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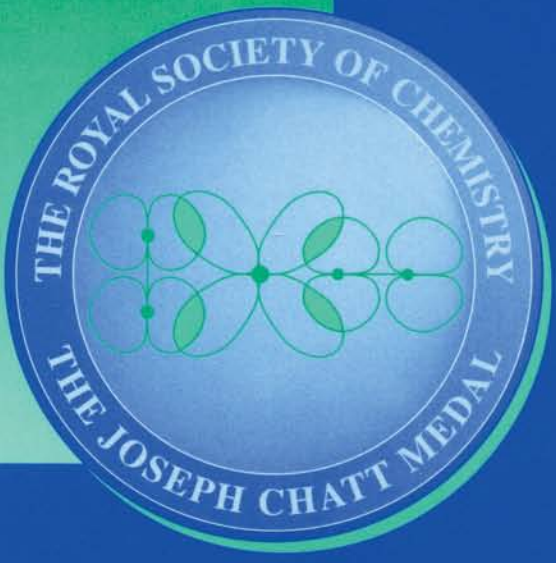

modern coordination chemistry

THE LEGACY OF JOSEPH CHATT

edited by G.J.LEIGH *and* N.WINTERTON

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Foreword

'The Child is Father of the Man'
William Wordsworth (1770–1850)

This book is dedicated to the work of Joseph Chatt. In this Foreword I should like to place Chatt's contribution in the perspective of chemistry when he entered the field, recognising that it was a very different field from that of the present day. Using the quotation above of another who was brought up in Cumberland, Wordsworth, I believe that his initial training in chemistry was an influence, perhaps the most important, on his attitude and approach to the subject. Chatt always talked with affection and gratitude of his mentor F. G. Mann. Mann was shy, but a remarkable chemist who viewed chemistry as a single subject and not as three branches: organic, inorganic and physical. He was a very careful and precise chemist who enjoyed producing crystals of high purity. It is reputed that the micro-analytical group in Cambridge often used his compounds to test their apparatus. Another characteristic that I found with F. G. was that he was never prepared to accept the immediate answer to any problem in his chemistry and viewed all reasonable alternatives. These are some of the characteristics that Joseph Chatt also exhibited.

The School of Chemistry in Cambridge was led by Sir William Pope, an organic chemist who was interested in the optical activity of elements other than carbon. F. G. Mann was his research assistant, and although Chatt was officially registered as a student with Pope his training was with Mann. It is of interest that by this time much of the work being carried out in the Cambridge laboratories was inorganic in nature but it was still classified as organic.

Joe Chatt was one of the leading inorganic chemists of his day. However, as was common at that time, his initial training was primarily in organic chemistry. His initial research project involved the preparation and bridge-splitting reactions of some dipalladium halogen-bridged phosphine complexes. The preparation of metal complexes of this type arose because Mann was interested in the use of phosphines in the preparation of optically-active phosphorus compounds and the platinum metals provided useful means of purifying and crystallising the phosphine compounds. After his initial work on these compounds, Chatt changed his research direction to a study of the stereochemistry of related arsenic compounds. This work led to the preparation of phenylene-1,2-bis(dimethylarsine), a compound utilised in coordination chemistry to great effect by Ron Nyholm. It was also during his period in Cambridge that Chatt became

acquainted with the olefin–platinum compounds that were to be of major interest when he started his independent career in inorganic chemistry.

On graduating, his interest in pursuing academic work was interrupted by the war and he was recruited into the scientific Civil Service. He was given initially a problem involving the preparation of organic nitro-compounds similar to TNT. This was an attempt to produce better explosives, an idea that originated with Robert Robinson, the leading British organic chemist of the day. However, the compounds proved to be of no major improvement on the explosives then available. Chatt's career then followed a chequered path within the Government service, from Swansea to Woolwich Arsenal, a major scientific laboratory in London, to a position as Deputy Chief Chemist at Peter Spence & Sons Ltd at Widnes in the North of England. This company was concerned with the production of aluminium chloride and oxide. However, he was not happy in these appointments and sought to return to an academic post in inorganic chemistry.

To appreciate Chatt's position at this time it is perhaps important to place the study of inorganic chemistry in perspective. Before the Second World War, it was very much the Cinderella of chemistry, often of minor concern in University chemistry courses. The subject was either omitted from the courses or taught by staff who had little interest in the subject, particularly from the point of view of research. Thus M. G. Evans, a leading physical chemist of his day and holder of the Chair of Physical Chemistry in Manchester, excluded any major teaching of the subject from the chemistry degree course.

When it came to the research in inorganic chemistry, which was not very extensive in the UK, the primary interest was in the study of the non-transition elements, with a particular emphasis on the similarity of the chemistry to that of related organic compounds. In many instances comparison with the carbon compounds was the prime aim. Thus there was a considerable interest in the chemistry of boron and silicon compounds and the relationship to their carbon analogues. As the compounds of these elements are particularly sensitive to water, and often to dioxygen, the main work involved the use of vacuum line techniques. In addition, the preparation of volatile compounds allowed the application of a range of physical methods that at that time were developed mainly to deal with volatile compounds. Methods for the determination of the structures of compounds in the solid and liquid states were not well developed. The X-ray structure of even relatively simple compounds could take years to complete. Paradoxically, Chatt thus obtained a very good training in an area of transition-metal chemistry, under the cloak of research in organic chemistry, when such chemistry was not being studied in any inorganic department. As his research work showed, this proved to be an extremely good training for the study of what was to become the coordination chemistry of the later transition elements.

The activities in the war brought about significant changes of emphasis in the study and role of chemistry, particularly of inorganic chemistry. The atomic-bomb project led to the preparation, isolation and study of the chemistry of the transuranic elements. This focused on a completely new area of inorganic chemistry. New techniques for the isolation and handling of chemical

compounds were developed and, in collaboration with physicists, new approaches to many problems were discovered. In particular, techniques such as ESR spectroscopy were developed which opened up the whole area of resonance methods.

This work led to a complete reassessment of inorganic chemistry, and, in particular, of the structural aspects of the subject, as chemistry, both inorganic and organic, was in those days dominated by the isolation and determination of the structures of compounds. It clearly took a while for these changes to be appreciated in the university system but it was with this changing approach to inorganic chemistry that Chatt took up his first university appointment as an ICI Fellow at Imperial College in 1946. This Fellowship was part of a scheme designed by ICI to make appointments in University departments for the best researchers until permanent staff appointments were available. However, Chatt found the environment at Imperial unsatisfactory and transferred to a new enterprise for fundamental research that was also being set up by ICI in a country house, The Frythe, just north of London. This laboratory, the Butterwick Laboratory, was subsequently called the Akers Laboratory. This was a great opportunity that was fully appreciated by Chatt. Initially there was an attempt to include him in the organic section, reflecting the view of the establishment as to the status of inorganic chemistry but Chatt put up a strong fight to have a separate inorganic section. This gave him the opportunity to research, for the first time, his own ideas and he chose to look at the chemistry of metal olefin and acetylene compounds. Chatt's work in these laboratories was at a time when there was the beginning of a surge of interest in inorganic chemistry in the UK and Europe in general. At this time Nyholm was also starting his work in coordination chemistry at University College in London. These two workers initiated what has been referred to as the Renaissance of Inorganic Chemistry in the UK. There was an air of expansion within the universities, and in chemistry this particularly applied to inorganic chemistry. It is perhaps important to recognise that in 1946 for the UK only 4% of the potential student cohort went to university and there were less than 30 universities or their equivalents in the country. If we compare this with the present situation of nearly 40% of the cohort and more than 100 universities, the changes have been enormous, and within the field of chemistry this is particularly true for inorganic chemistry.

The work described in this volume illustrates the wide range of contributions that Chatt made to inorganic chemistry, with over-spill into organic chemistry and biochemistry. His work attracted world attention and a large number of the most eminent inorganic chemists visited and worked in his laboratories, both at The Frythe and in Sussex. He attracted large numbers of postdoctoral workers, many of whom went on to make their own mark within chemistry and have contributed to this volume. On a purely personal level, in 1952 I debated long between an offer to work at The Frythe and a university appointment, finally deciding to take the university post.

The work carried out at The Frythe pioneered the basic chemistry that pervades much of organometallic chemistry today, with its overtures into catalysis. The work carried out at the University of Sussex was a major study in the

nitrogen fixation problem and led to fascinating developments in the chemistry of dinitrogen transition metal compounds.

Joseph Chatt was at the forefront in the development of inorganic chemistry, from what may be considered 'the dark ages' to the present day. His influence, both through his studies and the researchers with whom he worked, will be with us for decades. In addition to his many contributions to chemistry, Joseph will be remembered by many as a nice man and a good friend.

Lord Lewis of Newnham

Introduction

It is very appropriate that this volume, which deals with the scientific legacy of Joseph Chatt, should appear at this time. A decision was taken very early in the planning of the 34th International Coordination Chemistry Conference (ICCC34) to have a theme dealing with 'Joe Chatt Chemistry'. ICCC34 was held in the United Kingdom to celebrate the Golden Jubilee of the first meeting organised by Joseph Chatt at The Frythe, Welwyn, near London, which was then a corporate research laboratory of Imperial Chemical Industries. Since this first meeting ICCCs have grown steadily in size and importance with recent meetings attracting delegates from more than 50 countries.

As ICCC34 coincided with the New Millennium, it was appropriate to use the Joseph Chatt theme to provide a historical perspective of the development of coordination chemistry because, as this volume clearly demonstrates, Chatt was involved with an extraordinarily broad range of research activities. This historical perspective was backed by an exhibition organised by Paul O'Brien giving details of earlier meetings and many of the personalities who have been involved over the years.* More importantly, 'Joe Chatt Chemistry' was also used to provide a prediction of the likely future developments in coordination chemistry. Here the organisers faced a difficulty. Joseph Chatt's contributions to the subject have impacted on so many areas that it became difficult to draw a line defining the boundaries of topics that were to be considered under the theme of 'Joe Chatt Chemisty'. In many cases papers which could have been presented under this heading were included in the other sessions: Structure and Dynamics, 21st Century Materials, Biotechnology and Medicine, Technological Advances, and Chemistry of Life. The splendid range of papers included in this book illustrates how broadly Joseph Chatt contributed to the development of the subject. The editors should be congratulated on bringing together such an interesting and representative collection of papers defining his legacy.

Peter Tasker

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Preface

The historic threads of scientific enquiry that are woven into the fabric that is our understanding of the natural world (and the benefits that stem from its application in technology) should not simply be the province of scientific historians (nor even, heaven forbid, sociologists of science or cultural theorists); they should inform practitioners and the wider public alike of the debt today's scientists owe to their scientific forbears as well as demonstrating that the body of scientific knowledge is continually growing and some portion of it changing. Indeed, the processes, requirements and timescales of science, and the distinction to be made between them and those of technological development, need to be much better understood, particularly by those who formulate and execute public policy and those who direct and manage industrial, commercial and financial enterprises and not least by scientists themselves.

At the beginning of the 20th century, inorganic chemistry was overshadowed by developments in organic and physical chemistry, developments in both of which were to lay the foundations for the re-invigoration of inorganic chemistry and the sub-disciplines of coordination and organometallic chemistry that characterised the latter half of the century.

It is our purpose to provide a perspective of this formative period (and its manifestation in certain areas of contemporary inorganic chemistry) through the contributions of one of the foremost practitioners, Joseph Chatt.

Isaac Newton suggested that his own scientific vision was so great because he had 'stood on the shoulders of giants'. In a humbler sense, all scientists see further and deeper than they otherwise might, because of the work done by those who went before. However, with an ever-increasing volume of scientific publication, it is difficult for today's scientist to keep up with new material in his or her own field, let alone to explore and appreciate the wider significance of the earlier literature. While this is understandable, not only might they fail properly to acknowledge work with a bearing on their own, but they also lose sight of the methods (often very limited) available in the past that provide a proper testament to the magnitude of earlier contributions. We should know what it was that ensured that this earlier work has stood the test of time (particularly the test of modern scientific methodology). In addition, the over-dependence on computerised literature searching methods tends to reduce awareness of material published before the mid-1960s. This is significant, as the post-war period up to that point was the time when Joseph Chatt and his collaborators (as well as other major contemporary figures) were especially productive.

Today's science is much more of a team (one might even say a corporate) activity, with the idea of scientific leadership of the sort provided by Chatt (and amply exemplified by the various contributions in this volume from his former students and co-workers) being seen increasingly as old-fashioned. However, for today's research students and their supervisors at least, it should be informative if not instructive to be offered an appreciation of what it was like to work for such an individual, particularly the testing and challenging but essentially supportive environment in which Chatt's students researched.

There are those who look at the close involvement that exists today between science and business and are concerned that science is damaged by such interactions. It is significant then to draw attention to Chatt's employment and support by Imperial Chemical Industries Ltd during the period 1949 to 1962. (Chatt's internal ICI reports for the period have been archived at the John Innes Centre, Norwich, UK.) It says much about Chatt that his independence and strength of character saw to it that he produced fundamental work of the highest standard. It says much about ICI's very senior staff that they believed in the importance of participation in the scientific enterprise at its most fundamental. On the other hand one is also forced to conclude that there were others in ICI who tended to dismiss the workers at The Frythe as pampered academics and who did not regard Chatt's work as being of any value to them. Whether this was so, or simply appeared so to those unable to conceive of or appreciate its significance or potential, cannot now be gauged. One may simply speculate whether a greater understanding on both sides of the gulf that inevitably separates the output of purely scientific work from that needed to secure a commercial opportunity from a technological development based upon it (and the presence of some mechanism within the company purposefully designed to bridge this gap) might have led ICI to gain an advantage from the developments in coordination and organometallic chemistry potentially available to them. Suffice it to say that ICI was not the only large chemical corporation that found difficulty in reconciling the shorter-term demands of commercial operation and financial performance with the longer-term needs of research and development. Indeed, the problem remains a general and contemporary one.

Today's generation of academic scientists, particularly in the UK, have operated in an environment in which they have felt obliged to secure funding for their work primarily by stressing its 'relevance' or its potential for application, even when this has been at the expense of purely curiosity-driven research. Some argue that academics themselves are partly to blame because of their unwillingness to recognise and support creativity and adventurousness through the peer review process. Others argue that there is no incompatability between fundamental work done for its own sake and that done with some end in view. Indeed, this principle was well exemplified by the overall purpose of the Nitrogen Fixation Unit set up by the Agricultural Research Council at the University of Sussex under Chatt's direction. That it was so successful from a scientific point of view arose from a further principle that characterised Chatt's stewardship of the Nitrogen Fixation Unit, namely the recognition of the contributions to be made by different disciplines and by the purposeful interactions between them.

The gap between scientists and those seeking to develop the results of their science that was characterised in Chatt's time by ignorance and indifference may have been narrowed, though it may well now be more characterised by suspicion and antagonism arising from a failure of scientists and their sponsors to recognise the motivations, methods, language and timescales of each other. The wiser manager and investor do indeed recognise the long-term importance of 'pure' research (as well as understanding that the timescale is often measured in decades and not reflected by the demands of quarterly reporting of business performance!): there are just not enough of them to provide, business-wide, scientifically literate and technologically creative management. Today's successful academic should be at ease with a portfolio of fundamental research driven both by curiosity (particularly at the interfaces with other disciplines) and by technological or societal need and must be willing to appreciate the intellectual challenges associated with technological development (as well as its inevitable shorter-term focus). There are not enough of such academics either.

It is important to look back at the contributions of major figures of the past to assess, with a longer historical perspective, whether their reputation stands the test of time. We know that such assessments have been made about major figures such as Newton (and Hooke's contributions) and Darwin (and Wallace's contributions). In one particular sense, this volume provides a starting point for that assessment as far as Chatt is concerned.

As Peter Tasker's comments in his Introduction indicate, this volume grew out of the 34th International Coordination Chemistry Conference held at the University of Edinburgh, in July 2000. While most of the contributions presented to the 'Joe Chatt Chemistry' sessions are reproduced in expanded form here, we have also sought contributions from Chatt's contemporaries and students, whose reminiscences give a true measure of the man. There are, in addition, contributions which concentrate more on the chemistry with which Chatt was associated and, in various degrees, link Chatt's work, particularly on phosphine-, hydride-, olefin- and dinitrogen-metal complex chemistry and chemistry, biochemistry and biology of nitrogen fixation, with the very latest developments in these topics. These include chapters from recipients of the Chatt Lectureship, conferred by the Royal Society of Chemistry.

While this book is not solely biography, history, scientific text or conference proceedings, we hope that the mix of each will be of interest to many. We thank all the authors who have provided contributions and believe that they truly reflect the legacy of a great chemist to modern coordination chemistry.

G. J. Leigh and N. Winterton

Contents

Abbreviations

Hacac	acetylacetone; pentan-2,4-dione
Ala	alanine or alanate
Ar^F	perfluoroaryl
Asp	aspartic acid or aspartate
ATP	adenosine triphosphate
H_2atsm	$H_2NC(S)NHN{=}CMeCMe{=}NNHC(S)NH_2$
bipy	2,2′-bipyridyl
bipym	2,2′-bipyrimidine
Hbq	7,8-benzoquinoline
CDA	charge decomposition analysis
cod	cycloocta-1,5-diene
cot	cycloocta-1,3,5-triene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Hcupf	cupferron; *N*-nitrosophenylhydroxylamine
Cy	cyclohexyl
Cys	cysteine or cysteinate
dab	*N*,*N*′-disubstituted 1,4-diazabuta-1,3-diene
DCPIP	dichlorophenolindophenol
Hdct	2,6-dichlorothiophenol
depe	1,2-bis(diethylphosphino)ethane
diars	1,2-bis(dimethylarsino)benzene
digly	diethyleneglycol dimethyl ether
dmad	dimethyl acetylenedicarboxylate
Hdmavk	dimethyl-β-aminovinylketone
dme	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphino)ethane
dmso or DMSO	dimethyl sulfoxide
DMSOR	dimethyl sulfoxide reductase
DMS	dimethyl sulfide
Hdmt	2,6-dimethylthiophenol
dppe	1,2-bis(diphenylphosphino)ethane
dppf	$[Fe(C_5H_4PPh_2)_2]$

dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
dta	dithiooxamide
en	ethane-1,2-diamine
EDESI-MS	energy-dependent electrospray ionisation mass spectrometry
ESI-MS	electrospray ionisation mass spectrometry
HFc	ferrocene; $[Fe(\eta^5\text{-}C_5H_5)_2]$
FeMoco	iron–molybdenum cofactor of nitrogenase
Glu	glutamic acid
H_2gts	$H_2NC(S)NHN{=}CHCH{=}NNHC(S)NH_2$
HiPIP	high potential iron protein
His	histidine
hmpa	hexamethylphosphoramide
HOMO	highest occupied molecular orbital
INS	inelastic neutron scattering
IR	infrared
Leu	leucine
LUMO	lowest unoccupied molecular orbital
Lys	lysine
Me_8[16]aneS_4	2,4,6,8,10,12,14,16-octamethyl-1,5,9,13-tetrathiahexadecane
MeP	methyl propanoate
Mes	mesityl
mp	methyl propynoate
MPT	molybdopterin
NMR	nuclear magnetic resonance
$H_3(NN_3)$	$N(CH_2CH_2NHSiMe_3)_3$
$H_2(N_HS_4)$	$1,2\text{-}HSC_6H_4SCH_2CH_2NHCH_2CH_2SC_6H_4SH\text{-}1,2$
$H_3(NS_3)$	$N(CH_2CH_2SH)_3$
H_2(NPN)	$[PhP(CH_2SiMe_2NHPh)_2]$
Hoxin	8-hydroxyquinoline
H_2(2-pedt)	(2-pyridyl)ethylenedi-1,2-thiol
H_2(3-pedt)	(3-pyridyl)ethylenedi-1,2-thiol
H_2(4-pedt)	(4-pyridyl)ethylenedi-1,2-thiol
o-phen	1,10-phenanthroline
H(PNP)	$NH(SiMe_2CH_2PR_2)_2$

$H_2(P_2N_2)$	$PhP(CH_2SiMe_2NHSiMe_2CH_2)_2PPh$
H(PS)	$2\text{-}Ph_2PC_6H_4SH$
H(PSP)	2,6-(diphenylphosphino)thiophenol
$H_2(PS_2)$	$PhP(C_6H_4SH\text{-}2)_2$
$H_3(PS_3)$	$P(C_6H_4SH\text{-}2)_3$
$H_2(NH_2\text{-ptedt})$	2-amino-3-methyl-4-oxopteridinyl)ethylenedi-1,2-thiol
$H_2(NC(H)NMe_2\text{-}$ ptedt)	(2-*N*,*N*-dimethylaminomethyleneamino)-3-methyl-4-oxopteridinyl)ethylenedi-1,2-thiol
H_2ptsm	HMeNC(S)NHN=CMeCH=NNHC(S)NHMe
py	pyridine
H_2qedt	(2-(*N*,*N*-dimethylimino)-4-(qinoxalin-2-yl)ethylenedi-1,2-thiol
Hquin	2-quinaldic acid; 2-quinolinecarboxylic acid
RCM	ring-closing metathesis
Rd	rubredoxin
ROMP	ring-opening metathesis polymerisation
R-pyca	2-pyridine *N*-aryl carbaldimine
$H_2(S_4)$	$1,2\text{-}HSC_6H_4SCH_2CH_2SC_6H_4SH\text{-}1,2$
H_2salen	*N*,*N*′-bis(salicylidene)ethane 1,2-diamine
H_2sdt	$(2\text{-}C_6H_5)C(SH)=CH(SH)$
Ser	serine or serinate
SHE	standard hydrogen electrode
terpy	2,2′:6′,2″-terpyridine
TfOH	trifluoromethanesulfonic acid or triflic acid
thf	tetrahydrofuran
thpp	1,3,3a,6a-tetrahydropyrrolo[3,2-b]pyrrole
tht	tetrahydrothiophene
Htipt	2,4,6-tri-*iso*-propylthiophenol
TMAO	trimethylamine *N*-oxide
TMA	trimethylamine
tmen	*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine
Tol	tolyl; 4-methylphenyl
tren	tris(2-aminoethyl)amine
tripod	tris(diphenylphosphino)methane
Tyr	tyrosine
UV	ultraviolet
Val	valine

SECTION A:

Reminiscences of Joseph Chatt Drawn from Conversations and from the Recollections of Co-workers

Joseph Chatt worked in several different establishments during his career, and he has also given an account of his early life in a recorded conversation. Clearly he was very fondly regarded by those with whom he worked, and they continue to regard their time with him as a high point in their careers. To provide a background against which those who did not know him might wish to assess his life and work, we decided to ask some of those involved to write an account of their experiences working in the Chatt group. None of those approached needed any encouragement, and their contributions are presented in this section with only very light editing to avoid excessive overlap.

A Memoir of Joseph Chatt

G. J. LEIGH

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Joseph Chatt was born in the North East of England at Hordern, County Durham, on November 6, 1914. However, most of his early life was spent in the North West, in Cumberland. He once mentioned that, together with his father, he had observed German warships bombarding Hartlepool, though he must have been very young when that occurred, which was during the First World War. Nevertheless, he did have a fine memory, and his knowledge of the fundamental facts of inorganic chemistry was one of his great strengths. He had an almost personal understanding of the chemistry of the metallic elements, and his comments and advice on chemistry were generally sound, even when he could not explain why he had made them. His understanding was intuitive and inspirational, and though he was not afraid to admit he was wrong or even that he had made mistakes, everything he published was prepared with the utmost care and circumspection, often to the annoyance of his less patient and meticulous collaborators.

He inherited many of those qualities that are often regarded as characteristic of the northern Englishman. He was hard working, meticulous, blunt and honest. He was also very determined, and shrewd in his evaluation of people, even if he also had some related prejudices. He only slowly came to accept that women might also become good researchers, and he had a strong suspicion of men who sported beards. However, he could be persuaded by a demonstration of scientific ability, even if his initial reaction to some people was less than favourable. What sometimes inhibited his relationship with younger researchers, especially graduate students, was his unquestioning assumption that everyone in the laboratory had his interest in chemistry and also his enormous accumulation of knowledge. We, his colleagues, always called him Joseph, even after he retired. It was generally only colleagues from the United States who presumed to call him Joe.

Whatever he undertook to do he did with great thoroughness, whether it was chemistry or not. At one time he was interested in antique furniture, and I can recall being lectured on how to determine the age of a chair by examining the

construction of the seat. This was intended to help me in my purchase of furniture for a newly acquired house, though there was little enough money to spare on any furniture, let alone on antiques. He was actually very self-centred and rather insensitive, though certainly not mean. It was always necessary to ask him for help if you required it, because he was seldom aware that it might be necessary. However, once he was asked for help he always did his utmost to assist.

He was an avid collector of coins from his youth, and specialised in English and British Empire and Commonwealth coins. He had sets of Maundy money from every English (British) sovereign who had issued such coins. At his death he was working on a catalogue of Peace Medals, medals that were struck in towns all over Britain to celebrate the end of the First World War, but which had never been listed.

He was also very lucky. This showed not only in his career and perhaps in his chemical intuition, but also, sometimes, in his hobbies. He once bought a jardinière at a sale in aid of Sussex churches. It was said to be Sèvres, and it was not expensive. Subsequently he decided to take it to the Victoria and Albert Museum in London, to confirm that it was an imitation and not really a Sèvres product. The curator initially agreed that it could not be genuine, so Joseph asked to be shown the Museum collection, which, of course, consists only of genuine items. As they proceeded to inspect the display, starting at the later and moving to the earlier, Joseph's jardinière resembled more and more the Museum items, and finally the curator had to admit that the jardinière was a genuine and very rare early Sèvres piece, and certainly worth much more than he had paid for it.

When he was ten years old his family moved to a farm in Cumberland, at Welton, just south of Carlisle, and there began a formative time in his development. The farm was eventually inherited by his brother, and Joseph never became a farmer, even though the agriculturally pertinent topic of nitrogen fixation ultimately became his major professional interest. He enjoyed fell-walking and cycling, and was clearly very active. During this time he sustained damage to his leg that left him semi-crippled, though it was only towards the end of his life that he was forced to use a stick as well as special shoes and a leg-iron.

Cumbria and the Lake District are heavily mineralised, and the abundance of minerals in the rocks all around his home stimulated his interest in chemistry and also in exploring the hills. In this he was also aided by his uncle who was Chief Chemist in a steel works in Newcastle-upon-Tyne. The young Joseph visited him often and was given the run of the analytical laboratory. It was during this time that he developed a very refined experimental technique and also an interest in experimentation generally. Joseph learned how to make working models in glass of Hero's engine, starting with glass tubing. This required considerable skill, even more so when one realises that he must have been obliged to use soda glass. Until quite late in his career he required a bench to be kept in the lab for his particular use, though he seldom had the time to indulge himself in laboratory work.

Encouraged by learning that the Romans had once found gold in the Lake District, Joseph hunted for it in the fells around the family farm, though for once

he appears to have been unsuccessful. He set up a lighting system based on a dichromate cell in his bedroom, the control being the raising of an electrode from the acid bath using a piece of string. At that time one could buy chemicals from the local chemist (pharmacist) and the young Chatt was able to purchase things such as metallic sodium and aqua regia. He once claimed that he was one of the very few people to have observed the reaction of metallic sodium with aqua regia, and one would not wish to query this claim! It seems to have been rather spectacular. Somewhat later the destruction of some more of his sodium metal by throwing it into the water at Silloth Dock on the Cumbrian coast led to reports that the port had suffered an IRA attack, and apparently these have never been corrected. This story is told in detail elsewhere (G. J. Leigh, *Coord. Chem. Rev.*, 1991, **108**, 4), but Joseph was hesitant to publish the true details even in 1991, some fifty years after the event.

Joseph's family was not academic, and his father did not understand how the education system functioned at that time. Consequently, Joseph remained at the village school until he was fourteen. It is apparent that the family was never very flush with money, and spending some on educating a child beyond the minimum legal age in a private establishment required a considerable sacrifice. Nevertheless, at the age of fourteen he was admitted to the Nelson School in nearby Wigton, for which the normal age of entry was eleven. His promise was very quickly recognised, and he was given every encouragement by several of the teachers, some of whom are named in the above reference. As well as receiving local scholarships for financial support, he was given specific help with his mineralogy and chemistry, and he matriculated within two years instead of the usual four. Matriculation is a term no longer used, but it was then a qualification obtained at the age of fifteen or so, and was a necessary preliminary requirement for further study at a university.

Chatt's arrival at Cambridge owed everything to the mathematics master at the Nelson School. He thought that Joseph would benefit even more from Cambridge than he would from studying at Durham, which had been the original plan, and so in the late summer of 1935 Mr Burns went to Cambridge to try to encourage his own old college, St John's, to admit this promising young man who had already achieved so much and had already won at least two scholarships. The college was full, so he tried others, finally asking at Emmanuel College. They were also full, but the admissions tutor said that they generally lost a potential student 'falling down an Alp or something, in the long vacation'. So Joseph was given a place, on the understanding that he would obtain the required qualification in Latin, which was at that time regarded as an indispensable part of every person's University education. This he did in very short time, and he graduated in the summer of 1937.

He carried on with graduate work with F. G. Mann, for whom he always had the highest personal and scientific regard. Mann was one of those few pioneers who persisted with inorganic chemistry throughout the 1920s and 1930s, at which time inorganic chemistry was generally believed to have been finished and exhausted, and of no further interest. Mann wished to prepare organophosphine complexes of transition elements, because phosphines were known to produce

low-melting adducts with transition-metal salts and these adducts could be used to measure parachors. The parachor was expected to give information about the nature of the coordinate bond, and these two directions, phosphines and the coordinate bond, were to inform much of Chatt's earlier work at The Frythe (see below, pp. 8, 11, 18 and 25). Joseph's first six papers, published jointly with Mann, concerned phosphines and arsines and their complexes with elements such as palladium. The platinum metals also became an area of early interest.

Chatt graduated when the Second World War was beginning, and he was drafted immediately into work for the war effort. Because 1,3-dinitrobenzene proved to be a better explosive than had been expected, it was felt (apparently originally by Sir Robert Robinson) that 1,3,5,7-tetranitronaphthalene might be exceptionally good. There are 24 tetranitronaphthalenes, and Joseph was asked to make 200 g of this particular isomer in the Cambridge University laboratory. Unfortunately, the eight months' effort he needed to produce the compound were wasted as the compound proved to be a very disappointing explosive. In truth, the Ministry of Works, his then employer, had little idea of what a man of Chatt's calibre might achieve and a little later they were reasonably happy to let him resign. He took up employment with Peter Spence and Sons Ltd at Widnes, where he worked on various war-related projects such as the reduction of titanium tetrachloride to give aqueous titanium trichloride and the properties of activated alumina. He ultimately became Chief Chemist. Even then, he pursued his own private researches on olefin complexes in his spare time. It was at Widnes that he met his future wife, Ethel Williams.

Joseph had originally planned to pursue an academic career, and had even arranged to teach heterocyclic chemistry at St Andrews, but the war had put a stop to that. Once the war had ended he decided to try academe once more, and finally took up an appointment in inorganic chemistry at Imperial College. He found the life and the facilities at Imperial College completely unsatisfying. He was not able to do any research work, and to the end of his life he never really ever believed that a university chemistry department was the best place to do chemistry research. Afterwards, at the ICI laboratory at The Frythe and later, in the Nitrogen Fixation Unit at Sussex, he made great efforts to ensure that everyone realised that research was the prime and only significant activity of the laboratory, and that every person and thing in the organisation should operate in order to make the research as fruitful as possible. He was extremely successful, and his students and collaborators have carried the message across the world.

As a result of the frustrations he experienced at Imperial College, Chatt decided to go back to industry, and approached Dr R. M. Winter, who was then Controller of Research at ICI, for a job. As a result, he was appointed to a position at the ICI Butterwick Research laboratories at The Frythe, a large country house, near Welwyn Garden City. These laboratories were intended by ICI to be for fundamental research. After some local in-fighting, Chatt obtained the separate inorganic department he had been promised. With himself and just a single assistant he started what was probably the most productive period of his research career. Personal accounts of that period and the subsequent work at the

Unit of Nitrogen Fixation and the University of Sussex are to be found elsewhere in this book.

After his formal retirement from the Unit of Nitrogen Fixation in 1980, he moved his office into the then School of Chemistry and Molecular Science at the University of Sussex. He continued to pursue research, though he found it difficult to maintain his degree of productivity without the permanent professional support provided in the Unit. He was still a regular attender at chemistry seminars, and his understanding and insights were as keen as ever, even if his knowledge was becoming a little dated. He still enjoyed travelling, especially sea cruises, and had taken up painting. He was particularly pleased when, unexpectedly, someone bought one of his paintings at an exhibition. He was in reasonable health for his age, and supported his wife in her activities in local art societies.

Joseph died suddenly on May 19, 1994, whilst preparing himself for a joint photograph with the six Fellows of the Royal Society who were then working in chemistry at the University of Sussex. The sadness at his passing was tempered by the realisation that he had led a long, full and rewarding life, and had enriched the world of chemistry by his discoveries and example, perhaps by more than any of his contemporaries.

A Memorable Start to a Career

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In September 1949, I was just completing a PhD supervised by Richard Burkin, at University College, Southampton, examining the coordination chemistry of copper(I) complexes of long-chain aliphatic amines. As luck would have it, a position tailor-made for me had become available at the ICI Butterwick Research Laboratories in Welwyn. The work would involve fundamental research in a small group headed by Dr J. Chatt. I knew of his work with F. G. Mann at Cambridge before the war, and after an interview, I was delighted and not a little surprised, to be offered the position, which I accepted with alacrity! Years later, Joseph told me that my enthusiasm had won the day over some stiff opposition, which says more about him than about me.

The inorganic chemistry group headed by Dr Chatt consisted of Alan Williams and Alan Hart who were working towards degrees, and I was therefore the first of many graduates to join him. We were housed in a small building (hut might be a better description) of which there were many in the grounds of a Victorian mansion, The Frythe. It is appropriate here to say something about the establishment. There were a number of research groups. As well as inorganic, some others that I recall were organic, physical, microbiology and toxicology. My memory may be a little hazy about these and other matters! Most of us lived on-site in small huts, each housing a few people, and we were fed quite well in the main house. Some of the (mainly senior) scientists travelled from London daily and were picked up at Welwyn Garden City station. Joseph and Ethel Chatt had a house in St Albans.

It was a wonderful environment in which to get to know other scientists in different disciplines. I remember particularly the organic chemists who were working on the antibiotic griseofulvin. Some of these were John Grove, Jake Macmillan and Dunc (L. A. Duncanson, who was to enjoy a very fruitful collaboration with the inorganic group). There were 'relevant' overtones to our researches, but a fundamental approach was encouraged.

I can only endorse the views expressed by others[1] that Dr Chatt was friendly,

helpful, kind – and formal. He was Dr Chatt to me until some years after I left The Frythe, then Joseph, and occasionally Joe. It was a very friendly group that I joined and Joseph gave me an interesting problem that he had himself gone some way to resolving. I think that in this way he gave me some confidence and an early publication.[2] Beautiful canary yellow crystals are deposited when C_2H_4 is passed into a concentrated solution of $[\{PtCl_2(C_2H_4)\}_2]$ in acetone at $-70°C$. The product was shown to be dichlorobis(η^2-ethene)platinum(II), $[PtCl_2(C_2H_4)_2]$. The complex is thermally unstable and reverts to the orange dimer with loss of C_2H_4 on warming above about $-6°C$. In a cursory examination of the literature I have found little further reference to the compound and this is surprising since a structural determination, although tricky, would be worthwhile. Joseph thought the compound would have a *trans* conformation.

In September 1950, Joseph decided to invite about 30 coordination chemists to a meeting at The Frythe. This was to become the first International Coordination Chemistry Conference (international because both K. A. Jensen (Danish) and Gerold Schwarzenbach (Swiss) attended!). Little need be said about this meeting since it was featured in the exhibition of historical material from early ICCCs at the 34th ICCC (Golden Jubilee) held in 2000 at the University of Edinburgh. In 1950, all eleven talks took place over two days in the lounge of the main house at The Frythe. We also had a nice dinner and social evening at the Clock Restaurant in Welwyn. N. V. Sidgwick, who had just completed his mammoth two-volume work on the chemical elements,[3] gave a short talk and I recall that he reprimanded one speaker for using the phrase 'data is'! It was a splendid idea of Joseph's to bring together active workers in the area and I remember very well to this day the meeting and the impression it made on me. Now Leslie Orgel and I are the only speakers still around. I gave a talk about the preparation and equilibria between *cis*- and *trans*-complexes $[PtCl_2(ER_3)_2]$ (E = P, As or Sb), the study of which occupied most of my attention during my stay at The Frythe. It formed the basis of four papers[4] and Joseph presented the work at the ICCC in Copenhagen in August, 1953. We followed the equilibria using the vastly different dipoles of the two isomers.

We had a very sensitive meter, built in the excellent workshops on the site, to determine the dielectric constants of benzene solutions of the complexes from which dipole moments were calculated. Important findings were (1) that the total bond energy of the *cis* isomer is about 10 kcal greater than that of the corresponding *trans* isomer; (2) that the entropy differences between isomers, arising from the high dipole moment of the *cis* isomer, can control the positions of the equilibria; and (3) that traces of proligand (R_3E), either added (E = P) or autoproduced (E = As or Sb), are needed to establish the equilibria. These studies were the first of their kind and evoked immediate interest.

Since a good deal of the pioneering work on equilibria of complex ions was carried out in Sweden and Denmark, Joseph thought it would be a good idea to visit and talk with some of the people there who were known to us only as names. I was pleased when Joseph asked me to accompany him. We had an enjoyable and fruitful trip in June of 1952. We were fortunate to meet both Bjerrums (Nils and Jannik), Kai Jensen (who had done early studies of tertiary phosphine, arsine

and stibine complexes) and Sture Fronaeus, amongst others. Sten Ahrland has written about our meeting at Lund, which resulted in his joining the group in 1953 and starting a 'happy collaboration ... with a great scientist and also a true gentleman'.[5]

After an enjoyable and rewarding three years at The Frythe, I decided that I needed a change of direction. I went to the University of Southern California to learn about kinetics from Arthur Adamson. I believe, perhaps wrongly, that Joseph did not much like kinetics, indeed that he was uneasy with conclusions based on rate data. At the end of the year at USC, and mainly as a result of a chat between Joseph and Professor R. D. Howarth, chemistry department head at the University of Sheffield, I was encouraged to apply for a vacant lectureship there and was appointed, sight unseen (imagine that nowadays)!

I learnt a great deal in my three years with Joseph. Probably most important was scientific integrity. Facts published should be correct and as accurate as possible. Speculation should reside in ideas, which might very well turn out to be inaccurate.

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Joseph Chatt and The Frythe: A Memoir of the Early 1950s

GEORGE A. GAMLEN

One-time ICI employee at The Frythe

Joseph Chatt was successful and became famous because he was the right man in the right place at the right time. He deserved his glory because he knew what he wanted and he worked hard to get it. It goes without saying that he was a brilliant chemist, but in addition he had a phenomenal intuition rooted in his encyclopaedic knowledge of the subject.

In 1946, The Frythe was set-up by Sir Wallace Akers, ICI's Research Director, as a central research laboratory. It was hoped that chemists in ICI's manufacturing Divisions would follow the progress made at The Frythe, and pick up any results which might be of commercial value. Chatt arrived there in 1947, bubbling with enthusiasm and with a grandiose plan; he wanted to establish a world-class centre for inorganic chemistry that would rescue the subject from the doldrums. His main theme would be the nature of the coordinate link using complexes of the platinum-group metals as models. The first thing he needed was a very good laboratory. Drawing on his experience in Cambridge with organo-derivatives of the Group 15 and Group 16 elements, he installed powerful fume-cupboards including one floor-to-ceiling walk-in cupboard. Large quantities of compounds such as phosphines, arsines, selenides and tellurides were made in this and sealed in glass phials of convenient size. It was a test for newcomers that their first experimental work was usually to prepare one of these on the five-litre scale, using a Grignard reagent. Success, or the lack of it, was used as a measure of competence and potential usefulness to the department.

Chatt was very adept at experimental work and, for example, could usually induce crystallisation when others had failed. He kept a magnifying glass in his pocket to examine solutions for signs of crystals and if he spotted anyone scratching with a glass rod, he would take over. Holding the glass and the tube close to his eye, he would inspect the contents before beginning his own particular magic. Meanwhile, it was a matter of waiting with bated breath for the outcome – which was usually greeted with a sigh of relief. It used to be said that

nineteenth-century chemistry professors had large beards because they were a reservoir for seed crystals and I used to wonder whether the old-fashioned 1930s moustache (somewhere between Adolf and Groucho) that adorned Joseph's upper lip served the same purpose.

As the experimental work was so demanding, he carefully selected the school-leavers who were to be his lab. assistants and personally trained them in experimental methods. Some of these entrants later rose to senior academic or industrial positions as a result of their ability and good fortune in having such a fine teacher.

The utmost care was taken during preparations, but despite all the washing and scrubbing, the repulsive smell of the products seemed to stick to the skin and clothing. In this respect, the tellurides were particularly offensive. Lab. assistants going home used to note how seats around them on buses would quickly empty.

There was bench space in the laboratory for about eight workers who set up their apparatus in large enamel photographic trays. Any spillage could thus be caught and the precious metal recovered. Even so, there was the occasional loss which was signaled by a doleful rendering of a song beginning 'My plat'num has gone down the plug-'ole' (tune: 'My bonny lies over the ocean') but not if Chatt was in earshot. Precious metal recovery was a requirement of the experimental work and all the used filter papers and melting point tubes, ground up, were added to the residues.

The solvents commonly used were diethyl ether, benzene (not then recognised as a carcinogen), ethyl alcohol and acetone. Once the staff numbered four or five, a set-up to distil-off solvent from the collected reaction solutions ran every day so that the solid residues could be returned to Johnson Matthey for recovery. Chatt's first secretary still has a vivid recollection of the numerous fires that occurred (about once a month) but fortunately these were always put out before serious damage was done. On one occasion, when Chatt was bringing a distinguished visitor from the house to the lab., he noticed from a distance that a thick cloud of black smoke was pouring out of the fume-cupboard chimney and took the visitor to the arboretum to see an outstanding example of a maidenhair fern instead.

Chatt already had it in mind that physical measurements would be an important part of his work so there was a constant-temperature room which contained the dielectric constant machine and later a UV–visible spectrophotometer and a home-made calorimeter for measuring heats of *cis/trans*-isomerisation of complexes. L. A. Duncanson and his infrared spectrophotometer, with which the crucial spectra of the olefin–platinum complexes were measured, formed part of the Organic Chemistry Department in the next hut. As soon as he could, Chatt added an X-ray crystallography unit, run by his deputy, P. G. Owston, which was located in the old stables of the main house.

The site had its own microanalytical lab. with two first-class analysts. Some of the metal complexes were difficult to analyse accurately by standard methods because of the presence of the metal. The analysts' skill in solving these problems was a great help when new compounds were discovered.

Chatt's office was of modest size and he sat with his back to a wall that was pierced by a hatch. His secretary sat on the other side of the wall and as Joseph

finished each page of a new manuscript he would hand it through the hatch to the secretary for typing. He always wrote in pencil, selecting one from a jarful on the desk, and was careful to re-use the back of any paper that had been used for a previous draft. A small and grubby rubber was used (rather imperfectly) to make corrections and new material was inserted by writing above existing text. Sometimes he wrote a further insertion over the top of the first insertion and, as even his best writing was quite difficult to read, his long-suffering secretary struggled to cope. One day, when he had produced a particularly intricate and messy draft, he put it through the hatch, closed it and said, smiling, 'You know, I think that if I just scribbled a wavy line on the page, Celeste would be able to write the paper for me'.

Having established his base and begun experimental work at the bench, Chatt began to recruit staff. He was helped in this by knowing many of the Heads of university departments who recommended some of their best students to him. He loved scientific meetings and discussing chemistry with people and was delighted when the laboratory manager, M. T. Sampson, affectionately known as Sammy, encouraged him to hold a conference on coordination chemistry at The Frythe in 1950. This was later recognised as the First International Conference on Co-ordination Chemistry. With Ralph Wilkins, the first PhD member of his staff, he invited to attend everyone in Great Britain who had published on the subject, and some key figures from overseas as well. There were 23 from British institutions including the Australians, Craig, Maccoll and Nyholm; and three from abroad, Albert (Australia, temporarily based in London), Jensen (Denmark) and Schwarzenbach (Switzerland). There were also six from ICI Divisions in addition to the eight who attended from all the departments at The Frythe.

Two of the lectures were seminal for Chatt; Irving spoke on the stability constants of coordination compounds in aqueous solution (the Irving–Williams series) and Orgel on the significance of d-orbital hybridisation in coordination compounds. Chatt could see the possibility of another series of compounds akin to the Irving–Williams series based on donors other than oxygen and nitrogen, specifically the donors of Groups 15 and 16 and he knew how to get round the the problem of the insolubility in water of the platinum and palladium complexes by sulfonating the ligands. What he needed now was a good physical chemist, preferably with experience of determining stability constants. The first candidate he tried was British but proved unequal to the task and he had to look further afield. He found the ideal man, Sten Ahrland, at Lund University.

At that time, one of the main geographical areas where complex chemistry was a major topic of research was Scandinavia. In Denmark there was a long tradition of chemical excellence both on the preparative and physical side. Zeise, who in 1827 was the first to prepare an ethylene–platinum complex, was the first professor of chemistry at the University of Copenhagen. By a great coincidence, Jørgensen, who later was Werner's principal adversary, was not only born in the same village, Slagelse, as Zeise, but in a house on the same street. Jannik Bjerrum, son of Nils Bjerrum, signalled a major advance when he published his PhD thesis in 1941. In it, he described the stepwise formation of complex ions and the determination of stability constants. This, and other important papers which

were published in Denmark during the war, were well known in the other Scandinavian countries. Further groundbreaking work was done, for example, by Leden in Sweden and Flood in Norway.

Complex ions, a term which my mother always willfully misread, ('Oh, yes, my son is studying complexions') became a highly popular Nordic research field with Lars Gunnar Sillén in Sweden as the dominant figure until his sudden and premature death. Schwarzenbach in Switzerland was an early pioneer too, but, because of the war, the importance of complex ions in solution remained largely unknown in the UK for six or seven years. It was Irving and Williams who drew attention to Bjerrum's work late in the 1940s.

Sten Ahrland joined the team in 1953. It was a cold winter that year and I thought that, coming from Sweden, he would be used to it. In that I was wrong. Ahrland never did get used to how cold England was, and he explained to me how flats in Sweden were triple-glazed, and required by law to maintain a decent temperature whether they were occupied or not. It was particularly bad on Monday mornings at The Frythe as the heating was turned off over the weekend and the huts were poorly insulated. Ahrland would sit in his office wearing his overcoat, hat, scarf and gloves and place a two-bar electric fire on the desk in front of him, trying to keep warm. He was a very gentle giant with a highly developed sense of humour and a ready laugh. We did not meet again after he left The Frythe but corresponded until his death.

Luigi Venanzi arrived at The Frythe before Sten Ahrland. His antecedents seemed shrouded in some mystery, as he did not talk about them. He said he came from Trieste and had worked in North Africa and Germany. He arrived in England unable to speak a word of English but he had a gift for languages as well as for chemistry and within six months was speaking it fluently. It was only when he said 'abroad' which he pronounced 'abrode', that you knew he was not a native speaker. Venanzi adapted quickly to life in England. He was very elegant, carried a rolled umbrella when he went out and smoked a fine pipe. He became the epitome of an English gentleman with beautiful manners. In the laboratory he was immaculate in everything he did. His lab. coat was always clean, with no creases and completely stain free. His bench was always tidy and his notebooks written in a neat hand. He got through his work at a tremendous rate and made two or three new compounds every week. Venanzi occupied the bench adjacent to the front door so he was often the first person to greet the many visitors who now came to the lab.

Ralph Wilkins decided to join the brain drain and, encouraged by Fred Basolo, moved to the University of New York at Buffalo, so in 1952 I became the second Technical Officer that Chatt recruited onto his staff. When I went to The Frythe for interview, I was first taken to meet Mr. Sampson, who was in charge of The Frythe. He made two points to me: (a) that if I were appointed, he simply wanted me to do the best academic research that I could; and (b) that I should regard him as though he were my tutor and come to see him whenever I had a problem. I found it difficult to believe him on either score. I could not see why a large commercial organisation should pay people just to do academic research and Mr Sampson had a Roman nose in the middle of a face which might have

belonged to an emperor. There was also a touch of *hauteur* in his manner that seemed to belie his friendly words. Then I went down to the lab. and met Chatt. In those days he was shy and diffident when meeting people but he greeted me with 'Well, you're a pretty rare species' and was avuncular and helpful. I was thus emboldened to ask him if it was really true that we were only expected to do academic research. He confirmed this and showed me the papers that they had already published – a substantial collection for such a short time.

Later, I found that I had misjudged Sammy on the second count, too. At the end of the day, Chatt told Sammy that he wanted to offer the post to me and they immediately arranged a final interview at the ICI Headquarters in London, in two days time. It only took ten days from the time that I saw the job advertised in the paper to the visit to London when I was formally offered the post. My only worry was that I had already been accepted for the Scientific Civil Service at a salary of £830 a year and ICI only offered me £700. I explained this to Chatt in a letter and already felt on such good terms with him that I asked him what he thought I should do. He wrote a long reply filled with wise words, pointing out, for example, that ICI was such a big slice of the chemical industry that whatever they paid was going to be the average. He mentioned that he had also had experience of working for the Scientific Civil Service and ICI offered very much better working conditions. Finally he said that he wanted me to join him and if he could get me another £50 a year would I give a firm undertaking to accept the offer? I agreed, and never regretted the decision. In 1956, I transferred to one of ICI's main Divisional Research laboratories to study metal complexes as catalysts. Three weeks later there was a re-organisation of the management because the Division had decided to exploit the new fibre-reactive dyes that the Research Department had found. My new boss sent for me and said that the Division was not interested in my work. He gave me the option of starting dyestuffs research or leaving the Company, and he didn't mind which I chose. As there was really no choice, I started dyestuff research. Fortunately, I found that there were some good dyes which were cobalt and chromium complexes, so I worked on them. It turned out to be rather easy to make mixed-ligand metal complex dyestuffs. These gave tertiary shades at your whim, *e.g.* in an octahedral complex of chromium or cobalt, if three apices are occupied by a tridentate yellow chromophore and the other three by a blue the result is a green dyestuff. (Similarly, red plus yellow gives orange, *etc.*) Addition of a colourless reactive system to one of the chromophores then gives a fibre-reactive dye with excellent fastness properties. Useful, but trivial compared to what might have been. Seven years later, when Chatt left the Company, I was asked to take over the team that he would have led at the newly founded Corporate Research Labs., but by then the substantial time advantage we could have had was lost.

Joe Chatt and The Frythe were as great a success academically as Sir Wallace Akers, the ICI Director of Research responsible for setting up the laboratory, had hoped for, but people always ask, 'Did the Company get anything out of it?' They certainly did not get a mega-invention such as polythene (which had been developed in one of their Divisional labs.). There were certainly near-misses; at the Corporate Labs., Steve O'Brien found that zirconium tetra(π-allyl) was a

high-mileage catalyst for polythene. Somehow it didn't fit into the Company's operations, and the years dragged by. In the end, polythene was sold off, so the catalyst was never used.

The most disappointing miss for me, however, concerned Pharmaceuticals Division. While I was at The Frythe, I was responsible for sending samples of all the compounds we made to them for biological testing. Six months later and after well over a hundred compounds had been dispatched, we still had no results from them. I spoke to the man in charge of testing and he said that there were no results to send. None of the compounds was active so he hadn't thought it necessary to reply. In view of some of the elements that were contained in these compounds, it seemed surprising to me (as a non-expert) that none showed any activity. My opposite number replied that he was not a bit surprised as they normally tested thousands of compounds before they found one that was active. Keen to be sure, I asked whether not a single one had been of interest. It seems that one of them, a platinum complex, caused the test bacteria to swell up to many times their original volume, but that when the complex was washed out, the bacteria went back to their normal size. This compound was actually one I had made, *cis*-diammineplatinum dichloride! It seems that they already had so many other compounds with apparent potential that one exhibiting only 'temporary' activity was not of any great interest.

Squashed, I let it go at that. Years later, and especially when I found out the extraordinarily circuitous path by which cisplatin, the anti-tumour drug, was discovered, I realised with regret what an opportunity had been lost.

During the last years of The Frythe, some attempts were made to relate the chemistry to industrial problems and to surmount communications problems between The Frythe and the Divisions; for example, some staff from Divisional research labs. were seconded to The Frythe. They found that it was easier to make academic advances than to find useful new catalysts or processes. It was not realised that the evaluation and development work needed a much bigger specialist team than the pure chemistry research.

It was also decided to move responsibility for Chatt's group into the Heavy Organic Chemicals (HOC) Division, who were using the OXO process to make aldehydes with a cobalt catalyst and developing a process for vinyl acetate based on Wacker-type chemistry. At one of the liaison meetings, someone from Chatt's group mentioned an elderly Russian paper that described the catalytic activity of the platinum metals group and pointed out that rhodium was unusually active. The HOC chemists tried it and found that not only was rhodium more active than cobalt, so that milder conditions could be used, but that the product had a much more useful normal-to-iso ratio. There was only one snag: the existence of the Russian paper meant that the process could not be patented. However, the best efforts of the ICI physical and analytical chemists were unable to find any trace of rhodium in the polymer product so it was decided to keep the use of rhodium as a closely guarded secret. When Wilkinson published his famous paper on the rhodium catalyst that bears his name, there was an inscrutable smile on the face of the HOC chemists.

It may be said that the best reward for the Company as a result of setting up

The Frythe was the highly talented people who were attracted to join the company as a result of Chatt's work. Many of them later moved into academic life and a good number were appointed to Chairs. People from The Frythe and The Corporate Labs. who moved onto the industrial side also did very well. Two reached Directorial level inside the Company and several did equally well outside.

Was Sir Wallace Akers wrong to set up The Frythe as he did? In the sense that it proved unrealistic to expect the Divisions to see the possibilities for research that they themselves had not done, it may have been. On the other hand, it may take decades before an academic advance fructifies into a major invention. It is only now that we are beginning to see the emergence of new materials based on nanotechnology that are of great importance to the electronics and computing industries. Some of these are metal complexes and descendants of the chemistry that Chatt did so much to forward.

Sir Wallace's vision may thus still be realised, but it may not be ICI that benefits financially. This would not bother him unduly: his ultimate goal was to benefit mankind and the work at The Frythe most certainly did that.

Acknowledgements

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Recollections of Life with Joseph Chatt at The Frythe, 1958–62

DAVID M. ADAMS

One-time ICI employee at The Frythe

Joseph Chatt and The Frythe will always be associated in my mind, for it was there that I spent four and a half years in his Inorganic Research Group, a time of learning, fruitful collaboration, and real enjoyment for which I remain extremely grateful. Indeed, when ICI, our mutual employers, saw fit to close the Inorganic Group at the end of 1962, Joe and I were the last two members of the research group actually present on the final day, which I believe was Christmas Eve. The laboratories had been closed, and Joe had been banished for his few remaining days to a remote office upstairs in the old house that stood at the centre of the site. There it was that the two of us put the finishing touches to a paper for publication in *J. Chem. Soc.* It was the end of a remarkable era during which Joe had made outstanding contributions to the new field of transition-metal organometallic chemistry that had earned him election to the Fellowship of the Royal Society, as he became one of the UK's leading scientists, embellished the reputation of a none-too-grateful ICI, and launched a large group of co-workers into distinguished careers in industry and the academic world.

I had joined ICI at The Frythe in 1958 as a physical chemist, following a PhD plus post-doctoral year under the direction of one of the great scientists of the previous generation, Professor Sir Eric K. Rideal FRS. During my post-doctoral year I had applied infrared spectroscopy to the study of heterogeneous catalysts, which was then a technique in its infancy insofar as the field of catalysis was concerned. At that time we were able to study only the high frequency internal vibrations of the adsorbed species. A simple calculation based upon the entropy of adsorption showed that if we were to detect the stretching modes of the adsorbed species as it vibrated against its metal support, it would be necessary to work in what was termed the far-infrared, the region that lies between the infrared and microwave parts of the electromagnetic spectrum. No commercial instruments then existed for that region, so I began to design one.

It so happened that my daily travelling companion during that year was a

certain assistant lecturer at Imperial College, London, Dr Jack Lewis (now Professor Lord Lewis). One day he arrived on the railway platform with the news that a group in ICI was looking for someone to build an instrument to do far-infrared spectroscopy, and to apply it in transition-metal organometallic chemistry. Was I interested? About a week later I found myself in the delightful surroundings of The Frythe being interviewed by Joe Chatt and various of his co-workers. I was suspicious of entering industry, being bent on an academic research career, but the opportunity seemed too good to miss, and the money was good for those days – which was a consideration in only the second year of my marriage.

Joseph recognised early in his work on organometallic chemistry that structural and spectroscopic methods would be of particular importance to the field. It is greatly to his credit that he built in ICI a preparative organometallic research group with considerable strength in physical techniques of characterisation. Moreover, those of us on the physical methods side of the group were encouraged to work at the cutting edge of our respective fields and to pursue our own lines of research, whilst never forgetting that our primary reason for existence was support of the preparative studies.

During our time at The Frythe, X-ray methods were primitive by today's standards. Raw data were collected on film and then laboriously turned, spot by spot, into intensities. Rows of young ladies sat at mechanical calculating machines, processing the resultant numbers, writing each new result on a slip of card before moving to the next one. A single cycle of refinement could take three months. Not surprisingly, the same young ladies were notable for their liveliness at staff parties!

At such events Chatt was an avuncular presence. Unable to take an active part because of damage to his foot, he would hold court in a corner, telling anecdotes whilst sipping judiciously at a drink. Now and again, he and Ethel Chatt would invite the whole group to their home and these were always delightful times. They usually ended with extended viewings of Joe's slides from his latest American trip. On one such occasion, I recall him running back and forth through a series of slides on Niagara Falls and the related river system, until he was sure that all of us, from secretaries to senior section leaders, had grasped the details of the geology and hydrography of the region, meanwhile fielding hints from Ethel to the effect that, quite probably, these nice people had already grasped the essentials!

Life at The Frythe was good. The Frythe had a walled garden and many acres of surrounding land. During the Second World War it was used as a hush-hush research and development site by the Admiralty who, in particular, installed excellent machining facilities, and turned the walled garden into a car park. After the war ICI developed the site and built new state-of-the-art laboratories that were eventually occupied mainly by Joe Chatt's group. Complete with a reasonably well-stocked library, and a librarian, plus a good range of support staff, not to mention the absence of a teaching load, conditions for academic research were almost ideal. True, we lacked the daily contact with the wider community that a university affords, but conference attendance was encouraged and paid for, and

our daily tea and meal breaks were a fair approximation to the real thing. Our publication rate was the envy of many a university.

The Inorganic Group was not alone at The Frythe. There was a distinguished organic research group, also led by a Fellow of the Royal Society (Dr Bryant), which specialised in plant growth hormones, such as giberellins, and other natural products. These had obvious commercial prospects and therefore made the group popular with senior people in the Company. The site also housed the Industrial Hygiene Unit, a Company-wide resource entrusted with keeping an archive of data on chemical toxicities, especially with respect to ICI's manufacturing interests.

This mix of disciplines made for an interesting social life. Christmas celebrations at The Frythe always included devoting the final afternoon before closing for the festival to a concert party, more in the style of a pier show than a concert hall. The site harboured some remarkably talented individuals. In Joe's group alone we discovered one year a brilliant jazz pianist who could also act, and a gifted left-handed guitarist, recently joined from Oxford University, who announced in a bored voice that he was about to sing some madrigals that he had found in a dusty manuscript in the Bodleian Library. The music it is true, could have come from madrigals, but the words would have probably have been considered a shade too ripe even for *Carmina Burana*, although their inventiveness could not be faulted. One chronicled the exploits of a mediaeval knight, another the proclivities, ultimately tragic, of a warm-hearted Russian lady named Olga. The number of encores was a record.

Catering at The Frythe was of a high standard, being under the direction of a personable and somewhat formidable lady whose authority in her own field was fully the equal of Joe's in his sphere. My memory is of a constant stream of visitors of many nationalities to the Inorganic Group. Most of us would be called upon at some time to help out with this none-too-onerous task of entertaining, in the process becoming almost addicted to the standard Company tipple of gin and bitter lemon.

As a result of the supposed scientific standing and expertise of people in Joe's group, now and again one or more of us would be required to visit one of ICI's manufacturing Divisions for a spot of internal consulting. The conditions under which we travelled were in strict contrast to those most of us had left not far behind as research students. One set off from The Frythe, which was on the edge of Welwyn village, to the railway station in one of the Company's chauffeur-driven Rovers, all walnut fascia and leather upholstery. First-class tickets were permitted to those with five or more years service, or when travelling with a more senior employee, so one generally tried to engineer that. Met on arrival by another chauffeur, one would be whisked effortlessly to some dark satanic mill, there to do one's best, before the inevitable trek to the hospitality suite. It was a hard life.

Being experimental scientists, we also felt obliged to probe the limits of our expense accounts. This led on several occasions to strained interviews with senior staff, during which our scientific training in arguing a case and leading the reader to agree with our conclusions proved invaluable. It was never clear

whether or not the annual salary review was influenced by these discussions. Be that as it may, Joseph held the ultimate sanction within his Group of recommending whether, and, if so, how much, each of us was awarded annually, and he used it.

From time to time Joe would feel the urge to mount a small conference at The Frythe, generally aimed at widening our understanding of the field in which we worked. These were small, select affairs, with a distinguished visitor playing a key role. A. F. Wells, the noted crystallographer and a long-time employee of the Dyestuffs Division of ICI, was one such. He visited us not long before he was seduced to retire early and emigrate to the USA. Jack Lewis, then a lecturer at University College, delivered a series of lectures on physical-inorganic chemistry, with some emphasis on magneto-chemistry, all of which was very helpful as there was still not a lot in print at undergraduate level on that sort of thing. Leslie Orgel, then at the height of his fame at Oxford, was another welcome visitor, who also acted as a consultant before vanishing to California to study ageing before it was too late.

In retrospect, it was a remarkable time, a golden era, although probably few of us realised it then. Joe's group at The Frythe was just part of the tremendous world-wide renaissance of inorganic and organometallic chemistry, and a high proportion of those then involved, both in our group and elsewhere, later made it to positions of prominence and even glory. Being so close to London, it was easy to visit and participate in the Chemical Society meetings and conferences at Burlington House, Piccadilly, and therefore to meet most of the great and good as they passed through, or to drop into the Chemistry Department at University College, London for the latest news. There, Ron Nyholm, not yet an Fellow of the Royal Society, reigned genially over the Inorganic Department, and had gathered about himself an extraordinarily talented bunch of ex-patriot Aussies, every one of whom would later become distinguished in his own field. And probably as many research ideas were conceived at Schmidt's, a much-favoured German restaurant famous in season for its Strasbourg game pie, in nearby Goodge Street, as in the Department.

Now and again we would be caught up in some Company-wide scientific event. One of these jamborees was held at The Frythe about 1961. It included a banquet at a local restaurant that considered itself to be at the upper end of the market, a relative term even in those days. It so happened that one of the major scientific participants also doubled as the wine buyer for all the Company's canteens and hospitality suites. Service was good. We had all been served our main course and a glass of red wine when there was a commotion at the top table. Our wine buff had declared the vintage 'corked' and unsuitable for ICI employees. All of it was withdrawn and replaced. The manager was not a happy man, and there were more than a hundred of us in the party.

Quite early in the life of his group at The Frythe, Joe achieved a 'first' of considerable note in the field, and one that gave him much satisfaction. Specifically, he and Bernard Shaw synthesised the first complex metal hydride without supporting carbon ligands. This molecule contains a strong, stable metal-to-hydrogen bond, in this case platinum-to-hydrogen. A considerable series of

related platinum and palladium complex hydrides was made. The metal–hydrogen bond was shown to absorb infrared radiation near 2200 cm^{-1}, and to vary in frequency with the nature of the groups around the metal atom. Whilst this, together with other physical data, was convincing evidence of their claim, the final proof came in the form of an X-ray crystal structure analysis, also done in-house, and which itself was proof of Joe's foresight in establishing under one roof almost all the then-known physical methods needed for characterisation of organometallics.

This is not quite the end of the story. Joe's group was not alone in trying to make complex metal hydrides. Geoff Wilkinson, then recently arrived at Imperial College, London, following a distinguished period at Harvard and in the Atomic Energy programme, was also working on the problem. Joe achieved a double first in that he got into print ahead of the competition and, unusually for those days, provided the clinching evidence of the X-ray structure. Wilkinson was not happy. Having just come from Imperial College myself, I was able to give Joe the possibly apocryphal news that the Imperial College copy of the journal in which Joe's announcement appeared bore across his article the imprint of a muddy boot. True or not, it gave Joe a moment of the most exquisite pleasure, not to be repeated, to my knowledge, until the announcement of his Fellowship of the Royal Society.

Support services at The Frythe were excellent, and contributed greatly to the Group's research productivity, so much so that those of us who eventually returned to academia sometimes suffered re-entry problems. It was never necessary to chase an outside order: a man in the Purchasing Section did that automatically. Library services, glassblowing, machining and carpentry were all on tap. And there was that invaluable lower level of research help, the Assistant Experimental Officer (AEO) who might or might not be a graduate, available to do technically-demanding donkey work in support of the Group.

One such AEO underpinned the entire research effort of Joe's Group and was really the unsung hero of it. The principal stabilising ligands used in Joe's research were tertiary-, and sometimes di-tertiary- organophosphines. Synthesising these was generally far from trivial, particularly in the case of the di-tertiary members, all of which are highly air-sensitive and can be prepared only under an inert atmosphere. Due to their toxicity and penetrating smell, these materials were made in a downstairs laboratory lined with fume cupboards, dedicated to that purpose. There Mike Searle worked in glorious isolation. He devoted several years of his life to this task, becoming very expert in their production, and maintaining a steady supply of old and new types for the preparative team. As is inevitable in such work, Mike absorbed a proportion of these chemicals, probably though the skin. A tall, cheerful and convivial man with a strong West Country burr, he nevertheless found that this placed serious limitations on close social contacts of almost every kind.

Joe's election to the Fellowship of the Royal Society (FRS) gave much pleasure to the whole group, past and present. Many of us were headed for academic careers and it did us no harm to be seen to be part of such a distinguished team. Moreover, the superb conditions under which we worked had allowed us to

generate substantial numbers of publications that filled out our curricula and gave us a head start amongst our contemporaries.

Quite rightly, Chatt kept the pressure on in respect of getting our work into print. In part that was probably his way of keeping ICI's senior management quiet by pointing to the undeniable flow of publications in quality journals. In practice, none of us needed much urging as it was in our own interests as much as his and the Company's, to get the stuff out. The Company required us to issue each new paper first as an internal report (in green covers) that would be circulated within the Divisions for their perusal. Presumably this was to allow anyone within ICI to shout 'Hold it!' if they saw something of commercial value. Permission given, the paper would then follow the usual route into print. The number of publications from Joe's group was remarkable by any standards. I cannot quote a figure for the final tally, but I do recall a large set of filing shelves in his secretary's office, full from top to bottom with rows of reprints.

I remember the day the postman delivered the package of material that comes to every FRS upon his election. There were items bound in the classic maroon colour used by the Royal Society, there were things on parchment, a document to be filled in with his biographical details to form a factual basis for his eventual obituary, and goodness knows what else. He sat at his desk, dressed as usual in a smart suit of American origin, with these things spread out around him, doing very little but just quietly glowing with satisfaction, as well he might. And as we congratulated him again, his response was: 'There's no reason why any of you shouldn't do the same.' At least one did.

The powers that be at ICI acknowledged Joe's election to the Royal Society by throwing a banquet at their Millbank headquarters on the Thames, near the Houses of Parliament, and we and our wives all trooped down to celebrate. No expense was spared, and even the beer drinkers amongst us remarked on the quality of the wines served. Joe was not ICI's favourite son, but they were in a cleft stick and they did what was expected of them. True, the Main Board Research Director of the day, a lugubrious and inscrutable Scotsman, in a speech notable for the delicacy with which he placed his feet, did describe Joe as 'a complex character'. One had the suspicion that no double-entendre was meant.

Writing a paper for publication jointly with Joe was a process. The individual(s) concerned would write the first draft and have it typed, double-spaced. A copy went to Joe. In due time, one was called to his office and there would work through it, sentence by sentence, paragraph by paragraph, considering in turn the science, the accuracy of presentation, and the style. The majority of our work went to one or other of the journals of the Chemical Society, which at the time enjoyed the services of a senior editor of the old school whose mission in life was to train a generation of chemists in the correct, precise, and especially, concise use of English. I, personally, remain indebted to him for the training, although that was not the immediate response at the time.

Joe was a natural ally of the editor in this process, and he insisted that every detail be checked. I well remember one occasion on which two of us sat with him and were arrested at a sentence that contained the word 'co-ordination'. Joe thought that it should be written as 'coordination'. We instantly agreed with him,

having no axe to grind, and a pressing desire to go to lunch. We were rumbled. There followed an excruciating half-hour in which the three of us researched the use of the word: to this day I forget the outcome, but the trauma remains as fresh as ever!

A manuscript would commonly go through several revisions, being re-typed at each stage, complete with references. This, remember, was before the days of word processors, and copying machines were in short supply, so mostly we worked from carbon copies. Basically, secretaries were on the consumables budget! The final version of a manuscript would be checked for spelling and other infelicities by two or more of its authors, who were required by Joe to read the thing to each other in reverse word order, the theory being that since it made no sense that way, we would more readily spot the errors. Mostly it worked, although I do recall one instance in which a colleague and I had done just that. We took the faultless manuscript proudly to Joe, only to find that in our relief at completing the miserable task, we had failed to correct a typing error in the very first word. Joe was pleased!

Why did it end? Basically because the bean-counters in ICI couldn't see a return on their investment. Joe was never really at home in an industrial environment, not that The Frythe could even remotely be termed industrial in ambience. He was an academic to his fingertips and flourished in that atmosphere, as indeed he had done at Cambridge, and did later at Sussex University when he headed the Nitrogen Fixation Unit of the Agricultural Research Council. He never cultivated relationships within the company, finding the political side of life distasteful. Consequently, he was unprotected when a chill wind began to blow.

In retrospect, what was lacking in the Inorganic Research Group was any sustained attempt to develop applications of interest to the Company. Most of us in the group were new to organometallic chemistry when we joined Joe. It was an exciting time, being in at an early stage in a field that was taking off. There were so many new things to try, the Group was growing rapidly in international standing, and Joe was always flying off somewhere to spread the message. There *were* things that ICI could and should have profited from, but the Group was seen within the Company as too ivory tower, too far removed from the profit motive, and finding lucrative industrial applications was not Joe's forte or motivation. The Company should have added to the group personnel experienced in commercial development. In the end they just ran out of patience, and we ran out of time. But it was good while it lasted!

Joseph Chatt FRS: Some Memories of his Work at The Akers Research Laboratories of Imperial Chemical Industries Ltd, The Frythe, during the 1950s

L. A. DUNCANSON

One-time ICI employee at The Frythe

When given the opportunity to contribute to this publication commemorating the life and work of Joseph Chatt, three of his many attributes came immediately to my mind. First I remember his intense love of chemistry. Socially, Joe (as we referred to him informally) was hardly one to display his heart on his sleeve but in the research environment his passion for chemistry was an inspiration to all those fortunate enough to have the opportunity to collaborate with him. Secondly, I recall his outstanding empathy for people coupled with his profound understanding of human nature. Although his style of management was not flamboyant, he had a strong commitment to the personal well-being of his staff and to the development of their full potential as individuals. This, coupled with the creative working environment he provided, fostered a very strong sense of loyalty amongst the members of his research team whether they were *prima donna* scientists, laboratory technicians, or that unsung heroine, his secretary of many years, Inga Schmidt. Thirdly, I remember vividly Joe's sheer common sense and pragmatic approach to problem solving. It was always productive and rewarding to discuss, and argue, about scientific or other issues with Joe, and his counsel was always wise. In the 1950s it was not the fashion in industry to employ management consultants, but with people like Joe around they were not needed.

In short, Joe was not only a nice person but, in his quiet way, an excellent manager and a powerful scientific leader.

I was first made aware of Joe Chatt's work by the late Professor Ron Nyholm, one of his then sparring partners in the field of organometallic chemistry. Knowing that I wanted to marry the daughter of one of his Australian cricketing colleagues, but couldn't afford to on a part-time demonstrator's salary whilst wanting to continue with research, he suggested that I applied for a job in Imperial Chemical Industries at The Frythe. On arriving there I was asked to become an infrared spectroscopist, in support of the organic and inorganic chemistry being carried out in the laboratory. This turned out to be a most rewarding opportunity, not so much financially but in terms of exciting chemistry.

At that time one of Chatt's interests was the nature of bonding in olefin coordination to platinum. He was sure that the high mobility of ligands in the position *trans* to a coordinated olefin in square-planar platinum(II) complexes (the *trans*-effect) indicated a double bond between the olefin and the metal, involving a σ-bond between an electron pair of the olefin and a π-bond formed by back donation of electrons from a filled d-orbital of the metal. The infrared spectra of ethylene complexes were inconclusive regarding his original suggestion that the olefin had rearranged to form a methylidene radical in order to accept d-electrons into a vacant carbon orbital, producing a structure (CH_3–CH=Pt). However, propyleneplatinum(II) chloride was synthesised with some difficulty and found to have a strong absorption band in its infrared spectrum at 1504 cm^{-1}. This was easily assignable to a carbon–carbon double-bond stretching vibration. Re-examination of spectra of the ethylene complexes revealed only a very weak absorption band at this wavelength, indicating that the olefin was symmetrically bonded to the metal. This and other evidence led to the conclusion that the olefins were double-bonded to the platinum atom through sharing of the olefin's π-electrons to form a σ-bond and back donation of d-electrons into the vacant anti-bonding π-orbital of the olefin, similar to the structure proposed by Dewar for olefin complexes of silver ions. In the platinum(II) complexes the π-bond would be strengthened by hybridisation of a 5d orbital with a vacant 6p orbital of the metal.

Some time later, Rob Guy, whose chemical skills were much respected by the research team and who was also envied for his ability to charm ladies, managed to synthesise a range of acetylene complexes of platinum. Their infrared spectra indicated that bonding of the hydrocarbon to the metal was very similar to that in olefin complexes. Interestingly, it was observed that α-hydroxyacetylenes are chelated to platinum through interaction of oxygen lone-pair electrons with a vacant 6p orbital of the metal.

After this we embarked upon a comprehensive study of the infrared spectra of amine complexes of platinum and palladium. By we, I don't just mean Joe, the leader, and myself, but Alan Williams, George Gamlen, Bernard Shaw and last, but far from least, Luigi Venanzi who had the gift of being able to synthesise any compound you could think of which might have an interesting infrared spectrum. Incidentally I remember him not just for his chemical skills but as the most

outstandingly English Italian I have ever met. After he left The Frythe to become a fellow of Magdalene College Oxford, I vividly remember meeting him walking along The High with my very pretty baby daughter cradled in one arm and a furled umbrella on the other, not just looking the part, but actually being the perfect English gentleman.

The objective of the work we set out upon was to examine how the NH stretching frequencies of coordinated amines could provide information about the reactivity of transition metal complexes, with particular reference to the *trans*-effect. To be brief, let me just say that we measured the frequencies and absorption intensities of NH stretching modes in primary and secondary amine complexes of platinum and palladium containing a wide range of ligands in the position *trans* to the amines. These measurements led to the conclusion that the *trans*-effect operates by two mechanisms. First, an inductive effect upon the σ-bonding of the amine lone pair to the metal, but secondly a conjugative (mesomeric) effect involving the filled d-orbitals of the metal itself. These two factors influenced in different ways the mechanisms of substitution reactions of these coordination complexes.

We discovered also that there is inter-molecular hydrogen-bonding between the coordinated nitrogen atom of the amine and the Pt–Cl bonds of other molecules. We also observed a rather strange intermolecular hydrogen bond between the amine hydrogen atoms and the d-electrons of the coordinated platinum atom, whereby orbital following of the platinum d-electrons reduced the transition moment and hence the absorption intensity of NH stretching modes. In addition it was observed that conformational effects associated with restricted rotation about the Pt–N bond strongly influenced both the inter- and intra-molecular hydrogen bonding equilibria.

Although tempted, I will not bore the reader with more details of what still excites me personally as a rewarding field of research. Nor will I burden the typesetter with a lengthy list of references. The easy way to enrich and check the veracity of the above brief summary is to search under the key-words Chatt, Venanzi and infrared in the chemical literature of the 1950s and 1960s.

There followed many other exciting adventures involving studies of the infrared spectra of transition-metal complexes, but I will mention just one which I find particularly memorable. This followed the discovery by Bernard Shaw of a remarkably stable volatile platinum complex produced by reduction of $[PtCl_2(PEt_3)_2]$, the spectrum of which had a very strong and sharp absorption band near 2200 cm^{-1}.

This seemed only assignable to a Pt–H stretching vibration. Joe, being as rigorous as ever, was not completely convinced until a similar strong, sharp, absorption was found at 1600 cm^{-1} in the spectrum of the corresponding deuterium compound, precisely where expected from the mass difference between hydrogen and deuterium. The complex $[PtClH(PEt_3)_2]$ was the first in which the stretching frequency of a metal–ligand bond was observable in the spectral range available to us at the time. We used this to make direct measurements of the bond strength of a coordinate link. It was found that the Pt–H stretching frequencies of a range of hydride complexes with different anionic

ligands showed a strong correlation with the magnitudes of the anionic *trans*-effects as established by Chernyaev in 1927.

Incidentally, on this question of why are we what we are, I remember being told by a previous mentor, C. K. Ingold, that he took up chemistry because he had been told at Imperial College in the early 1900s that Maxwell had already finished physics! I would not want to enter into discussion about the relative impacts of Chatt and Ingold on chemistry, but in my personal opinion based on experience of both of them, they were level pegging in their research leadership qualities. Be that as it may, I welcome this opportunity to remember and record the strong bonds of affection and respect which I am certain all of my co-workers at The Frythe still have for Joseph, as I know his wife Ethel always preferred us to address him. I sincerely hope that, after all this time, she will forgive me for using the affectionate diminutive that seemed so natural to us all.

SECTION B:

Recent Developments in the Synthesis, Bonding Modes and Reactivity of Hydrido and Dihydrogen Complexes

Hydrido complexes of transition metals have been known since the early 1930s, largely from the pioneering work of Hieber on the preparation of the hydridometal carbonyls $[FeH_2(CO)_4]$, $[MnH(CO)_5]$ *and* $[CoH(CO)_4]$. *Subsequent work was driven in part by the recognition that transition-metal hydride complexes are important intermediates in a range of homogeneously catalysed reactions, such as synthetically and industrially important hydrogenations, olefin isomerisations and polymerisations, hydroformylations and hydrosilations.*

Chatt's discovery and characterisation of $[PtClH(PEt_3)_2]$ *and related complexes, reported first in 1957, and Wilkinson's report of* $[ReHCp_2]$ *in 1955 represent further major advances in transition metal hydride chemistry. Such work opened up the field which has led to a greater understanding of the structures, bonding, stereochemistry and reactivity of transition metal hydrides and of the nature of the metal–hydrogen bond. The discovery of* $[PtClH(PEt_3)_2]$ *arose serendipitously from attempts to obtain cyclobutadiene complexes of platinum*(0). *The product, an air stable, monomeric and sublimable solid which analysed as* $[PtCl(PEt_3)_2]$, *could also be isolated from aqueous solution from the reaction of* $[PtCl_2(PEt_3)_2]$ *with hydrazine. At the time, the oxidative and thermal stabilities of* $[PtClH(PEt_3)_2]$ *(it can be distilled unchanged at 130°C/0.01 mmHg) were unique. Typical thoroughness was shown in the structural and spectroscopic characterisation of these materials (as described above by Adams), including an early application of nuclear magnetic resonance spectroscopy (carried out in C.E.H. Bawn's laboratory at the University of Liverpool), a technique which has played a critical role in more recent developments. The availability of a large series of tractable complexes enabled the role of the hydride ligand to be fully characterised, including the demonstration of its high* trans-*effect and ligand field strength. The demonstration of the reaction of* $[PtClH(PEt_3)_2]$ *with ethylene to give* $[Pt(C_2H_5)Cl(PEt_3)_2]$,

another milestone in organometallic chemistry, followed shortly. It was known from the early work of Hieber and others that the hydrogen in metal hydride complexes can display both hydridic and protonic character. Crabtree summarises recent developments on metal hydride complexes in which interactions between hydridic and protonic hydrogens ('dihydrogen bonding' or 'proton hydride interactions') are evident. Chaudret and Ito describe further developments in the chemistry of the interaction of hydrogen and transition metals, including the synthesis, characterisation and reactivity of polyhydride, dihydrogen and silane complexes, particularly of ruthenium and molybdenum.

Hydrides, Hydrogen Bonding and Dihydrogen Activation

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1 Introduction

Chatt[1a] was one of the principal pioneers of hydride chemistry in the third quarter of the 20th century, when the chemistry of terminal and bridging hydrides was mainly developed. The area has expanded very greatly since the mid-1980s. The most important advance was the recognition that molecular hydrogen complexes ($M–H_2$) are not only common but can also have an important role in the reactivity of molecular hydrogen in metal complexes. Chatt[1b] was also a pioneer in bioinorganic chemistry, so it is of particular interest that M–H and $M–H_2$ intermediates have been proposed[2] as the key species in Ni-Fe hydrogenases, the enzymes that convert H_2 to protons and electrons.

As a result of my being a doctoral student in his group during his Sussex University period, our own subsequent work has been heavily influenced by the Chatt legacy. Of our first two problems at Yale, our work on hydride complexes started as a direct development of Chatt chemistry. It was the exceptionally high formal oxidation states and coordination numbers in metal polyhydrides that persuaded me that they must have some interesting physical or reactivity properties. As a testament to their hold on my attention, of the many fields we have tackled, this is the only area that has been a focus of continuous work from my very first paper,[3] resulting from undergraduate work in Malcolm Green's lab., right up to the present. The other area, C–H activation, was something Chatt held as an important goal for the future even if he had himself only carried out a few early but influential experiments in the field.[4]

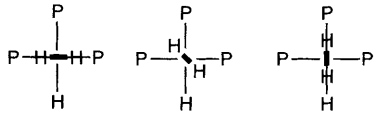
After completing our work on C–H activation in 1985,[5] we participated in the development of the chemistry of dihydrogen complexes[6] by showing their generality and that they can be synthesised by protonation of compounds with a terminal M–H bond (Equation 1).[7a]

$$[IrH_5(PCy_3)_2] + H^+ = [IrH_2(H_2)_2(PCy_3)_2]^+ \quad (1)$$

(Cy = cyclohexyl)

Such compounds can be hard to characterise by classical methods, so we suggested[7b] use of the excess T_1 relaxation of the hydride signal in the ^1H NMR spectrum as a criterion for M–H_2 binding. This work[7c] has long been published so in the present review we concentrate on developments in the hydride area since 1994, with the rise of dihydrogen bonding. This term refers to the attractive interaction between a protonic and a hydridic hydrogen in an M–H···H–N or M–H···H–O group. These interactions are distinct from classical hydrogen bonds,[8] A–H···B (AH = acid; B = base) in that the proton acceptor is an M–H hydride instead of a lone pair of the base, B.

The first indications in this area date from 1990, when attractive A–H···H–M interactions were first proposed to explain the close contact (H···H, 2.4 Å) between the IrOH proton and the Ir–H hydrogen in a neutron diffraction study of *cis*-[IrH(OH)$(PMe_3)_4$].[9] This H···H distance is rather long and about equal to the sum of the van der Waals' radii for two H atoms and so the interaction may be relatively weak. A truly short *d*(H···H) of 1.86 Å was found by neutron diffraction[10a] in *mer*-[Fe$(H)_2(H_2)(PEt_2Ph)_3$], a study originally carried out to test our earlier spectroscopic assignment[11] of this species as a dihydrogen complex. The H_2 ligand was found in a canted orientation that Eisenstein recognised from an extended Hückel analysis[7a] and from an *ab initio* calculation[7b] as a compromise (**2**) between **1** (H–H ⊥ to *cis*-Fe–H) that leads to the strongest back donation and **3** (H–H ∥ to *cis*-Fe–H) which leads to the maximal attraction between the protonic Fe–H_2 group and the hydridic Fe–H. She used the term '*cis*-effect' for this phenomenon, which can now alternatively be considered as dihydrogen bonding because of the very short H···H distance (1.86 Å).

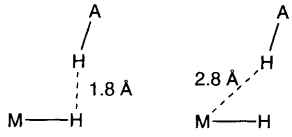


1 **2** **3**

From 1995, we and Morris' group found a long series of metal hydrides in which a transition metal M–H bond acts as the weak base (proton acceptor) in a hydrogen bond with OH or NH protons (= A–H) as the weak acid partners. This was shown by the short H···H distance (*ca.* 1.8 Å) and by studies that identified the A–H···H–M interaction strength as *ca.* 4–8 kcal mol^{-1}. Classical hydrogen bonds,[8a] A–H···B, require a lone pair on the base, B, and both A and B are electronegative. In A–H···H–M, the lone pair of the weak base, B, is apparently replaced by the M–H σ-bond, and both M and H are much more electropositive than the N, O or F atoms common in the classical type, so we have a new class of hydrogen bond. Morris[8b] has used an alternative descriptive term, proton–hydride interaction.

The conformational preference usually seen in compounds having a dihydro-

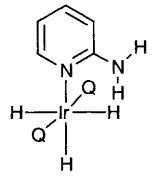
gen bonded H···H interaction is such that the NH or OH bond approaches the M–H bond in a side-on direction (as in **4**), although linear examples were also found in cases where conformational or steric effects hinder a bent geometry. Indeed, Eisenstein found in DFT calculations that the potential energy surface is rather flat, so distortions from the ideal geometry are not very costly.[12]



4 **4a**

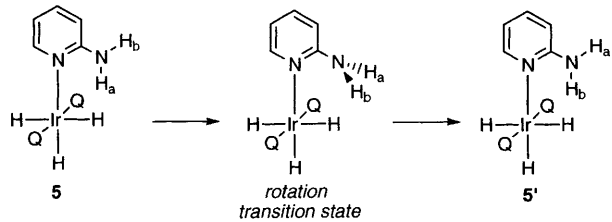
2 Intramolecular Interactions

The effect was easiest to study first in intramolecular cases because this allows NMR to be used to best effect. Complex **5** proved to be a useful test bed so as to get some idea of the energetics of the interaction.



5 (Q = PPh_3)

Our NMR method for estimating the H···H bond energy involves looking at the C–NH_2 rotation barrier by variable temperature NMR in species such as **5**. In the transition state for **5** → **5′**, shown in Equation 2, the H···H bond is broken and the energy for the delocalisation of the N lone pair into the pyridine ring is lost. We estimated the intrinsic C–N rotation barrier in the absence of dihydrogen bonding using a combination of experimental data and Hartree-Fock calculations. By measuring the barrier and subtracting our estimate of the delocalisation energy, we arrive at a reasonable estimate of the H···H bond energy: 5.0 kcal mol^{-1} for **5**.[13]



(2)

One of the *trans* hydrides in **5** can readily be replaced by any of a variety of anions, Y, to give **6** (Equation 3). Unlike **5** and **5′**, **6** and **6′** are not equivalent:

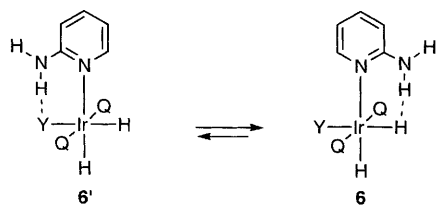
Table 1 *Some H···H bond strengths for* **6**

Y	*H···H bond strength (kcal mol^{-1})*
H^-	5.0
CO	3.7
CN^-	3.4
I^-	3.3
MeCN	3.1
Br^-	3.0
Cl^-	2.9
F^-	< 2.9

data taken from ref. 13

while **6** has an H···H hydrogen bond, **6′** has a classical H···Y hydrogen bond. Apart from the bond strength method used for **5**, estimates of the relative H···H/H···Y hydrogen bond strengths were also possible in this case from the ratio of **6** to **6′**. These two species can be distinguished by NMR spectroscopy at − 80°C in the equilibrium of Equation 3. The C–N rotation barriers and the resulting H···H bond strengths in **6** were very strongly dependent on the nature of the *trans* ligand, Y, indicating the presence of a substantial *trans* effect on the H···H interaction. Where Y is H^-, the H···H bond energy was highest (5.0 kcal mol^{-1}). When Y becomes more electron withdrawing, the H···H interaction energy falls until, for Y = F^-, the energy is < 2.9 kcal mol^{-1} (Table 1). Since H ligands *trans* to high *trans* effect ligands tend to be particularly hydridic,[14] this implies that a basic hydride is best for dihydrogen bonding, in accord with the electrostatic bonding model mentioned above. Epstein, Berke and co-workers[14] have recently used the *trans* effect of a nitrosyl *trans* to H to encourage particularly strong dihydrogen bonding in an intermolecular case.

The presence of the other isomer, **6′**, allowed the N–H···Y hydrogen bond strengths to be determined and, even for Y = F^-, this proved to be only just a little more (5.2 kcal mol^{-1}) than for the N–H···H–Ir bond where Y = H^- (5.0 kcal mol^{-1}). The system was designed to have a conformation that is most favourable for formation of an N–H···H–Ir dihydrogen bond, however, so there is probably some size mismatch for the larger Y groups. This may be largely compensated by the ability of the pyridine ring to rotate about the Ir–N bond and so move out of coplanarity with the H–Ir–Y group and allow hydrogen bonding even for large Y groups. Fluoride being very similar in size to hydride, however, a valid comparison is probably possible in this case.



(3)

From the decrease in hydrogen-bonding energies[8] on moving from the classical lone pair H-bond, N–H···(lone pair) {4–8 kcal mol^{-1}}, to the N–H···π case in which the proton acceptor is usually an arene π system, $\leqslant$ 2 kcal mol^{-1}, one might expect that any N–H···σ type, where the acceptor is a σ bond, would have a negligible bond energy < 1 kcal mol^{-1}. In contrast, we find N–H···H–E interaction energies of 4–8 kcal mol^{-1} which are almost as large as for the N–H···(lone pair) case. This requires E to be an electropositive element such as B or a transition metal, so that the hydrogen has significant hydridic character, and even then we usually also need a high *trans* effect ligand *trans* to the H in question. It is still not entirely clear why the dihydrogen bonding energies in species such as **5** are quite as large as we find, however. The H···H distance of 1.8 Å is essentially the same as the H···B distance in the classical hydrogen bond, so an unusually close approach of donor and acceptor atoms is not the critical factor.

We suggested fast T_1 relaxation as a criterion for the presence of close H···H distances in dihydrogen complexes, and Morris *et al.*[8b] and our own group[8c] have detected a substantial excess relaxation for H···H bonding. Making the usual assumptions, the excess T_1 in cases such as **5** and **6** can be interpreted in terms of an H···H distance of about 1.8 Å in all the cases studied, a value consistent with the structural data in related systems.

3 The Nature of A–H···H–E Hydrogen Bonding

In the first A–H···H–M hydrogen bonds found by us[8c] and by Morris,[8d] the weak acid AH was an acidic NH or OH group and M was a d^6 transition metal (*e.g.* **5**, **6**). Since a d^6 metal such as iridium(III) has d_π nonbonding electrons, these could in principle interact with the A–H proton (Figure 1). The reason the AH proton is always close to the MH hydride could be nothing to do with a proton–hydride interaction. Instead, the AH might in fact interact with these d_π nonbonding electrons adjacent to the M–H bond simply because H is the sterically smallest ligand present and allows the NH to approach the metal most closely. In that case, the A–H···H–E bond is really no different from the classical A–H···B

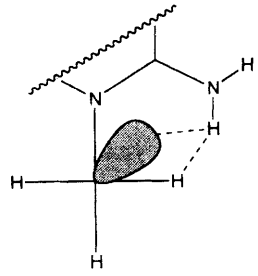


Figure 1 *Since the d^6 metals involved in the M–H···H–A interaction have d_π electrons, the hydrogen bond might have been of the classical A–H···(lone pair) type. The work discussed here suggests it is best described as an interaction between the AH proton and the H–M bond*

hydrogen bond and the true interaction is between AH and a nonbonded d_π electron pair on M (**4a**). On this idea, the H···H part of the interaction would be *repulsive.*

A study of $BH_3{\cdot}NH_3$ and its derivatives was useful to resolve this question because neither B nor N has nonbonding electrons. This approach suggested itself because a sample of this compound happened to be located in a prominent place in the laboratory. The striking feature of $BH_3{\cdot}NH_3$ is that it is a solid, unlike its isoelectronic analogues, such as C_2H_6. Indeed, its melting point of $+104\,^\circ C$ is almost 300 degrees higher than that of ethane (m.p., $-183\,^\circ C$). Such a large m.p. elevation is similar to that found for H_2O and CH_4, a classic case in which the difference is ascribed to hydrogen bonding, albeit of the classical variety.

In this study, the Cambridge Crystallographic Database (CSD) provided data on intermolecular N–H···H–B hydrogen bonds[15a] in a series of organic amine-boranes. The nature of the interaction proved essentially identical structurally in the transition metal and main group examples and so the d_π nonbonding electrons play no more than a minor role. The H···H distances in both main group and transition metal cases range from 1.7–2.2 Å, which should be compared with 2.4 Å,[18] the sum of the van der Waals' radii for two hydrogens.

At first we only found data for the organic derivatives. The unsubstituted example, $BH_3{\cdot}NH_3$, not being an organic compound, was in the *inorganic* database. According to the reported coordinates, it had an entirely different configuration from that shown in **4**. This species had been examined by X-ray crystallography on several prior occasions but the B–H···H–N configuration found was the reverse of the one in **4**: B–H···H appeared to be almost linear and N–H···H appeared strongly bent. In collaboration[15b] with Klooster and Koetzle of Brookhaven National Labs., we were able to look at $BH_3{\cdot}NH_3$ by neutron diffraction (Figure 2). By comparison of the neutron and X-ray work it was clear that the B and N had previously been misassigned as N and B, respectively; the true assignments produced a normal BHHN configuration as expected. The B/N assignment is definitive by neutron diffraction because the neutron scattering diameters are so different for the two nuclei.

A DFT calculation on the $BH_3{\cdot}NH_3$ dimer[15a] shows a conformation for the BH···HN group that is very similar to that of **4**. The H···H bond energy was calculated to be 6.6 kcal mol^{-1} per bond, comparable to that seen for transition metal dihydrogen bonding. The calculated charge distribution suggested that the BH bonds are polarised on forming the H···H interaction, which may help explain the relatively high interaction energy, and that the boron is more negatively charged than the hydride. The latter is consistent with the presence of a significant $B^-\cdots H^+$ component in the interaction, or alternatively, one could view the entire B–H bond as being the true proton acceptor. The H···H bonding is not entirely electrostatic, however, because $^1J(H^-\cdots H^+)$ coupling in the range 2–7 Hz is seen in the ^1H NMR spectrum of compounds such as **5** and **6**. Similar small couplings between the A–H proton and the base have recently been seen for classical A–H···B hydrogen bonds.[16]

Other theoretical work has proved valuable. Calhorda *et al.*[15c] found a large

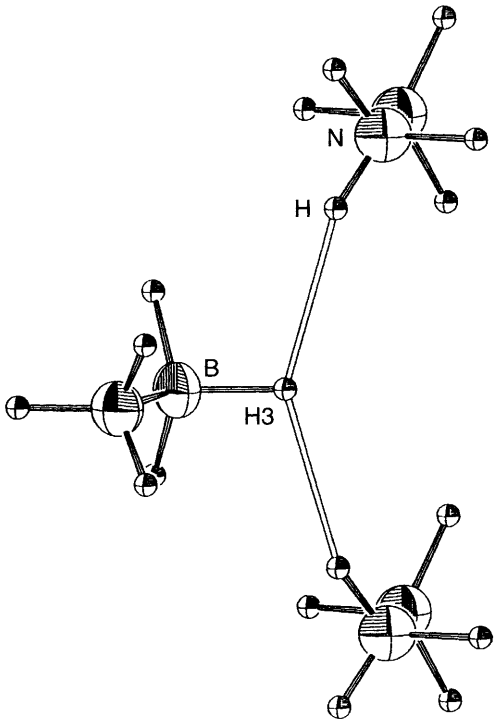


Figure 2 *The neutron diffraction structure of $BH_3{\cdot}NH_3$ showing intermolecular dihydrogen bonding*
Reproduced from ref. 15b with the permission of the American Chemical Society

number of complexes in the CSD database with short MH···H(O,N) distances and carried out a DFT study for $[(IrH(OH)(PH_3)_4]PF_6$ that concluded that the counter-ion must be included to obtain good agreement with experiment. Lledos, Eisenstein *et al.*[17] have written an excellent review on theoretical methods applied to hydride complexes.

4 Intermolecular Interactions

In **5** and **6**, the NH bond is held in a rigid chelate conformation and this could affect the conformation of the A–H···H–M substructure, so the metric parameters for such systems might be artefacts. In addition, the measured interaction energies for **5** and **6** might be affected by the rigid geometry. In an extreme revisionist interpretation, the whole dihydrogen bonding phenomenon might be considered an artefact.

To resolve this problem, we therefore studied intermolecular interactions such as are found when an acid HA co-crystallises with a metal hydride (M). In this

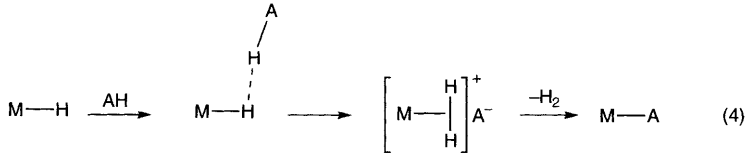
case, each moiety can find its most appropriate orientation in the co-crystal. However, in practice, HA and M most often crystallise separately, however. To favour co-crystallisation, we chose an acid, indole (**7**), that is a liquid and therefore cannot crystallise, and a base, $[ReH_5(PPh_3)_3]$ (**8**) that forms poor quality powders rather than good quality crystals on attempted crystallisation on its own; this gave satisfactory results. An X-ray structure by Rheingold confirmed the co-crystal formulation and suggested the H···H distance was short (< 2 Å). In one crystallisation attempt, large, very high quality crystals were obtained for the adduct between **7** and **8**. These allowed Koetzle and Albinati to obtain a high quality neutron diffraction structure.[12] This showed essentially the conformation **4** previously seen and confirmed that this was not a result of the constraints of chelation. The H···H distance of 1.73 Å in this structure remains the smallest to have been reliably determined. The value is much smaller than the sum of the van der Waals' radii for two hydrogens (2.4 Å).[18]

Energetics were also estimated for the intermolecular case. Approximate values were first found *via* IR spectroscopy with the modified Iogansen equation,[19] relating the low energy shift of the ν(NH) or ν(OH) band in the IR spectrum to the interaction energy. Applied[12] to $[ReH_5(PPh_3)_3 \cdot \text{indole}]$ (3.6 kcal mol^{-1}), and $[ReH_5(PPh_3)_3 \cdot ArOH]$ (5.6–5.8 kcal mol^{-1}), the results seem reasonable (Table 2). They agree quite well with UV–vis data from full equilibrium studies,[20] which give a ΔG of 5 kcal mol^{-1} binding energy for $[ReH_5(PPh_3)_2(C_5H_5N)]$ and indole.

Epstein, Berke *et al.*[14] have used the Iogansen method to obtain intermolecular association energies of *ca.* 5.5 kcal mol^{-1} between acidic alcohols such as $(CF_3)_2CHOH$ and the hydridic hydride, $[WH(CO)_2(NO)(PMe_3)_2]$. Equilibrium constants for the same systems gave an interaction energy of 4.9 kcal mol^{-1}.

5 Reactivity

Using the information discussed above, protonation of metal hydrides can now be considered as going *via* the following pathway (Equation 4).



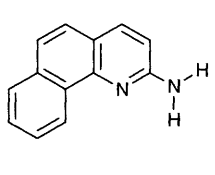
(4)

In one case, Chaudret and Sabo-Etienne[21a] have seen an equilibrium between $[RuH_2(dppm)_2]$ [dppm = bis(diphenylphosphino)methane] and a dihydrogen complex formed as a result of proton transfer from an alcohol such as $(CF_3)_2CHOH$ (Equation 5). Other related reactions have been reported.[21b]

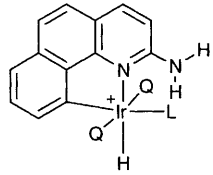
$$[RuH_2(dppm)_2 \cdot HOR] \rightleftharpoons [RuH(H_2)(dppm)_2]^+(OR)^- \qquad (5)$$

6 Intramolecular Effects of Pendant Groups

Enzymes often catalyse reactions because the hydrogen bonding and other reactive groups that surround the active site stabilise the transition state for the reaction. We felt that this biomimetic approach might usefully be extended to organometallic chemistry and we have now added pendant reactive groups to a cyclometallated benzoquinolate (bq) ligand in the hope of seeing binding and reactivity effects including ones resulting from hydrogen bonding. A variety of groups can easily be introduced at the 2-position of the benzoquinolinate. Cyclometallation of the bq gives species of type **9**, in which the amino group is adjacent to the site *trans* to the bq carbon, where a variety of ligands L readily bind. The rigid geometry prohibits the group from binding to the metal – it can only interact with the ligand L bound to the metal at the *cis* binding site.

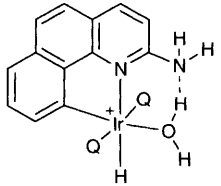


bqNH$_2$

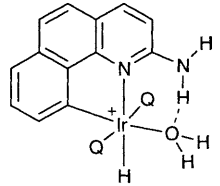


9

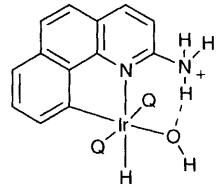
The labile aqua complex[22a] **9** (L = H_2O) is a very useful precursor in this area, but it was hard to characterise fully, even with an X-ray crystal structure, because the hydrogen bonding pattern remained ambiguous: out of **9a–c**, the experimental data led us to prefer **9a**, but only marginally.



9a



9b



9c

The DFT (B3PW91) calculations of Clot and Eisenstein[22b] predict that **9a** should be preferred. Subsequent to the DFT work, cooling of **9** to − 80 °C led to

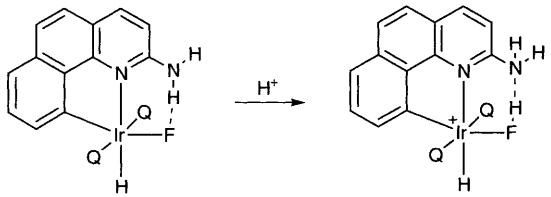
Table 2 *Some dihydrogen bond strengths (kcal mol^{-1}), deduced from Δν(NH) and Δν(OH) IR spectroscopic data, for intermolecular adducts of some d^0 and d^2 complexes with typical proton donors, indicating that direct X–H···M hydrogen bonding is not predominant; data taken from ref. 12b*

H-bond donor	$[ReH_5(PPh_3)_3]$	$[ReH_7$(dppe)][a]
indole	3.6	3.3
2,4,6-$Me_3C_6H_2OH$	5.6	4.7
d^n configuration	d^2	d^0

[a]dppe = 1,2-bis(diphenylphosphino)ethane

the water peak in the proton NMR spectra being resolved into a 1:1 pattern, consistent with structure **9a**.

The $bqNH_2$ system can also stabilise an HF complex – the first of its kind – by hydrogen bonding (**11**).[22] Protonation of the neutral fluoride (**10**) at $-80\,^{\circ}C$ in CD_2Cl_2 gave the new complex shown in Equation 6. The presence of a J(H,F) of 440 Hz in the NMR spectrum at $-80\,^{\circ}C$ is only consistent with the presence of a hydrogen-bonded H–F ligand. The J(H,F) in the parent **10** is a mere 52 Hz. The J(F,P) and J(F,H) couplings seen in **11** but with reduced values relative to the parent fluoride, **10**, indicate that the HF is still bound to the metal in **11**.



10 **11** (6)

The HF compound was too unstable to survive to room temperature or to be crystallised, so we were not able to obtain an experimental structure. The DFT (B3PW91) calculations[22b] predict the structure (Figure 3) and that the HF binds to the complex in a bidentate fashion involving a coordinate and a hydrogen bond of about equal strengths and with a total binding energy of 28.2 kcal mol^{-1}, a much larger value than when the NH_2 pendant group is replaced by H (18.0 kcal mol^{-1}) when no HF complex is detectable experimentally. The HF distance of 1.042 Å in **11** is only slightly elongated from free HF (0.922 Å) but the IrF distance elongates significantly from 2.123 Å in the fluoride **10** to 2.262 Å in the HF complex, **11**. The N···HF distance of 1.43 Å in **11** indicates it contains a very strong H-bond.

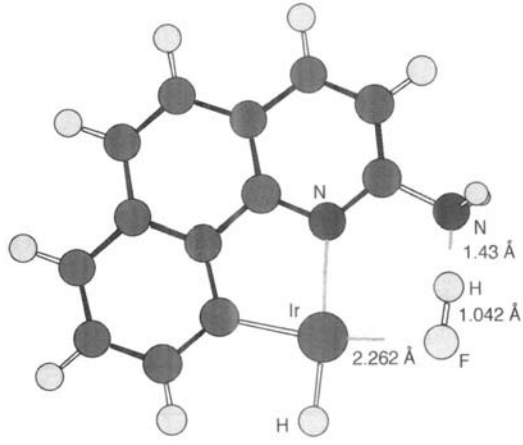
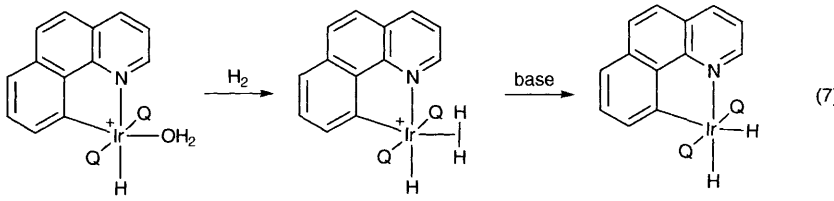


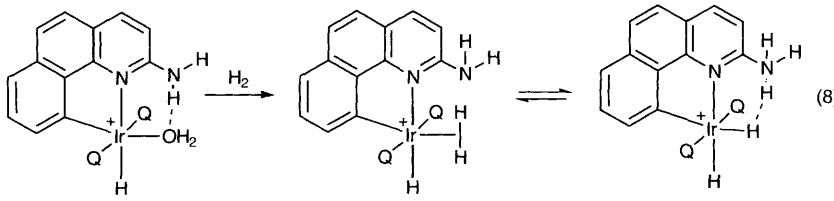
Figure 3 *The calculated structure for the HF complex* **11** *from DFT (B3PW91). Adapted from ref. 22b. PH_3 ligands not included*

7 Heterolytic H–H Activation

In order to identify the pendant group effects more securely, we have compared the behavior of the $bqNH_2$ complexes with analogues that lack a pendant group, that is, with the bqH derivatives. For example, in Equation 7, H_2 displaces water from the precursor to give a molecular hydrogen complex that is deprotonated by external base. In Equation 8, the corresponding situation with $bqNH_2$ and Q = PPh_3 yields the hydride **12b** where the coordinated H_2 has been deprotonated by the pendant amino group.[23]



(7)



(8)

12a **12b**

Clot and Eisenstein carried out DFT calculations on a model system with Q = PH_3 which predicted that **12a** should be stabler than **12b**, in contrast with experiment. To try to reconcile theory with experiment, we replaced the PPh_3 with the more basic phosphine PBu^n_3. The dihydrogen complex, **12a**, now proved to be the stable isomer. The same species **12a** was also seen for Q = $PMePh_2$ and PMe_2Ph. When the theoretical model PH_3 was replaced by weaker donors PFH_2, PF_2H and PF_3 in the calculations, **12b** became the stabler isomer, in line with experiment (Q = PPh_3).

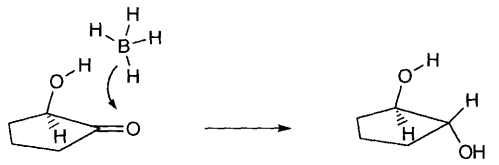
Since the Q = PCy_3 case shows splitting of the H_2, factors other than basicity seem to be at work here and we are continuing our studies on the problem to resolve the situation. The advantage of the joint theory–experiment approach is that in the absence of the theoretical result, we would not have gone beyond the PPh_3 case and would not have seen the M–H_2 isomer.

8 Consequences of H···H Bond Formation

Many metal hydrides protonate to give H_2 complexes,[24] but kinetic protonation can take place on M–H to give an M–(H_2) complex, even when protonation at the metal is thermodynamically favoured. Protonation of [FeH(dppe)Cp*] (Cp* = pentamethylcyclopentadienyl) gave the dihydrogen complex at $-80\,^{\circ}C$, followed by rearrangement to the dihydride at $25\,^{\circ}C$.[25] Kinetic protonation by

A–H at M–H is consistent with the presence of a dihydrogen-bonded A–H···H–M precursor adduct as intermediate. Proton transfer in the adduct gives the H_2 complex and conversion to the *trans*[16] dihydride is slower because motion[26] of the heavy atoms is needed.

Gatling and Jackson[27] have shown how dihydrogen bonding to an OH group of a hydroxyketone can direct the attack of borohydride to one face of the molecule; indeed, the product is 99.7% *trans* (Equation 9). The effect was suppressed by addition of F^-, a species that disrupts the hydrogen bonding. Under the conditions used, formation of an intermediate borate ester can be excluded.



99.7% *trans*

(9)

The role of dihydrogen bonding in stabilising the transition states for solid state reactions involving loss of H_2, such as in the thermal decomposition of triethanolamine/$LiBH_4$ or of $BH_3{\cdot}NH_3$ has been emphasised very recently both in experimental[28] and theoretical[29] work.

9 Conclusion

A combination of computational and experimental approaches gives an understanding of the proton–hydride interaction. This new type of hydrogen bond, the dihydrogen bond, is shown to influence the physical properties and reactivities of a number of main group and transition metal compounds. It seems to be important in cases of protonation of hydrides by acids HA.

10 Acknowledgements

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Hydrides and Dihydrogen Ruthenium Complexes: a Continuation of Joe Chatt's Chemistry

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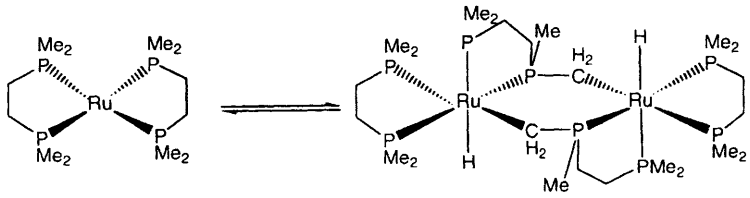
1 Introduction

Joe Chatt has been a pioneer of modern organometallic chemistry involving transition metal phosphine derivatives and in particular hydride complexes. In this article, we will emphasise the link between the pioneering work of Joe Chatt and the present interest in σ-bond complexes and their reactivity. This article concentrates on the chemistry of ruthenium derivatives and is divided into a brief historical overview, giving a perspective of the evolution of the chemistry of ruthenium hydride complexes and a part describing recent achievements in this field, mainly from our research group.

2 Historical Aspects

The first transition metal hydride $[FeH_2(CO)_4]$ was discovered by Hieber in 1931,[1] but the organometallic chemistry of metal hydrides really started in the mid-fifties with the synthesis of $[ReHCp_2]$ by Geoffrey Wilkinson *et al.*[2] and of $[PtClH(PEt_3)_2]$ by Joe Chatt *et al.*[3] The ruthenium hydride phosphine chemistry, which is rich in a great number of catalysts for a variety of organic transformations, started with a family of octahedral complexes of general formula $[RuClH(chel)_2]$ (chel = a chelating dihapto ligand such as dmpe [1,2-bis(dimethylphosphino)ethane], depe [1,2-bis(diethylphosphino)ethane], diars [1,2-bis(dimethylarsino)benzene], *etc.*) reported in 1961 by Chatt and Hayter.[4] These compounds have been used as starting materials for a variety of deriva-

tives among which are the hydrido alkyl and aryl complexes $[RuRH(chel)_2]$ and the dihydrides $[RuH_2(chel)_2]$.[5] The latter was the first polyhydride of ruthenium. Among the compounds described in the early report of 1961 was the ruthenium(0) complex, $[Ru(dmpe)_2]$ able to undergo the tautomeric equilibrium described in Scheme 1. This reaction is remarkable in several respects: (i) it is an early example of a C–H activation reaction and led the DuPont group of Ittel, Tolman and co-workers to study in detail C–H activation processes in the late seventies;[6] (ii) the reaction is far from being straightforward and implies an approach of the two ruthenium centres and presumably the presence of an intermediate in which C–H bonds of one ruthenium centre are weakly coordinated to the other centre; (iii) it is also remarkable that the weak C–H interactions present in the intermediate lead to a modification of the geometry at ruthenium with the diphosphines now coordinated *cis*. This behaviour can also be described as an early example of 'molecular recognition'.



Scheme 1

The development of homogeneous catalysis, following, for example, the demonstration of the hydrogenation of olefins by $[RhCl(PPh_3)_3]$,[7] and the need for available coordination sites has led to the synthesis of ruthenium complexes accommodating different monophosphines, and in particular PPh_3. The first complex in the series was $[RuCl_2(PPh_3)_3]$.[8] This complex displays an interesting early example of a weak C–H agostic interaction blocking a coordination site. Such interactions are evidenced by X-ray crystallography but are usually difficult to characterise by other methods, such as NMR, since the coordination energy of the C–H group is usually very low. However, recent NMR investigations have demonstrated the presence of such interactions in several cases, including a ruthenium phenylpyridine complex described hereafter.

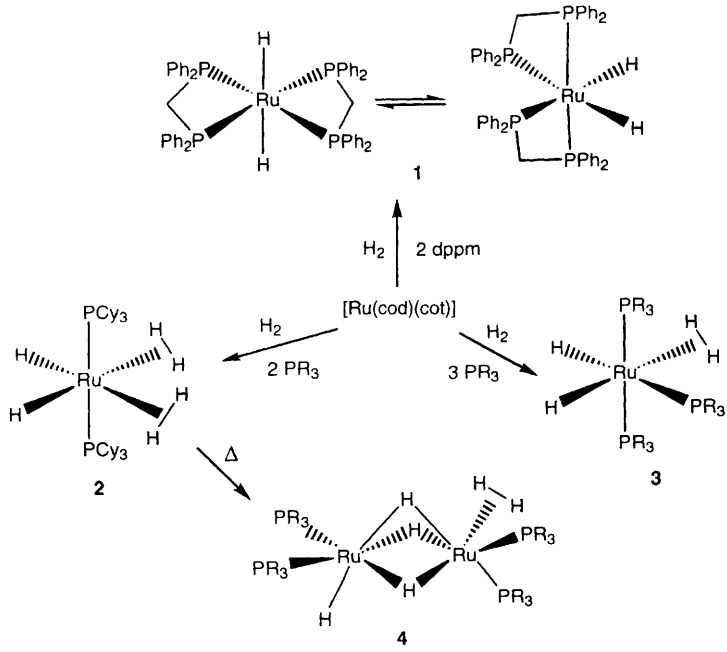
In order to investigate the mechanism of hydrogenation reactions, hydride complexes were synthesised, including $[RuClH(PPh_3)_3]$,[9] a fast and selective catalyst for olefin hydrogenation. This was followed by the synthesis in 1970 by the group of Yamamoto of the dihydride $[RuH_2(PPh_3)_4]$ analogous to $[RuH_2(chel)_2]$, but which, thanks to the easy dissociation of triphenylphosphine, was found to be an extraordinary precursor for inorganic and organometallic complexes as well as a catalyst for many organic transformations.[10] However, the presence of four triphenylphosphine ligands on $[RuH_2(PPh_3)_4]$ was a problem in some reactions. Other attempts to produce polyhydride derivatives led in the early seventies to the synthesis of two other complexes, $[RuH_4(PPh_3)_3]$[11] and $[RuH_2(N_2)(PPh_3)_3]$.[12] The tetrahydride exhibited characteristic features of polyhydrides such as $[IrH_5(PPh_3)_3]$ or $[ReH_7(PPh_3)_2]$, popular at that time. However its high field ^1H NMR spectrum showed only a broad signal and its reactivity was similar to that of the dinitrogen compounds and resulting from an

easy dissociation of one mole of dihydrogen from the complex. Similar observations on cationic ruthenium trihydrides led Singleton to propose that dihydrogen could exist as such in the coordination sphere of ruthenium compounds.[13]

The need for highly reactive complexes which could also be precursors of transient species displaying a very low coordination number led us in 1982 to the synthesis of the 'hexahydride' $[RuH_6(PCy_3)_2]$ (Cy = cyclohexyl).[14] One of the major goals was the generation of active species for C–H activation reactions. The characterisation and reactivity of this compound and of related species towards σ-HX bonds (X = H, C, Si) will be briefly presented in the section below.

3 Ruthenium Hydride and Dihydrogen Complexes

During the early eighties, we developed a strategy for synthesising new hydride derivatives, controlling precisely the quantity of phosphines added. This is based on the hydrogenation of the zerovalent precursor [Ru(cod)(cot)] (cod = cycloocta-1,5-diene; cot = cycloocta-1,3,5-triene) in the presence of the desired amount of ligands. The complexes $[RuH_2(dppm)_2]$ (**1**) [dppm = bis(diphenylphosphino)methane],[14] $[RuH_6(PCy_3)_2]$ (**2**),[14a,15,16] $[RuH_4(PR_3)_3]$ (R = Cy, **3a**; Pr^i, **3b**)[15] and $[Ru_2H_6(PR_3)_4]$ (R = Cy, **4a**; Pr^i, **4b**) were prepared in this way.[15] The demonstration by Kubas in 1984 of dihydrogen coordination without dissociation in $[M(CO)_3(H_2)(PCy_3)_2]$ (M = Mo or W)[17] and the reinvestigation of the structure of $[RuH_4(PPh_3)_3]$ which led Crabtree to propose the formulation $[RuH_2(H_2)(PPh_3)_3]$[18] prompted us to reconsider the structure of complexes **2**–**4** (see Scheme 2).



Scheme 2

3.1 $[RuH_2(dppm)_2]$, Dihydrogen Bonds and Proton Transfer

$[RuH_2(dppm)_2]$ is another example of bis(chelate) derivatives similar to those originally reported by Chatt and co-workers. The compound exists as a mixture of the *cis*- and *trans*-isomers, which are in equilibrium at room temperature in solution.[14] It was found in the eighties to be a good precursor for heterobimetallic derivatives, the best examples being $[RuRhH_3(dppm)_2]$[19] and $[RuMoH_2(CO)_4(dppm)_2]$.[20]

In contrast to other complexes of general formulation $[RuH_2(chel)_2]$ which can be easily protonated to yield a series of *trans* hydrido dihydrogen derivatives, $[RuH(H_2)(chel)_2]^+$,[21] $[RuH_2(dppm)_2]$ does not produce a stable dihydrogen complex upon protonation, but leads after dihydrogen evolution to the cationic monohydride $[RuH(S)(dppm)_2]^+$ (S = solvent). However, we have recently studied the interaction of $[RuH_2(dppm)_2]$ with phenol in toluene solution and demonstrated the presence of hydrogen bonding between one hydride and phenol and, moreover, the presence of a dynamic proton transfer at low temperature ($< -30°C$):[22]

$$\textit{trans}\text{-}(dppm)_2HRuH \cdots HOPh \rightleftharpoons [RuH(H_2)(dppm)_2]^+(OPh)^-$$

The reaction is reversible and upon allowing the solution to warm to room temperature the dihydride is quantitatively recovered. This reaction is interesting for several reasons: (i) it was the first NMR observation of such a dynamic proton transfer; (ii) this method allows the observation of unstable species otherwise not detectable; (iii) this reaction is specific since only the *trans*-isomer reacts with phenol.

We have extended this method to another complex: $[RuH_3(PCy_3)Cp^*]$ (Cp^* = pentamethylcyclopentadienyl). This complex was the first derivative reported to display 'quantum mechanical exchange couplings', a consequence of the *ortho–para* transition of dihydrogen which is observable by NMR when the barrier to exchange of two hydrogens is sufficiently low (*ca.* 10 kcal mol^{-1}).[23] Addition of an acidic alcohol to this complex induced hydrogen bonding between a hydride and the alcohol proton. This kind of interaction thus modifies the exchange barriers of the hydrogens and therefore the magnitude of the exchange couplings. We can in this way classify the strength of the hydrogen bonding interaction of various alcohols, the strongest ones being observed with the most acidic alcohols, namely hexafluoro-isopropanol and nonafluoro-*tert*-butanol. In this case, proton transfer was observed at low temperature to give the otherwise inaccessible complex $[RuH_2(H_2)(PCy_3)Cp^*]^+$.[24]

3.2 $[RuH_2(H_2)_2(PCy_3)_2]$ (2)

Complex (**2**) has long been the only thermally stable derivative containing two dihydrogen ligands and one of the few complexes containing two coordinated σ-bonds. Its infrared spectrum displays two bands of strong intensity, presumably because of the coupling between the Ru–H and $Ru–H_2$ stretches. The X-ray crystal structure of the compound was solved recently and, although an ambiguity concerning the real space group of the molecule remains, the refinements in

both the symmetrical (P1) and unsymmetrical ($P\bar{1}$) space groups are consistent with the dihydride bis(dihydrogen) formulation.[25] The presence of dihydrogen ligands is confirmed by NMR (T_1 measurements) and by inelastic neutron scattering (INS). The use of the latter technique for the characterisation of dihydrogen complexes was developed by Eckert. It involves the measurement of the *ortho–para* transition of dihydrogen and allows an estimation of the rotation barrier of dihydrogen, which in the present case is close to 1 kcal mol^{-1}.[26]

$[RuH_2(H_2)_2(PCy_3)_2]$ (**2**) has been found to be a very efficient starting material for the preparation of a great variety of new ruthenium hydride derivatives, in particular those accommodating σ-bonds.[16] We will not describe all the chemistry of this compound but concentrate on four examples: hydrogen transfer and metallation reactions, reactions with halocarbons, reactions with proton donors and reactions with silanes, and in each case related reactions.

3.3 Hydrogen Transfer and Hydrocarbon Activation

The coordinated dihydrogen molecules of **2** may be easily substituted sequentially to give a variety of new hydride and dihydrogen derivatives. The dihydrido(dihydrogen) complex $[RuH_2(H_2)(PCy_3)_3]$ can thus be obtained by substitution of H_2 by a phosphine or directly from [Ru(cod)(cot)]. This compound and the analogous $[RuH_2(H_2)(PPr^i{}_3)_3]$ lose reversibly a phosphine in solution to give a transient species $\{RuH_2(H_2)(PR_3)_2\}$ (R = Cy, Pr^i) able to catalyse rapid H/D exchange between the deuterium of C_6D_6 and the protons of the phosphine ligands.[16] This behaviour suggests a high potential for C–H activation reactions, confirmed by the reaction with ethylene. Thus, after substitution of H_2, we can observe in the presence of excess ethylene the sequential dehydrogenation at room temperature of cyclohexyl groups present on **2** to give $[RuH(C_2H_4)(PCy_3)(\eta^3\text{-}C_6H_8PCy_2)]$ (**5**).[27] In the presence of 3,3-dimethylbut-1-ene, it is possible to isolate successively $[RuH_3(PCy_3)(\eta^3\text{-}C_6H_8PCy_2)]$ which is better described as a monohydride complex accommodating a stretched dihydrogen ligand (see Figure 1)[28a] and $[RuH(\eta^3\text{-}C_6H_8PCy_2)(\eta^2\text{-}C_6H_9PCy_2)]$ in which both phosphine ligands have been dehydrogenated.[28b] Interestingly, **5** has been found to be an excellent and selective catalyst for the dehydrogenative silylation of ethylene.[27]

3.4 16-Electron Hydrido(dihydrogen) Complexes: Reactions of $[RuH_2(H_2)_2(PCy_3)_2]$ with Halocarbons and Related Reactions

After substitution of H_2, addition of CH_3I to **2** produces the 16-electron dihydrogen complex $[RuHI(H_2)(PCy_3)_2]$.[29] Analogous complexes of general formulation $[RuHX(H_2)(PCy_3)_2]$ (X = Cl or SR) have been obtained from the reaction of **2** with dichloromethane and thiols. $[RuHI(H_2)(PCy_3)_2]$ reacts with an excess of dihydrogen to give the following equilibrium which can be detected by NMR:[30]

$$[RuHI(H_2)(PCy_3)_2] + H_2 \rightleftharpoons [RuHI(H_2)_2(PCy_3)_2]$$

Further reaction with chloroform produces the ruthenium(IV) dihydride

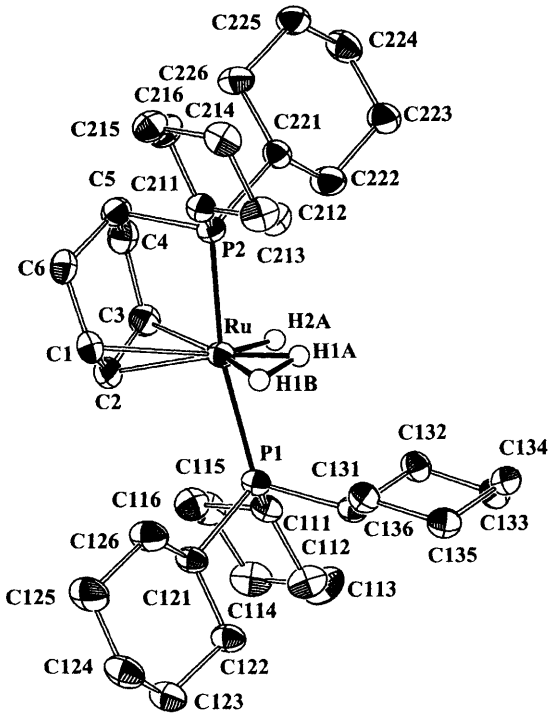


Figure 1 *Molecular structure of* $[RuH(H_2)(PCy_3)(\eta^3\text{-}C_6H_8PCy_2)]$

$[RuCl_2H_2(PCy_3)_2]$ which exists as a mixture of isomers and in equilibrium with the ruthenium(II) dihydrogen derivative $[RuCl_2(H_2)(PCy_3)_2]$. Interestingly, Caulton has recently reported that the prolonged reaction of **2** with CH_2Cl_2 produced the carbene complex $[RuCl_2(PCy_3)_2(=CH_2)]$,[31] a member of Grubbs' carbene family, and an excellent precursor for metathesis and ROMP reactions.[32]

3.5 18-Electron Hydrido(dihydrogen) Complexes, Proton Transfer and C–H Activation

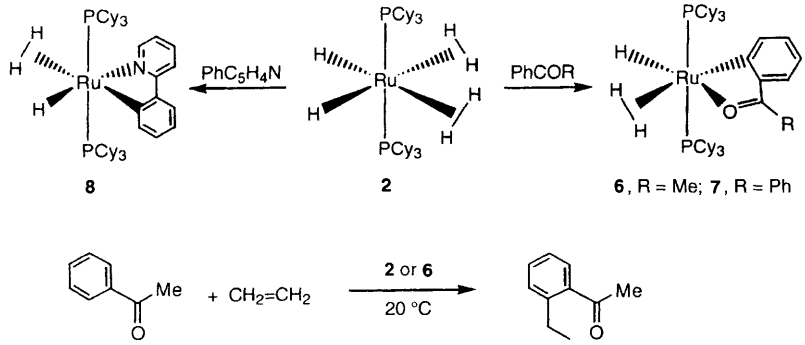
Addition of proton donors to $[RuH_2(H_2)_2(PCy_3)_2]$ gives, after substitution of the two dihydrogen ligands, new hydrido(dihydrogen) derivatives, as is the case with carboxylic acids:[33]

$$[RuH_2(H_2)_2(PCy_3)_2] + RCOOH \rightarrow [RuH(H_2)(OCOR)(PCy_3)_2] + 2\,H_2$$

Similar reactions were carried out with various good σ-donors which are also proton donors such as hydroxo-, amino- or thio-pyridine or quinoline (HE–L) thus producing a new series of complexes $[RuH(H_2)(E\text{-}L)(PCy_3)_2]$ in which, because of the high electron density induced by the presence of these ligands, a significant vibrational mode of the H–H bond is observed in the IR

spectrum. In addition, an H–H distance of *ca.* 1.3 Å was calculated for $[RuH(H_2)(OC_5H_4N)(PCy_3)_2]$ from the relaxation time T_1 of the hydride signal and from the H–D coupling constant observed after partial deuteration of the compound.[34]

Analogous reactions of **2** were carried out with phenyl derivatives, *viz.* acetophenone, benzophenone or phenylpyridine, to give, after activation of a C–H bond, complexes containing a metal–carbon bond. A series of compounds of general formula $[RuH(H_2)(PCy_3)_2(C_6H_4R)]$ (R = COMe, **6**; COPh, **7**; C_5H_4N, **8**) were prepared in this way (see Scheme 3). The chemistry of these compounds is very rich but that of the complexes of nitrogen donors (**8**, and also the analogous triisopropylphosphine complex $[RuH(H_2)(PrP^i_3)_2(C_6H_4C_5H_4N)]$ (**9**) and the corresponding benzoquinoline derivative) is very different from that of the oxygen donors.[35]



Scheme 3

Dihydrogen can be eliminated from **9** to give the 16-electron species $[RuH(PPr^i_3)_2(C_6H_4C_5H_4N)]$ or substituted by various small molecules to give $[RuH(L)(PPr^i_3)_2(C_6H_4C_5H_4N)$ (L = N_2, O_2, CO or C_2H_4). Ethylene can easily be removed from the last complex but no sign of insertion into the Ru–H or Ru–C bonds is observed.

This is in marked contrast with the reactivity of **6** and **7** which catalyse the insertion of ethylene into the *ortho* C–H bond of the phenyl ring of acetophenone and benzophenone (see Scheme 3). This reaction has been previously described by Murai using various ruthenium catalysts, the most efficient being $[RuH_2(CO)(PPh_3)_3.]$[36] It is derived directly from the early metallation reactions of Joe Chatt and displays a high potential in organic synthesis. Moreover, it avoids the production of salts which are the by-products of similar alkylation or arylation reactions such as Heck or Suzuki couplings. However, Murai's reaction operates at 130 °C probably because of the need for the complex to eliminate one PPh_3 and one CO ligand for the reaction to proceed. Our system operates at room temperature but the drawback is the formation of the inactive bis(metallated) complex $[Ru(PCy_3)_2(C_6H_4COR)_2]$.[35b]

$[RuH(H_2)(PPr^i_3)_2(C_6H_4C_5H_4N)$ can be protonated to give a new complex, $[RuH(H_2)(\mathit{H}\text{-}C_6H_4C_5H_4N)(PPr^i_3)_2]^+$ (**10**), accommodating two σ-bonds: a dihydrogen molecule and an aromatic C–H bond (Figures 2 and 3).[37] The agostic phenyl ring exhibits a hindered rotation process on the NMR time-scale

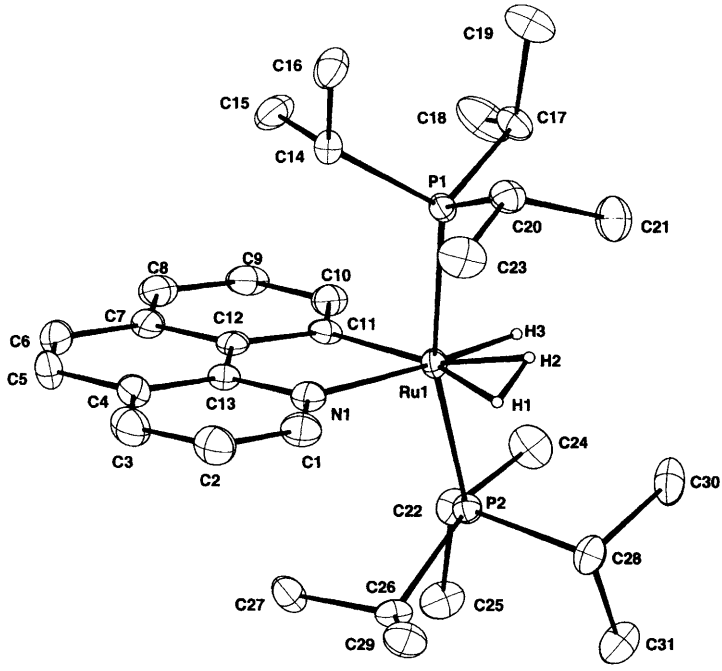


Figure 2 *Molecular structure of* $[RuH(H_2)(PPr^i_3)_2(C_6H_4C_5H_4N)]$ **(9)**

with a barrier of activation, $E_a = 35.6 \pm 1.8$ kJ mol^{-1}; $\Delta G^{\ddagger} = 42.0 \pm 5.6$ kJ mol^{-1} at -30°C. This barrier represents the maximum value of the bonding energy of the C–H bond to ruthenium. Interestingly, the corresponding carbonyl complex $[\overline{RuH(CO)(PPr^i_3)_2(H\text{-}C_6H_4C_5H_4N)}]^+$ shows a similar process with a higher rotation barrier: $E_a = 44.5 \pm 1.8$ kJ mol^{-1}. Since all other electronic and steric factors of the ligands are strictly the same, this result demonstrates the better π-accepting properties of CO which allow a stronger coordination of the agostic C–H bond.

10 undergoes a reversible proton transfer process in thf to give the metallated dihydrogen derivative $[Ru(H_2)(thf)(PPr^i_3)_2(C_6H_4C_5H_4N)]^+$ according to the following equation:

$$[\overline{RuH(H_2)(PPr^i_3)_2(H\text{-}C_6H_4C_5H_4N)}]^+ \underset{H_2}{\overset{thf}{\rightleftharpoons}} [Ru(H_2)(thf)(PPr^i_3)_2(C_6H_4C_5H_4N)]^+$$

This process occurs through the transient formation of a cationic bis(dihydrogen) complex which rapidly loses H_2. This is a facile C–H activation reaction, the mechanism of which may involve either a classical oxidative addition or a direct proton transfer from carbon to hydride, a process analogous to σ-bond metathesis. However, DFT calculations by Eric Clot strongly suggest the occurrence of a ruthenium(IV) derivative in the transition state and therefore of a classical oxidative addition process.[37]

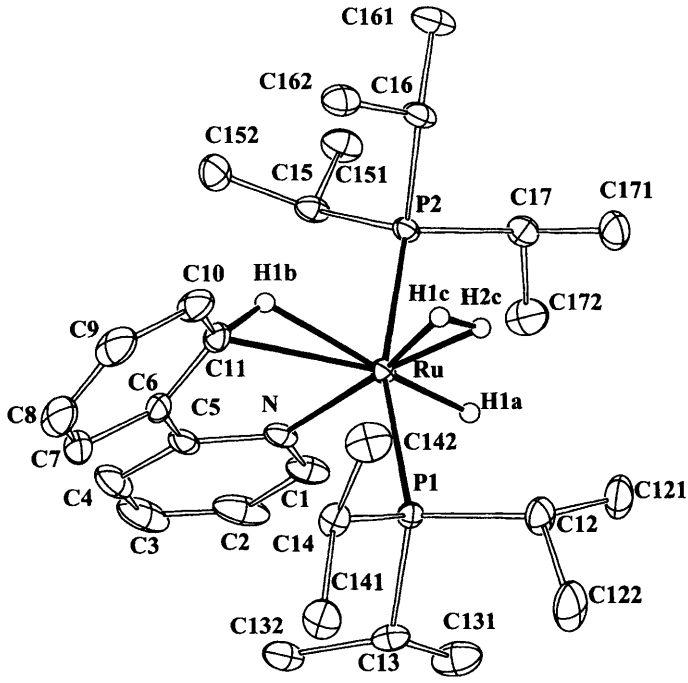
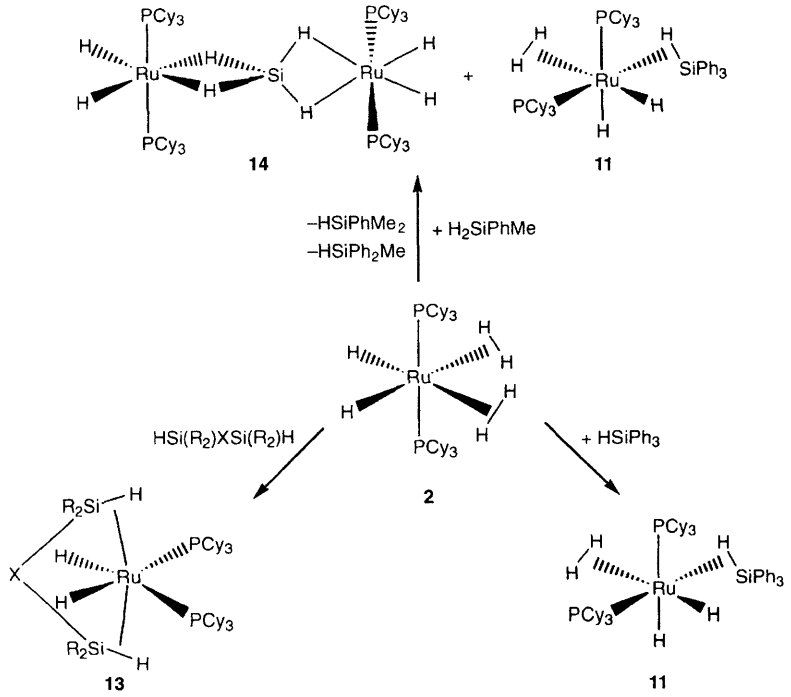


Figure 3 *Molecular structure of* $[\widetilde{RuH(H_2)(H}\text{-}C_6H_4C_5H_4N)(PPr^i_3)_2]^+$ **(10)**

3.6 Silane Complexes and Substitution Reactions of $[RuH_2(H_2)_2(PCy_3)_2]$

As observed earlier, the dihydrogen ligands of **2** are very labile and can be reversibly substituted by weakly coordinating ligands, dihydrogen evolution to the gas phase being the driving force of the reaction. For example, this is possible with N_2; the complex $[RuH_2(N_2)_2(PCy_3)_2]$ can be isolated and the mixed $[RuH_2(H_2)(N_2)(PCy_3)_2]$ may be observed.[38] No evidence for hydrocarbon adducts has been obtained but the reaction with bulky silanes leads cleanly to the substitution of one dihydrogen molecule to give complexes accommodating both a H–H and a Si–H σ-bond, such as that with triphenylsilane $[RuH_2(H_2)(HSiPh_3)(PCy_3)_2]$ (**11**) (see Scheme 4). This complex has been characterised by different techniques including X-ray crystallography at low temperature.[39] The most unexpected aspect of this structure is the bending of the P–Ru–P angle. It is close to 180° in **2** and decreases to 109.71(5)° in **11**. This is associated with additional weak interactions between the terminal hydrides and silicon, one 'non-bonding' Si ··· H distance being very short: 1.83(3) Å. The molecule was modelled by Barthelat and co-workers[39] who clearly evidenced the presence of two additional weak Si–H interactions in the complex which stabilise the bent form at the expense of the expected *trans* configuration. According to the level of calculation, the bent form is more stable by *ca.* 8–17 kJ mol^{-1}. A



Scheme 4

similar complex is obtained when a germanium hydride is used, *viz.* $[RuH_2(H_2)(HGePh_3)(PCy_3)_2]$ (**12**).[38] Whereas all the hydrides of **11** exchange rapidly on the NMR time-scale, even at low temperature (100°C), a decoalescence is observed in the case of **12** between the germanium hydride, the two hydrides and the dihydrogen molecule.

Using a disilane $HSiR_2XSiR_2H$, both dihydrogen molecules of **2** may be substituted to yield the corresponding bis(silane) complexes accomodating two σ-Si–H bonds, $[\widehat{RuH_2(H\text{-}SiR_2XSiR_2\text{-}H)}(PCy_3)_2]$ (R = Me, X = O, C_2H_4, C_3H_6, C_6H_4 or $OSiMe_2O$; R = Ph, X = O) (**13**) (see Scheme 4 (X = $OSiMe_2O$) and Figure 4).[40] Like **11**, the new complexes **13** display a bent geometry with a P–Ru–P angle of 104–108° due to the presence of four additional non-bonding interactions between the terminal hydrides and the silicon atoms of the disilane ligands. The chelating effect of the disilane ligand is only a minor factor in the stabilisation of the corresponding bis(silane) complex. These complexes are fluxional and rapid exchange between terminal and silicon hydrides may be observed by NMR, the coalescence temperature depending upon the ligand. These processes presumably involve a ruthenium–dihydrogen intermediate.

All these complexes are catalytically active for hydrosilylation and dehydrogenative silylation of ethylene. High turnovers and high selectivity for vinyl derivatives may be obtained using both mono- and bis-silanes as reagents.[27,41]

However, perhaps the most interesting complexes have been prepared through the reaction of **2** with silanes (see Scheme 4). Thus, a redistribution reaction

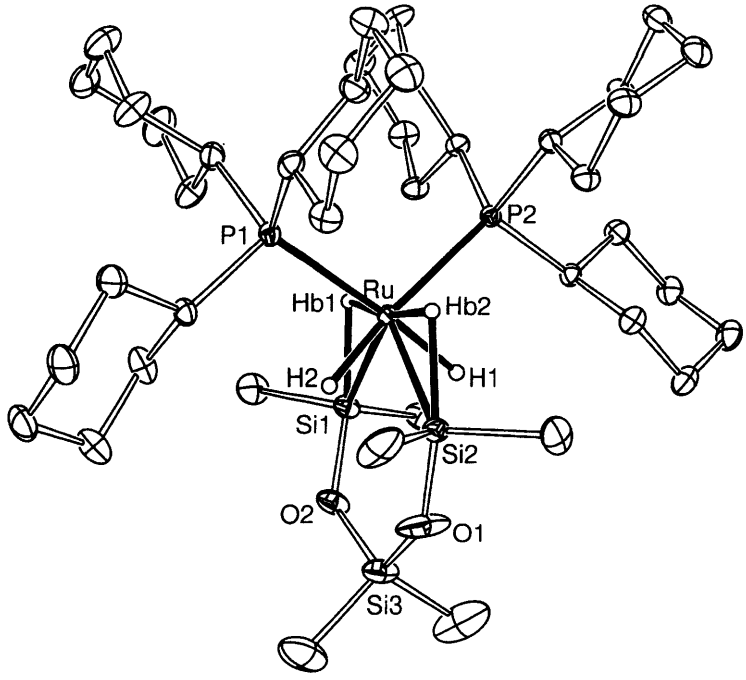


Figure 4 *Molecular structure of* $[\overline{RuH_2(H\text{-}SiMe_2OSiMe_2OSiMe_2\text{-}H)}(PCy_3)_2]$ **(13)**

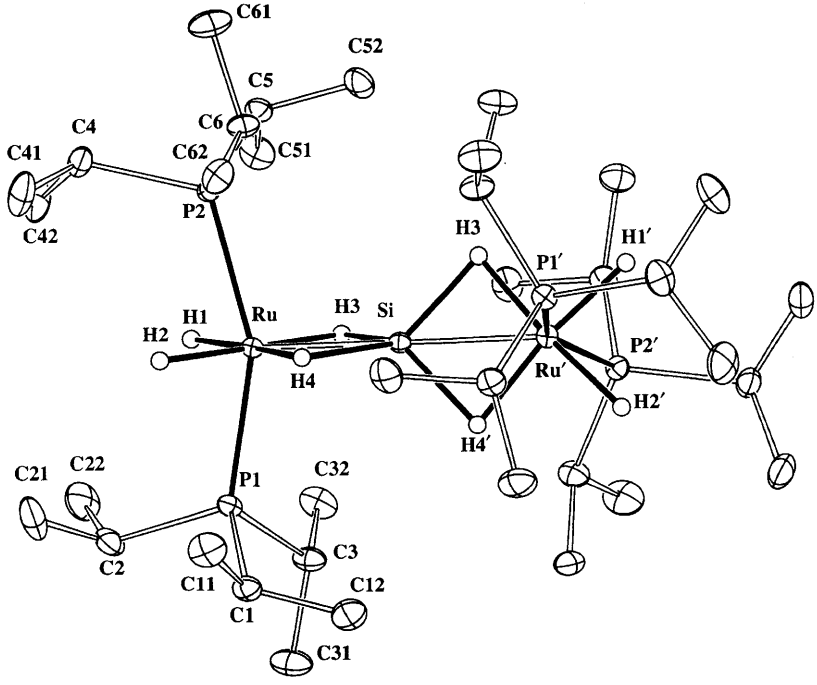


Figure 5 *Molecular structure of* $[\{RuH_2(PCy_3)_2\}_2(\mu\text{-}SiH_4)]$ **(14)**

is observed at room temperature which leads to **11** and to the remarkable complex $[\{RuH_2(PCy_3)_2\}_2(\mu\text{-}SiH_4)]$ (**14**) (see Figure 5).[42] The SiH_4 molecule lies between two ruthenium dihydride units. The Ru–Si distances are the shortest reported (2.1875(4) Å) but no direct Ru–Si bond is present. The silane molecule is attached to ruthenium by four σ-bonds and, uniquely, the back-bonding occurs into a σ^* orbital of Si–H bond linked to the other ruthenium. The ease of this reaction and the rich reactivity of **14** will lead us to study in detail further transformations of silanes in the coordination sphere of ruthenium.

4 Conclusion

Using ruthenium hydride chemistry to provide milestones, it is possible to appreciate the innovative character of Joe Chatt's research and to understand the evolution of the field for the past 45 years. In the early days, it was important to demonstrate the possibility for various ligands to coordinate to transition metals. Some of these ligands introduced by Joe Chatt have become the prototypes of ancillary ligands; this is the case for phosphines, for example. Other ligands have proved to be extremely useful tools in organometallic chemistry. This is particularly true for hydrides, the chemistry of which is also associated with the name of Joe Chatt. The first purpose of the early days was the demonstration of the existence of various types of complex. This purpose is not completely outdated since, for example, the quest for an isolable alkane complex is still a target of several research groups. However, with the demonstration by Kubas of the possibility for σ-bonds to give stable complexes, we have probably now reached the point of having defined and isolated all potential coordination modes between a transition metal and various potential ligands. Hence, electronic doublets or electronic vacancies as well as bonds, whether σ or π, and all combinations of these elementary modes of bonding may be involved in ligand coordination to transition metals. It is also evident that the famous Chatt, Dewar and Duncanson model used for understanding ethylene coordination to a transition metal is also usable for understanding σ-bond coordination. The SiH_4 complex discussed above represents a new version of this model in a bimetal system.[42] To these modes of binding we must add the closed sphere interactions, famous for gold(I) (aurophilic interactions) which have recently led to the isolation of a gold–xenon complex.[43]

These results bring us to the main difference between the present research and that of the late fifties. The main objective of present research is to find new species displaying a selective reactivity, for example for the functionalisation of hydrocarbons, whether unsaturated (hydroboration, hydrosilylation, selective and enantioselective hydrogenation of various functions, polymerisation of various substrates including stereospecific polymerisation of polypropylene, *etc.*) or saturated. Weak interactions appear to play an increasingly important role in this field, whether hydrogen bonding, interaction of σ-bonds ('agostic' bonds), hydride silicon interactions, *etc.* These weak interactions will eventually lead to the tuning of the selectivity in catalytic reactions by modelling the coordination sphere of the complexes. This is presently a very active area of research.

5 Acknowledgements

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Hydrido Complexes of Group 6 Transition Metals – Formation of the Pentadentate Ligand with a P–P–Si–P–P Framework

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1 Introduction

One day at the end of June, 1970, I knocked at the door of Professor Joe Chatt's office at the Unit of Nitrogen Fixation in the University of Sussex and met him for the first time. This was the very day I started research on the transition metal hydride complexes. I cannot forget that Professor Chatt was so kind that he drove me in his own car to find accommodation for my family, my wife and two little daughters.

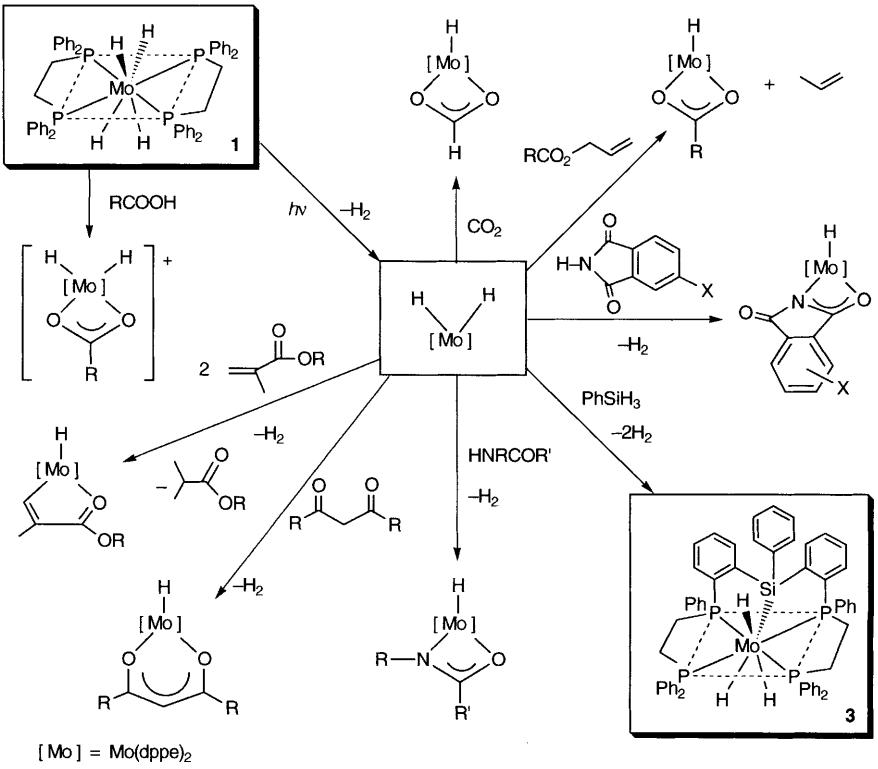
The research theme I undertook as a postdoctoral fellow during the two years under the warm and severe supervision of Professor Chatt spread over a wide range of transition metal complexes, studies of which were performed in collaboration mainly with Drs Jeff Leigh and Jon Dilworth.

On coming back to Professor Akio Yamamoto's group in 1972, I started a research programme on molybdenum chemistry, which has lasted until now.

My research programme on the Group 6 transition metal hydrides mainly concerns two kinds of starting complexes, one being of the type $[MH_2Cp_2]$ originally prepared by Wilkinson, Green, *et al.*,[1] and the other of the type $[MH_4(dppe)_2]$ (**1**) [dppe = 1,2-bis(diphenylphosphino)ethane] which was prepared for the first time by Pennella in 1971.[2] In this article, our recent research results relating to the latter hydrido complex will be described, focusing mainly on its reactions with primary and secondary silanes.

The tetrahydrido complex **1** has shown versatile reactivities, some of which are

typical of polyhydrido complexes, especially due to a high reactivity of the coordinatively unsaturated intermediate species, $\{MH_2(dppe)_2\}$ or $\{Mo(dppe)_2\}$, generated on either light irradiation or heating at 110 °C in solution. Examples hitherto reported by us are shown in Scheme 1.[3]



Scheme 1

2 Reactions of $[MH_4(dppe)_2]$ with Primary and Secondary Silanes

A typical method of formation of a transition metal–silicon bond is the oxidative addition of silane derivatives, involving either Si–H or Si–Si bond cleavage, to a low valent, coordinatively unsaturated transition metal complex. Various kinds of transition metal silyl or silylene complexes have so far been synthesised *via* this method. However, in contrast to the rich chemistry of the late transition metal complexes with an M–Si bond, a limited number of syntheses of Group 6 metal complexes with an M–Si bond have been reported.[4]

In expectation of obtaining oxidative addition products of the general formula $H–\{Mo\}–SiR_3$, which are readily envisaged from the series of reactions reported, we examined the thermal reactions of tetrahydride **1** with silanes. On reaction of **1** with phenylsilane $PhSiH_3$ in refluxing toluene, an oxidative addition reaction

involving Si–H bond cleavage to give an Mo–Si bond did in fact occur, although the final product isolated was a little more complicated than that expected from simple oxidative addition.[5]

Thus, heating a toluene solution of **1** under reflux in the presence of more than two equivalents of phenylsilane for 3 h afforded a yellow solid in 78% yield, which was characterised as **2** (shown in Scheme 2) spectroscopically as well as by an X-ray crystallographic study (Figure 1). The high-field region of the ^{1}H-NMR spectrum of **2** in C_6D_6 at room temperature showed two resonances with integration 1:1; a broad multiplet at δ −4.5 and a broad, apparent triplet at δ −5.4 ppm. The results indicate that there are two sets of magnetically inequivalent protons that may be assignable to two hydrido ligands. Complex **2** represents the first example of the simultaneous activation of an Si–H bond and two aromatic C–H bonds giving rise to the formation of a pentadentate ligand which contains a P–P–Si–P–P framework.

Later, the detailed study of this reaction revealed that reaction of **1** with only one equivalent of $PhSiH_3$ under similar conditions afforded a greenish yellow solid, which was assignable as the trihydride **3a** in 87% yield. Complex **2** was also derived from trihydride **3a** by its reaction with an excess of $PhSiH_3$ in refluxing toluene. When *o*- or *p*-tolyl silanes were used in place of phenylsilane, trihydride complexes **3b** and **3c**, respectively, were obtained, although the disilyl complexes corresponding to **2** were found to be too unstable to be isolated (Scheme 2).

When secondary silanes such as $Ph(Me)SiH_2$ or Ph_2SiH_2 were employed in a similar reaction with **1**, the trihydrido complex **4**, instead of **3**, with a tridentate ligand P–P–Si was isolated, and was structurally characterised by X-ray analysis (Scheme 3).[6]

A possible reaction path from **1** to **3** is shown in Scheme 4: $PhSiH_3$ may

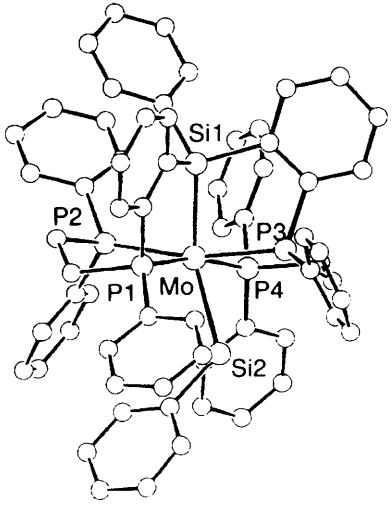
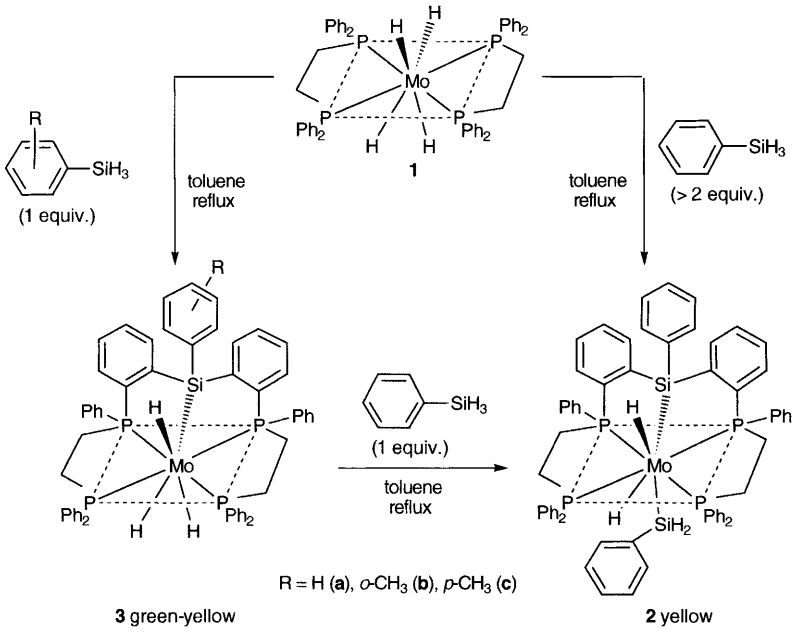
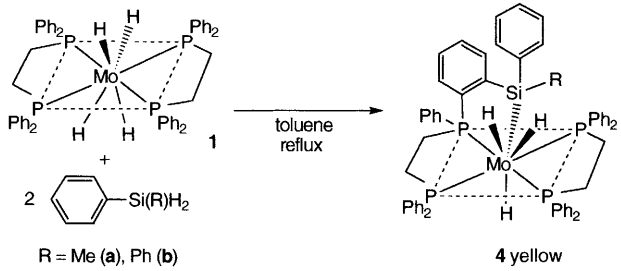


Figure 1 *Molecular structure of* **2**

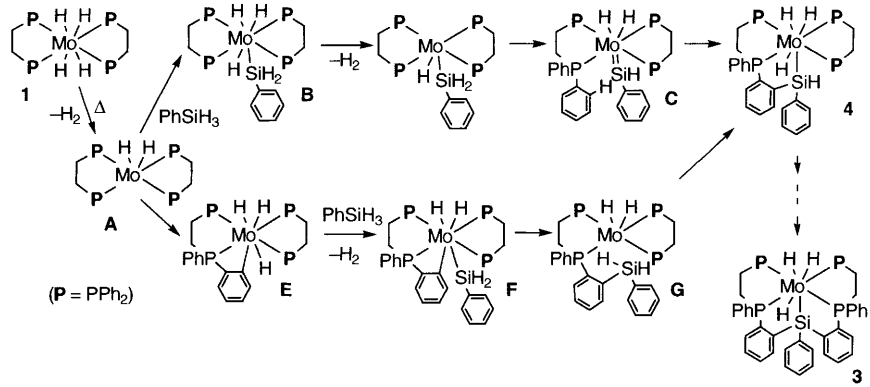


Scheme 2 *Thermal reactions of* **1** *with primary arylsilanes*



Scheme 3 *Thermal reactions of* **1** *with secondary arylsilanes*

oxidatively add to the 16-electron reactive intermediate **A**, generated thermally from **1** on release of one mole of H_2, to give a phenylsilyl-molybdenum intermediate **B**. Since the direct substitution of the *ortho* hydrogens of phenyl groups in the dppe ligand with Si in the coordinated SiH_2Ph ligand seems to be less likely, intervention of a silylene intermediate such as **C** in the Scheme, formed *via* an α-hydrogen elimination of the silyl group, seems to be more plausible. Activation of *ortho* C–H bonds in the phenyl groups of dppe ligands with the Mo=Si bond may result in the formation of the tridentate ligand complex corresponding to **4** which is isolated when secondary silanes are employed. In the case of a primary silane, further α-hydrogen elimination from **4** followed by the insertion of an Si=Mo bond into the *ortho* C–H bond may lead to the formation of the pentadentate ligand complex **3**. The alternative path involving oxidative



Scheme 4 *Possible reaction path from* **1** *to* **3**

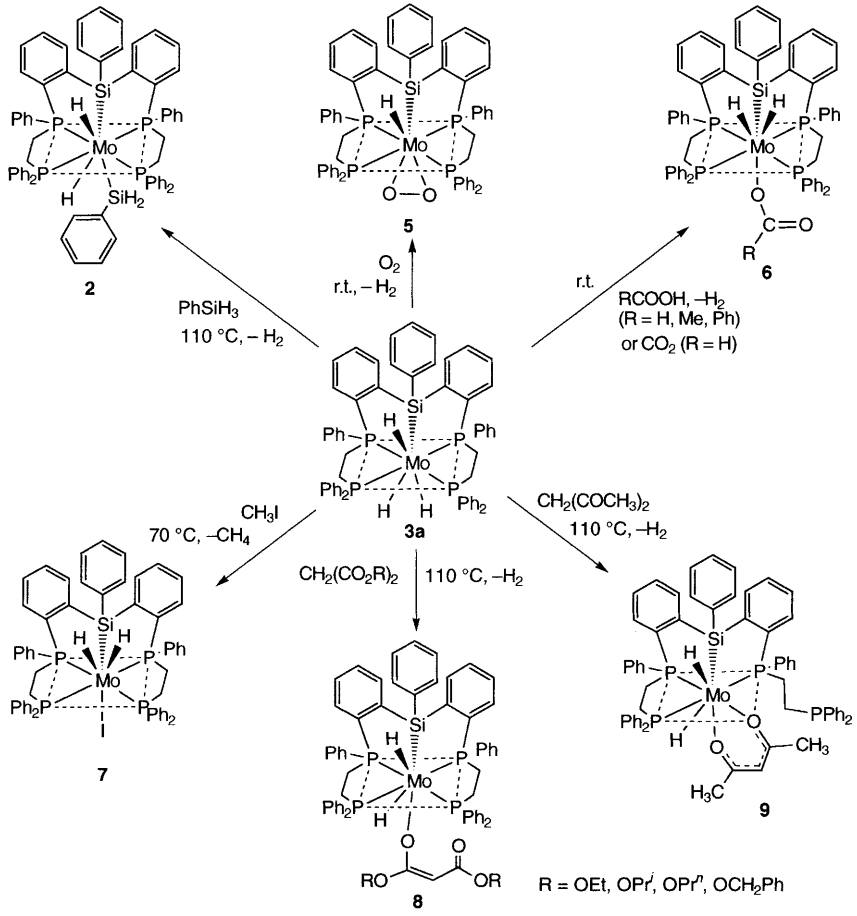
addition of the *ortho* C–H bonds of dppe, reductive elimination of Mo–C and Mo–Si bonds, and oxidative addition of an Si–H bond (the path involving **E** through **G** in Scheme 4) without intervention of the silylene intermediate, however, cannot be ruled out.[5]

3 Some Reactions Involving Trihydrido Complex $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ar)Si\text{-}P,P,P,P,Si\}]$ (3)

The trihydrido complex **3** was found to undergo versatile reactions, generally maintaining the unique pentadentate ligand intact, as summarised in Scheme 5.

As is described above, **3a** reacts with a further mole of phenylsilane to give **2**. Solutions of complexes **3** in thf were found to be very susceptible to air and changed from yellow to greenish in the presence of even trace amounts of air. When dioxygen was bubbled through a thf solution of **3a** at room temperature, a similar colour change was immediately observed. The work up of the solution afforded green crystals which were analysed as a peroxo complex of the type $[MoH\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ph)Si\text{-}P,P,P,P,Si\}(\eta^2\text{-}O_2)]$ (**5**) on the basis of spectral and X-ray structural analyses.[6] The analogous dioxygen complexes corresponding to **3a** were obtained similarly for tolyl derivatives **3b** and **3c**. Evolution of a significant amount of H_2 was detected by GLC when the reaction of **3** with O_2 was conducted in a sealed system.[6] The presence of the P–P–Si–P–P type of pentadentate ligand in **5** seems to be crucial in stabilising the peroxo-type dioxygen complex as suggested by the two observations: (1) treatment of the parent complex $[MoH_4(dppe)_2]$ (**1**) with O_2 in solution resulted only in decomposition of the complex; (2) the trihydrido complexes with a P–P–Si tridentate ligand (complexes **4** in Scheme 3) did not give any dioxygen complex similar to **5** on their treatment with O_2 but decomposed.

Carboxylic acids such as formic, acetic, and benzoic acids reacted with **3a** to give corresponding carboxylato complexes **6** in which the carboxylato ligand



Scheme 5 *Some reactions of trihydrido complex* **3a**

coordinates to the metal in a unidentate mode through one oxygen atom as shown spectroscopically as well as by the single crystal X-ray analysis.[7] If one considers that most of the related carboxylatomolybdenum complexes so far reported possess the bidentate-type carboxylato ligand, the rigid double chelate framework consisting of Si, four phenyl carbons and two P atoms in **6** seems to have hindered the coordination of the second oxygen atom of the carboxylato ligand. The same unidentate formato complex **6** (R = H) was obtained by the reaction of **3** with gaseous carbon dioxide in a toluene solution (Scheme 5).[8]

On heating a thf solution of **3a** or **3b** at 70°C in the presence of two moles of CH_3I, the reddish orange iodo complex **7** was obtained, accompanied by evolution of methane (Scheme 5). The similarity between **6** and **7** in the pattern and the chemical shift of the ^1H NMR signal assignable to the hydrido ligand strongly suggests that the latter has a similar molecular arrangement to the former, the structure of which was confirmed by X-ray structure analysis.

The reaction of **3a** with malonates in refluxing toluene, as shown in Scheme 5,

afforded the malonato complex **8** which has a unique unidentate malonato ligand bonded *via* one enolic oxygen atom to the metal, with the pentadentate P–P–Si–P–P framework being kept intact. [9] The highly stable nature of the framework seems to have hindered the chelation of the malonato ligand.

In contrast, when pentan-2,4-dione was allowed to react with **3a** under similar conditions, chelated pentan-2,4-dionato complex **9** was obtained in which one of four phosphorus atoms of the framework is dissociated.[9] This result of the unique reaction was confirmed by the X-ray structure analysis of the complex **9**. Although the explanation of these results obtained for two types of β-dicarbonyl compounds, malonate and pentan-2,4-dione, is not straightforward at present, the difference in the steric congestion between two dicarbonyl compounds seems to be responsible.

Since the trihydrido complex of the type **3** with a unique pentadentate ligand is interesting in view not only of its formation itself but also of its reactivity, we are now exploring the related reactions utilising the tungsten analogue of **1** as well as the primary and secondary germanes.

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SECTION C:

The Chemistry of Phosphines

When Chatt first became involved in phosphine chemistry it was a minority sport. Apparently the interest in such compounds was then based upon the property of solubility in organic solvents that they conferred upon their adducts with metal halides. This opened up the possibility of determining parachors, a function that, it was hoped, would shed some light on the nature of the co-ordinate bond.

That this never transpired is one of the ironies of chemical history. What phosphine complexes have enabled us to do has been much more significant. Chatt's early work concentrated on platinum group metals, and this was consonant with the interest in complexes containing hydrides, olefins, alkyl groups, or aryl groups. When Chatt left The Frythe, the work had just about reached the iron group, with minor excursions beyond.

It was natural that the Unit of Nitrogen Fixation should continue to exploit phosphine complexes, and this was richly rewarded. Apart from opening up osmium and rhenium phosphine chemistry, work also advanced to Group 6. Progress further to the left in the Periodic Table is much more difficult if one insists upon using tertiary phosphines, but even so Group 6 gave series of dinitrogen complexes to add to the series obtained with osmium and rhenium. In fact some chemists became so blasé that when a manuscript describing only the second extensive series of dinitrogen–phosphine complexes, based upon rhenium, was submitted to Chemical Communications, *a referee recommended rejection, saying that this was just another series of dinitrogen complexes. Chatt was no less angry than the rest of his collaborators.*

It is possible that our concentration upon the use of phosphines has unbalanced current perceptions about the coordination chemistry of dinitrogen. However, phosphines have opened so many new vistas in inorganic and organometallic chemistry that, be it due to luck or to exceptional insight, the debt of the chemical community to Chatt, and also to pioneers such as F. G. Mann, is difficult to over-estimate.

This section contains three contributions: that of Mingos describes some of the historical background as well as developing some recent ideas about cone angles; that of McAuliffe describes some unexpected compounds stabilised by phosphines

which do not, at first sight, obey the normal rules elucidated for them; and that of Heaton deals with new materials based substantially upon phosphines. The story of phosphine coordination chemistry still has a long way to run.

Some New Insights into the Steric Effects of Tertiary Phosphine Ligands via *Data Mining*

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1 Introduction

Joseph Chatt made many valuable contributions to coordination and organometallic chemistry, but perhaps his most significant and widely applicable legacy resulted from his promotion of tertiary phosphines as flexible ligands in transition metal chemistry.[1] He demonstrated very clearly that their presence enabled chemists to develop reactions at the metal centre which were unique and resulted in the ligation at the metal of many unusual and novel organic ligands and fragments. His PhD training with F. G. Mann at Cambridge[2] had introduced him to the distinct advantages of using triethylphosphine as a ligand in the preparation of air-stable and crystalline samples of platinum metal complexes. He recognised that having complexes which were soluble in a range of organic solvents opened up reactions which could only be undertaken in non-protic solvents. Of course he also learned the skills associated with making and safely handling such ligands. Indeed his postgraduate research had resulted in the first synthesis of bis(dimethylarsino)benzene (diars) – a ligand which was destined to become the workhorse of the extensive research efforts of the Nyholm group during the 1950s and 1960s.[3,4]

With the benefit of hindsight, it is instructive to look back at those features of phosphine which excited Chatt's enthusiasm and interest and also indicate how he advanced the field so that their advantages became more widely appreciated by other chemists all over the world. In the late 1930s the absence of spectroscopic techniques for characterising complexes and the extreme difficulty of completing a single crystal X-ray crystallographic analysis[5] because of the phase

problem meant that it was essential to have a pure compound which could be analysed by classical techniques. Indeed, the assignment of coordination geometries had been closely associated with the formation of distinct isomers which could be separated by fractional crystallisation techniques. Therefore, Chatt and Mann's research at that time represented an extension of the methodology which had been so successfully developed by Werner at the turn of the century. Werner's research had been based primarily on ammonia and amines coordinated to substitutionally inert transition metal ions, and such complexes could be made and recrystallised from aqueous solutions. Of course, Werner's classical work on the separation of enantiomorphs of tris(ethylenediamine) complexes of cobalt(III) required the introduction of organic substituents onto the nitrogen ligands in such a way that the methodology of working in aqueous solutions could be maintained. Chemists at this time had studied the complex formation of tertiary amines, but discovered that they did not form complexes which were as stable as the comparable complexes of ammonia. The first report of a tertiary phosphine complex of a transition metal has been attributed to Hofmann in 1857.[6] Mann came into the field in the 1930s and recognised that tertiary phosphines and arsines formed particularly stable complexes and he extended the range of known platinum and palladium complexes.[7]

2 Historical Background

When he set up an independent research group at The Frythe, Chatt recognised the following important qualities of tertiary phosphines as ligands:

1. They imparted organic solubility on the complexes which were formed from them. The solubility in a particular solvent could also be modified by changing the length of the alkyl substituent and introducing phenyl substituents.
2. The resulting complexes would produce highly crystalline samples if the appropriate phosphine were used. Of course, crystallising compounds was at that time, and indeed still is, as much an art as a science and Chatt himself had various intuitive feelings about the desirability of using specific phosphines. When I worked with him he had a distinct preference for triethylphosphine and diethylphenylphosphine as ligands which he thought formed highly crystalline and therefore easily separable complexes. In contrast, he was not at all in favour of using triphenylphosphine. The relative insolubility of *cis*-$[PtCl_2(PPh_3)_2]$[8] had led him to disfavour this ligand – an oversight which perhaps allowed others to develop the important chemistries of the following complexes: $[Pt(PPh_3)_{3,4}]$ (Malatesta, Allen);[9] $[RhCl(PPh_3)_3]$ and $[RuCl_2(PPh_3)_3]$ (Wilkinson);[10] $[IrCl(CO)(PPh_3)_2]$ (Vaska);[11] and $[CoH(PPh_3)_4]$ (Yamamoto, Sacco).[12,13]
3. I think that the discovery that he could make complexes which were soluble in non-polar and relatively unreactive solvents such as benzene (more widely used in those days than now) and diethyl ether (tetrahydrofuran did not become readily available until the late 1950s) proved to be a particularly important observation, because it opened up the possibility of doing meta-

thetical reactions of chloro-complexes of the transition metals with reactive organic reagents such as Grignards and lithium aluminium hydride. This was a development of the types of reaction which had become familiar to him as a PhD student when he was making tertiary phosphines and arsines.

4. The solubility in non-polar solvents was also important to Chatt because he early recognised the value of making dipole moment measurements on complexes in order to provide valuable stereochemical information and to gain some insight into the polarities of the metal–ligand bonds. His subsequent routine use of this technique built on the foundations which had been developed previously by Sutton and his group at Oxford.[14,15] Of course, the advent of first proton and then phosphorus NMR spectroscopy led coordination chemists, and particularly Bernard Shaw and his co-workers, to use methyldiphenyl- and dimethylphenyl-phosphine more extensively.[16] These ligands have particularly simple and yet informative proton NMR spectra, especially in the light of the virtual coupling phenomenon of *trans* phosphines noted by Shaw and his co-workers.
5. Chatt appreciated early on that phosphine ligands are particularly effective in forming stable complexes with the platinum metals. Indeed his determination to put this characteristic on a more quantitative basis led to the important Class (a) and Class (b) classification scheme of metal–ligand interactions proposed jointly with Ahrland and Davies.[17] This work was subsequently subsumed into Pearson's general 'Hard and Soft' acid and base classification scheme.[18]
6. Chatt recognised that substituents on the phosphines could alter the steric requirements of phosphine ligands, but it was not a central concern of his research at that time. He was particularly interested in ligands which coordinated strongly to transition metals and remained coordinated to the metal when the metal was modified by introducing hydride, alkyl and aryl ligands *via* metathetical reactions.[19] The ability of ligands such as triphenylphosphine to generate empty and potentially reactive coordination sites was first indicated by Malatesta's work on $[Pt(PPh_3)_4]$ which showed that it lost a phosphine to give $[Pt(PPh_3)_3]$ on recrystallisation from benzene[9] and this observation became a critical part of the mechanism proposed by Wilkinson and Osborn for alkene hydrogenation catalysed by $[RhCl(PPh_3)_3]$.[20] It was also mechanistic studies by Tolman on the hydrocyanation catalyst $[Ni(PR_3)_4]$ (R = alkyl, aryl, alkoxy or aryloxy) which led him to quantify for the first time the relative steric effects of phosphine and related ligands.[21]

   Therefore, it was Tolman rather than Chatt who was able to show how steric effects associated with phosphine ligands could be put on a more quantitative basis using the cone angle concept.[22] A mathematically defined cone was projected from the metal atom to the surface of the ligand as defined by the van der Waals' radii of the atoms on the surface of the ligand. I suspect that Chatt, Wilkinson and Malatesta all probably had an appreciation of the importance of steric effects, but in my opinion they lacked the mathematical background to articulate it in a way which could be readily appreciated by other coordination chemists.

7. In the early 1950s the relative stabilities of comparable tertiary amine and phosphine adducts with Lewis acids were interpreted in terms of the availability of 3d orbitals at phosphorus. This view no longer prevails,[23] but it led Chatt and Nyholm to propose that the retrodative bonding which had been developed earlier for metal–alkene complexes could also be applied to phosphine ligands, with which the conventional Werner dative bond could be augmented by back-donation from filled metal d orbitals into empty d orbitals on phosphorus.[24] Of course, the relative strengths of the two components could be modified by changing the substituents on the phosphorus. Chatt recognised that on this basis PF_3 would be a superior π-acid ligand and this led him to attempt to synthesise $[Ni(PF_3)_4]$.[25] This work was taken up by others who demonstrated that PF_3 was as good as CO at stabilising low oxidation state transition metal compounds.[26] He also appreciated that PPh_3 and $P(OPh)_3$ may be able to stabilise low oxidation states of the platinum metals. This led to the isolation of complexes such as $[Pt(alkyne)(PPh_3)_2]$,[27] but Chatt did not explore this idea to any great extent until the mid-1960s when it became apparent that the isolation of stable dinitrogen complexes could only be achieved when low oxidation state complexes were generated.
8. Chatt's PhD work had led him to understand the importance of bidentate phosphine and arsine ligands and he, together with Davidson and Watson,[28,29] later used the ligand $Me_2PCH_2CH_2PMe_2$ to develop some classical organometallic chemistry which for example demonstrated how C–H bonds may be activated by transition metals.

3 Discussion

The introduction and background presented above have underlined the important contributions which Chatt made to the development of phosphine-stabilised transition metal chemistry and also suggest why it was Tolman rather than he who quantified the relative steric contributions of phosphine ligands.

Tolman's original proposal (see Figure 1) depended on the direct physical measurement of cone angles from idealised space-filling CPK models.[22] Subsequently other methodologies have been developed for calculating the steric effects of ligands and the subject has been well documented in White and Colville's recent review.[30] These methods sought to rectify the basic disadvantage of the Tolman method, which does not take into account the variation in cone angle with ligand conformation. The cone angle concept has subsequently been profitably extended to other important classes of ligands, notably amides such as $N(SiMe_3)_2^-$, substituted cyclopentadienyl and arene ligands, substituted polypyrazolylborates, substituted alkyls and aryls including mesityl and supermesityl.[31] A common theme of modern main group and transition metal chemistry has been the isolation of compounds with low coordination numbers and the kinetic stabilisation of multiply-bonded compounds using sterically demanding ligands.[32]

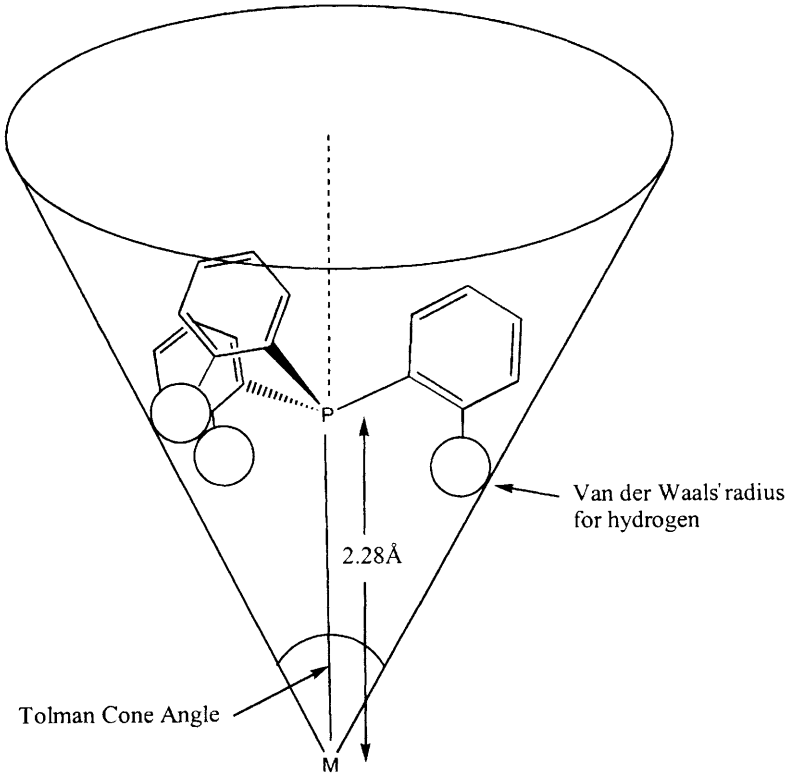

Figure 1 *Illustration of the definition of the Tolman cone angle for a typical aryl phosphine ligand*

Since the Cambridge Crystallographic Database[33] has a wealth of structural data on phosphine ligand complexes, Thomas Müller and I[34] decided to determine whether it could provide a statistically based analysis of the variation of cone angles from complex to complex. Just as Dunitz and Burgi used the results of structural analyses to map out the reaction coordinates for many basic reactions and polytopal rearrangement processes, so we felt that the calculation of cone angles for all reliably determined structures of phosphine complexes in the database could record how the cone angle changed in response to the different environments in the whole range of complexes. Orpen[36] had previously completed a Dunitz and Burgi-type analysis on phosphine ligands and showed how the dihedral angles of the ligands varied in a concerted manner, but a similar statistical analysis of cone angles had not previously been attempted.

The crystallographic data define the positions of the nuclei for heavy atoms and the Tolman angle calculation requires a knowledge of the van der Waals' surface of the ligand. The crystallographic coordinates and the Tolman cone angle were inter-related by the geometric relationships illustrated in Figure 2.

To make the calculations consistent with those reported by Tolman, the

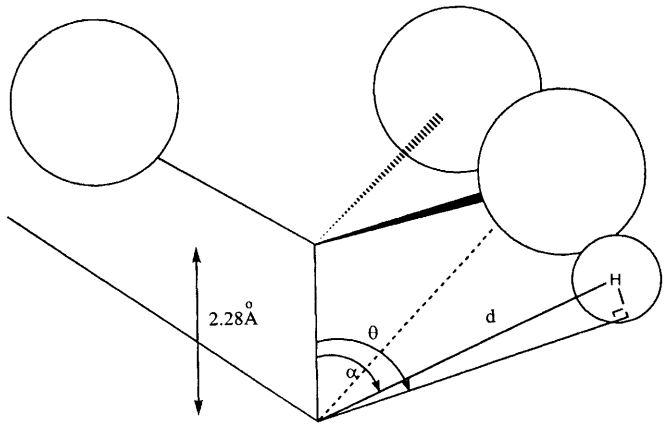

Figure 2 *Calculation of the Tolman cone angle from X-ray crystallographic data*

metal–phosphorus bond length was initially set constant at 2.28 Å and a van der Waals' radius of 1.00 Å was used for hydrogen. This leads to the calculation of cone angles in individual structurally characterised molecules, rather than being based on idealised molecular models or geometries derived from molecular mechanics calculations. The calculations do introduce a small error since hydrogen atom positions are generally defined on the basis of calculated positions which assume a C–H distance of 0.98 Å. This distance gives a better description of the electron density distribution in the C–H bond rather than the value of 1.08 Å, which defines the internuclear distance. However, the small systematic error introduced is more than compensated for by access to the thousands of structures in the Cambridge Crystallographic Database. The following questions become accessible by using such a statistical analysis.

1. Is there a direct correlation between these data and the original cone angles proposed by Tolman?
2. Do the cone angles vary greatly from complex to complex?
3. Does this variation depend on the rotational freedom of the ligands?
4. When there is more than one phosphine ligand in a complex, do they share a common cone angle? For a particular ligand, does a deviation from the normal cone angle occur in those complexes where the phosphine ligands intermesh and the phenyl ligands may occupy space which may also be apportioned to the cone of an adjacent ligand?
5. Are there any systematic variations in cone angle either across or down the periodic table?

Table 1 summarises the results of the cone angle calculations for more than 4000 phosphine-containing compounds based on the ligands PMe_xPh_{3-x}, PEt_3 and PCy_3 (Cy = cyclohexyl). The results of the statistical analyses may be presented as bar charts, which may be idealised into normal distribution curves (see Figure 3). Such an analysis provides a mean cone angle for each ligand and also a standard deviation.

Table 1 *Comparison of computed average cone angles for tertiary phosphine ligands with their Tolman cone angles*

	PPh_3	PPh_2Me	$PPhMe_2$	PMe_3	PEt_3	PCy_3
No. of structural determinations of ligands	2388	185	547	1203	354	108
Av. M–P–C (°)	114.8(1.2)	115.2(1.3)	115.7(1.3)	116.8(1.5)	115.4(1.5)	112.7(1.4)
Tolman cone angle	145	136	122	118	132	170
Crystallographic cone angle (°)	148(5)	135(5)	120(5)	111(2)	137(5)	160(5)
Range of cone angles (°)	129–168	121–153	108–139	96–121	124–159	146–172

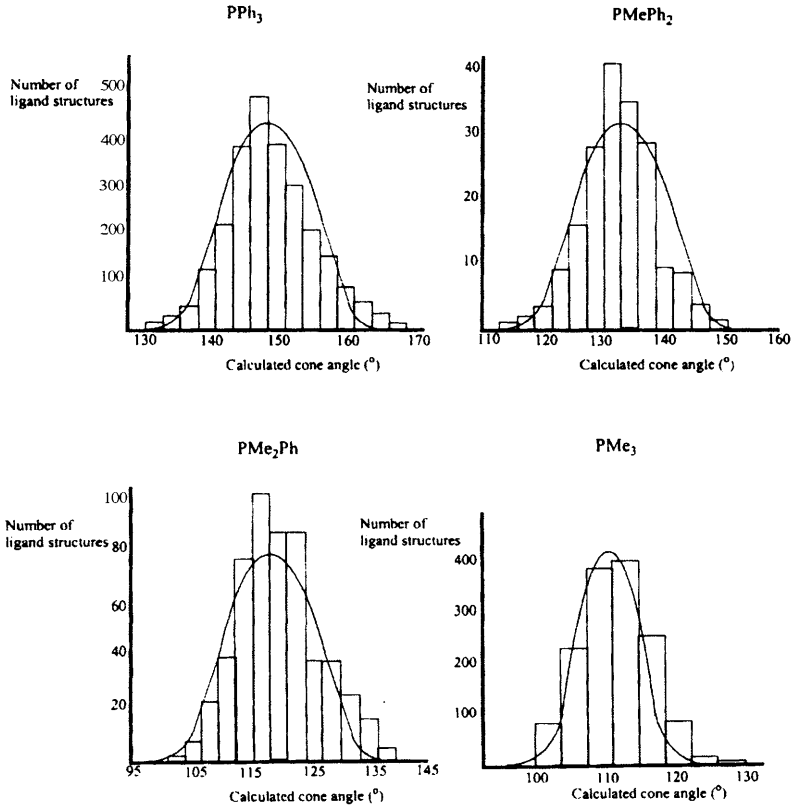

Figure 3 *Histograms and idealised normal distribution functions for the cone angles of some tertiary phosphine ligands*

It will be recalled that for an idealised Gaussian distribution three standard deviations each side of the mean define a 99% probability of finding a compound with a cone angle in that range. The statistically derived cone angles for these phosphines generally correlate well with the Tolman cone angles. For example, for PPh_3, $PMePh_2$, PMe_2Ph and PEt_3 the differences are less than one standard deviation. For PMe_3 and PCy_3 the difference is approximately two standard deviations. Some have suggested previously that Tolman may have over-estimated the cone angle of PCy_3 and an alternative cone angle of 157° has been proposed, which agrees better with our calculated value than the original Tolman cone angle.

The standard deviations of the cone angles provide an indication of the variation of the cone angles from complex to complex and therefore reflect the ability of a ligand to change its conformation in order to optimise the packing of the ligands within the molecule and the crystal. In general, the phosphine ligands have a standard deviation of 5°, suggesting a spread of cone angles of 30°. In contrast the standard deviation for PMe_3 is only 2.4°, reflecting the limited degrees of rotational freedom available to this ligand. Consequently the spread of cone angles for this ligand is only 15°.

Even within one complex the cone angles can vary significantly. For example, for complexes containing three triphenylphosphine ligands, the average cone angle is 150°, close to the global mean cone angle for this phosphine of 148°. However, in some of these complexes the cone angles of the PPh_3 ligands differ by as much as 16°, approximately three standard deviations. In such complexes, two of the three triphenylphosphines have cone angles close to the global mean and the third deviates greatly from it. In these sterically crowded molecules the restricted degrees of freedom available to the ligands lead one of the phosphines to adopt a conformation with a much larger cone angle. These differences underline the limitations of using a cone to define the space occupied by ligands which have a propeller-like structure.

The standard deviations associated with the cone angles therefore provide an indication of the ability of the phosphines to adapt to different environments. For example, trimethylphosphine, which has limited scope for intermeshing with other ligands because of the absence of large degrees of freedom associated with the methyl groups and the absence of the flat phenyl rings, has the smallest standard deviation. Therefore this phosphine has well defined steric requirements. In contrast the other phosphines studied have a much wider spread of cone angles, and this is reflected in the larger standard deviations.

There are groups of complexes for which the cone angle of the triphenylphosphine is much smaller than the global mean of 148° and cone angles as low as 120° have been noted. In many of these complexes a small cone angle is demanded by the presence of bulky and inflexible co-ligands. For example, in carborane metal complexes containing triphenylphosphines, the steric pressure of the demanding carborane ligand may result in a reduction of the cone angle of the phosphine. Similarly, multidentate ligands which have limited degrees of freedom when located *trans* to the triphenylphosphine ligands cause a reduction

of the cone angle. Examples of such ligands include thia-crown ethers and porphyrins. The carborane and multidentate ligands share a disc-like structure and a reluctance to distort in order to permit the phenyl rings of the triphenylphosphine ligand to adopt a conformation with a cone angle close to the mean.

In contrast, those complexes for which the calculated cone angle of triphenylphosphine is consistently larger than the mean cone angle also belong to an identifiable group. Many of the examples are complexes of gold and mercury, where the metal has a lowish coordination number and where the co-ligands are sterically not very demanding. In these complexes the triphenylphosphine can take advantage of the greater space around the metal atom to expand its cone angle.

It has been noted previously that the metal–phosphorus–carbon (M–P–C) bond angle varies significantly in triphenylphosphine complexes. Indeed there are Periodic regularities. A plot of cone angle for PPh_3 against the Periodic Group number shows a progressive change in the angle across the transition series. The average cone angle increases from *ca.* 142° to 155°, and this may be related to the decrease in the average M–P–C bond angle. This trend has been noted previously and has been interpreted in terms of the change in *s* character in the P–C bond, which is larger for complexes of the later transition metals. This change in *s* character results in an opening up of the M–P–C angle and a larger cone angle. The high proportion of complexes of the later transition metals with large cone angles may be related to this.

We have also investigated the effect on the cone angle calculations of using the crystallographically determined M–P distance rather than the putative 2.28 Å distance proposed by Tolman. The 2.28 Å distance is smaller than the mean M–P distance of 2.32(9) Å calculated for all triphenylphosphine complexes. The calculated mean cone angle based on observed metal–phosphorus distances is 146.9(6)° which contrasts with an angle of 148(5)° based on the standard metal–phosphorus bond length proposed by Tolman.

In summary, this statistical analysis has provided some interesting insights into the Tolman cone angle concept. Specifically, it has demonstrated that the cone angles in real complexes vary much more than previously believed and that there are systematic periodic differences in the average cone angles. The cone angles may also be affected by the steric requirements of the co-ligands and the coordination number of the complex. More surprisingly, the analysis suggests that even within one complex containing several phosphine ligands the cone angle may vary considerably.

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Synthesis of New and Unusual Metal Complexes from the Reaction of Dihalogen Adducts of Tertiary Phosphines with Unactivated Metal Powders

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1 Introduction

In 1847 Paul Thenard synthesised trimethylphosphine from the reaction of methyl chloride with impure calcium phosphide at 180–300 °C.[1] The subsequent discovery of aliphatic amines established the link between amines and phosphines and stimulated Hofmann and Cahours[2] to develop this area of chemistry. A major development was the synthesis of triphenylphosphine by Michaelis[3] in 1885.

In 1973 one of us edited a volume on transition metal complexes of Group 15 ligands.[4] When approached to get his permission to dedicate the compilation to him, Joseph Chatt, with characteristic generosity, requested that the book be dedicated to Frederick Mann. The latter, said Chatt, invented the area of metal complexes of phosphines. A subsequent volume was dedicated to Chatt.[5]

Indeed, Mann's studies initiated an explosion of interest in transition metal phosphine chemistry.[6] Chatt was Mann's student, and it is interesting to reflect that Chatt employed transition metal salts as a means of derivatising tertiary phosphines. Little did they realise how this area would expand! Chatt's influence on metal–phosphine chemistry was profound, and out of it sprung the employment of phosphine complexes as tools for investigations into metal hydrides, nitrogen fixation, the stabilisation of unusual oxidation states, synthesis of metal alkyls and aryls, and the immense practical area of homogeneous and heterogen-

eous catalysis. The Chatt 'family' is large: Shaw, Venanzi, Leigh, Richards, and their students. If we may be forgiven a personal statement: we view our pedigree as Mann → Chatt → Venanzi →McAuliffe → Godfrey and Levason. Reasonably, this may be seen as a very parochial view, since this area has been globally researched. However, it was Mann and Chatt's British School with the Antipodeans Dwyer and Nyholm who spearheaded this now vast area.

2 Background

There are four comprehensive reference texts on phosphine coordination chemistry.[4,5,7,8] Two are somewhat out-of-date,[4,5] but the article by Levason is more recent.[7] However, all four give much useful information on synthetic procedures for the preparation of primary, secondary and tertiary phosphines; diphosphines; multidentate and macrocyclic phosphines; mixed Group 15 donor and mixed Group 15/16 donor systems; and phosphorus-containing heterocycles. The coordination chemistry of phosphorus has expanded to include P_4 fragments, P_6 rings, and even naked phosphorus atoms, for example, nine-coordinate P and η^6-P_6 systems.[8]

The cone-angle concept has been comprehensively reviewed (see Reference 8 and the preceding article by Mingos). It was Tolman[9] who introduced the idea of the *cone angle* to describe in quantifiable terms the bulk of (mainly) phosphine ligands. This term is especially applicable to Group 15 proligands. On binding to metals they increase the coordination number of the donor atom to four, with tetrahedrally disposed bonds that, rotated around an apical axis, describe a cone. It is this that makes the term particularly appropriate for pnictide ligands. It is important to appreciate that cone angles are not necessarily the dominant steric/structural effect on ligand behaviour, and that steric bulk and cone angle are not necessarily synonymous.

There has been much discussion of the nature of the M–PR_3 bond in metal complexes, and the relative importance of the σ and π contributions. Useful background to this can also be found in References 4, 5, and 8.

3 Work at The University of Manchester Institute of Science and Technology (UMIST)

One evening in 1989, one of us (C. A. M.) was enjoying an after-work drink in The Lass O'Gowrie (a pub on Charles Street, near the UMIST campus) with a close friend and colleague, Tony Mackie, and we began to discuss the synthesis of metal–phosphine complexes. We recognised that the traditional and much employed synthesis was the reaction of a metal salt with a quantity of a tertiary phosphine (Equation 1).

$$MX_n + yPR_3 \rightarrow MX_n(PR_3)_y \qquad (1)$$

We recognised that this was the reaction of an oxidised metal with a phosphorus(III) centre, and wondered if it would be possible for an 'unoxidised' metal to react with an oxidised phosphine, *i.e.* a phosphorus(V) centre. We both

thought that this was unlikely, since most metals have a somewhat impenetrable surface oxide coating, as those of us who have enjoyed the challenge of initiating a Grignard reagent preparation will attest.

We therefore planned to investigate the reactions of X_2PR_3 (X = Br or I) with unactivated metals (Equation 2).

$$M + nX_2PR_3 \rightarrow ? \quad (n = 1 \text{ or } 2) \tag{2}$$

To our delight we found that the activation of crude metal powders by reagents X_2PR_3 in dry diethyl ether at about ambient temperatures is facile and led to the isolation of known, and, more frequently, previously unknown and unexpected products (see below).

3.1 Nature of PR_3X_2 (X = Cl, Br or I)

Because of the success we initially experienced in the synthesis of coordination complexes, we decided to investigate the structural chemistry of the reagents PR_3X_2 isolated from the reaction of stoichiometric quantities of dihalogen with tertiary phosphines in diethyl ether.

Prior to our investigations, there were two recognised structural groups for PR_3X_2 compounds: molecular trigonal-bipyramidal *trans*-$[PR_3X_2]$ and the ionic $[PR_3X]X$. Somewhat to our surprise we found that a single crystal X-ray analysis of PPh_3I_2 revealed it to have a tetrahedral four-coordinate structure, Ph_3P–I–I, a charge-transfer complex of molecular iodine and triphenylphosphine. As expected, the I–I separation in molecular diiodine, 2.71 Å, is lengthened to 3.161 Å in PPh_3I_2.[10] There had been much previous work on dihalogen adducts of tertiary phosphines, such as the solution studies by Harris and his co-workers[11] and by Du Mont.[12] A subsequent study of a large number of PR_3I_2 (R_3 = Ph_3, substituted triaryl, mixed arylalkyl, or trialkyl) showed that the four-coordinate 'spoke'/charge transfer structure was common in the solid state.[13] Moreover, this 'spoke' structure in the solid state was also exhibited by Ph_3P–Br–Br.[14] We studied 20 other R_3PBr_2 compounds and found that in $CDCl_3$ solution they exist in the ionic $(R_3PBr)Br$ form, except for $(C_6F_5)_3PBr_2$ which has a molecular five-coordinate structure both in $CDCl_3$ solution and in the solid state,[15] presumably due to the very low basicity of the parent tertiary phosphine.

These results posed the question: what are the solid-state structures of tertiary phosphine adducts of mixed halogens, such as PR_3IBr? For all compounds (R_3 = $(p\text{-}ClC_6H_4)_3$, Ph_3, Ph_2Pr^n, Ph_2Me, $PhMe_2$ or $Bu^n{}_3$) the 'spoke' structure predominates, but other structures are present in small proportions. In particular, PPh_3IBr exists as Ph_3P–I–Br, with a little Ph_3P–Br–I.[16]

The conclusions from our investigations are that the solid-state structures of PR_3X_2 (X = Br or I) depend crucially on the nature of R and the solvent of preparation. For example, when employing diethyl ether as the solvent the ionic $[(Me_2N)_3PI]I$ is produced, but $PPhMe_2I_2$ has the molecular 'spoke' structure.[17]

Despite the fact that compounds of stoichiometry R_3PCl_2 have been known

for over 120 years,[18] their solid-state structural nature has remained largely unexplored, even though PPh_3Cl_2 is a widely used chlorinating agent in organic reactions and is commercially available. Our X-ray crystallographic study[19] of PPh_3Cl_2 crystallised from CH_2Cl_2/Et_2O revealed it to be $[Ph_3PCl^+ \cdots Cl^- \cdots {}^+ClPPh_3]Cl$, and not a molecular trigonal-bipyramidal adduct, not a molecular charge-transfer complex, and not the simple ionic species $[Ph_3PCl]Cl$. This contrasted with conclusions from all spectroscopic data recorded on compounds of stoichiometry PR_3Cl_2 by earlier workers[20] and represents the first compound of this formulation to be crystallographically characterised. However, we have shown from ^{31}P-{H} NMR studies that these compounds are ionic in $CDCl_3$ solution. For those parent tertiary phosphines that are weakly basic (or more acidic), a trigonal-bipyramidal structure was revealed in the solid state and this also persists in $CDCl_3$ solution. It is evident that all reported PR_3F_2 compounds contain five-coordinate phosphorus centres. However, for PR_3Cl_2 and PR_3Br_2 the nature of R crucially determines the structure.[21] This phenomenon has also been observed for AsR_3Br_2: the parent $AsPh_3$ is a relatively weak base and thus $AsPh_3Br_2$ is trigonal-bipyramidal, whereas the stronger base, $AsMe_3$, forms a molecular four-coordinate species $Me_3As{-}Br{-}Br$.[22]

In conclusion, the structural chemistry of dihalogen adducts of tertiary phosphines is clearly diverse and is sensitive to the nature of R and X; moreover the central atom E (E = P, As[22] or Sb[23]) can play a crucial role, as can the solvent of preparation. There has been some discussion about the bonding of P to the X moiety.[24–27] Finally, although we have discussed here 1:1 adducts of R_3E with X_2, different ratios can lead to more complex compounds. For example one polymorph of PPh_3I_4[27] reveals a strong interaction between the cation $[PPh_3I]^+$ and a triiodide anion, and the individual $[PPh_3I]$ units are further linked into a polymer by weak interactions between the triiodide anions. Further, the compound $PPr^i{}_3I_4$ contains two $[PPr^i{}_3I]^+$ cations weakly linked independently to one of the two terminal iodine atoms of the same triiodide anion.[28]

3.2 The Activation of Crude Metal Powders by Reagents PR_3X_2

Our investigations have revealed several surprising results:

(i) crude, inactivated metal powders react readily with these reagents and form metal complexes;
(ii) complexes of metals in high oxidation states result from a one-pot synthesis;[29–37]
(iii) stable complexes which defy Chatt's class (a)/class (b) categorisation and the HSAB principle, *e.g.* $[CoI_3(SbPh_3)_2]$, can be synthesised;[34]
(iv) low-oxidation-state gallium(II) and indium(II) complexes are accessible;[38,39]
(v) even a noble metal such as gold can be oxidised readily.[36]

We now exemplify briefly the above observations.

Iron. In contrast to the well-established coordination of nickel salts with monotertiary phosphines, reports of corresponding iron complexes are relatively

rare, and only $[FeCl_3(PMe_3)_2]$ and $[FeCl_3(PPh_3)_2]$ are known for the oxidation state III.[40]

Iron powder reacts with two equivalents of $PPhMe_2Br_2$ in Et_2O to form a white solid, which is acutely sensitive to dioxygen.[29] At exposure to low O_2-partial pressures (< 100 ppm) it is possible to isolate an intensely purple trigonal-bipyramidal complex $[FeBr_3(PPhMe_2)_2]$, with the phosphines *trans* to each other and in the apical positions. It might have been expected that exposure of the initial white material, presumably an iron(II) species, would have yielded a μ-oxo complex.

We were interested to know if other zerovalent iron species could be oxidised by these reagents. Reaction with $[Fe_2(CO)_9]$ yielded a series of diverse products: ionic $[ER_3X][FeX_3(ER_3)]$ (E = P, R_3 = Ph_3, Me_2Ph or $(p\text{-}MeOC_6H_4)_3$, X = I; R_3E = Me_3As, X = Br or I), $[(Ph_3E)_2Br][FeBr_4]$, and the surprising ionic adduct, $[SbPh_4][FeI_4]\cdot SbPh_3I$, remarkable not only for phenyl migration to the antimony atom, but also for the formation of the rare $[FeI_4]^-$ anion from a zerovalent iron carbonyl precursor.[30]

Manganese. The X-ray crystal structure of $[MnI_2(PPhMe_2)]$ made by direct reaction of MnI_2 with $PPhMe_2$ in Et_2O has been reported by King and co-workers,[41] and shows an infinite chain of MnI_2 units with two $PPhMe_2$ molecules additionally co-ordinated to alternate manganese atoms, producing a sequence of manganese coordination numbers 4,6,4,6... However, when $PPhMe_2IBr$ reacts with crude manganese powder the reaction of Equation 3 occurs.

$$2PPhMe_2IBr + 2Mn \rightarrow 2[MnBr_2(PPhMe_2)] + [MnI_2(PPhMe_2)] \quad (3)$$

An X-ray crystal structure analysis[29] of the iodo-product revealed that it, too, was polymeric, but with a 5,5,5,5 structure, indicating that our new synthetic method can produce isomeric forms of the complexes made by more conventional means. Both isomers, however, react with O_2 to form a 1:1 adduct.

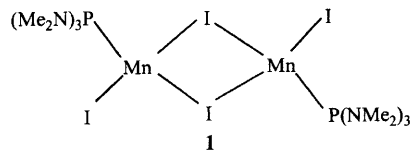
That subtle changes can significantly influence[42] the product is illustrated in Equation 4.

$$2PPh_3I_2 + 2Mn \rightarrow [MnI_2(PPh_3)_2] + MnI_2 \quad (4)$$

Further structural variety was found in the product from the reaction in Equation 5.

$$P(NMe_2)_3I_2 + Mn \rightarrow [Mn\{P(NMe_2)_3\}I_2] \quad (5)$$

The adduct **1** has the previously recognised 1:1 MnI_2:phosphine stoichiometry, but it is a dimer rather than polymeric (Scheme 1). Even more surprising were the results of the 1:1 reaction of manganese powder with PMe_3I_2.[32] This produced a polymeric complex of 1:1 stoichiometry, $MnI_2(PMe_3)$, **2**, but this had the 4,6,4,6 structure. Complex **2** showed intriguing reactions with molecular oxygen. $[Mn_2I_5(PMe_3)_3]$, **3**, is unique in two respects: although mixed-valence manganese complexes are well established with ligands involving O- and N-donor systems, no such system was known for P-donors.



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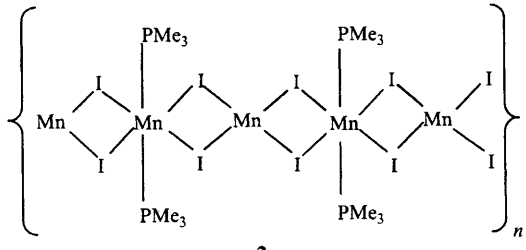

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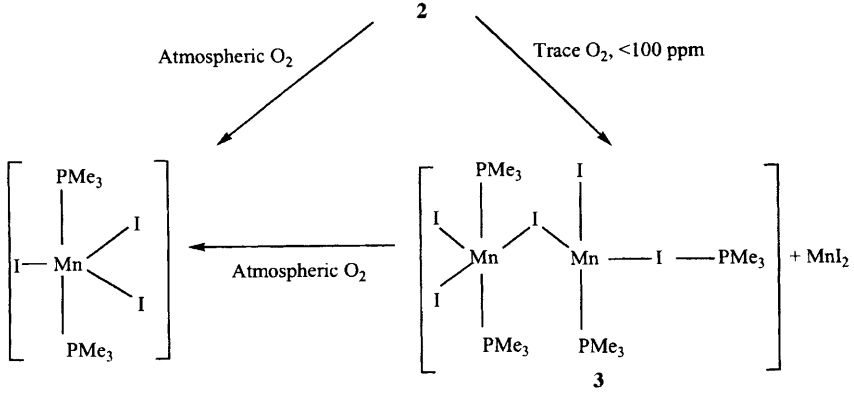

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Scheme 1

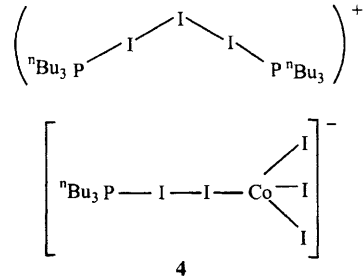
Additionally, there is a PMe_3 molecule in the lattice, but it is surprising that the material is not pyrophoric in air.

Cobalt. The reaction[31] of cobalt metal with two mole equivalents of PMe_3I_2 yields $[CoI_3(PMe_3)_2]$ (Equation 6).

$$Co + 2PMe_3I_2 \rightarrow [CoI_3(PMe_3)_2] + \tfrac{1}{2}I_2 \qquad (6)$$

This complex is trigonal-bipyramidal. In contrast, when the reagent $PBu^n{}_3I_2$ was employed an intermediate species with the unusual formula $[CoI_8(PBu^n{}_3)_3]$ was isolated. This proved to be $[(Bu^n{}_3PI)_2(\mu\text{-}I)][(Bu^n{}_3PI)(\mu\text{-}I)CoI_3]$, **4**, and provides a 'snapshot' of the reaction of these reagents with bare metals. Note that cobalt is 'capturing' iodines from the reagent, and that at this point no Co–P bonds exist.

The reagent $AsPh_3I_2$ oxidises $[Co_2(CO)_8]$ (6:1 molar ratio) to produce the novel $[(Ph_3AsI)_2(I)][CoI_3(AsPh_3)]$ in quantitative yield. As well as being the first crystallographically characterised complex containing a cobalt(II) tertiary arsine



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bond in the tetrahedral $[CoI_3(AsPh_3)]^-$ anion, it also contains the unusual linear cation $[Ph_3As–I–I–I–AsPh_3]^+$.[43] When two mole equivalents of PMe_3I_2 react with cobalt (or nickel) powder, Equation 7, the M^{III} complexes are produced quantitatively in a simple one-step reaction.[33,34]

$$2PMe_3I_2 + M \rightarrow [MI_3(PMe_3)_2] + \tfrac{1}{2}I_2 \quad (7)$$

In contrast, $AsMe_3I_2$ and Co produce a mixed product, Equation 8.

$$4AsMe_3I_2 + 2Co \rightarrow (AsMe_3I)[CoI_3(AsMe_3)] + [CoI_3(AsMe_3)_2] + \tfrac{1}{2}I_2 \quad (8)$$

Textbooks refer to Chatt's class (a) and class (b) acceptors, a concept subsequently developed in Pearson's HSAB principle. In contrast to this perceived wisdom, the complex $[CoI_3(SbPh_3)_2]$, which contains a hard metal centre and extremely soft iodide and $SbPh_3$ ligands, is quite stable.[34] Its formation is thought-provoking.

$$2I_2SbPh_3 + Co \rightarrow [Ph_3SbI][CoI_3(SbPh_3)] \rightarrow [CoI_3(SbPh_3)_2] + \tfrac{1}{2}I_2 \quad (9)$$

Nickel. The synthesis of unusual metal complexes by our new synthetic method is shown by the formation of the square-planar cation[44] in $[Ph_3PI][Ni(PPh_3)I_3]$, whereas, according to conventional wisdom, 'large' ligands such as PPh_3 and iodide should force tetrahedral geometry around nickel(II).

Gold. Gold has always been considered as the most noble of all metals. Only one oxide of gold is known, Au_2O_3, and even this is unstable, decomposing to produce gold metal at the moderate temperature of 160°C. Consequently, to produce gold complexes it is necessary to solubilise the metal, usually by using rather severe conditions, such as treatment with *aqua regia* and/or cyanide. Clearly, the development of a new reaction route starting with elemental gold to produce gold complexes under ambient conditions in a chemically inert solvent is highly desirable.

We found[36] the following reaction, Equation 10.

$$3I_2AsMe_3 + 2Au \rightarrow 2[AuI_3(AsMe_3)] + Me_3As \quad (10)$$

The product is square-planar. Even more interesting is the reaction shown in Equation 11.

$$2I_2PMe_3 + Au \rightarrow [AuI_3(PMe_3)_2] + \tfrac{1}{2}I_2 \quad (11)$$

This complex has a trigonal-bipyramidal structure with the phosphines in the *trans*-apical positions, and is apparently the first structure where this geometry is not forced upon the gold(III) by the steric requirements of the ligands.

These reactions indicate not only that even gold can be activated and oxidised by EMe_3I_2 (E = P or As), but they show that distinctly different products form as a result of quite subtle changes in the reagents. $AsMe_3I_2$ yields square-planar $[AuI_3(AsMe_3)]$ and I_2PMe_3 yields trigonal-bipyramidal $[Au(PMe_3)_2I_3]$, complexes that differ both in stoichiometry and geometry.

Tin. The reaction[37,45] of a series of PR_3I_2 reagents with tin powder has yielded complexes of empirical formula $SnI_4(PR_3)_2$, indicating that these reagents can oxidise tin(0) to tin(IV) in one step. Tin(IV) complexes have hitherto proven difficult to synthesise by conventional methods. The X-ray crystal structure of octahedral *trans*-$[SnI_4(PPr^n{}_3)_2]$ shows that all the iodine atoms are in the same plane.

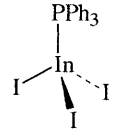
Gallium and Indium. Virtually nothing was known about the coordination chemistry of indium with tertiary phosphines until the pioneering work of Carty and Tuck.[46] We allowed I_2PR_3 (R = Ph, Pr^n or Pr^i) to react with indium metal powder, and obtained a series of interesting and novel complexes, Equations 12–14.

$$3PPh_3I_2 + 2In \rightarrow \underset{\mathbf{5}}{[InI_3(PPh_3)_2 \cdot InI_3(PPh_3)]} \quad (12)$$

$$2PPr^n{}_3I_2 + 2In \rightarrow [\{InI_2(PPr^n{}_3)\}_2] \quad (13)$$

$$3PPr^i{}_3I_2 + 2In \rightarrow 2[InI_3(PPr^i{}_3)] \quad (14)$$

Complex **5** was shown by X-ray crystallography to contain both tetrahedral, **6**, and trigonal-bipyramidal, **7**, indium(III) in the unit cell.[39] No complex of indium(III) of this stoichiometry had previously been identified. Finally, a reaction



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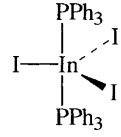

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with gallium metal powder[38] was performed with the diiodine adducts of tertiary arsines, $As(p\text{-}MeOC_6H_4)_3I_2$ and $AsEt_3I_2$, to produce $[GaI_3\{(p\text{-}MeOC_6H_4)_3As\}_3]$ and $[Ga_2I_4(AsEt_3)_2]$, respectively. The last is a unique example of a gallium-tertiary arsine complex containing a Ga–Ga bond, and these complexes serve to illustrate the subtle effect of the organic substituent on the chemistry of the arsenic atom.

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NMR Studies of Metal Complexes and Clusters with Carbonyls and Phosphines

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1 Introduction

It was with great pleasure that I accepted the invitation to participate in the ICCC at Edinburgh in the session devoted to Joe Chatt and to write this article about the enduring influence he had on the chemistry I have been involved with since I started my D. Phil. with him at Queen Mary College (QMC), London in July 1964. At that time, Joe Chatt had just started the Unit of Nitrogen Fixation. At The Frythe, he had built up a large internationally-recognised team, including experts such as Bernard Shaw and Luigi Venanzi, and it must have been very difficult for him at QMC to have only an inexperienced group of three research students. This was cushioned to some extent by being able to retain his former secretary from ICI, Inga Wass (née Schmidt), who helped him enormously.

On my first day I was asked if I would like to move to the University of Sussex since there was not enough space to develop the new Unit of Nitrogen Fixation at QMC. As a result, we moved to Sussex in October, 1964 and our group was among the first to occupy the purpose-built chemical laboratories at Sussex. These were opened officially later in the year by the Queen. Designed by Sir Basil Spence, this new University was a very exciting and stimulating place to be. Nevertheless, although the architecture on the University campus was very pleasing, there were initial problems in the laboratory design. This resulted in Chatt and his collaborators spending much time with the architects in designing the new Unit of Nitrogen Fixation, which was occupied subsequently after 1967.

At the end of my first post-graduate year, I did not have too many results! Most of my time had been devoted to establishing the laboratory and to developing the necessary preparative expertise. During this period, Chatt's group started to expand rapidly and my development was greatly assisted by the arrival of permanent nitrogen fixation chemists, Ray Richards and Jeff Leigh and

overseas visitors such as Paolo Chini who spent six months in 1965 with Chatt as a NATO fellow. He and I worked on benches opposite each other, and I learned much of my preparative technique from him. It was natural some years later to start our long and productive collaboration on NMR studies of clusters, discussed below.

It is interesting to reflect on the state-of-the-art equipment being used during my D. Phil. work, which involved the preparation of water soluble phosphorus-ligand complexes *via* the hydrolysis of ligands containing P–Cl bonds. Far IR spectrometers had just become available. This enabled the assignment of ν(Pt–X) in, for example, $[PtX_2(PR_3)_2]$ (X = Cl or Br) so that *cis* and *trans* isomers could be distinguished. This allowed the very time-consuming dipole moment measurement, which had previously been routinely used at The Frythe, to be dispensed with. The modern NMR methods were still a long way off! We were using continuous wave NMR spectrometers with either permanent (^{1}H, 60 MHz) or electromagnets (^{1}H, 100 MHz) and a Computer of Average Transients (CAT) for ^{31}P NMR measurements! Using a CAT was a pretty hit-and-miss exercise because we did not know which region to scan and because of the very small spectral sweep width. Nevertheless, I was taught the fundamentals of NMR spectroscopy by Alan Pidcock who had just taken up a Lectureship at Sussex having obtained his doctorate with Luigi Venanzi, then at the University of Oxford.

These early measurements stimulated my interest in NMR spectroscopy, and, on moving to the University of Kent at Canterbury (1972), we were lucky to be able to buy the first Fourier Transform NMR spectrometer in the UK. This instrument was still based on an electromagnet (^{1}H, 100 MHz) but allowed faster acquisition of NMR spectra and enabled the development of multinuclear NMR spectroscopy. This permitted me to start collaborating with Paolo Chini who had taken up an appointment at the University of Milan where he was developing metal carbonyl cluster chemistry. In Milan, Chini had access only to an IR spectrometer that aided the clean preparation and subsequent crystallisation of clusters, and, importantly, an X-ray diffractometer for their structural characterisation.

In this article are reviewed some of my more important multinuclear NMR contributions made in the areas of metal carbonyl and metal phosphine complexes involved in homogeneous catalysis.

2 Metal Carbonyls

Chatt's group attracted Chini because Booth and Chatt had noticed that addition of base to $[PtCl_2(CO)_2]$ produced various intense colours.[1] Work in 1965 at Sussex allowed the isolation of bright red $[Pt_3(\mu\text{-}CO)_3L_x]$ ($x = 3$, L = PPh_2Bz; $x = 4$, L = PPh_3) and black $[Pt_3(\mu\text{-}CO)_4L_3]$ (L = PPh_3 or PMe_2Ph).[2] These were all isolated by careful fractional crystallisation using a variety of solvents. Subsequently, the initial observation of Booth and Chatt was shown to be due to the formation of Pt_3-triangular stacks, $[Pt_{3n}(\mu\text{-}CO)_{3n}(CO)_{3n}]$ ($n = 1$–6).[3,4] This remarkable series of clusters showed that the Pt_3-triangles were almost eclipsed

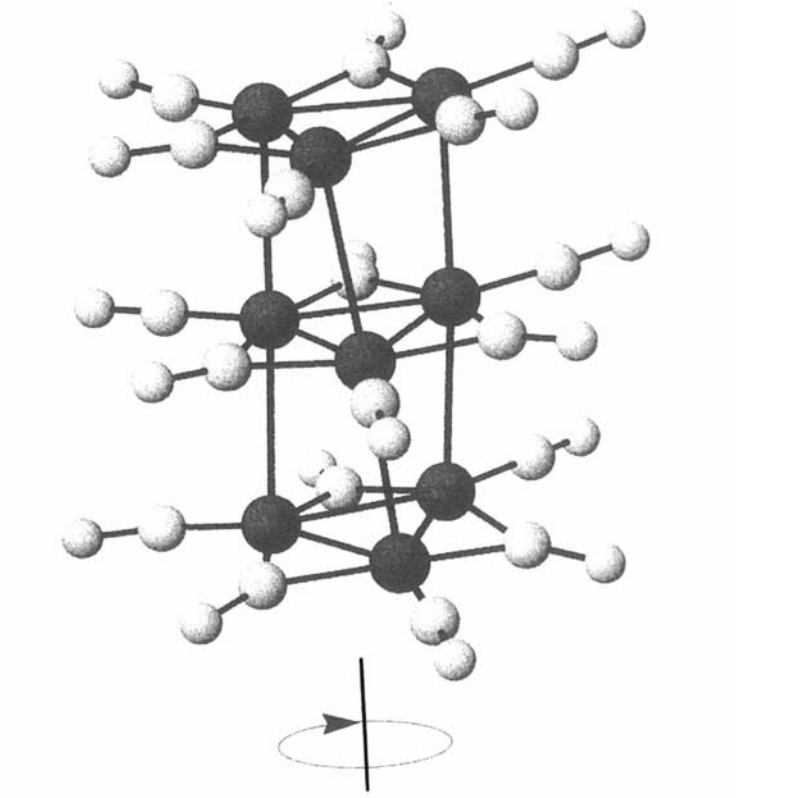


Figure 1 *Schematic representation of the X-ray structure of* $[Pt_9(\mu\text{-}CO)_9(CO)_9]^{2-}$ *and the rotation of the* $[Pt_3(\mu\text{-}CO)_3(CO)_3]$ *groups about the pseudo-three-fold axis in solution*

in the solid state but ^{13}C and ^{195}Pt NMR studies in solution showed that, for $n = 3$, there was ready rotation of the intact $[Pt_3(\mu\text{-}CO)_3(CO)_3]$-groups about the pseudo-3-fold axis (Figure 1), together with inter-exchange of $[Pt_3(\mu\text{-}CO)_3(CO)_3]$ groups between the Pt_9 and Pt_{12} clusters (Equation 1).[5]

$$\begin{array}{c} [\{Pt^*_3(C^*O)_6\}_3]^{2-} \\ + \\ [\{Pt_3(CO)_6\}_4]^{2-} \end{array} \rightleftharpoons \begin{array}{c} [\{Pt^*_3(C^*O)_6\}_{3-n}\{Pt_3(CO)_6\}_n]^{2-} \\ n = 1\text{–}3 \\ + \\ [\{Pt^*_3(C^*O)_6\}_{4-n}\{Pt_3(CO)_6\}_n]^{2-} \\ n = 1\text{–}4 \end{array} \qquad (1)$$

This was the first example of a facile, intra-molecular, metal polyhedral rearrangement in a transition metal–carbonyl cluster. Other work showed that related metal polyhedral rearrangements occur when the metal polyhedra are not well close-packed, as when they contain a hetero-interstitial atom, *e.g.* $[Rh_9E(CO)_{21}]^{2-}$ (E = P or As),[6] $[Rh_{10}E(CO)_{22}]^{n-}$ ($n = 3$, E = P or As; $n = 2$,

E = S)[6,7] and $[Rh_{12}Sb(CO)_{27}]^{3-}$.[3-6]

The initial work on Rh-containing carbonyl clusters relied heavily upon the coupling patterns and relative intensities obtained from one-dimensional NMR spectra, together with appropriate isotopic-labelling experiments. Thus, it was possible to determine unambiguously the source of the interstitial carbide in the trigonal-prismatic cluster, $[Rh_6C(CO)_{15}]^{2-}$ (Equation 2).[8]

$$6[Rh(CO)_4]^- + {}^{13}CCl_4 \rightarrow [Rh_6{}^{13}C(CO)_{15}]^{2-} + 4Cl^- + 9CO \qquad (2)$$

Related work proved the presence and determined the source of the interstitial nitride in the isoelectronic cluster $[Rh_6N(CO)_{15}]^-$,[9] and the facile interconversion of the trigonal prismatic and octahedral clusters (Equation 3).[10]

$$\underset{\text{trigonal prism}}{[Rh_6C(CO)_{15}]} \underset{+2CO}{\overset{-2CO}{\rightleftharpoons}} \underset{\text{octahedron}}{[Rh_6C(CO)_{13}]^{2-}} \qquad (3)$$

Interestingly, the observed migration in solution of seven COs around one of the three Rh_4-square planes of the Rh_6-octahedron in $[Rh_6C(CO)_{13}]^{2-}$ is exactly in accord with the librations of the same COs around the same Rh_4-square plane in the solid state.[11] This provided the first example of a correlation between CO fluxionality in solution and thermal motion in the solid state. However, there is still much more to be done to be able to predict both the migrational pathways and to clarify the exact mechanism – even in small clusters.[12,13]

Acquisition of ^{103}Rh NMR data using direct methods originally required the use of 15 mm tubes containing *ca.* 1 g of cluster and the use of high field spectrometers because of the insensitivity of this nucleus, despite being 100% naturally abundant. In the 1970s and 1980s measurements were done on the then highest field spectrometer (360 MHz) available, which was provided by the EPSRC service at Edinburgh. Clearly, this was neither very convenient nor easy to arrange from Canterbury and indirect methods were developed; a ^{13}C–$\{^{103}Rh\}$ probe was developed at the University of Kent[14,15] and a ^{1}H–$\{^{103}Rh\}$ INDOR probe at the University of Bristol.[16] The ^{13}C–$\{^{103}Rh\}$ NMR measurements allowed unambiguous assignment of resonances and clear elucidation of CO migrational pathways.[17] ^{1}H–$\{^{103}Rh\}$ INDOR measurements also provided important information about both H-site occupancies and H migration in clusters.[16,17] A particularly interesting series of clusters is $[H_xRh_{13}(CO)_{12}(\mu\text{-}CO)_{12}]^{(5-x)-}$ (x = 1–4) which, in solution, all exhibit interstitial H-migration and migration of all but the three bridging COs in the Rh_6-hexagonal plane. At low temperature, it was possible to stop both H and CO migration for $x = 3$ and show that the hydrogens occupy square-faces of the hexagonal close-packed Rh_{13} skeleton. It was reasoned that the preferential site occupancy of these different square-faces decreases with increasing μ-CO occupancy of the square-face and this hypothesis has recently been substantiated by the neutron diffraction determination of the structure of $[H_2Rh_{13}(CO)_{12}(\mu\text{-}CO)_{12}]^{3-}$ (Figure 2).[18] For $x = 2$ in solution it was impossible, even at

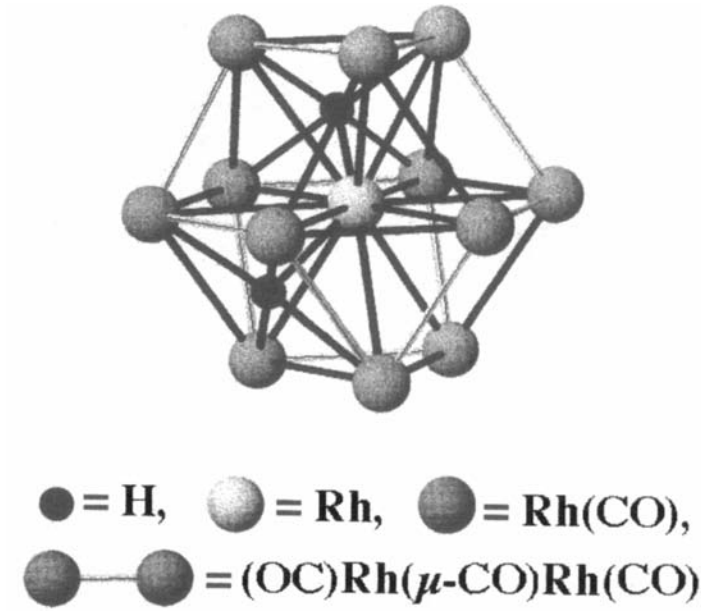


Figure 2 *Schematic representation of the neutron diffraction structure of* $[H_2Rh_{13}(\mu\text{-}CO)_{12}(CO)_{12}]^{3-}$; *each H is co-planar with a* Rh_4*-square-face*

very low temperature, to stop H-migration. However, H-migration is much less facile in the solid state and, as expected from the static neutron diffraction structure (Figure 2), two equally intense high-field ^{1}H resonances are observed in the solid-state ^{1}H NMR spectrum. Comparative variable temperature solution and solid-state NMR studies on other clusters substantiate this general view but probably the most spectacular result is observed for $[HCo_6(CO)_{15}]^-$. In this case, neutron diffraction studies show the presence of an interstitial hydride which gives rise to δ(H) at + 1 ppm whereas in solution the resonance appears at + 23.2 ppm, due to H-migration from inside to outside the cluster.[20]

Recently, indirect 2D NMR methods have been developed for obtaining ^{103}Rh NMR data (HMQC measurements) for rhodium clusters containing edge- and face-bridging carbonyls.[7,21,22] For such clusters, multiple quantum effects become important because of the presence of 100% ^{103}Rh and non-conventional delays are required. These methods are now used routinely to collect data on substituted clusters, which, since there is a reference point (substituted Rh), allow unambiguous assignments.[17,21,22]

The predominant patterns of monodentate phosphine substitution in tetrahedral and octahedral rhodium clusters have been established[17,23] and recent work on trigonal prismatic clusters suggests the following pattern (see Figure 3).[22,24] Thus, only one of the three possible isomers of $[Rh_6C(\mu\text{-}CO)_9(CO)_4(PPh_3)_2]^{2-}$ is detected in solution; further substitution occurs, but the structures of these derivatives have not yet been established. There are few reported ligand-substituted clusters containing seven or more metal atoms and

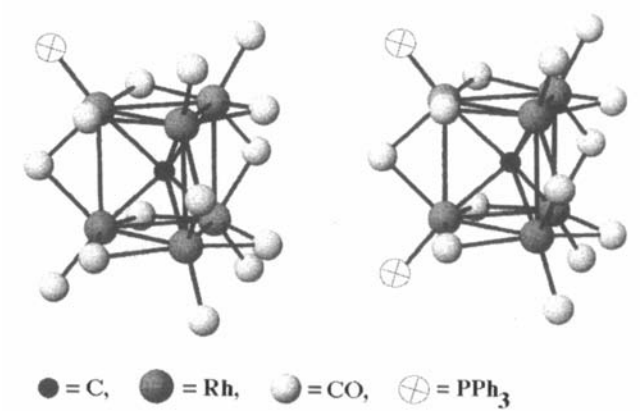


Figure 3 *Schematic representation of the solution structures of* $[Rh_6C(\mu\text{-}CO)_9(CO)_{6-x}(PPh_3)_x]^{2-}$ *(x = 1 or 2)*

there is clearly much more work to be done on both hetero- and homo-metallic lower and higher nuclearity clusters to understand better non-carbonyl mono- and multi-dentate ligand site occupancies.

For N-donor ligands (*e.g.* pyridine and dipyridyl, py and bipy), reaction with $[Rh_4(CO)_{12}]$ results surprisingly in disproportionation (Equations 4 and 5), and the solution structures of the products (established from VT HMQC measurements) are subtly different, depending upon whether the ligand is mono- or bi-dentate (see Figure 4).[24]

$$3[Rh_4(CO)_{12}] + n\text{py} \xrightarrow{CO} 2[Rh(CO)_2(py)_2][Rh_5(CO)_{15-x}(py)_x] \quad (4)$$
$$n = 4 \text{ or } 8,\ x = 0, 1, \text{ or } 2$$

$$3[Rh_4(CO)_{12}] + n\text{bipy} \xrightarrow{CO} 2[Rh(CO)_2(bipy)_2][Rh_5(CO)_{15-2x}(bipy)_x] \quad (5)$$
$$n = 2 \text{ or } 4,\ x = 0 \text{ or } 1$$

All of the above work involved neutral or anionic clusters with $\nu(CO) < 2145$ cm^{-1}. Recently, there has been a significant number of new metal carbonyls with $\nu(CO) > 2145\ cm^{-1}$.[25,26] Most of these complexes are mononuclear and contain metals in relatively high oxidation states. We recently reported only the second example of a dinuclear carbonyl in this class. Surprisingly, $[Pt_2(CO)_6]^{2+}$ **1**, which is colourless and very moisture-sensitive, is formed by the slow dissolution of black PtO_2 in concentrated H_2SO_4 on stirring under an atmosphere of CO for a few days at room temperature (Equation 6).

$$PtO_2 + CO \xrightarrow[RT/1\ atm]{\text{Conc } H_2SO_4} [Pt_2(CO)_6]^{2+} \quad (6)$$

The structure of complex **1**, which has not yet been isolated in the solid state, was established by ^{13}C and ^{195}Pt NMR measurements in solution using both

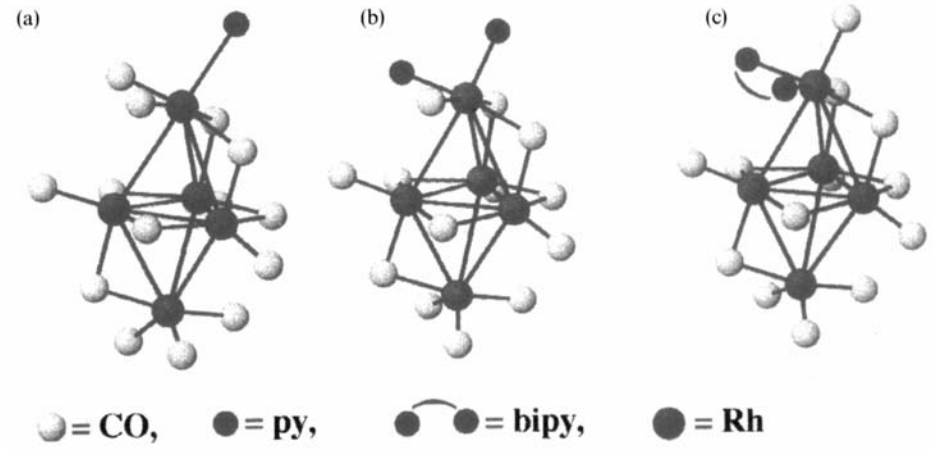
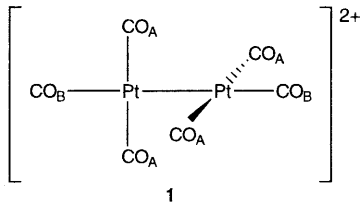


Figure 4 *Schematic representation of the solution structures of:* (a) $[Rh_5(\mu\text{-}CO)_6(CO)_8(py)]^-$ (b) $[Rh_5(\mu\text{-}CO)_6(CO)_7(py)_2]^-$ (c) $[Rh_5(\mu\text{-}CO)_6(CO)_7(bipy)]^-$



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natural-abundance ^{13}CO and 99%-enrichment. This formulation was subsequently substantiated by Raman, EXAFS and other measurements.

Even for dinuclear platinum complexes, both ^{13}C and ^{195}Pt NMR spectra quickly become very complicated with increasing ^{13}C-enrichment due to the increasing abundance of the different isotopomers, which results in long-range coupling and the appearance of second-order spectra (see Figure 5). This probably also accounts for our lack of good NMR results on higher nuclearity, crystallographically characterised clusters[28,29] such as $[Pt_{19}(CO)_{22}]^{4-}$ and $[HNi_{38}Pt_6(CO)_{48}]^{5-}$ although the influence of metal character with increasing cluster size could also be important. In this connection, it is perhaps significant that, even for clusters containing metals without a spin, no NMR data have been reported on any high nuclearity (> *ca.* 30 metal atoms) structurally-characterised cluster, including the recently reported three-shell cluster, $[Pd_{145}(CO)_x(PEt_3)_{30}]$.[30]

3 Mechanistic *in situ* Homogeneous Catalytic Studies on Metal–Phosphine Complexes

Chatt was one of the early pioneers in furthering our understanding of the nature of the coordinate link in metal complexes containing phosphine ligands.[31]

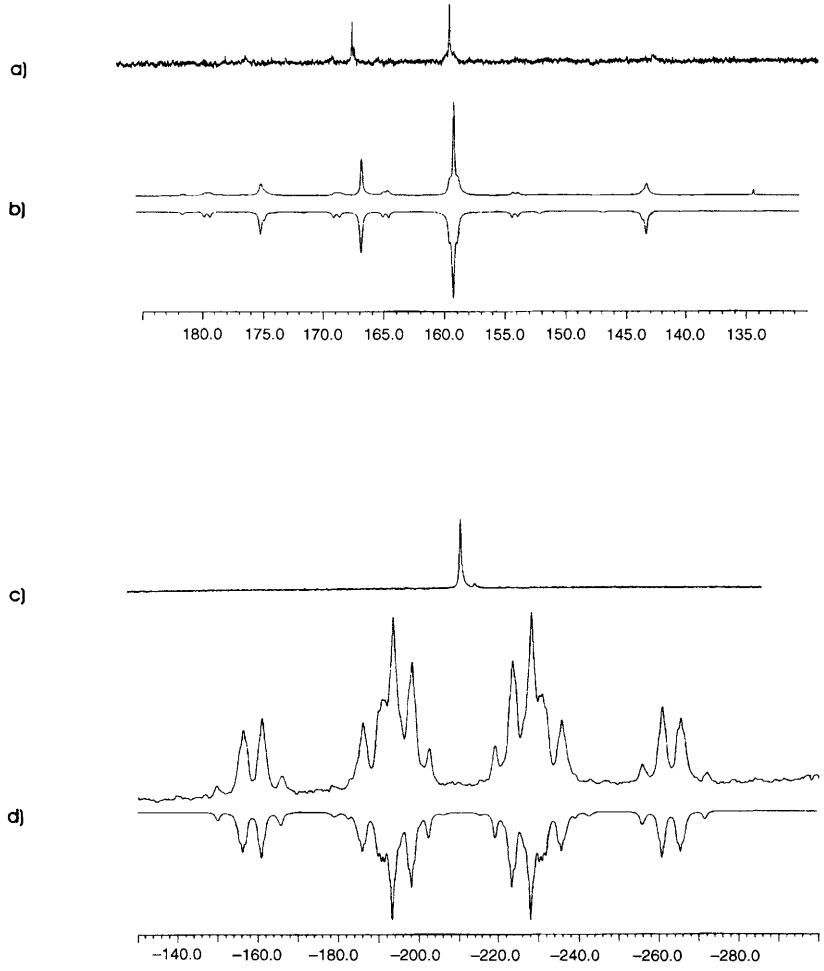


Figure 5 *NMR spectra of* $[Pt_2(CO)_6]^{2+}$: *(a) Observed* ^{13}C *at 1.1%* ^{13}CO; *(b) Observed/simulated* ^{13}C *at 99%* ^{13}CO; *(c) Observed* ^{195}Pt *at 1.1%* ^{13}CO; *(d) Observed/simulated* ^{195}Pt *at 99%* ^{13}CO δ (CO_A) *158.7,* δ (CO_B) *166.3,* δ *(Pt) −211.2,* $^1J(Pt\text{-}CO_A)$ *1595.7,* $^1J(Pt\text{-}CO_B)$ *1281.5,* $^1J(Pt\text{-}Pt')$ *550.9,* $^2J(Pt\text{-}CO_A)$ *−26.2,* $^2J(Pt\text{-}CO_B)$ *199.6,* $^2J(CO_A\text{-}CO_B) = {}^3J(CO_A\text{-}CO_B) = 0$, $^3J(CO_B\text{-}CO_B) = 19.8$

Nowadays, metal–phosphine complexes are widely used as catalysts for a variety of industrially important homogeneous catalytic reactions, which often require an elevated pressure of reactant gas.

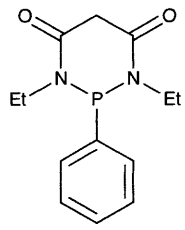
In order to improve the selectivity and efficiency of the catalytic reaction, it is important to have a detailed knowledge both of the nature of the intermediates and of the rates of the individual steps involved in the catalytic cycle *in situ*. Possession of this knowledge also avoids patent litigation.

The initial NMR measurement under a high pressure of gas, aimed at spectroscopic characterisation of species present under these conditions, was carried out in the early 1980s;[32] this was followed by Roe's introduction of the now commonly used sapphire tube.[33] Although the sapphire tube is easy to use, it suffers from the following problems.

1. Poor gas/solution mixing, which often results in rate-limiting step gas dissolution. Furthermore, without agitation dissolution of H_2 (30 atm) in $CHCl_3$ at room temperature can take up to *ca.* 10 h before equilibrium is reached.
2. Inability to measure/maintain constant pressure. This presents serious problems for rapid reactions because of gas depletion in both 5 and 10 mm NMR tubes.

All these problems have been overcome by Jon Iggo at Liverpool through the design of a flow cell[34] which allows multinuclear NMR measurements to be made at constant pressure (< 200 atm) from -40 to $+190$°C. This cell can be used not only to characterise structurally catalytic intermediates but also to carry out meaningful kinetic measurements, which compare favourably with kinetic data from reactions carried out in a stirred autoclave. For rhodium-catalysed hydroformylation reactions, the rates determined in the flow cell are an order of magnitude higher than those obtained from a sapphire tube.

Recently, this cell, together with complementary high-pressure IR measurements, has been used to investigate the mechanism of the rhodium-catalysed hydroformylation using a monodentate biuret-based phosphorus diamide ligand, **2**.[35] The major rhodium acyl species observed *in situ* is $[Rh\{C(O)R\}(CO)_2L_2]$ which has a trigonal-bipyramidal structure with two equatorial ligands, L. The equatorial CO is found to exchange with dissolved CO at a much faster rate than the apical CO. Although the generally accepted mechanism proposed by Wilkinson[36] is confirmed, the overall kinetics are rather complicated; the rate-determining stage of the hydroformylation reaction for this system is *not* due to a single step but is strongly dependent on the conditions used.[35]



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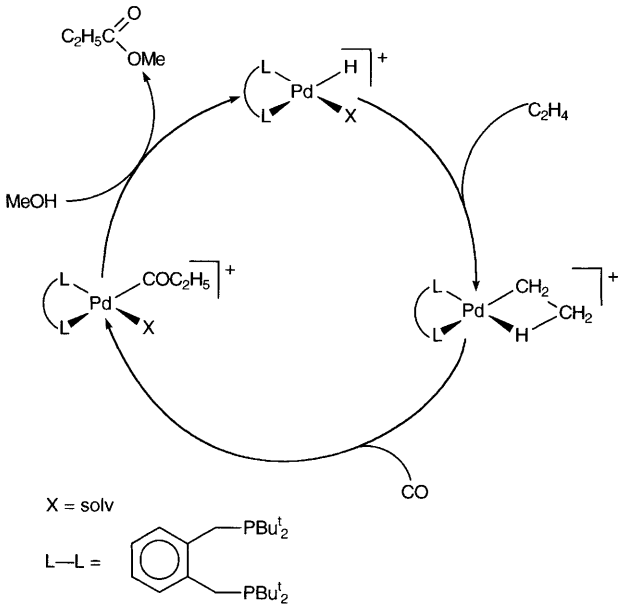
There is much current industrial interest in the palladium-catalysed methoxycarbonylation of ethene to give methyl propanoate (MeP), the precursor to methyl methacrylate. The Pd^0 catalyst precursor contains a novel bis(phosphine), for example, 1,2-$(CH_2PBu^t_2)_2C_6H_4$, and, under reaction conditions, gives MeP with high turnover and selectivity (99.98%).[37] We have inves-

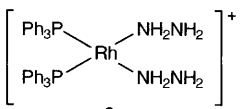
tigated this reaction and have spectoscopically characterised *all* the Pd^{II} intermediates involved in the catalytic cycle (see Scheme 1).[38] For none of the intermediates in Scheme 1 is there evidence for dissociation of the bidentate phosphine and it is surprising that the Pd–Et intermediate exhibits a β-C–H interaction, even in polar solvents such as RCN (R = Me or Et); in both the other intermediates shown in Scheme 1, the fourth site is occupied by solvent. There is no evidence for the involvement of Pd–OMe species which, together with Pd–Hs, have been proposed to be involved in the related copolymerisation of alkenes with CO to give the commercially available copolymer, Karilon.[39]



Scheme 1 *Spectroscopically characterised intermediates involved in the Pd-catalysed methoxycarbonylation of ethene*

The characterisation of all the species in Scheme 1 provides one of the few homogeneous transition metal-catalysed cycles which has been completely elucidated.

Earlier work on the *in situ* characterisation of rhodium–phosphine/hydrazine complexes was instrumental in the successful outcome of patent litigation between Hovione (Portugal) and Pfizer (USA). Here, we were able to prove conclusively by ^{31}P, ^{15}N, and ^{105}Rh NMR spectroscopies that in the hydrogenation of doxycycline to methacycline, rhodium complexes with N-donor ligands such as **3** and **4** were involved, rather than $[RhCl(PPh_3)_3]$.[40,41]



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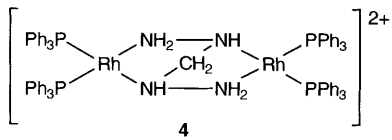

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Chatt showed that hydrazine is one of the intermediates involved in some nitrogen fixation pathways and it was a pleasant coincidence for me to carry out this work on hydrazine complexes and to be able to prove their involvement in catalytic hydrogenation reactions.

4 Acknowledgements

For the cluster work, it is a pleasure to thank the groups in Milan, Bologna, Osaka, Canterbury, Liverpool, and more recently St Petersburg, who have contributed to this work over the years; I am most grateful to all the people whose names appear in the references. For the catalytic work, my thanks go to Taro Eguchi for his help with building/designing/tuning probes in the early high-pressure NMR experiments and for passing on his expertise, to Jon Iggo who has developed the unique high-pressure NMR flow cell, to Chacco Jacob for involvement in the catalytic hydrogenation work, to Stefano Zacchini for elucidating the mechanism of the methoxycarbonylation of ethene and to Robin Whyman for his general contributions to our catalytic studies and for his expertise on high-pressure IR spectroscopy. I am also grateful to EPSRC, Hovione, Enios Acrylics, and BP Chemicals for providing the necessary financial support.

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SECTION D:

Transition Metal Complexes of Olefins, Acetylenes, Arenes and Related Isolobal Ligands

Modern organometallic chemistry of the transition metals has its origins in materials first described in the 19th and the early 20th centuries. These include Zeise's salt, early examples of metal carbonyl compounds such as Mond's nickel tetracarbonyl discovered in 1888, and the so-called polyphenylchromium compounds in 1919. Further milestones of the 20th century include the discovery in 1930 of butadienetricarbonyliron and of ferrocene described in 1951.

It was Zeise's salt, a compound believed to contain C_2H_4 *bound to platinum, which had first caught Chatt's young eye after reading Keller's Chemical Review on metal–olefin complexes published in 1941. He had been intrigued by Gel'man's suggestion that four electrons were involved in bonding between Pt and* C_2H_4*, including two platinum d electrons. Chatt was also struck by the divergence of view between that he recollected from F. G. Mann's undergraduate lectures on olefin complexes in which Mann had suggested that the C=C π-electrons acted as a lone pair in a donor bond to the metal and Keller's scepticism that such bonding or Gel'man's model were possible.*

Elucidating the constitution and structure of $K[PtCl_3(C_2H_4)]\cdot H_2O$ *had represented a challenge to chemists ever since it had been first isolated from the reaction of platinum(II) chloride and ethanol by William Christopher Zeise in 1825. From early arguments about its constitution to later efforts to characterise its structure and describe the nature of the metal olefin bond some 125 years after its discovery, Zeise's salt continued to fascinate chemists. As is often the case, such fascination brought forth new and important ideas on chemical bonding as well as deeper understanding that grew to have technological and industrial significance. Some of this early work, particularly relating to the contributions of M. J. S. Dewar and Chatt, is reviewed by N. Winterton. G. Frenking describes more recent developments arising from the application of modern quantum chemical methods to the so-called Dewar–Chatt–Duncanson model of bonding of olefins to transition metals.*

The scope of discovery that arose following the later work of Chatt and others and the patterns of bonding and reactivity among isoelectronic ligands and metals is reflected in the other contributions brought together in this section. These include chapters by H.-W. Frühauf (on 1,3-dipolar additions to a series of 1,4-diazabutadienemetal carbonyl and isonitrile complexes), by V. C. Gibson, the Royal Society of Chemistry's Chatt Lecturer for 2001–2002 (on studies of metal imido complexes which reveal and explore their isolobal relationship with metal cyclopentadienyl complexes), by M. Abou Rida and A. K. Smith (on the preparation of ruthenium–rhodium bimetal complexes and their use in olefin hydroformylation) and by M. A. Bennett and J. R. Harper (on tethered arene–metal complexes).

Gibson's chapter also includes a brief historical commentary on the 'distortional' or 'bond-stretch' isomerism debate concerning green and blue forms of $[Mo(O)Cl_2(PMe_2Ph)_2]$ *initiated by Chatt, Manojlovic-Muir and Muir in 1971.*

Some Notes on the Early Development of Models of Bonding in Olefin–Metal Complexes

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1 Models of the Olefin–Metal Bond

In 1951, in a discussion[1] following his paper[2] reviewing π-complex theory, M. J. S. Dewar proposed a model (Figure 1) to describe the bonding of an olefin to silver(I) or copper(I). The model suggested that, in addition to σ-donation of olefin π-bonding electrons to the metal, d_π electrons on the metal would also interact with antibonding orbitals of π-symmetry on the olefin. No experimental evidence was provided to support this proposal nor, indeed, was explicit mention made of Zeise's salt or other platinum–olefin complexes. From a study of *Chemical Abstracts* **41** (1947)–**75** (1971), it would appear that Dewar did not follow up his proposal with more detailed studies, possibly indicating that this was not a prime focus of his own interests in MO theory and its application to

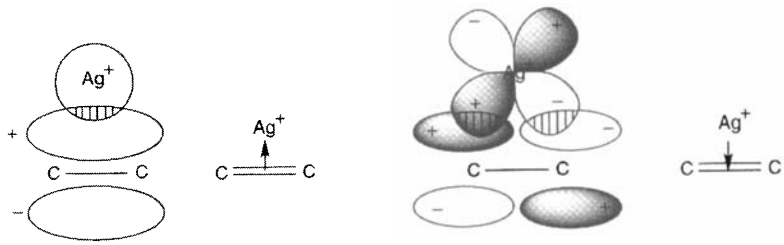

Figure 1 *Model of bonding of olefins with silver(I) proposed by M. J. S. Dewar (taken from ref. 1)*

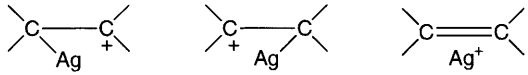

Figure 2 *Valence bond description of bonding of olefins with silver(I) (taken from Winstein and Lucas, ref. 6)*

organic chemistry.[3a] Indeed, in the brief discussion[3b] of bonding in metal–olefin complexes in his classic text[3a] (published in 1969), he cites only ref. 1 and no later theoretical or experimental work (either his own or that of other workers) on this topic.

The interactions of unsaturated hydrocarbons and metal ions, particularly silver(I), was an active area of research and had been reviewed by Keller[4] in 1941. A highly relevant paper[5] appeared in the same year (though not in time to be included in Keller's review) in which Taufen, Murray and Cleveland provided convincing spectroscopic evidence of olefin coordination to silver (albeit in solution) in a mode that was consistent with the valence-bond formulation (Figure 2) proposed by Winstein and Lucas.[6] Such evidence would also have supported Dewar's own formulation, though the paper by Taufen *et al.* was cited in neither Dewar's *Bull. Soc. Chim. Fr.* paper[2] nor in the subsequent discussion.[1] However, it should be noted that the discussion section is not supported by references. If Dewar was aware of Taufen *et al.*'s work and its significance it is odd that he made no mention of it.

Chatt and Duncanson, who developed Dewar's proposal in their seminal paper[7,8] of 1953 on metal–olefin complexes, do cite the paper of Taufen *et al.*[5] (as well as of Dewar), though Chatt had not done so in an earlier relevant paper of 1951.[9,10] Precisely when Chatt became aware of Taufen's work in not known.

While ref. 7 has been cited more than 500 times since 1981, Dewar's paper[2] about 250 times and the associated discussion[1] more than 200 times during the same period, the Taufen *et al.* paper, ref. 5, has been cited only seven times, an astonishing result bearing in mind the paper's significance. This work indeed merits wider recognition.

While it is surprising that Dewar and Chatt may not immediately have become aware of a paper from such a well known journal on its publication in 1941 (and, apparently, were unaware of it ten years later), it must remembered that sea-borne communication at the critical time (1941 onwards) was subject to wartime hazards, and the material may only have become more generally known after the war.

According to an interview,[11] Chatt had become interested in olefin complexes long before joining ICI in 1947 and had been fascinated by the suggestion by Anna Gel'man[12] that the metal–olefin bond involved four electrons, including two d electrons on platinum as well as the π-electrons of the olefin. Gel'man considered '*unsaturated molecules ... as acceptors and donors at the same time*', though in the model the metal was formulated as platinum(IV).

Early on, Chatt had not been able to find evidence of interaction between trimethylborane and ethylene.[9,10] He concluded from this indirect experimental

evidence that simple donation of electrons from the olefin to a transition metal was insufficient to be responsible for bonding of an olefin to a transition-metal ion and that bonds involving metal d orbitals were required, similar to those invoked in models developed for transition metal–CO and –NO bonding.

Chatt had first suggested in a note[13,14] (though without new supporting experimental detail) that olefin coordination in complexes of the sort $K[PtCl_3(RCH{=}CH_2)]$ involved coordination of an ethylidene moiety (Figure 3), drawing analogies with the role of d orbitals on platinum in π-bonding to the carbon of coordinated CO. After discussions with C. K. Ingold,[11] Chatt was persuaded to have another look at the structure and this proposal was subsequently abandoned.

Concurrently, Chatt pursued other highly productive studies on the constitution, structure and bonding of related complexes, developing ideas (such as the origin of the *trans* effect) concerning the role of π-bonding of organophosphine, -arsine and -stibine and carbon monoxide ligands proposed earlier. During this period, with Williams, Chatt[15,16] made an important contribution by demonstrating that the role of d orbitals in bonding might be enhanced by the presence of strongly electronegative groups attached to the ligating atom and this was demonstrated by the synthesis and isolation of platinum complexes of phosphorus trifluoride, a development also reported at about the same time by Wilkinson.[17] The suggestion had originally been made by Chatt in 1949 in a note[18,19] in *Nature*.

As Chatt acknowledges in the abstract of his paper with Duncanson[7] (and had also noted in a paper presented to a conference in March 1952[20]) only the Dewar model of olefin coordination was supported by his new infra-red evidence adduced for platinum complexes. As Chatt's interview[11] with Leigh reveals, this change came about following conversations with Dewar, who pointed out to Chatt the discussion section[1] following the *Bull. Soc. Chim. Fr.* paper,[2] which Chatt had not seen. Chatt's particular contribution was to develop the model, providing both the basis for predictions regarding its structural consequences (orientation of the C–C group with respect to the plane defined by the metal and the other donor atoms, changes in C–C bond length change, state of hybridisation at C and C–C–H bond angle changes) as well as experimental and spectroscopic evidence in its support. The Figure used in ref. 7 (Figure 4) has been widely reproduced. A crystal structure study of Zeise's salt, published in 1954[21] with a

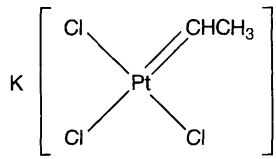

Figure 3 *Early proposal by J. Chatt of bonding between ethylene and platinum(II) in Zeise's salt (taken from ref. 13)*

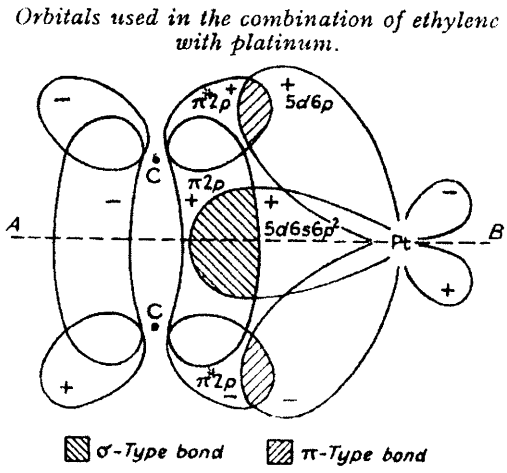

Figure 4 *MO description of bonding between ethylene and platinum(II) in Zeise's salt by Chatt and Duncanson (taken from ref. 7)*

correction in 1955,[22] first[21] corrects Chatt's structural inferences in ref. 13 and then offers support[22] to the Chatt–Duncanson proposal in ref. 7. The key point for Chatt, as he says, was that, '*this was the first time that any structure for the olefin compounds had been suggested* and *reasonably proven. Of course, there had been many others, all suggestions, as listed in R. N. Keller's review*[4] *and in a review by A. D. Gel'man, none proven any more than had been Dewar's proposed silver ion–olefin structure*'. This comment may be considered questionable in the light of the Taufen paper, though, at that particular time, compared with today, the weight given to evidence for proposed structures of species in solution may have been much less than that given to those of stable isolated solids. There had also been a brief report in 1950 of the crystal structure of $[Ag(C_6H_6)]ClO_4$,[23] though, at the time, Chatt was not convinced of the relevance of such structures to bonding in transition metal–olefin complexes.

However, there is no doubt that Chatt always acknowledged Dewar's vital role, as he did in the key paper with Duncanson[7] and subsequently.[e.g. 24,25]

So how, since this time, have chemists viewed the relative contributions of Dewar and Chatt to what has become known[26] as the Dewar–Chatt–Duncanson model (a term to which Dewar subsequently took exception[27] and one which Chatt himself apparently never used)?

The crystal structures of Zeise's salt[21,22] and of two analogous palladium–olefin complexes were published,[28,29] shortly after the publication of the Chatt–Duncanson paper.[7] They confirmed the structural proposals made by Chatt, but none of these papers cites Dewar,[1,2] though metal–olefin bonding models were not discussed. Two short reviews on the history of Zeise's salt,[30,31] (one[31] part of a more general discussion of the history of organometallic chemistry) also only refer to Chatt's contribution, though neither specifically address questions of bonding.

Emeléus and Anderson[32] discuss *both* the structure *and* bonding in platinum–olefin complexes citing explicitly Chatt and Duncanson's 1953 paper and

their infra-red studies (as well as the crystallographic studies[21,22,28,29]). They reproduce a version of the Chatt–Duncanson (and not Dewar's original) MO description. Dewar's paper is cited at the end of this section, curiously prefaced with '*cf*'.

On the other hand, in an organic text,[33] in which the role of transition metal–olefin complex intermediates is reviewed,[34] the bonding scheme is described (in a section heading) as '*Dewar's MO picture*', which, in later text, was '*soon extended by Chatt and Duncanson to platinum complexes*...'.

Cotton[35] in 1960 writes '*The geometry of the olefin-metal system ... is in accord with the type of bonding discussed by Chatt and Duncanson following the proposal by Dewar*'. In Cotton's review the work of Taufen *et al.*[5] is given due prominence.

Guy and Shaw[36] in 1962 also indicate the prior contribution of Dewar, though forbear from characterising the scheme as the Dewar–Chatt–Duncanson model.

Similarly, Green[37] in 1968 says beneath an MO diagram, '*... description originally proposed by Dewar and in a modified form by Chatt*'.

The various editions of Cotton and Wilkinson[38] deal with the matter in different ways: in the first and second editions the model is attributed to Dewar alone, though Chatt and Duncanson's spectroscopic work is cited; the third edition refers to the Dewar–Chatt description; in the fourth edition, Dewar only is mentioned.

Later reviews[39,40] published in the 1970s and a key paper[41] dealing with a neutron diffraction study of Zeise's salt continue to refer to the Dewar–Chatt–Duncanson model. Even very recent work,[42] such as the ^{13}C and ^{2}H NMR study of Zeise's salt in the solid state, cites both Dewar[1] and Chatt and Duncanson.[7]

An interesting final perspective on the foregoing is provided by the theoretical work of Böhme, Wagener and Frenking[43] (elaborated further by Frenking in the next chapter[44]) who conclude from their calculations that bonding in $\{Cu(C_2H_4)^+\}$ is better described by an electrostatic model rather than one involving back bonding. Some authors have reached similar conclusions for $\{Ag(C_2H_4)^+\}$. However, there continues to be much discussion on this point (not reviewed here but see refs. 45 and 46). As in the case of Chatt's ideas concerning the π-acidity of empty 3d orbitals on the phosphorus of PY_3 bound to a suitable transition metal, which more recent work[47,48] has shown possibly to be less important than interactions involving empty σ^* orbitals of PY_3, it now seems possible that the systems about which Dewar speculated[1] are not the best exemplars of back-bonding involving alkenes. However, in both cases the earlier thinking created the opportunity for improved models to be developed and refined.

In my view, Greenwood and Earnshaw[49] summarise matters most appropriately: '*The key to our present understanding of the bonding in Zeise's salt and all other alkene complexes stems from the perceptive suggestion by M. J. S. Dewar in* 1951 *that the bonding involves electron donation from the* π*-bond of the akene into a vacant metal orbital of* σ *symmetry; this idea was modified and elaborated by J. Chatt and L. A. Duncanson in a seminal paper in 1953 and the Dewar–Chatt–Duncanson theory forms the basis of most subsequent discussion*'.

Perhaps, this is how history, finally, should judge this important joint contri-

bution of theory and experiment from Dewar and Chatt and those that followed.

2 Addendum

After this brief survey was written, Seyferth[50] published a further perspective on Zeise's salt, reviewing again much of the early discussions of its synthesis and disputes about its composition and formulation. In a section devoted to the development of bonding models and more recent structural studies, Seyferth cites an earlier review by Olsson[51] that covers much of the discussion of the present paper, and reaches a broadly similar conclusion concerning Chatt's contribution in developing Dewar's earlier suggestion. I thank L. I. Elding for providing a copy of Olsson's publication. I also gratefully acknowledge receipt from Professor D. M. P. Mingos of a copy of a manuscript prior to publication.[52]

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The Dewar–Chatt–Duncanson Bonding Model of Transition Metal–Olefin Complexes Examined by Modern Quantum Chemical Methods

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1 Introduction

There is probably no bonding model that has proven to be more useful for explaining metal–ligand interactions in transition metal (TM) complexes than the suggestion which was originally made by Dewar to describe the bonding of an olefin coordinated to silver(I) and copper(I).[1] Chatt and Duncanson[2] realised that this model and their spectroscopic data of Zeise's salt gave a coherent picture and, for the first time, an understanding of the bonding of a compound which had been a puzzle for chemists ever since it was accidentally synthesised in 1825.[3]

Figure 1a shows a schematic representation of the Dewar–Chatt–Duncanson (DCD) model. The pivotal idea is that the olefin serves as a donor and an acceptor at the same time. There is ligand → metal donation and metal → ligand back-donation. The former interaction involves a donor orbital of the ligand which has π symmetry in the free ligand but σ symmetry in the complex. The metal acceptor orbital is mainly the d_{z^2} orbital of the metal. Quantum chemical calculations have shown that the valence s orbital of the metal is less important as an acceptor orbital than the d_{z^2} orbital.[4] The metal → ligand back-donation takes place *via* a d(π) orbital of the metal and the π^* orbital of the olefin.

The picture shown in Figure 1a has become a standard model in textbooks of inorganic and organometallic chemistry to explain the bonding in TM compounds. However, it was soon realised that there are TM compounds with olefin

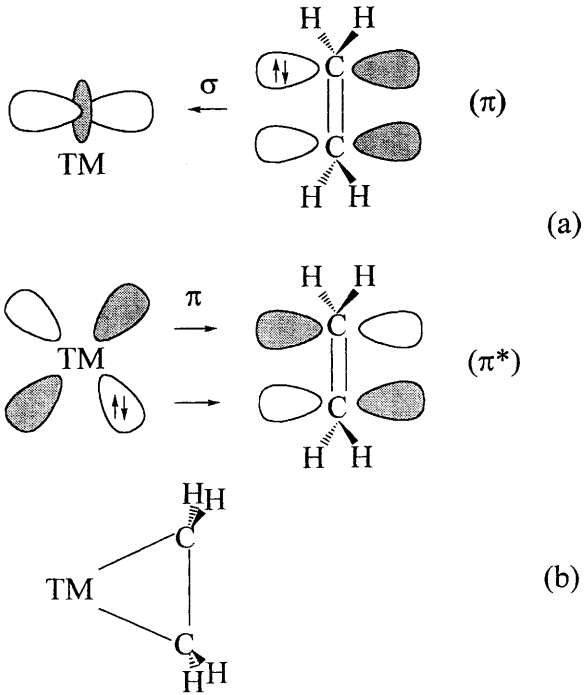


Figure 1 *Schematic representation of (a) the DCD model for TM–olefin bonding and (b) a metallacyclopropane*

ligands which would better be described as metallacyclopropanes as shown in Figure 1b. The latter compounds have two electron-sharing covalent[5] metal–carbon bonds instead of a donor–acceptor bond. The dichotomy of two bonding modes, *i.e.* donor–acceptor bond and electron-sharing covalent bond, has also become a very helpful device for the understanding of TM complexes with other ligands such as alkynes, carbenes and carbynes.[6]

The DCD model has been used for decades as a heuristic device to explain the structures and properties of TM complexes without the nature of the metal–ligand interactions having been examined by theoretical methods. The progress in quantum chemical methods in the last decade has made it possible for calculations on TM compounds to be carried out with high accuracy.[7] The electronic structure can then be analysed with modern charge and energy partitioning methods.[4,8] A charge-partitioning method has been developed with respect to the DCD model which makes it possible to quantify the amount of ligand → metal donation and metal → ligand back-donation.[9] Application of charge decomposition analysis (CDA) to a wide range of TM compounds shows that it can be used as a quantitative expression of the DCD model.[8a,10] Details of CDA can be found in the literature.[8a,9,10]

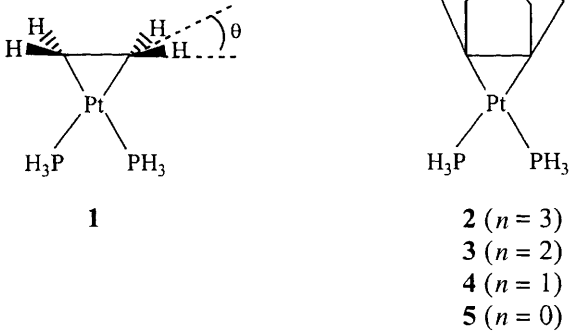
In this paper we present a summary of three theoretical investigations of TM olefin complexes, which show that the original bonding model of Dewar[1] and its ingenious application to metal–olefin interactions by Chatt and Duncanson[2]

stand the test of examination by quantum chemical methods. The strength of the DCD model comes to the fore as a result of calculations which show that changes in the donor or acceptor moiety of the complex induce concomitant changes in the metal–ligand interactions and in the properties of the complexes, which can be understood by the model. Analysis of the calculated data shows the scope but also the limitation of the DCD bonding model. The calculations reveal examples of olefin complexes which are not properly described by the DCD model. We will present only results which are important in the context of this paper. For details we refer the reader to the original publications.

2 Platinum Complexes of Strained Olefins

Olefins become more reactive when steric constraints enforce a nonplanar geometry on the $R_2C{=}CR_2$ moiety. A twisted or pyramidal geometry of the olefin weakens the double bond. The energy level of the occupied π orbital increases while the unoccupied π^* orbital becomes lower in energy. The change in the energy levels of the π and π^* orbitals should enhance the metal–ligand donation and back-donation and thus should strengthen the metal–olefin bond. We studied this effect by calculating the structures and bond energies of the platinum complexes $[PtL(PH_3)_2]$ where L is ethylene or a strained tricyclic olefin as shown in Figure 2.[11]

The strain in the olefin moiety of the tricyclic compounds becomes larger when the chain length n of the bridging $(CH_2)_n$ group becomes smaller. This becomes evident from the calculated pyramidalisation angle θ and the C=C bond lengths of the free olefins which are shown in Table 1. The calculations also show that the C=C distances of the olefinic moiety become longer in the complexes and that the pyramidalisation angle θ becomes bigger than in the free olefin. The increase



1

2 (n = 3)
3 (n = 2)
4 (n = 1)
5 (n = 0)

Figure 2 *Calculated platinum olefin complexes* **1–5** *and definition of the pyramidalisation angle* θ

Table 1 *Theoretically predicted pyramidalisation angles θ (degrees) and C=C bond lengths (Å) of the platinum complexes* **1–5** *and the free olefins. Calculated metal–olefin binding energies D_e (kcal mol^{-1}). Results of the CDA calculations of ligand → metal donation d, metal → ligand back-donation b and ratio d/b*[a]

Molecule		*Sym.*	*θ* (Δ*θ*)[b]	*C=C*(Δ*C=C*)[b]	D_e	*d*	*b*	*d/b*
Compounds								
$[Pt(C_2H_4)(PH_3)_2]$	**1**	C_{2v}	24.1 (24.1)	1.427 (0.096)	99.9	0.511	0.383	1.33
$[Pt(C_{11}H_{16})(PH_3)_2]$	**2**	C_1	48.4 (20.5)	1.446 (0.104)	147.1	0.477	0.396	1.20
$[Pt(C_{10}H_{14})(PH_3)_2]$	**3**	C_2	53.9 (11.7)	1.460 (0.111)	200.3	0.498	0.429	1.16
$[Pt(C_9H_{12})(PH_3)_2]$	**4**	C_{2v}	60.2 (6.5)	1.480 (0.118)	244.7	0.504	0.460	1.10
$[Pt(C_8H_{10})(PH_3)_2]$	**5**	C_{2v}	66.6 (4.7)	1.513 (0.133)	293.5	0.517	0.500	1.03
Olefins								
C_2H_4 (ethene)		D_{2h}	0.0	1.331				
$C_{11}H_{16}$ ($n = 3$)		C_s	27.9	1.342				
$C_{10}H_{14}$ ($n = 2$)		C_2	42.2	1.349				
C_9H_{12} ($n = 1$)		C_{2v}	53.7	1.362				
C_8H_{10} ($n = 0$)		C_{2v}	61.9	1.380				

[a]Taken from reference 11

[b]The values in parentheses give the differences between the values in the complex and the free olefin

of the C=C distance upon complexation has the same trend as the bond dissociation energies of the Pt–L bonds **1** < **2** < **3** < **4** < **5** (Table 1). This means that the change in the carbon–carbon bond lengths of the coordinated olefin reflects nicely the bond strength. We want to point out that this holds only within a series of compounds which has the same kind of bonding interactions. It will be shown below that the change of geometry does not always correlate with the bond strength because different types of metal–olefin bonds may have a different influence on the geometry. Note that the further increase of the pyramidalisation angle θ of the olefin ligands in the complexes becomes less for the more strongly strained ligands (Table 1).

What about the correlation of the DCD model of metal–olefin bonding with the calculated changes of the geometries and the bond dissociation energies? Table 1 also shows the CDA results of the olefin → $Pt(PH_3)_2$ donation *d* and the $(PH_3)_2Pt$ → olefin back-donation *b*. We wish to point out that the absolute values of the donation and back-donation have little meaning. It is the ratio *d/b* of the two terms which should be used for a comparison of different complexes or different ligands. Table 1 shows that the ethylene complex **1** has *d/b* = 1.33, *i.e.* the calculated charge donation is larger than the back-donation. The *d/b* values of the other olefin complexes decrease in a regular fashion with the trend **1** > **2** > **3** > **4** > **5**. It means that the $(PH_3)_2Pt$ → olefin back-donation becomes more important when the coordinated olefin is more strained. It follows that the energy lowering of the LUMO of the olefin is more important for increasing the bond energy than the energy increase of the HOMO. Figure 3 shows a diagram

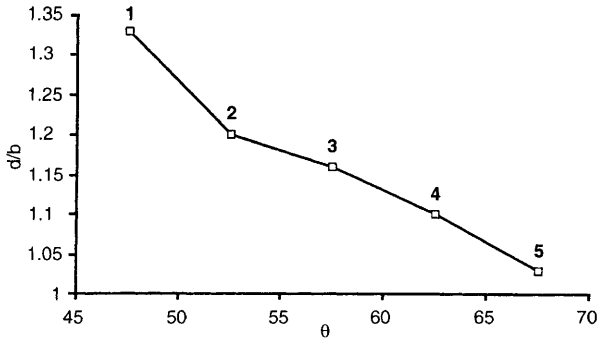


Figure 3 *Plot of the d/b ratio of olefin → Pt donation and Pt → olefin back-donation against pyramidalisation angle θ (degree) of compounds* **1–5**
Reproduced with permission from reference 11

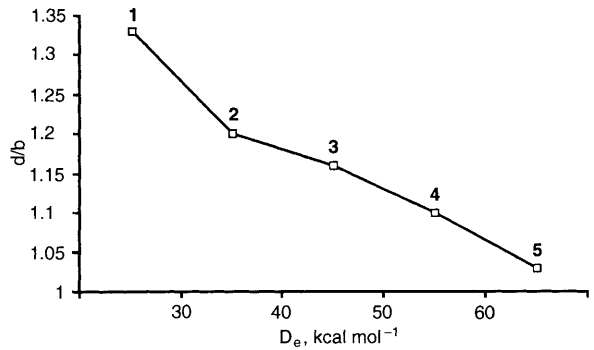


Figure 4 *Plot of the d/b ratio of olefin → Pt donation and Pt → olefin back-donation against the bond dissociation energies D_e (kcal mol^{-1}) of compounds* **1–5**
Reproduced with permission from reference 11

where the *d/b* ratio of **1–5** given by the CDA is correlated with the pyramidalisation angles *θ*. Figure 4 shows a plot of the calculated bond energies and the *d/b* ratio. The diagrams nicely demonstrate that partitioning of the electronic structure of molecules in terms of the DCD model yields a quantitative correlation between the *d/b* ratio of the metal–ligand interactions and the geometries and bond energies of the compounds.

3 Olefin Complex *versus* Metallacyclopropane

The dichotomy of the two bonding models which are sketched in Figure 1 has been investigated by us with the help of CDA calculations using the model compounds $[W(CO)_5(C_2H_4)]$ (**6**) and $[WCl_4(C_2H_4)]$ (**7**) as examples.[8a,12] Figure 5 shows the calculated geometries and the theoretically predicted bond dissocia-

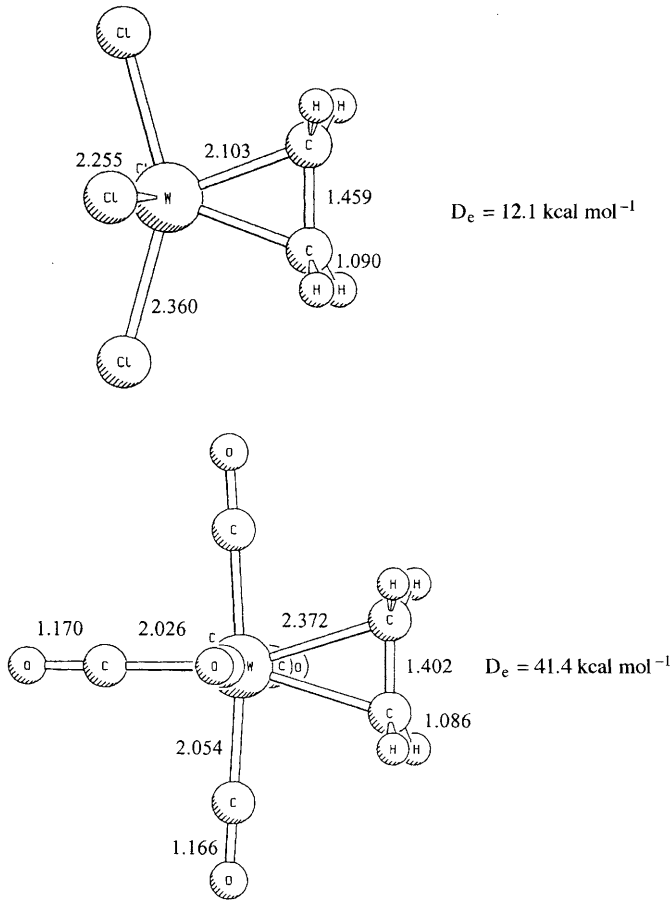
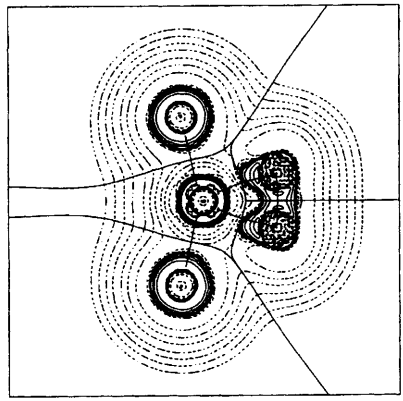
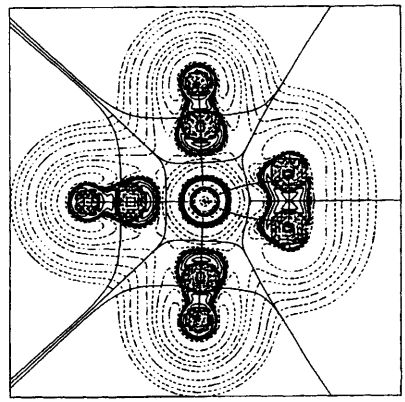


Figure 5 *Calculated geometries and W–C_2H_4 bond dissociation energies (kcal mol^{-1}) of* [$WCl_4(C_2H_4)$] **7** *and* [$(W(CO)_5(C_2H_4)$] **6**. *Bond lengths are given in Å Reproduced with permission from reference 12b*

tion energies of the molecules. It becomes obvious that the W–C distance of **7** (2.103 Å) is substantially shorter than in **6** (2.372 Å). The shorter W–C bond length of the former compound suggests stronger metal–ethylene interactions than in the latter molecule. Stronger tungsten–ethylene bonding is also indicated by the C–C distances in the two compounds. The C–C bond length in **7** (1.459 Å) is clearly longer than in **6** (1.402 Å). A direct proof for stronger metal–ligand interactions in the former complex comes from the topological analysis of the electron density distribution.[13] Figure 6 shows the contour line diagrams of the Laplacian $\nabla^2\rho(\mathbf{r})$ in the plane which contains the WC_2 moiety. Areas of charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$) are depicted with solid lines while areas of charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$) are drawn with dashed lines. Visual inspection of the shape of the Laplacian shows that the electronic charge of the ethylene ligand in **7** is much more distorted than in **6** . There is a much larger area of charge



(a)



(b)

Figure 6 *Contour line diagrams of the Laplacian distribution* $\nabla^2\rho(\mathbf{r})$ *of* (a) $[WCl_4(C_2H_4)]$ **7** *and* (b) $[W(CO)_5(C_2H_4)]$ **6** *in the plane containing the* WC_2 *moiety. Dashed lines indicate charge depletion* ($\nabla^2\rho(\mathbf{r}) > 0$) *and solid lines indicate charge concentration* ($\nabla^2\rho(\mathbf{r}) < 0$). *The solid lines connecting the atomic nuclei are the bond paths, and the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the plane. The crossing points of the bond paths and the zero-flux surfaces are the bond critical points*
Reproduced with permission from reference 8a

concentration at the ligand carbon atoms in the former compound pointing toward the tungsten atom than in the latter species.

The calculated $W–C_2H_4$ bond dissociation energies (BDEs) do not correlate with the geometrical parameters. The compound **7** has a surprisingly low BDE $D_e = 12.1$ kcal mol^{-1} while **6** has a much stronger bonded ethylene ligand with $D_e = 41.4$ kcal mol^{-1}. What is the reason for the much stronger metal–ethylene interactions in the former compound leading to such a low BDE? It is important to recognise that strong electronic interactions do not necessarily mean a strong

bond in a thermodynamic sense. The BDE is the energy difference between the molecule and the fragments in the electronic ground states, which may not be the electronic reference state in the molecule. The analysis of the electronic structure in terms of the two bonding models shown in Figure 1 did not give only an understanding of the bonding situation in the two ethylene complexes. It also gave a plausible explanation for the low BDE of **7**. However, we must give a short outline of the CDA in order that the results of the calculations can be understood.

The CDA method considers the bonding in a complex in terms of fragment molecular orbital interactions between two closed-shell fragments. In the present case, the fragments are $\{W(CO)_5\}$ and C_2H_4 for **6** and $\{WCl_4\}$ and C_2H_4 for **7**. The mixing of the occupied orbitals of C_2H_4 and the unoccupied orbitals of $\{W(CO)_5\}$ or $\{WCl_4\}$ gives the electron donation *d*. The mixing of the unoccupied orbitals of C_2H_4 and the occupied orbitals of $\{W(CO)_5\}$ or $\{WCl_4\}$ gives the back donation *b*. The mixing of the occupied orbitals of the two fragments gives the repulsive polarisation *r*. The mixing of the vacant orbitals of the fragments gives the residual term Δ. It should be zero because mixing of unoccupied orbitals cannot physically contribute to the electron density. It was found that the residual term Δ is a sensitive probe which shows if the electronic structure of a compound can reasonably be described by donor–acceptor interactions of the chosen fragments. For example, the electron density of ethylene cannot be described by interaction of two methylene fragments in the $^1A_1$ state but only in the $^3B_1$ state. A CDA of ethylene using ($^1A_1$) CH_2 as building blocks gives values for Δ which are very large. Thus, a significant deviation of $\Delta = 0$ beyond numerical noise indicates that the compounds cannot be described by the interactions of the chosen fragments.

Table 2 shows the CDA results of **6** and **7**. The data suggest for **6** that ethylene is a stronger donor than acceptor. The total amounts of donation and back-donation are larger than in $[Pt(C_2H_4)(PH_3)_2]$ (Table 1) but the *d*/*b* ratio of the two complexes is similar. The calculated value for Δ is close to zero which indicates that the bonding situation in **6** can be discussed in terms of donor–acceptor interactions between $\{W(CO)_5\}$ and C_2H_4. The results for **7** are very different. The calculated amounts of donation and back-donation are negative, which is a physically unreasonable result. The same conclusion comes from the calculated residual term $\Delta = 0.351$. The CDA results clearly show that the bonding situation in **7** should not be discussed in terms of donor–acceptor

Table 2 *Charge decomposition analysis of* $[WCl_4(C_2H_4)]$ (**7**) *and* $[W(CO)_5C_2H_4]$ (**6**)[a]

	7	**6**
d	−0.263	0.225
b	−0.194	0.148
r	−0.318	−0.422
Δ	0.351	−0.025

[a]Taken from reference 8a

interactions between the closed-shell fragments $\{WCl_4\}$ and C_2H_4. The latter compound should rather be considered as a metallacyclopropane where the W–C bonds arise from the electron-sharing interactions between two open-shell fragments. This explains why the BDE of the W–C_2H_4 bonds are so low. Ethylene has a closed-shell electronic ground state. In order to promote C_2H_4 from the ground state to the triplet excited state which is the reference state for the binding interactions with $\{WCl_4\}$ (which has a triplet ground state) a large amount of excitation energy is necessary. The singlet → triplet excitation of ethylene is ~ 100 kcal mol^{-1}. Thus, the interaction energy between $\{WCl_4\}$ and C_2H_4 is much higher ($D_e = 12$ kcal mol^{-1} plus the excitation energy) than the BDE. The value of ~ 112 kcal mol^{-1} correlates nicely with the calculated bond lengths of **7**.

4 Electrostatically-bound Olefin Complexes

The olefin complexes discussed above could either be classified as belonging to the DCD bonding scheme or metallacyclopropanes. Now we want to introduce yet another type of strongly bonded TM–olefin complex which is held together mainly by electrostatic interactions.

In the course of a theoretical investigation of model compounds for ethylene and acetylene bonded to copper atoms on a metal surface we calculated the structures and bond energies of $\{Cu(C_2H_4)\}$ and $\{Cu^+(C_2H_4)\}$.[14] Figure 7 shows the optimised geometries of the molecules. The C–C distance is slightly longer than the calculated value of free ethylene (1.336 Å). We want to point out that the carbon–carbon bond length and the pyramidalisation of the ethylene ligand in $\{Cu(C_2H_4)\}$ and $\{Cu^+(C_2H_4)\}$ are nearly the same and that the Cu–C distance of the latter compound (2.095 Å) is only slightly shorter than in the former molecule (2.122 Å). However, the positively charged species has a much higher BDE $D_e = 43.9$ kcal mol^{-1} than the neutral compound which has only BDE = 4.2 kcal mol^{-1}. The weak copper–ethylene bond of $\{Cu(C_2H_4)\}$ suggests that the compound should be considered as van der Waals' complex. But what about the bonding in $\{Cu^+(C_2H_4)\}$?

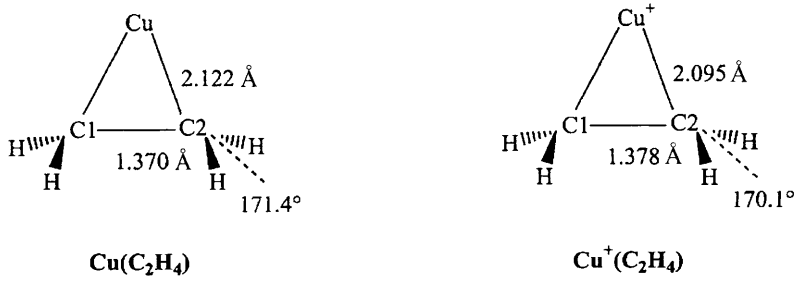


Figure 7 *Calculated interatomic distances (Å) and bond dissociation energies D_e (kcal mol^{-1}) of $\{Cu(C_2H_4)\}$ and $\{Cu^+(C_2H_4)\}$*
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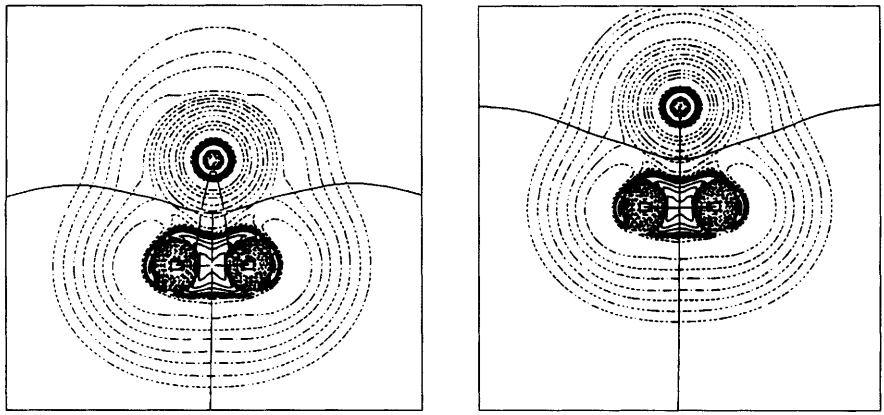

Figure 8 *Contour line diagrams of the Laplacian distribution* $\nabla^2\rho(\mathbf{r})$ *of (a)* $\{Cu(C_2H_4)\}$ *and (b)* $\{Cu^+(C_2H_4)\}$
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Figure 8 shows the Laplacian distribution of $\{Cu(C_2H_4)\}$ and $\{Cu^+(C_2H_4)\}$. Visual inspection of the shapes of the areas of charge concentration (solid lines) and charge depletion (dashed lines) shows hardly any difference between the two compounds. The most prominent difference is that in neutral $\{Cu(C_2H_4)\}$ there are bond paths between each C atom and Cu, besides the bond path between the carbon atoms. There is also a ring critical point in the CuC_2 moiety of $\{Cu(C_2H_4)\}$. Thus, the topological analysis defines the latter compound as a cyclic molecule. The positively charged $\{Cu^+(C_2H_4)\}$, however, does not have bond paths which connect Cu^+ with the carbon atoms. There is only a bond path from Cu^+ to the midpoint of the C–C bond. Thus, the topological analysis suggests that $\{Cu^+(C_2H_4)\}$ has a T-shaped structure and that it should not be considered as a cyclic compound. The bonding interactions arise from the charge attraction between positively charged Cu^+ and the negative charge accumulation in the C–C bond region. The Natural Bond Orbital analysis[15] of $\{Cu^+(C_2H_4)\}$ shows that the copper atom carries a positive charge of $+0.91$. There is very little ethylene $\rightarrow Cu^+$ charge donation in the compound. $\{Cu^+(C_2H_4)\}$ is neither a donor–acceptor complex which can be described by the DCD model nor a metallacyclopropane. Rather, it is a electrostatically bonded species which is held together mainly by Coulomb attraction between Cu^+ and the π charge of ethylene.

5 Summary

The DCD bonding model of TM olefin complexes is supported by accurate quantum chemical calculations which quantify the amount of ligand $\rightarrow$ metal donation and metal $\rightarrow$ ligand back-donation. The geometries and bond energies

of olefin complexes which can be described by the DCD model show a nice correlation with the strengths of the donation and back-donation. Modern charge partitioning schemes show that there are other types of olefin complex for which bonding interactions are not well described by the DCD model. The bonding in metallacyclopropanes comes from electron-sharing covalent bonding between a metal fragment and the olefin which have electronic triplet states. There are also compounds such as $\{Cu^+(C_2H_4)\}$ where the bonding between the metal and the olefin is mainly due to electrostatic attraction. The different types of TM–olefin complexes exhibit a different correlation between bond strength and bond length.

6 Acknowledgements

The author thanks his co-workers who contributed to the publications which are described in this work. This research has been supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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Cycloaddition Reactions with Metalla-1,3-Dipoles

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1 Introduction

Much of the work described in this article has previously been presented at International Coordination Chemistry Conferences, including the latest piece (Section 3.3.1), in the session on Joe Chatt Chemistry at the 34th ICCC in Edinburgh, which resulted in the invitation to write this paper.

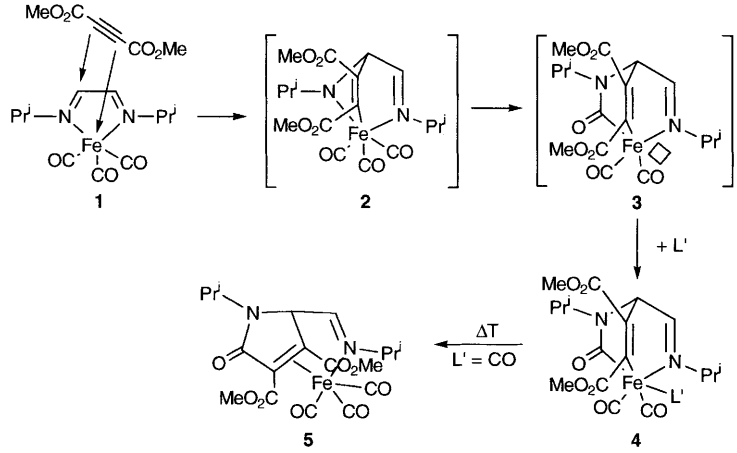
When the reader scans through this introduction and the rest of the paper, he will find ligands such as olefins, acetylenes, or phosphines/phosphites. They could be taken from a key-word list of the published work of Joseph Chatt and make clear the connection to his seminal work.

The chemistry that is described in this account arose from an attempt to prepare the first iron(0) η^2-alkyne complex. In an investigation on [$Fe(CO)_2$(η^2-olefin)(1,4-diaza-1,3-diene)] complexes[1] it was found that the stability of the iron–olefin bond increased strongly with increasing π-acidity of the olefin. So the idea was, in analogy with the preparation of the olefin complexes, to substitute photochemically a CO-ligand in [$Fe(CO)_3$(diazadiene)] for the supposedly very good π-accepting dimethyl acetylenedicarboxylate (dmad). As it turned out, it was not possible to irradiate the tricarbonyl complex in the presence of dmad, because a very fast thermal reaction immediately consumed the reactants. This was readily recognised from the immediate disappearance of the intense colour of the [$Fe(CO)_3$(diazadiene)] complex on the addition of dmad. All [$Fe(CO)_3$(diazadiene)] complexes have a very intense MLCT transition in the visible region which, depending on the diazadiene, makes them intensely red, violet (*N*,*N*′-disubstituted 1,4-diazabuta-1,3-dienes, dab), blue (2-pyridine-*N*-aryl carbaldimines, R-Pyca), or green (bipy, o-phen). The fascinating chemistry that arose from this initial observation will be summarised in this account.

2 1,3-Dipolar Cycloaddition of Activated Alkyne to the Fe–N=C Fragment

2.1 The Reaction of $[Fe(CO)_3(dab)]$ with Dimethyl Acetylenedicarboxylate

The original reaction mentioned in the introduction is shown in Scheme 1. In the ^1H NMR of the reaction mixture, two apparently isomeric products could be identified in a ratio of *ca.* 9:1. In an attempt to separate them by column chromatography, the isomer ratio was inverted to 1:9. From this it was obvious that **4** was an intermediate and **5** was the final product. Compound **5** could be isolated and fully characterised, including by X-ray structural analysis.[2] So it was concluded that the isomerisation consisted of a reductive elimination to form the 1,5-dihydropyrrol-2-one and recoordination of its olefinic double bond.



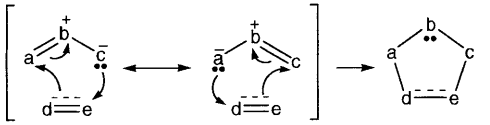
Scheme 1

The thermally labile intermediate **4** could also be isolated (and was characterised by X-ray analysis[3]) when the reaction was performed in the presence of trimethyl phosphite L′ in place of carbon monoxide. As a consequence, the metal becomes more electron-rich and reductive elimination does not occur. With the structure of **4** being firmly established, the pathway shown in Scheme 1 was proposed and it was realised that the Fe–N=C fragment resembles a 1,3-dipole.[4] By ^{13}CO labelling studies[5] and from the X-ray structure of **4** with L′ = $P(OMe)_3$ it was shown that the additional ligand L′ is always stereospecifically incorporated *trans* to the inserted carbonyl. The initial bicyclo[2.2.1] cycloadduct **2** could not be observed even at very low temperatures – evidently because CO insertion is faster than its formation. Later, when the 1,3-dipole was modified (*cf.* Section 3), stable analogues of **2** could be obtained. The crystal and molecular structures of homologues of **2** could be determined in the iron system,[4,6] for ruthenium[7] and manganese.[8]

With the formation of **2**, two interdependent stereocentres are formed, the bridgehead iron and carbon atoms. The imine carbon atoms in **1** are prochiral, and the alkyne can approach either of them from either the *re*- or the *si*-face. With chiral substituents at the nitrogen atoms, the approach of one face may be favoured over the other. This would lead to diastereoselectivity which has been investigated with different types of diazadiene ligands and a series of chiral *N*-substituents.[9] Depending on both the type of diazadiene (C_2 and non-C_2 symmetric) and the chiral *N*-substituents, diastereoselectivities from 0 to $> 99\%$ have been observed.

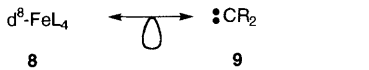
2.2 The Isolobal Relation of the Fe–N=C Fragment with an Azomethine Ylide

Huisgen defined a 1,3-dipole[10,11] as a species that may be described (as in Equation 1) by zwitterionic octet structures **6a** ↔ **6b**,* and which may undergo cycloaddition reactions of the type 3 + 2 → 5 with suitable multiple bonds (dipolarophile d=e) to give a neutral five-membered ring **7**.

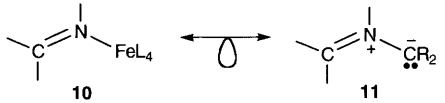


6a **6b** **7** (1)

This general description of a 1,3-dipole can be easily recognised in the iron–imine system with the aid of the isolobal relation **8** and **9** (Equation 2) and, derived from it, **10** and **11** (Equation 3).



8 **9** (2)

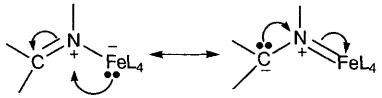


10 **11** (3)

In the well-known isolobal analogy[12,13] between a d^8 ML_4 fragment **8** and a carbene **9**, the four ligands L at the iron correspond to, *e.g.*, the three CO ligands and one of the two imine units in **1**. If, by way of N-donation, an imine is added to **8** and **9**, respectively, structures **10** and **11** are obtained, of which **10** is equivalent to **1**, while **11** resembles one resonance structure of an azomethine ylide, a classical 1,3-dipole. When the relevant atom arrangement in **10** is substituted into the general formula **6a** ↔ **6b** of a 1,3-dipole, the resulting organometal

* The formal 1,3-dipole results from localising two of the four electrons at the onium centre b^+, which gives rise to the sextet structures $^+a\text{–}b\text{–}c^-$ ↔ $^-a\text{–}b\text{–}c^+$. They demonstrate the ambivalence of 1,3-dipoles, which may have both nucleophilic and electrophilic properties at each end.

1,3-dipole **12a** ↔ **12b** in fact represents a valence-bond description of the dab. Earlier MO calculations on the model compound $[Fe(CO)_3(HN{=}CH{-}CH{=}NH)]$[14] had shown that the frontier orbitals of **1** are C=N–Fe based, *i.e.* both the HOMO and LUMO have strongly mixed metal d and ligand π^* character.[15]



12a **12b**

From this it seemed reasonable to formulate the initial reaction step (Scheme 1) in terms of a 1,3-dipolar cycloaddition reaction of the alkyne across the Fe–N=C fragment, resulting in the (unobserved) ferrabicyclo[2.2.1] intermediate **2** from which the isolated products **4** and **5** are readily derived.

3 Adding Variety to the 1,3-Dipolar System

The concept of 1,3-dipolar cycloadditions was supported by CAS-SCF calculations by Dedieu and Liddel[16] on both the organic and inorganic species. Both are nucleophilic dipoles with relatively high HOMO and LUMO energies, the metalla-1,3-dipoles at slightly higher energy. Cycloaddition reactions of nucleophilic 1,3-dipoles are HOMO-controlled, *i.e.*, the interaction of the dipole HOMO with the dipolarophile LUMO is predominant, and the reactivity of the dipole can be increased either by decreasing the HOMO–LUMO gap, and/or increasing the HOMO energy.

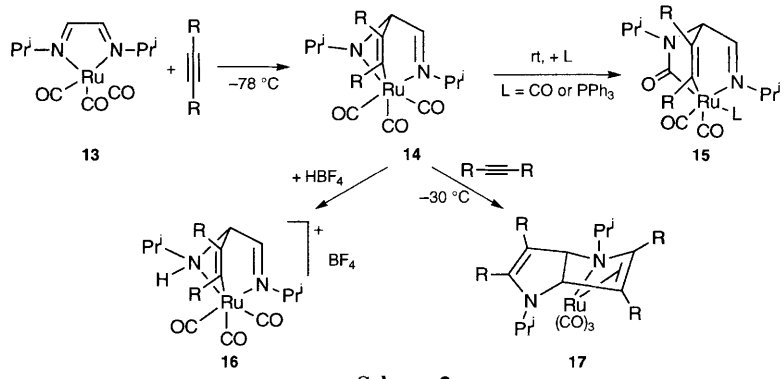
Variations to the system, to explore their influence on reactivity, can be brought about by changing the metal atom, the hetero atom, or the electronic properties of the additional ligands on the metal.

3.1 Changing the Metal

3.1.1 Reactions of $[Ru(CO)_3(dab)]$

With ruthenium instead of iron,[7,17] the 1,3-dipolar reactivity markedly increased. The same reaction pathway is followed, but the activation barriers further along the reaction coordinate are different. The reaction of **13** with one equivalent of dmad (Scheme 2)[7] proceeds instantly at − 78 °C and, in contrast to the iron system, the bicyclo[2.2.1] adduct **14** is stable at that temperature. After protonation of the amido nitrogen with HBF_4, which inhibits CO-insertion, **16** is stable at room temperature, and its X-ray structure could be determined. On warming the solution of **14** to room temperature in the presence of CO or PPh_3, CO-insertion occurs, as in the iron system, to give **15**.

3.1.1.1 Double cycloaddition. In the presence of an excess of dmad, the increased 1,3-dipolar reactivity of **13**, or rather **14**, leads to a second cycloaddi-



Scheme 2

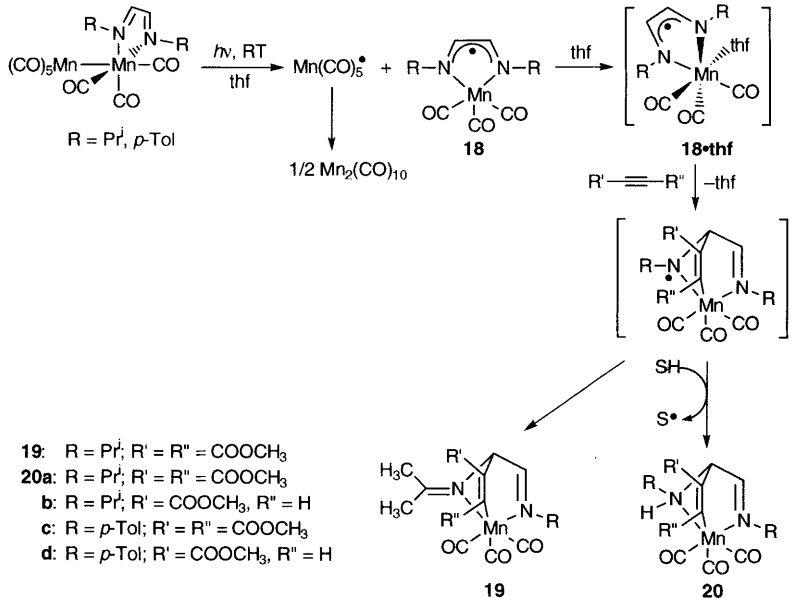
tion to give the 1,4,3a,6a-tetrahydropyrrolo[3,2-*b*]pyrrole (thpp) complex **17**. In **17**, the coordination of thpp to the metal is highly dynamic[7,18,19] and at $T > 30\,°C$ it readily dissociates from the metal. The $\{Ru(CO)_3\}$ fragments immediately form $[Ru_3(CO)_{12}]$ and, unfortunately, cannot be intercepted by an excess of diazadiene to regenerate **13** in order to make the formation of thpp catalytic. In the iron system, the double cycloaddition to thpp could only be observed when the dipole was further activated by exchanging the CO ligands for isocyanides (see Section 3.2).

3.1.1.2 Olefins as dipolarophiles. The reactivity of **13** is also sufficient to cycloadd olefins such as dimethyl fumarate and maleate.[17] The conservation of the *cis*- and *trans*-configuration of the olefins in products formed on *N*-protonation and insertion of CO into the Ru–N bond of the cycloaddition product indicates that the reaction is stereospecific and most likely to be a concerted process. The CO ligands in **13** are thermally labile, for which reason **13** is only stable in solution under an atmosphere of CO.[20] It is therefore not surprising that the substitution products in which a CO is replaced by dimethyl fumarate or maleate are formed as side-products.

3.1.2 $[Mn(CO)_3(dab)]^{\bullet}$: *a test-case for the isolobal relation*

Stufkens *et al.*[21,22] had shown by means of ESR spectroscopy that in $[Mn(CO)_3(dab)]^{\bullet}$ radicals, obtained photochemically by homolytic cleavage of the metal–metal bond in dinuclear complexes $[Mn_2(CO)_8(dab)]$, the unpaired electron does not reside at the metal atom, but is mainly localised in the π^*-orbital of the dab. The radical $[Mn(CO)_3(dab)]^{\bullet}$ (**18**) is therefore best described as a 16-electron d^6 manganese(I) species, *i.e.* $[Mn^+(dab^{\bullet -})(CO)_3]$. Comparing this with the homologous $[Fe(CO)_3(dab)]$ (**1**) shows that now we have a d^6 ML_4 fragment instead of the d^8 ML_4 fragment in **1** which was an isolobal analogue of carbene. If the isolobal concept holds, the C=N–Mn^IL_4 present in **18** should not behave as a 1,3-dipole. Indeed, when $[Mn_2(CO)_8(dab)]$ was irradiated in hexane (to generate **18**) in the presence of dmad or methyl propynoate (mp) as dipolarophiles, no cycloaddition took place but

extensive decomposition.[8] The only product that could be identified was $[Mn_2(CO)_6(dab)]$, which is also formed in the absence of any other reactants or ligands.[21] When the same experiments were performed instead in thf, a coordinating solvent, the bicyclo[2.2.1] cycloaddition products **20**, and in case of R = Pr^i, a mixture of **19**/**20a** (Scheme 3) was obtained in 60–70% yields. A donor molecule (thf) can coordinate weakly to the 16-electron species **18**, and hence act temporarily as an additional ligand in **18·thf**. In that case, a d^6 ML_5 fragment is obtained, which is isolobally related to a d^8 ML_4 fragment, and consequently the corresponding $L_5Mn{-}N{=}C$ fragment is isolobal with the azomethine ylide and hence a 1,3-dipole. The bicyclo[2.2.1] cycloadducts **19**/**20** cannot undergo migratory CO-insertion because the nitrogen has no lone pair with which to attack nucleophilically a carbonyl carbon. Unfortunately, the only crystalline material suitable for X-ray analysis turned out to be a mixed crystal with **19** and **20a** both present in the unit cell. The two could not be distinguished individually. The geometry of the nitrogen bridge was therefore disordered and averaged between sp^2 and sp^3.



Scheme 3

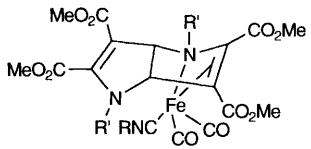
Complexes $[M(CO)_4(dab)]$ (M = Cr, Mo or W), which like **18·thf** contain a d^6 ML_5 fragment, do not react with dipolarophiles. This can be rationalised in the following way: (i) the extra electron in the LUMO, or rather SOMO, of the dab ligand in **18·thf** increases the reactivity of the 1,3-dipole sufficiently, and (ii) the carbonyl ligands in $[M(CO)_4(dab)]$ bind too strongly to the metal and cannot be lost as easily as thf from manganese in order to avoid an increase of the coordination number to seven during the cycloaddition.

3.2 Changing the Additional Ligands: Isocyanides for Carbon Monoxide

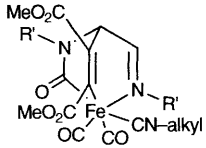
The decision to replace carbonyls in **1** for isonitriles is based on two reasons: (i) while CO is a pronounced π-acceptor, isocyanides R–NC are better σ-donating/less π-accepting,[23–28] and their electronic and steric properties can be varied by the choice of R. Increased donation to the metal should raise the HOMO-energy of the 1,3-dipole and increase its reactivity; (ii) like CO, isocyanides are known to undergo insertion reactions,[23–24,29] and their introduction opened the possibility of obtaining new, isocyanide inserted compounds, and further, in mixed complexes, of studying a possible intramolecular competition between CO and isocyanide insertion in the initial cycloadducts.

3.2.1 *Reactivity of* [*Fe*(*CO*)$_2$(*RNC*)(*dab*)] (**21**)

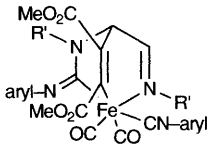
With Pd/C catalysis, one CO in complex **1** can be selectively substituted for an isonitrile R–NC to give **21**.[30] When **21** is reacted with dmad at $-60\,^{\circ}C$, three types of product, **22–24**, are obtained in 60–95% total yields after column separation.[18]



22



23



24

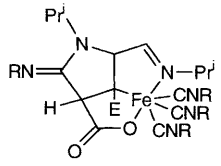
The product distribution depends on the isocyanide used. Only with aromatic (R = *o*-tolyl or 2,6-xylyl), and not with aliphatic isocyanides (R = Bu^t, Bu^s or benzyl) are isonitrile insertion products **24** formed. Aryl isocyanide insertion is obviously very fast since the competing formation of **23** from CO insertion is not observed; complexes **22** are only minor products. With aliphatic isocyanides, the thpp complexes **22**, from double cycloaddition of dmad (*cf.* Section 3.1.1), are the major products (70 to >95% of the product mixture) and indicate a strongly increased 1,3-dipolar reactivity, *i.e.* the intermolecular second cycloaddition is preferred to the intramolecular CO insertion. Compared with the ruthenium compound **17**, the thpp in **22** is strongly bound to the metal and can only be decomplexed oxidatively with cerium(IV), or under 80 bar of CO.

3.2.2 *Reactions of* [*Fe*(*RNC*)$_3$(*dab*)] (**25**) *with dmad,*[31] *olefins*[32,33] *and heteroallenes*[34–36]

Complexes **25** had been described in the literature[37] with spectroscopic evidence only, and were supposedly very labile. However, it was possible to prepare **25a–c** (**a**: R = 2,6-xylyl, **b**: R = Bu^t, **c**: R = Cy) in synthetically useful amounts.[31] In particular **25a** proved to be the optimally activated 1,3-dipole, which not only

reacts with the greatest variety of dipolarophiles, but also exhibits some very surprising and interesting consecutive reactions.

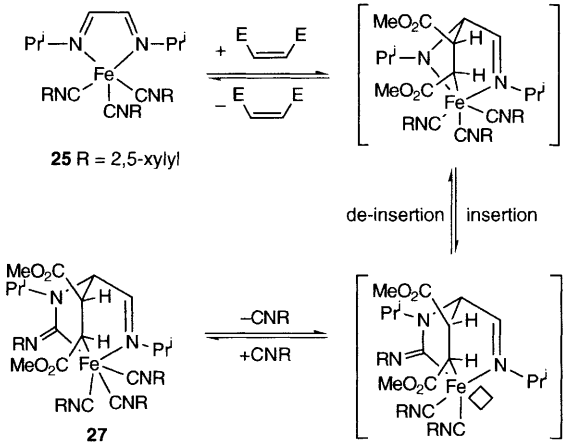
The reaction of **25a–c** with dmad[31] proceeds in a manner completely analogous to the reaction of **21**, *i.e.* giving thpp complexes by double cycloaddition in case of the aliphatic isonitriles (**b**, **c**), and isonitrile insertion with the aromatic 2,6-xylyl isonitrile **a**. Just as complexes **4** with L′ = trimethyl phosphite (Scheme 1) and **23**, the corresponding trisisonitrile bicyclic complex does not reductively eliminate a pyrrolinone imine, probably again due to the σ-donor capacity of the ligands that increase the electron density at the iron(II) centre. However in the presence of water, this trisisonitrile bicyclic analogue of **23** finds an alternative pathway for which a plausible sequence of steps involves hydrolysis of one ester function to the acid. The hydroxyl group then oxidatively adds to the electron rich iron(II) centre forming an intermediate with a formal iron(IV) centre. Simultaneously, the imine moiety is displaced from the metal. From the high oxidation state, a reductive elimination regenerates the iron(II) oxidation state by forming a 1,5-dihydro-2-iminopyrrole followed by recoordination of the double bond. The stable tricyclic end product **26**, the structure of which has been established by X-ray crystallography, is formed by formal insertion of the ring double bond into the metal–hydrogen bond and recoordination of the pendant imine group. That the new proton originates from water has been confirmed by performing the reaction in D_2O instead of H_2O. ^2H NMR unequivocally proved the incorporation of deuterium at the former alkyne carbon atom.



26 R = 2,6-xylyl
E = CO_2Me

The reaction of **25a**, containing the aromatic 2,6-xylyl isocyanide ligands, with dimethyl maleate in pentane (Scheme 4)[32,33] proceeds with stereospecific cycloaddition of the *cis*-olefin and subsequent isocyanide insertion to form the bicylo[2.2.2] complex **27**, which precipitates as a yellow powder in 95% isolated yield. The structure of **27** has been confirmed by X-ray crystallography. Very surprisingly, at slightly elevated temperature the whole reaction sequence is cleanly reversed, a process that can be monitored by temperature-dependent NMR spectroscopy. When a solution of pure **27** in C_6D_6 is kept at 60 °C, the signals of **27** disappear and the signals of **25a**, dimethyl maleate, and 2,6-xylyl isocyanide grow in and finally replace them until the solution is cooled down again. It is an indication of the microscopic reversibility of the reaction that the reverse reaction is also stereospecific, with only dimethyl maleate and no fumarate being formed. This temperature-controlled molecular self-assembly and disassembly is unique, considering all the steps involved, and the ease with which these steps occur. During the process, C–C, C–N, Fe–C σ-bonds, and an Fe–CNR donor bond are formed and broken. Another intriguing aspect of the

reverse disassembly reaction is that the reaction represents the first unequivocally established case of an isocyanide deinsertion reaction.

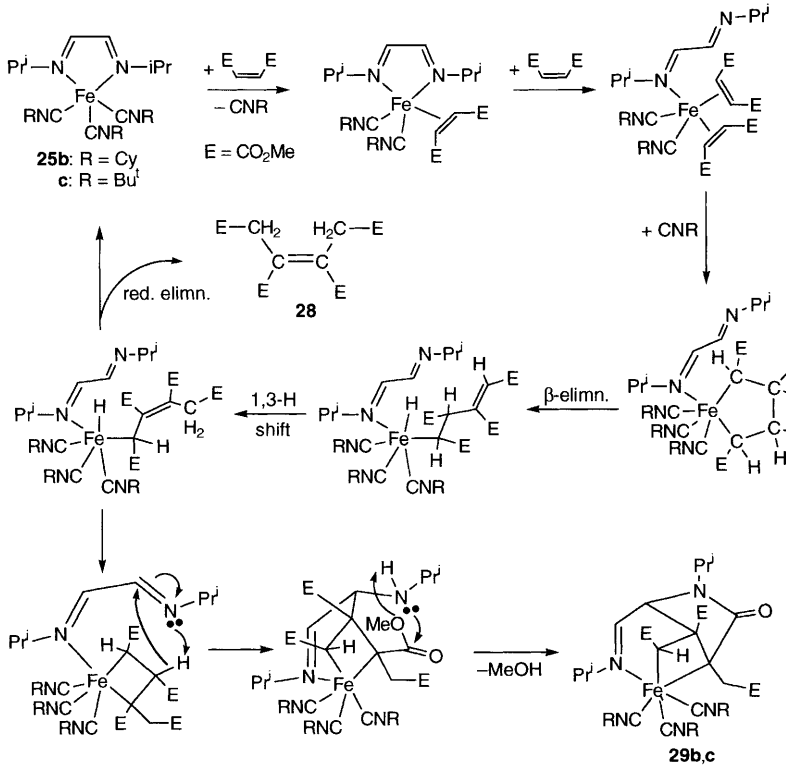


Scheme 4

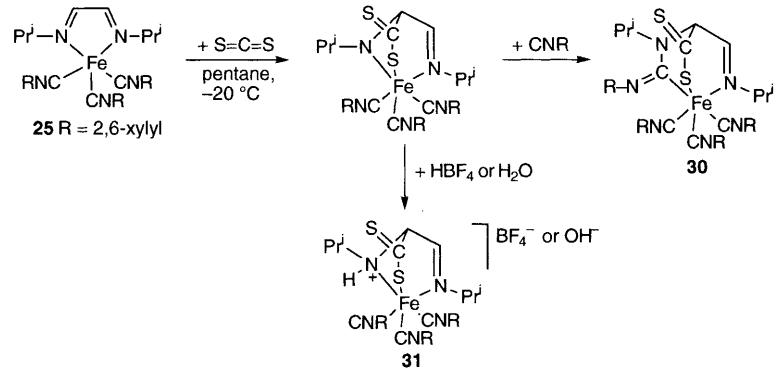
The influence of the type of isonitrile on the reactivity of **25** towards olefins is dramatic. With the aliphatic isonitriles **b** and **c**, a totally different reaction with dimethyl maleate is observed. Scheme 5 shows the isolated products **28** and **29b,c** and the proposed reaction pathway.[33]

The observation that the reaction is strongly slowed down by an excess of isocyanide suggests that the reaction starts with the substitution of an isocyanide by an alkene. The rest of the reaction sequence is more or less speculative, but in any case there is a high degree of stereoselectivity. The final tricyclic complex **29** contains five chiral centres, yet only one diastereomer is observed, the structure of which has been confirmed by X-ray crystallography. The relative amount of the organic olefin dimer **28** depends on the reaction temperature. At $-30\,^{\circ}C$, the ratio **28**/**29** is 1/4, and at $0\,^{\circ}C$ it is 6/4, *i.e.* at higher temperature, reductive elimination of **28** becomes faster than olefin insertion into the Fe–H bond. The fact that complexes **25b,c**, with three strongly electron-donating aliphatic isocyanides, give only cycloaddition with the very reactive dipolarophile dmad, and not with dimethyl maleate, must be a consequence of the high electron density at the metal and the weaker metal–isocyanide coordinative bond in **25b,c** (weaker π back-bonding as compared to the aromatic isocyanides). The substitution of one of the terminal aliphatic isocyanides for a better π-accepting olefin *via* a dissociative pathway apparently becomes much faster than a cycloaddition reaction.

Complexes **25** also cycloadd the C=S double bonds in heteroallenes CS_2, COS,[34] and aryl isothiocyanates.[35,36] The reaction of **25a** with CS_2 (Scheme 6) gave an 80% yield of the expected bicyclo[2.2.2] complex **30**, the structure of which has been established by X-ray crystallography.[34] When the reaction was performed in the presence of water or HBF_4, the amido nitrogen bridge in the initial bicyclo[2.2.1] adduct was protonated, which inhibited the insertion of isocyanide, and **31** was isolated in 80% yield.



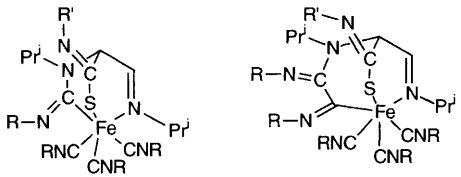
Scheme 5



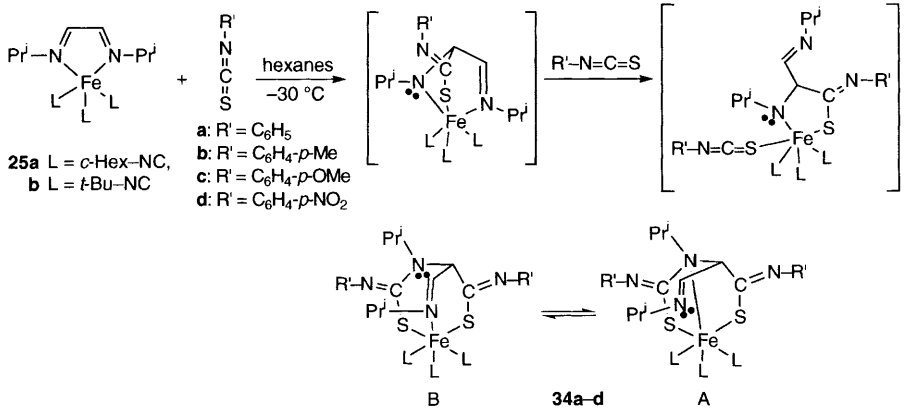
Scheme 6

With aryl isothiocyanates, 4-XC_6H_4NCS, (X = H, Me, OMe or NO_2), complex **25a** reacted in the familiar way by cycloaddition of the C=S bond and isocyanide insertion to form the bicyclo[2.2.2] adducts **32**.[35] The structure of **32**, X = H, has been determined by X-ray crystallography. In the presence of a second equivalent of isocyanide, the bicyclo[3.2.2] products **33**, resulting from a second isocyanide insertion, could be isolated. This reaction is cleanly thermally

reversible, and for the first time, the thermodynamic parameters of an isocyanide insertion/deinsertion reaction could be determined by temperature-dependent NMR spectroscopy. At high temperatures the reaction sequence is reversed all the way to **25**. However, at these temperatures the thermal stability of **25** is not sufficient to establish a stable equilibrium. The crystal structure of **33** could not be determined, because the equilibrium between **32** and **33** was obviously not frozen even at very low temperatures. When a saturated solution of pure **33**, X = OMe, in ether/dichloromethane (5/1) was stored at − 80 °C, after several months crystals of **32**, X = OMe, were obtained. So, the dynamic equilibrium had completely shifted towards the side of **32**, X = OMe, as a result of its lower solubility.



The labilisation of the coordinative bonds due to the strong σ-donation of the aliphatic isocyanide ligands in **25a,b**, which has already been mentioned above, obviously also plays a role again in the reaction of **25a,b** with aryl isothiocyanates (Scheme 7).[36] The X-ray structure of **34c**, L = Bu^{t}NC indicates a [3.2.0] bicyclic complex with a coordinated amido nitrogen and an uncoordinated imine nitrogen (A). However, temperature-dependent NMR spectroscopy indicates a dynamic competition of these two nitrogen atoms for the coordination site. As in all previous cases, the terminally coordinated aliphatic isocyanides do not insert in the initial bicyclo[2.2.1] cycloadduct, but rather an external isothiocyanate is inserted, most likely after precoordination by displacement of the imino group.



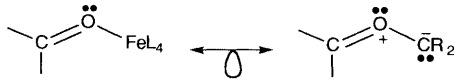
Scheme 7

3.3 Changing the Heteroatoms

Like the variations of the metal (Section 3.1) and of the additional ligands (Section 3.2), the variation of the heteroatom in the 1,3-dipole cannot be done arbitrarily. A suitable synthetic route to and the stability of the resulting starting compound are the limiting factors. So, like the complexes $[Ru(CO)_3(dab)]$ (**13**) and $[Fe(RNC)_3(dab)]$ (**25**), several of the 1,3-dipoles in this section had to be prepared and reacted *in situ*. Their identity, however, was beyond doubt – either through spectroscopic characterisation and comparison with stable representatives of the same type, or from a complete characterisation of their reaction products.

3.3.1 Oxygen instead of nitrogen: α-imino ketones and α-imino esters

The previously mentioned CAS-SCF calculations[16] had already shown that the isolobal analogy between an azomethine ylide and the $L_4Fe–N=C$ fragment (Equation 3) may be extended to an $L_4Fe–O=C$ fragment **35** and a carbonyl ylide **36** (Equation 4), and that the oxygen homologues would have slightly higher HOMO and LUMO levels, and a smaller HOMO–LUMO gap. From these properties, an increased 1,3-dipolar reactivity could be expected.

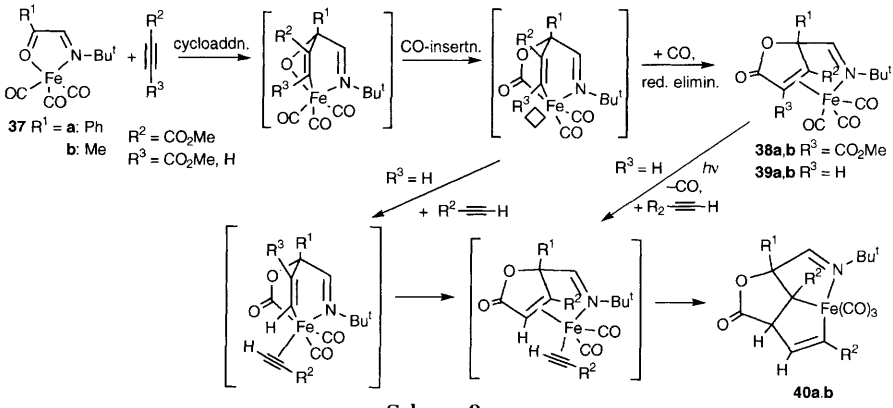


(4)

35 **36**

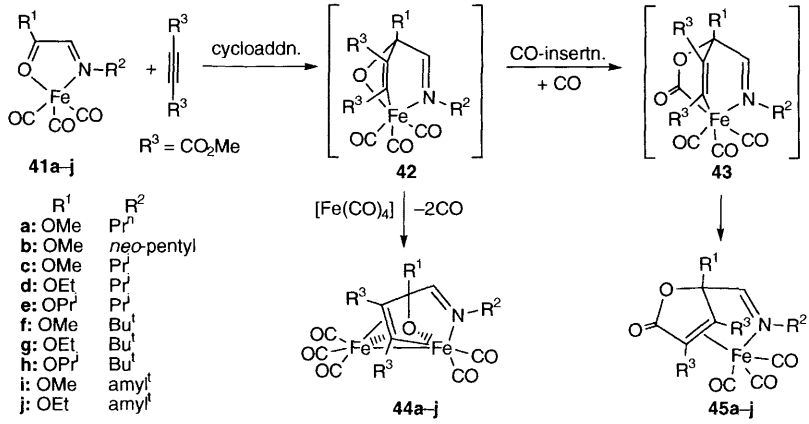
In order to compare the 1,3-dipolar reactivity of the $L_4Fe–N=C$ and the $L_4Fe–O=C$ fragments, *i.e.* to investigate the chemoselectivity of a dipolarophile towards them, a series of suitable complexes with an Fe–N=C and an Fe–O=C fragment within the same molecule, namely $[Fe(CO)_3(\alpha\text{-imino ketone})]$ (**37**)[38,39] and $[Fe(CO)_3(\alpha\text{-imino ester})]$ (**41**),[40–42] were prepared and allowed to react with activated alkynes (Schemes 8–10).

When complexes **37a,b** reacted in pentane solution at −78 °C under an atmosphere of CO with dmad (Scheme 8), the butenolide complexes **38a,b** were formed in clean reactions and could be isolated in 85 and 65% yields,[39] *i.e.* the reaction proceeded with complete chemoselectivity for the Fe–O=C fragment. When the same reaction was performed at − 50 °C and − 30 °C, respectively, with methyl propynoate (mp) as dipolarophile,[38] the butenolide complexes **39a,b** with the hydrogen next to the inserted carbonyl group were formed with complete chemo- and regio-selectivity. Complexes that had incorporated two moles of the alkyne (**40a,b**) were observed as minor side-products. In the absence of CO, and with two equivalents of mp, the tricyclic complexes **40a,b** were formed exclusively in moderate yields. Complexes **40a,b** can also be prepared in almost quantitative yields by irradiation of the corresponding complexes **39a,b** in the presence of an excess of mp at room temperature, an observation that strongly supports the pathway indicated in Scheme 8. X-Ray structural analysis of **40b** has confirmed that, of the possible regioisomers, only the one shown in Scheme 8 is formed.

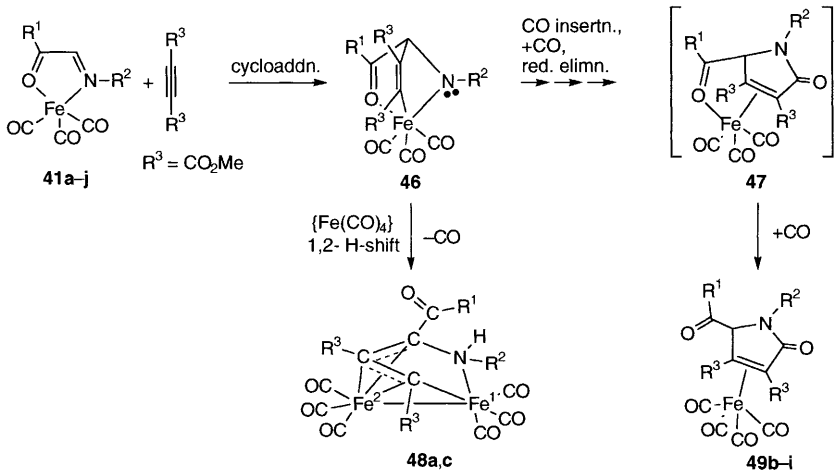


Scheme 8

The effect of reaction temperature on the cycloadditions of **37a,b** with dmad and mp (*vide supra*) already indicated that not only has the dipolarophile a marked influence on the reactivity, but so has the substituent R^1 (phenyl *vs.* methyl) in the 1,3-dipole. However, in both cases the cycloaddition was completely selective for the Fe–O=C moiety. In order to probe how far the reactivity of the Fe–O=C dipole could be further attenuated by the choice of R^1, an extended series of imino ester complexes **41**[41] was reacted with the two dipolarophiles dmad and mp.[42] Instead of the aryl or alkyl groups R^1 in **37**, complexes **41** bear an electronegative oxygen atom. The less reactive dipolarophile mp again reacted exclusively with the more reactive Fe–O=C dipole. However, with the more reactive dmad, the Fe–N=C dipole becomes competitive, and both the butenolide complexes **45** (Scheme 9) and pyrrolinone complexes **49** (Scheme 10) are formed. The weakly coordinating ester carbonyl group in **47** is displaced by an extra CO in **49**. The initial bicyclo[2.2.1] cycloadducts **42** and **46** also undergo a side reaction with an $\{Fe(CO)_4\}$ species present from the *in situ* preparation of **41**, to give the binuclear products **44** and **48**. All product structures have been confirmed by X-ray crystallography.



Scheme 9



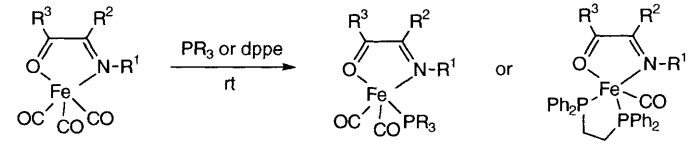
Scheme 10

The steric bulk of both substituents R^1 and R^2 clearly influences the product distribution. Increasing the bulk of R^1, *e.g.* in the series **c** → **e**, or **f** → **h**, results in an increasing preference for the Fe–N=C fragment, while increasing the bulk of R^2 (**a**, **c**, **f**) favours the Fe–O=C fragment.

In the stable and isolable imino ketone complexes **37a** and **37c** (Scheme 11), at room temperature, one or two carbonyls could be exchanged for phosphorus ligands **k–n** [**k** = $P(OMe)_3$, **l** = PPh_3, **m** = PEt_3, **n** = PPr^n_3] or dppe ($Ph_2PCH_2CH_2PPh_2$).[6] The resulting complexes **50**/**51** were prepared in the expectation that the increased donor capacity of the phosphorus ligands, as opposed to CO, would increase π-back-donation into the imino ketone LUMO and thus increase the reactivity of the 1,3-dipole. This was indeed the case, and complexes **50**/**51** were found reactive towards acetylenes (dmad, mp, phenyl acetylene), olefins (dimethyl maleate) and aryl isothiocyanate. Not all cycloaddition products were isolable though, and could only be characterised spectroscopically. The most remarkable result, however, was that for the first time in the iron system the initial bicyclo[2.2.1] adduct was directly observable. In the reaction of the dppe complex **51a** with dmad (Equation 5), complex **52** was the stable end product of which single crystals could be grown to determine its X-ray structure. CO insertion does not occur in this case, which is obviously due to the *trans* disposition of the oxygen bridge and the single carbonyl ligand, as evidenced by the crystal structure of **52**.

3.3.2 Sulfur instead of nitrogen: dithiooxamide

The coordination chemistry of dta towards carbonyl iron has been studied to find out if it was possible to prepare at least *in situ* mononuclear chelate [$Fe(CO)_3$(σ-S,σ-S′-dta)] (dta = dithiooxamide) complexes (**53**) in order to investigate their 1,3-dipolar behaviour.[43] This proved successful with dta **a–d** (Scheme 12). However, only the reaction of **53a** with dmad gave an isolable [3 + 2]

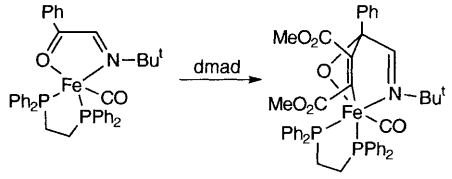


37
a: R^1= Bu^t, R^2= H, R^3= Ph
c: R^1= Me, R^2= Ph, R^3= Ph

50a,c,k–n
k: R = OMe
l: R = Ph
m: R = Et
n: R = Pr^n

51a,c

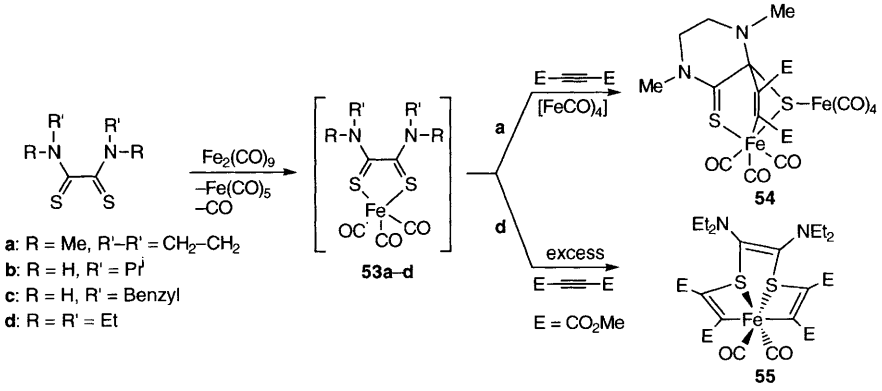
Scheme 11



(5)

51a **52**

cycloadduct **54a**. In **54a**, an $\{Fe(CO)_4\}$ fragment, present in solution from the *in situ* generation of **53a**, has coordinated to the sulfide bridge. This inhibits carbonyl insertion and stabilises the cycloadduct. Extensive decomposition is observed when the reaction with dmad is done with pure **53a**, *i.e.* in the absence of $\{Fe(CO)_4\}$, and the only isolable product is a small amount of **54a**. When **53d** reacts with an excess of dmad, no [3 + 2] cycloaddition takes place, and only small amounts of **55d** formed by two [2 + 2] cyloaddition reactions can be isolated.



a: R = Me, R'–R' = CH_2–CH_2
b: R = H, R' = Pr^i
c: R = H, R' = Benzyl
d: R = R' = Et

53a–d **54** **55**

Scheme 12

4 Acknowledgements

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A Journey in Metal–Ligand Multiple Bond Chemistry

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1 Introduction

In the late 1970s, whilst an undergraduate at the University of Sheffield, and under the tutelage of Maitlis, McCleverty and Fenton, I was first introduced to the many seminal contributions to inorganic and organometallic chemistry of Joseph Chatt: the simple but 'universal' bonding model for alkenes binding to a transition metal centre, the chemistry of metal–ligand multiple bonds, carbon–hydrogen bond activation, and not least of all his work on dinitrogen complexes at the Nitrogen Fixation Unit, to highlight but a few. At that time, as an undergraduate, I could only dream that I would myself one day be researching some of the very same areas into which Joe Chatt had provided such great insight and inspiration. The chemistry outlined in this chapter is a personal journey which started in the mid-1980s with my appointment to a lectureship in inorganic chemistry at the University of Durham and which led me along a path that would enter some of the subject areas which had been so dramatically influenced by Chatt.

Starting with a desire to answer a simple question in metal oxo chemistry, the journey quickly broadened to take in metal imido systems and to explore applications of these complexes in olefin metathesis, especially ring-opening metathesis polymerisation (ROMP), and later in α-olefin polymerisation. The structure of this chapter broadly reflects the original itinerary, with a few diversions along the way. It is inevitable that an account of this type glosses over the many important contributions by other researchers in the field. I apologise unreservedly to them and hope readers will refer to the citations of their work contained within the accompanying references.

2 The Elusive $[M(O)Cl_2Cp]$ Complexes of Niobium and Tantalum

Embarking on an academic career in the mid-1980s, one of the first questions I wanted answered was why terminal oxo-ligands are so abundant for certain transition metals but not for others? The explanation for late transition metals was relatively straightforward since the hard π-basic oxo-ligand is less compatible with *d* electron-rich metals, leading to the filling of anti-bonding M–L molecular orbitals. However, the answer was less clear for early transition metal systems and especially so it seemed for the Group 5 metals, vanadium, niobium and tantalum. $[V(O)Cl_2Cp]$ (**1**), a volatile and thermally robust three-legged piano stool molecule (Figure 1), had been described by E. O. Fischer in 1958,[1] yet 30 years later the niobium and tantalum analogues (**2** and **3**) had still not been described. These, therefore, presented tantalising targets.

My first PhD student, Terry Kee (now on the faculty at the University of Leeds) set about trying to make the niobium and tantalum compounds by reaction of $M(O)Cl_3$ with a variety of Cp sources. We tried them all! All failed, and all we were able to salvage from this initial endeavour were improved syntheses of the $M(O)Cl_3$ starting materials.[2] Other obvious routes, *e.g. via* reaction of $[MCl_4Cp]$ with $(Me_3Si)_2O$ also proved unsuccessful, in the case of $[TaCl_4Cp^*]$ (Cp^* = pentamethylcyclopentadienyl) affording $[\{TaCl_3Cp^*\}_2(\mu\text{-}O)]$ and $[TaCl_3(OSiMe_3)Cp^*]$.[3] Terry, however, would not be thwarted, and he switched from looking at high-valent routes to exploring the potential for low-valent precursors. He was subsequently able to show to our surprise that the half-sandwich tertiary phosphine tantalum(III) complex, $[TaCl_2(PMe_3)_2Cp^*]$ (**4**), reacted with carbon dioxide to yield $[\{Ta(O)Cl_2Cp^*\}_2]$ (**5**), along with $[TaCl_2(CO)_2(PMe_3)Cp^*]$ (**6**) as the main by-product[3] (Figure 2). The characterising data for **5** revealed a dinuclear structure with bridging rather than terminal oxo ligands. It was about this time that Alan Shaw joined the group and he and Terry were able to provide the answer as to the elusivity of these compounds[3,4] by showing that **5** is in fact unstable converting, at room temperature in chloroform solution and at elevated temperature in toluene, to a mixture of the trinuclear oxide cluster, $[Ta_3O_4Cl_4Cp^*_3]$ (**7**),[5] and the dinuclear species, $[\{TaCl_3Cp^*\}_2(\mu\text{-}O)]$ (**8**). It was also found to react with $(Me_3Si)_2O$ to give a mixture of the same dinuclear compound and $[TaCl_3(OSiMe_3)Cp^*]$ (**9**), which explained the failure of our earlier attempts to prepare $[Ta(O)Cl_2Cp^*]$ *via* the

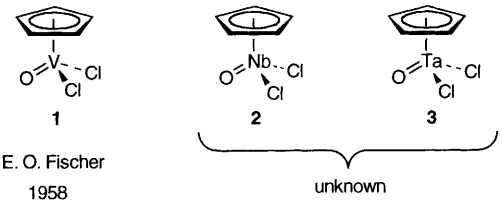


Figure 1 *Half-sandwich oxychlorides of the Group 5 metals*

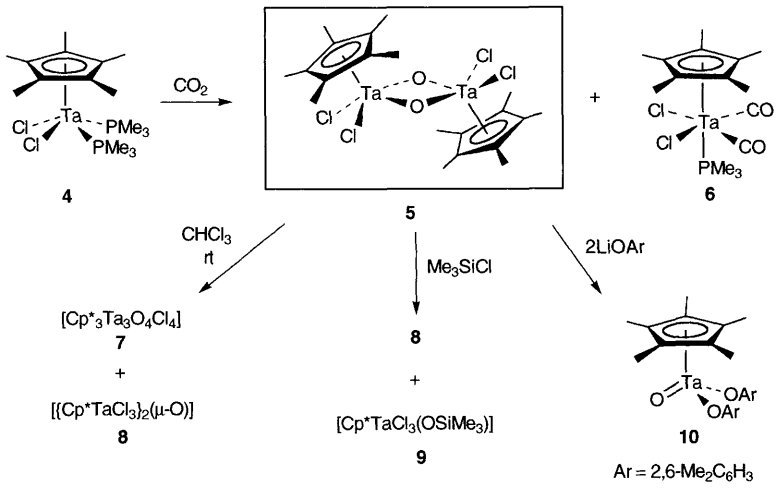


Figure 2 *The low valent route to* $[Ta(O)Cl_2Cp^*]$ *and derivative chemistry*

reaction of $[TaCl_4Cp^*]$ with $(Me_3Si)_2O$. Ultimately, Alan was able to show that it is possible to stabilise terminal oxo half-sandwich tantalum species by exchanging the chlorides for phenoxide ligands (compound **10**).[4] However, the question was essentially answered: for tantalum, at least, the elusive nature of terminal oxo complexes was attributable to the greater stability afforded by bridging oxo ligand environments. Unfortunately, this low-valent pathway proved to be unsuited to the niobium analogue.

3 Half-sandwich Imido Compounds of Niobium and Tantalum

The lack of stability of terminal oxo compounds of the heavier Group 5 metals led us naturally to the door of the isoelectronic imido (NR) ligand, where the availability of a substituent attached to the multiply-bonded group would allow both steric and electronic modulation of the products' stability and reactivity. There had been a handful of half-sandwich imido complexes of the Group 5 metals synthesised by other workers, especially for vanadium[6] and tantalum,[7] but at that time none were known for niobium. A half-sandwich imido compound of niobium we considered, therefore, a prime target.

David Williams was able to show that heptamethyldisilazane, $(Me_3Si)_2$-NMe, reacts with $[NbCl_4Cp]$ to give moisture-sensitive, yellow-orange $[Nb(NMe)Cl_2Cp]$ (**11**),[8] the crystal structure of which revealed a monomeric three-legged piano stool structure (Figure 3). By subsequent judicious choice of silylated amine reagents, he was able to generalise this synthetic entry to access a wide family of half-sandwich niobium and tantalum imido compounds (**12**, Figure 3) and set about developing their derivative chemistry.[9]

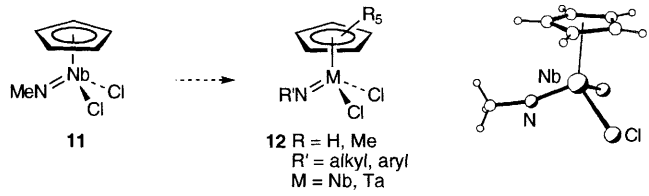


Figure 3 *Half-sandwich imido complexes of the heavier Group 5 metals, and the molecular structure of* $[Nb(NMe)Cl_2Cp]$

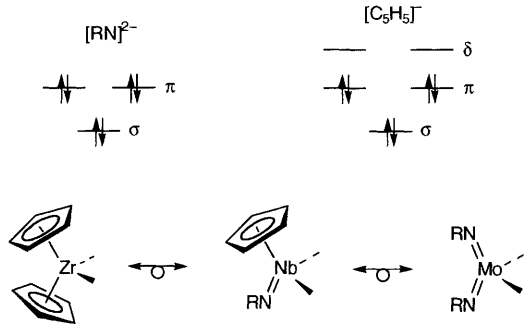


Figure 4 *The isolobal relationship between imido and cyclopentadienyl species*

At about this time, we were enjoying a collaboration with Dick Schrock at MIT, applying his well-defined molybdenum metathesis catalysts to new materials synthesis (in conjunction with Jim Feast at Durham), and we had often found ourselves, over various liquid refreshments, discussing the relationship between the simple imido moiety and cyclopentadienyl ligands. At first sight they might appear as different as chalk and cheese, but on closer examination some striking similarities become apparent. Although possessing different formal charges, these six-electron ligand fragments should present the same symmetry combinations of frontier orbitals to a metal centre (Figure 4), thereby allowing an intriguing isolobal parallel to be drawn between the Group 4 metallocenes, half-sandwich imido compounds of the Group 5 metals and bis(imido) compounds of the Group 6 metals (Figure 4). The relationship appeared to work in bis(imido)tungsten systems under investigation in Dick's labs at MIT[10] and we directed our attention to testing this hypothesis on the half-sandwich Group 5 metal imido system.

Elegant theoretical studies by Lauher and Hoffmann[11] had established the molecular orbital description of the Group 4 metallocenes and so David Williams turned his hand to MO calculations on the [Nb(NMe)Cp] system. The outcome was a frontier orbital picture showing only minor differences to the $\{MCp_2\}$ fragment.[9] Moreover, the interaction of trimethylphosphine with $[Nb(NMe)Cl_2Cp]$ provided experimental evidence for the similar orientations of the complex LUMOs in $[MX_2Cp_2]$ and $[M(NR)X_2Cp]$.[9]

4 Exploiting the Isolobal Relationship Between Cyclopentadienyl and Imido Ligands

In order to place the isolobal analogy between Group 4 metallocenes, half-sandwich imido compounds of the Group 5 metals and bis(imido)metal complexes of the Group 6 metals on a firm experimental footing, we set about probing similarities and differences in their structures and reactivity. Andrew Poole was able to show that the bis(phenyl) complex, [Nb(*N*-2,6-$Pr^i_2C_6H_3$)$(Ph)_2$Cp*] reacts in much the same way as [$ZrPh_2Cp_2$] upon treatment with trimethylphosphine.[12,13] In both cases, elimination of benzene occurs resulting in formation of a stable benzyne complex (see **13**, Figure 5 for the niobium derivative). The close similarity of the bond lengths within the benzyne ring and the orientation of the benzyne ligand provided further support for the metallocene-like nature of the frontier orbitals of the {Nb(NR)Cp*} fragment.

In an analogous reaction, the bis(benzyl) species [Nb(*N*-2,6-$Pr^i_2C_6H_3$)$(CH_2Ph)_2$Cp*] was found to eliminate toluene upon treatment with trimethylphosphine to give the benzylidene complex, [Nb(*N*-2,6-$Pr^i_2C_6H_3$)(=CHPh)(PMe_3)Cp*] (**14**).[12,13] Here, the substituents of the alkylidene ligand are orientated towards the Cp* and imido ligands allowing overlap of the carbene carbon p orbital with the d_π symmetry 'metallocene-like' frontier orbital of the {Nb(NR)Cp*} fragment. The olefin complexes, [Nb(*N*-2,6-$Pr^i_2C_6H_3$)$(CH_2=CHR)(PMe_3)$Cp′] (Cp′ = Cp or Cp*; R = H or Me)[14,15] *e.g.* **15**, revealed similar orientational preferences consistent with 'metallocene-like' frontier orbitals for the half-sandwich imido fragment. Furthermore, their method of synthesis, *via* treatment of the dihalide precursors with two equivalents of alkylmagnesium chloride in the presence of trimethylphosphine, is entirely analogous to that employed in the preparation of their metallocene relatives. It proved possible to extend the series to acetylene complexes (**16**) by two routes: either by direct displacement of the olefin[14] or *via* exchange of an acetylene for one of the PMe_3 ligands in [Nb(NR)$(PMe_3)_2$Cp*].[15]

Having synthesised a family of 'metallocene look-alikes', we were interested to

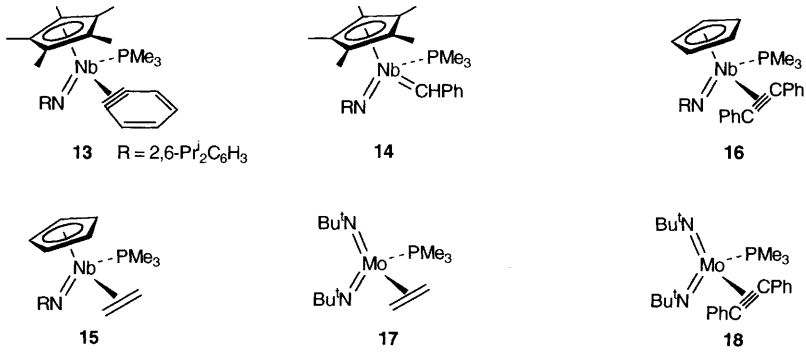
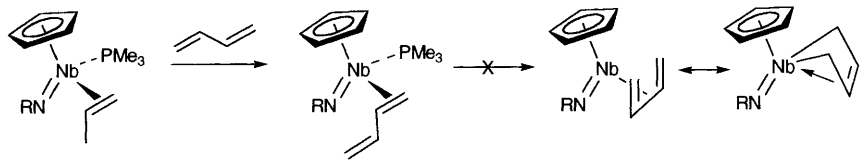


Figure 5 *Metal-imido relatives of the zirconocene family*

explore their derivative chemistry, especially potentially useful C–C bond-forming reactions. However, we had not reckoned with the over-zealous binding of the trimethylphosphine ligand which we unsuccessfully attempted to displace from the niobium centre with a variety of unsaturated organic substrates. This is most graphically illustrated by the reaction of $[Nb(NAr)(\eta^2\text{-}C_3H_6)(PMe_3)Cp]$ (**19**) with butadiene (Figure 6). Although the propylene can be displaced to give an η^2-butadiene complex (**20**, as four isomers),[16] prolonged warming did not result in displacement of the trimethylphosphine to give the η^4-butadiene product. This is in contrast to the zirconocene system which not only readily forms the η^4-butadiene species, but also has been shown to furnish synthetically useful carbon–carbon bond forming reactions.[17]

Two ways forward appeared open to us: either we could find an alternative less strongly binding ligand which could be displaced from niobium, or we could look to its neighbour tantalum, which, according to the diagonal relationship, should bear a closer electronic resemblance to zirconium. Andrew Poole decided to set about developing the chemistry of the tantalum system. Disappointments were in store, however. For example, the tantalum benzylidene species was not formed cleanly on thermolysis of $[Ta(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CH_2Ph)_2Cp^*]$ in the presence of trimethylphosphine, nor could evidence be obtained for the formation of a tantalum–benzyne species on thermolysis of $[Ta(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(Ph)_2Cp^*]$. Only paramagnetic decomposition products were produced.[16] These disappointments turned out to be a good omen, reflecting as they did the greater lability of the tertiary phosphine ligand.

The tantalum-olefin derivatives provided the advance we were seeking. The ethylene complex, $[Ta(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(C_2H_4)(PMe_3)Cp^*]$ (**21**) was found to react with an excess of ethylene to give the tantalacyclopentane (**22**) complex shown in Figure 7.[16,18] It also proved possible to synthesise the same complex in better yield by reaction of $[Ta(N\text{-}2,6\text{-}Pr^i_2C_6H_3)Cl_2Cp^*]$ with two equivalents of ethylmagnesium chloride in the presence of an excess of ethylene. In behaviour reminiscent of zirconacyclopentanes, the half-sandwich tantalacyclopentane species does not undergo facile β-elimination to afford but-1-ene due to the conformational constraints within the MC_4 metallacycle that prevent the β(C–H) bonds from accessing the metal-centred LUMO. It does, however, undergo slow exchange with C_2D_4 to give the perdeuteriated metallacycle (**22**–$\mathbf{d_8}$), indicating that the reverse β-C–C bond cleavage occurs to generate the bis(alkene) species. Two of the C–C bond coupling processes, with acetonitrile



19 R = 2,6-$Pr^i_2C_6H_3$ **20**

Figure 6 *The displacement of propylene to give an η^2-butadiene species*

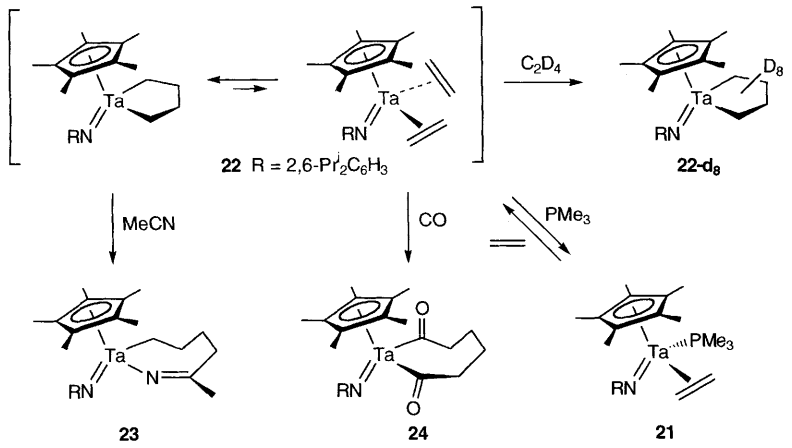


Figure 7 *Some reactions of the tantalacyclopentane complex* **22**

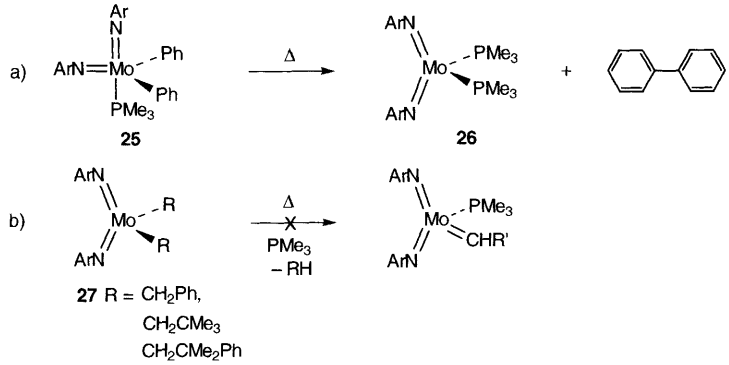


Figure 8 *Attempts to synthesise a) benzyne and b) alkylidene complexes of molybdenum*

(**23**) and carbon monoxide (**24**), are shown in Figure 7, revealing the potential for new C–C coupling reactions.

As part of his PhD studies, Phil Dyer (now on the faculty at the University of Leicester) was given the task of extending the relationship to the bis-(imido)molybdenum system. He was able to synthesise the four-coordinate olefin and acetylene complexes, $[Mo(NBu^t)_2(C_2H_4)(PMe_3)]$[19] (**17**) and $[Mo(NBu^t)_2(PhC{\equiv}CPh)(PMe_3)]$, (**18**)[20] but benzyne and alkylidene derivatives proved elusive. Although potential precursors such as the bis(phenyl) complex $[Mo(NAr)_2(Ph)_2(PMe_3)]$ (**25**) could be made quite readily, the resultant thermolysis product was not the anticipated benzyne species. Rather, in this case biphenyl is generated, along with the Mo^{IV} complex, $[Mo(NAr)_2(PMe_3)_2]$[21] (**26**, Figure 8), which Phil had isolated earlier from the magnesium reduction of $[Mo(NAr)_2Cl_2(dme)]$ in the presence of PMe_3.[22]

A range of dialkyls (**27**), including the dibenzyl, were also investigated as potential precursors to alkylidene products, but these proved to be too stable.

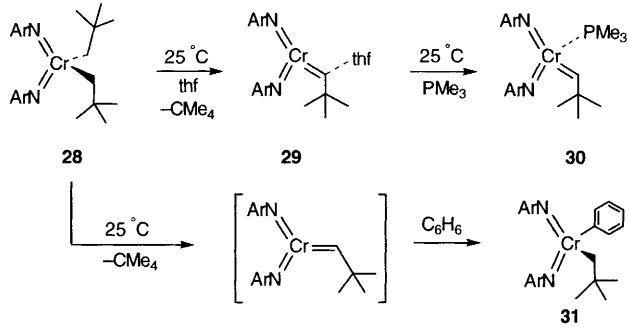


Figure 9 *Chromium*(VI) *alkylidene species*

Heating the samples above 100°C (up to 150°C) resulted in decomposition rather than in the formation of an isolable alkylidene species[23] (Figure 8). In fact, it was quite some time before a bis(imido) alkylidene complex of the Group 6 metals proved accessible and, to our surprise, chromium proved to be the metal that provided the solution (Figure 9). Martyn Coles (now on the faculty at the University of Sussex) synthesised the neopentyl complex, $[Cr(NAr)_2(CH_2CMe_3)_2]$ (**28**), and found that, in thf solvent at room temperature, a smooth elimination of neopentane occurred to give the Cr^{VI} alkylidene species, $[Cr(=CHCMe_3)(NAr)_2(thf)]$ (**29**).[24] The PMe_3 derivative, $[Cr(=CHCMe_3)(NAr)_2(PMe_3)]$ (**30**), can be prepared straightforwardly by subsequent treatment of the thf adduct with one equivalent of the phosphine. These represented the first Cr^{VI} alkylidene species to prove isolable. To our surprise, in the absence of a donor solvent, the transiently formed alkylidene species is capable of activating one of the C–H bonds of benzene to give a neopentyl/phenyl product (**31**, Figure 9), which was first identified as a result of activation of the deuterio-benzene NMR solvent.[24] A bigger surprise was the fact that this same C–H bond activation occurs in the presence of acyclic olefins and norbornenes. This was unexpected since high-valent alkylidene complexes of the other Group 6 metals, molybdenum and tungsten, are invariably efficient olefin metathesis catalysts.

5 Alkyl and Alkylidene Complexes of Molybdenum: Routes to Olefin Metathesis Catalysts

The work of Osborn[25] and Schrock[26] in the late 1980s had established synthetic entries into low-coordinate molybdenum and tungsten alkylidene species which were to prove of tremendous significance in the field of olefin metathesis, affording 'living' polymerisation systems for the ROMP (ring-opening metathesis polymerisation) of cyclic olefin monomers, as well as the more recently developed application of ring-closing metathesis (RCM). The route they developed to the catalysts was based on protonation of an imido ligand followed by an α-H abstraction with elimination of alkane, to give the stable alkylidene complex (Figure 10a,b). Osborn found that, for *tert*-butylimido derivatives, the products

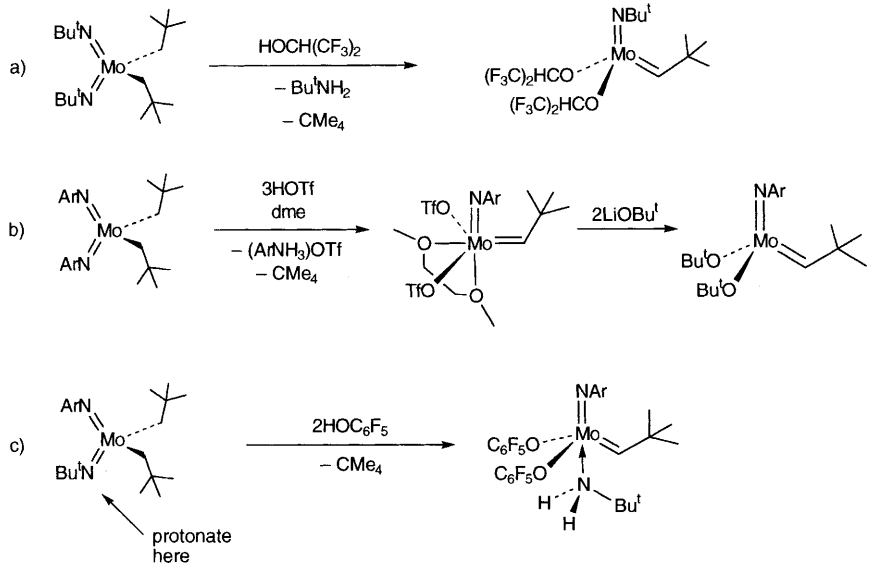


Figure 10 *Osborn's* (a), *Schrock's* (b) *and the selective protonation route* (c) *to molybdenum*(VI) *alkylidene complexes*

are usually oils which can lead to handling difficulties, and the methodology was restricted to alkoxides that are relatively electron-withdrawing. Schrock's approach employs precursors containing 2,6-diisopropylphenylimido ligands whose alkylidene products are, in general, more amenable to manipulation. However, a drawback in the preparation of arylimido catalysts is the necessity for triflic acid (CF_3SO_3H, HOTf), an expensive and potentially hazardous reagent, to 'protonate off' the much less basic arylimido ligand.

During our investigations on the half-sandwich Group 5 metal imido and Group 6 bis(imido) metal systems, we found that a convenient way of changing the imido ligand was to treat the relatively electron rich *tert*-butylimido metal species with a variety of anilines. This, for example, allowed us to access conveniently a range of new imido complexes of vanadium,[27] chromium[28] and molybdenum[29] systems. Ed Marshall adapted this methodology to the synthesis of molybdenum metathesis catalysts (Figure 10c). He synthesised bis(imido)molybdenum precursors containing a combination of *tert*-butylimido and 2,6-diisopropylphenylimido ligands and was able to show that a less strong acid such as pentafluorophenol can be used to 'protonate off' selectively the more electron-rich *tert*-butylimido group thereby generating the target arylimidomolybdenum alkylidene species.[30]

6 Olefin Polymerisation Catalysts

The isolobal analogy between cyclopentadienyl and imido ligands held promise for the development of new α-olefin polymerisation catalysts based on imido ligation. However, our early endeavours were to prove disappointing. Cationic

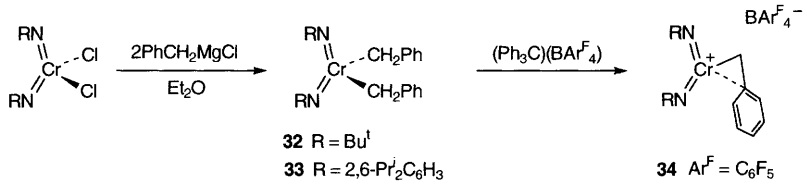


Figure 11 *Well-defined cationic chromium alkyl catalysts for ethylene polymerisation*

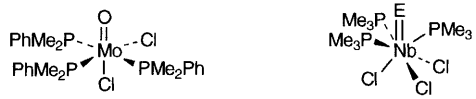
alkyl complexes based on niobium and molybdenum, of the type $[Nb(NAr)RCp]^+$ and $[Mo(NAr)_2R]^+$ respectively, gave disappointingly low activities in ethylene polymerisation.[31] We tried a tantalum analogue of the niobium system and this too proved to be of very low activity.[31] There seemed only one way to go for imido systems from there and that was to chromium, a metal with a track record of producing highly active ethylene polymerisation catalysts when supported on silica. Bis(imido)chromium chemistry was less well developed than for its heavier Group 6 congeners molybdenum and tungsten. Nevertheless, Martin Coles and Chris Dalby, in a project sponsored by BP Chemicals, soon showed that it was possible to prepare the complexes $[Cr(NBu^t)_2(CH_2Ph)_2]$ (**32**) and $[Cr(NAr)_2(CH_2Ph)_2]$ (**33**) and they showed that the cationic monobenzyl species $[Cr(NBu^t)_2(CH_2Ph)](B(C_6F_5)_4)$ (**34**) could be generated using $(Ph_3C)(B(C_6F_5)_4)$ or $(PhNMe_2H)(B(C_6F_5)_4)$.[32] In the case of the anilinium reagent, mono- and bis-amine adducts are formed with the liberated *N,N*-dimethylaniline. The compounds were tested for ethylene polymerisation activity in conjunction with BP Chemicals and were found to give reasonable activities and with negligible loss of performance over three hours.[31,32]

The relatively short journey from the Group 4 metallocenes on the left hand side of the transition series to Group 6 bis(imido) metal systems in the middle of the series has led to a continuing journey towards the late transition metals in a quest for new olefin polymerisation catalysts. This journey is still in progress and so an account of the outcome of these studies will have to wait until another occasion.

7 Distortional Isomerism

This account would not be complete without mention of *distortional isomerism*, a term Joe Chatt was to coin in describing two isomeric forms of the six-coordinate compounds, $[Mo(O)Cl_2(PMe_2Ph)_3]$ (**35**, Figure 12) in a short communication published in *Chem. Commun.* in 1971, but which later was to spark an intense debate into the reality or otherwise of the phenomenon of *bond stretch isomerism*. We followed the debate with some interest, since we had inadvertently stumbled across seven-coordinate oxo and sulfido compounds of niobium of the type $[Nb(E)Cl_3(PMe_3)_3]$ (E = O or S; **36**) which seemed to show a closely related effect.[33]

In their 1971 paper Chatt, Manojlovic-Muir and Muir[34] proposed the term *distortional isomerism* to describe two forms of $[Mo(O)Cl_2(PMe_2Ph)_3]$, one blue



35 **36** E = O, S

Figure 12 *Six-coordinate molybdenum and seven-coordinate niobium complexes which appeared to display the phenomenon of bond-stretch isomerism*

with ν(Mo=O) at 954 cm^{-1} and the other green with ν(Mo=O) at 943 cm^{-1}. These were members of a range of analogous blue and green oxomolybdenum compounds with high or low (Mo=O) vibrational frequencies, respectively, reported earlier by Butcher and Chatt and thought at first to be *cis* and *trans* isomers.[35] X-ray structure determinations showed that blue $[Mo(O)Cl_2(PMe_2Ph)_3]$ and the green diethylphosphine derivative [ν(Mo=O) = 940 cm^{-1}] in fact possessed similar *cis–mer* configurations, but with strikingly different organophosphine orientations and markedly different Mo=O bond lengths. Based on these observations Chatt and co-workers proposed a new form of isomerism involving 'two equilibrium arrangements of ligands which differ in the distortions of the highly strained coordination polyhedron of the metal'. They suggested that the blue and green forms of *cis–mer* $[Mo(O)Cl_2(PMe_2Ph)_3]$, which they concluded had different organophosphine orientations (resulting in C_s symmetry in the blue complex and C_1 in the green), exhibited this type of *distortional isomerism.*

In his study of the system, Parkin was able to show that small M=O bond length differences can be caused by an isomorphous contaminant, $[MoCl_3(PMe_2Ph)_3]$ in this case.[36] Also, since $[MoCl_3(PMe_2Ph)_3]$ is yellow, a mixture of blue $[Mo(O)Cl_2(PMe_2Ph)_3]$ and yellow $[MoCl_3(PMe_2Ph)_3]$ would readily account for the green 'isomer'. This explanation, however, did not provide an answer as to why *two* stretches were seen in the IR spectra recorded by Chatt (since only one would be expected), and led Enemark[37] to conclude that Chatt's assignment of two Mo=O stretches had been erroneous. It was on this basis that the simple and persuasive contaminant theory gained widespread acceptance as providing an explanation for all the spectroscopic and crystallographic observations surrounding Chatt's *distortional isomer* system.

We, however, were sceptical that Chatt would have made an error of this kind, especially given the importance attached to IR spectroscopy as a characterisation technique at the time the original study was carried out. We resolved to investigate further. Mary McPartlin (who had determined the structures of our niobium oxo compounds) and I discussed the issue with Joe, and learnt that Tony Butcher, who had carried out the original work in Chatt's Sussex laboratory, had made a successful career in business, and was living in Cambridgeshire. After making contact, Tony was adamant that there had been two different stretches in the IR spectra of the blue and green 'isomers'. Indeed, his keenness to resolve the issue led him to make available various spectroscopic facilities at his Company, and he even volunteered to do some of the work himself! Oliver Robinson, a PhD student in my group set about repeating the synthesis of the Chatt–Butcher compounds following the original procedure and was able to

make and grow crystals of the blue isomer (Figure 13). A structure determination carried out by Mary McPartlin revealed different phosphine orientations from the blue isomer studied by Parkin and Enemark, and moreover the new blue isomer had a Mo=O stretch at 954 cm^{-1}, the same value observed by Chatt. We then determined the structure of the blue isomer prepared under the conditions described by Enemark and Parkin and also the structures of the two bromo isomer analogues (Figure 14). This confirmed beyond all doubt the existence of two isomeric forms of pure $[Mo(O)X_2(PMe_2Ph)_3]$ (X = Cl or Br).[38] Thus, two stretches in the IR could be explained by the presence of two different blue isomers, and that the only difference between these two isomers is the orientation of the phosphine ligands. Whatever one's view of the phenomenon of *bond stretch isomerism* the description *distortional isomers* would still seem to be an appropriate description of the relationship between these compounds.

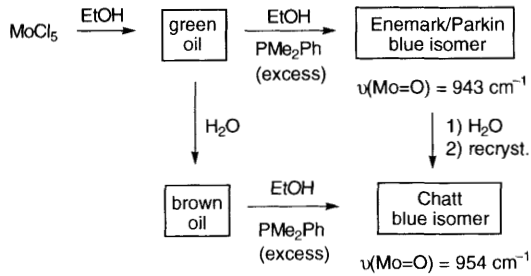


Figure 13 *Routes to the two blue isomers of* $[Mo(O)Cl_2(PMe_2Ph_2)_3]$

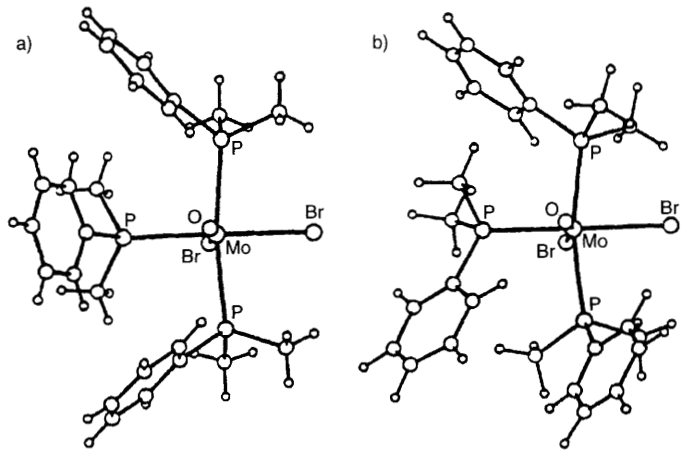


Figure 14 *The structures of the two forms of* $[Mo(O)X_2(PMe_2Ph)_3]$ *(X = Cl or Br), illustrated for X = Br:* (a) *the structure of* C_s *symmetry for the high-frequency form and* (b) *the structure of* C_1 *symmetry for the low-frequency form*

8 Acknowledgements

This author is indebted to the many students and postdocs who, through their dedication and hard work, have enlightened and enlivened the journey described here. The largest debt of gratitude, however, is owed to Joe Chatt for the many fundamental insights he provided into the stucture, bonding and reactivity of transition metal coordination and organometallic compounds, and for his boundless enthusiasm which has inspired so many others to enter the field.

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Synthesis, Characterisation and Catalytic Activity of Heterobimetal Complexes

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1 Introduction

Heterobimetal complexes have been the subject of much interest in view of the catalytic potential associated with the proximity of the metal atoms even in the absence of any metal–metal bond.[1] Ring-opening (or metal-insertion) reactions of chelated bidentate phosphine ligands provide a useful route to ligand-bridged heterobimetal complexes.[2–4] In these reactions the reactant is usually a mononuclear complex containing a chelating phosphine as part of a four-membered ring. On reaction with an appropriate metal complex, this four-membered ring opens to produce a ligand-bridged bimetal complex in which the bidentate ligand becomes part of a less-strained five-membered ring. We have exploited this synthetic route to produce a range of heterobimetal complexes, using both bidentate and tridentate phosphine ligands. In addition, a major goal of this research was to demonstrate that two or more metal centres can cooperate in the homogeneous catalysis of the hydroformylation of alkenes.

2 Synthesis of Ruthenium–Rhodium Heterobimetal Complexes

The synthesis of a number of heterobimetal complexes of the type $[(RhRuCl_2Cp)(\mu\text{-}CO)_2(\mu\text{-}\eta^2\text{-L-L})](Rh\text{–}Ru)$ {L-L = dppm, [dppm = bis-(diphenylphosphino)methane][5] $Ph_2PC(=CH_2)\text{-}PPh_2$,[5] $Ph_2PNHPPh_2$ or dppp[6] [dppp = bis(diphenylphosphino)propane]} has been carried out. These complexes are readily prepared by treatment of the chelating phosphine complexes

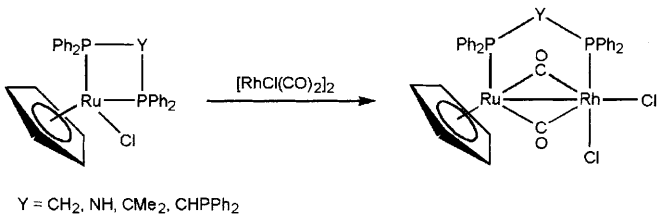

Figure 1 *Synthesis of ruthenium–rhodium heterobimetal complexes*

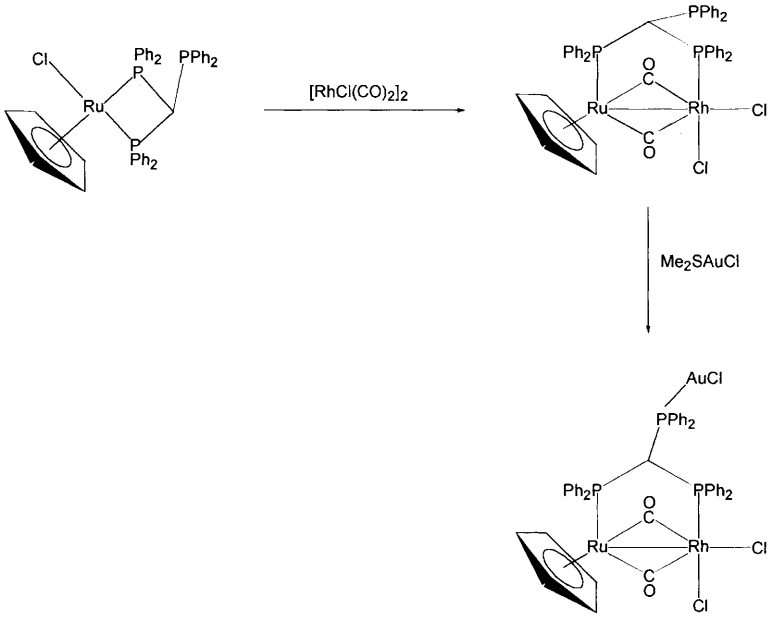

Figure 2 *Synthesis route to the ruthenium–rhodium–gold trimetal complex* **3**

[RuCl(L-L)Cp] with $[RhCl(CO)_2]_2$ (Figure 1). The reaction proceeds rapidly and quantitatively at room temperature. Many diphosphines that give four-membered rings upon chelation can be used in this reaction. Ligands that chelate to a metal atom forming a five-membered ring do not generally undergo this ring-opening reaction, except for dppe, which undergoes a ring-opening reaction to produce a rather unstable heterobimetal complex which was characterised spectroscopically, but which could not be isolated in a pure state. These heterobimetal complexes, which are not very soluble in organic solvents, may be regarded as complexes of a rhodium(I) anion and a ruthenium(II) cation with a donor-acceptor ruthenium–rhodium bond.

We have also reported some of the reactions of these complexes with CO under a range of conditions of temperature and pressure. A notable reaction is the completely reversible reaction of $[CpRu(\mu\text{-}CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-L-L})RhCl_2]$ with CO to give $[RhCl_2(CO)_2]^-$ and $[Ru(CO)_2(\eta^1\text{-L-L})Cp]^+$.[7]

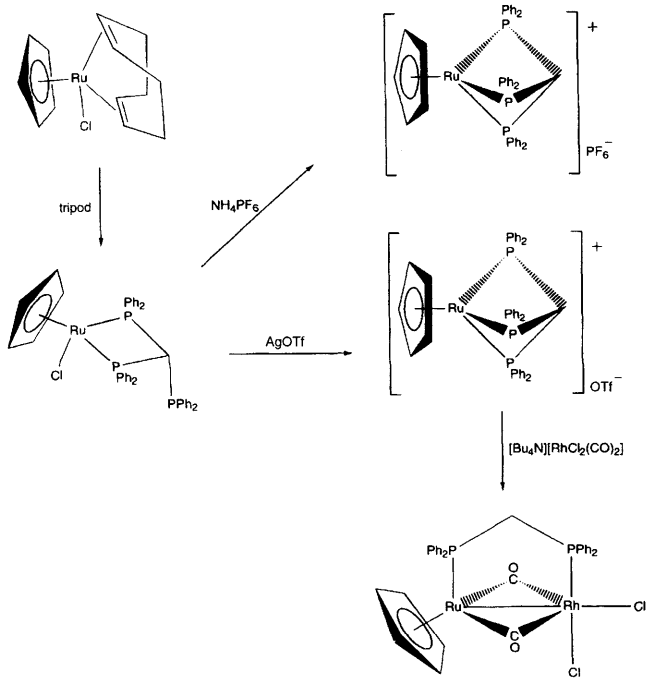

Figure 3 *Synthesis of the* η^3*-tripod complex* **4** *and the reaction of complex* **4** *with* $[RhCl_2(CO)_2]^-$. *HOTf* = $HOSO_2CF_3$

The tridentate ligand 1,1,1-tris(diphenylphosphino)methane, $CH(PPh_2)_3$, known as tripod, offers attractive potential and a variety of modes for coordinating to transition metals. Many complexes in which $CH(PPh_2)_3$ can act as an η^1-monodentate ligand[8], an η^2-chelating ligand[8,9], an η^3-μ_2-bridging-chelating ligand[8,10] or an η^3-μ_3-bridging ligand[11–19] have been synthesised. In addition, the dangling arm or arms provide potential coordination sites for other metals.

As an example of the utility of tripod in constructing heterometal complexes, we have recently investigated the reaction of the monometal complex $[RuCl(\eta^2\text{-}HC(PPh_2)_3)Cp]$ **1** with $[RhCl(CO)_2]_2$. This reaction gives rise to the heterobinuclear complex $[CpRu(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC(PPh_2)_3\}RhCl_2]$ **2**. Subsequent reaction of complex **2** with $[AuCl(SMe_2)]$ gives the heterotrinuclear complex $[CpRu(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}HC(PPh_2)_3\}RhAuCl_3]$ **3** (Figure 2).

The η^2-tripod complex **1** is converted into the η^3-tripod complex $[RuCp(\eta^3\text{-}HC(PPh_2)_3)](OTf)$ **4** by treatment with Ag(OTf). When complex **4** is treated with the anionic rhodium complex $[RhCl_2(CO)_2]^-$, a ring-opening and a P–C bond cleavage reaction occurs to generate the known μ-dppm heterobimetal complex $[CpRu(\mu\text{-}CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}dppm)RhCl_2]$ **5** (Figure 3).

3 Hydroformylation of Oct-1-ene

The hydroformylation of oct-1-ene was studied at 115 °C using complexes **1** and **5** as catalysts. The reaction was carried out with an oct-1-ene concentration of 9.55×10^{-3} mol cm^{-3}, catalyst concentration of 1.9×10^{-5} mol cm^{-3} and a total pressure of ($P_{CO} + P_{H2}$) 60 atm (at ambient temperature; CO: H_2, 1: 1).

With complex **5** as the catalyst, straight chain and branched aldehydes are formed. These are the only reaction products under these reaction conditions (Figure 4). About 50% of the oct-1-ene is converted after 40 hours. Nonanal was the major product with a relatively constant *n/iso* ratio of 2.8. At higher temperatures, isomerisation and hydrogenation reactions take place in addition to hydroformylation.

The catalytic activity and selectivity of **2** was also studied towards the hydroformylation of oct-1-ene. The mole number-time profile of oct-1-ene and reaction products is shown in Figure 5. With this bridging tripod complex the activity is about the same as that of dppm complex **5** (50% conversion after 40 hours); however, the *n/iso* ratio is much higher, between 8 and 9. The presence of the extra phosphine on the central carbon atom clearly has a marked effect on the selectivity of the reaction.

Since the regioselectivity (expressed as *n/iso* ratio) to linear aldehyde using the tripod bridging complex **1** is higher than that of the analogous bridging dppm complex **5**, we suggest that the presence of the free diphenylphosphine group on the central carbon atom in **1** has a strong effect in controlling the selectivity of the reaction. This may be explained essentially by steric effects.

This result is in accordance with virtually all other phosphine- or phosphite-coordinated rhodium hydroformylation catalysts, where an excess of phosphine

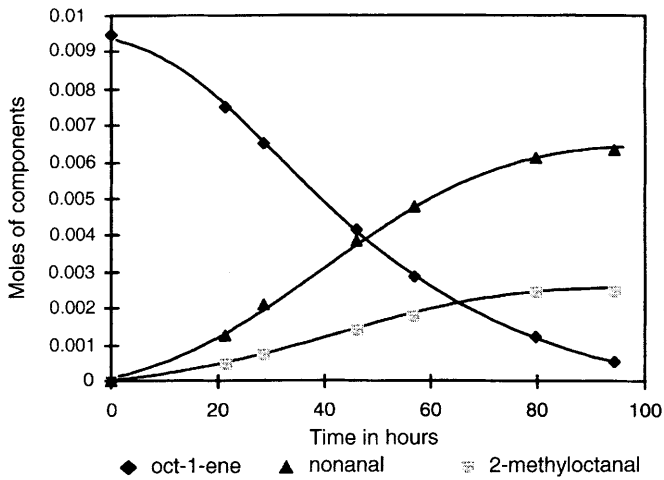

Figure 4 *Hydroformylation of oct-1-ene with complex* **5** *as catalyst*

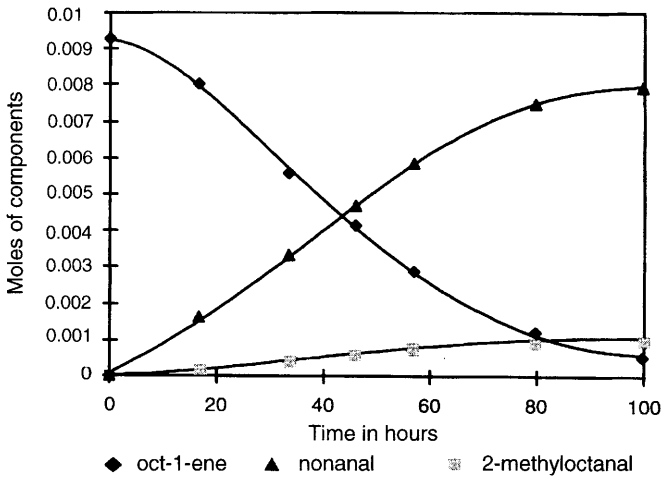

Figure 5 *Hydroformylation of oct-1-ene with complex* **2** *as catalyst*

(PPh_3) is needed to maintain good selectivity or stability. The need for excess PPh_3 in mononuclear rhodium catalysts arises from the relatively weak Rh–PPh_3 (or phosphite) bonding. In order to maintain the coordination of two PPh_3 ligands, which are required for good regioselectivity, a large excess of PPh_3 is required to force the dissociation equilibrium to favour $[RhH(CO)(PPh_3)_2]$.[20] In our case the free dangling phosphino group of the tripod seems to play an analogous role.

It is important to note that complexes **1** and **5** are recovered unchanged from the reaction mixture following catalysis, and ^{31}P NMR spectroscopy of the product solution showed no other phosphorus-containing species present.

We explored the hydroformylation reaction for monometal model complexes that represent one 'half' of the bimetal catalysts **1** or **5**. These tests give us an idea about whether each metal centre is functioning as a conventional mononuclear catalyst or whether there is some cooperativity. Thus the catalytic activity and selectivity of the complexes $[RuCl(\eta^2\text{-}Ph_2PCH_2PPh_2)Cp]$, $[RuCl\{\eta^2\text{-}HC(PPh_2)_3\}Cp]$ and $[\{RhCl(CO)_2\}_2]$ were studied under the same conditions as described above.

The complexes $[RuCl(\eta^2\text{-}Ph_2PCH_2PPh_2)Cp]$ and $[RuCl\{\eta^2\text{-}HC(PPh_2)_3\}Cp]$ are extremely poor hydroformylation catalysts. They showed less than 0.5% conversion of alkene to aldehyde after 30 hours, linear to branched ratios of one or less, and undesirable amounts of alkene isomerisation and hydrogenation products.

The complex $[\{RhCl(CO)_2\}_2]$ is a much more active catalyst with a relatively high turnover frequency of 156 (at 50% conversion), and 97% conversion of oct-1-ene after three hours. The products are exclusively the straight chain and the branched aldehydes with an *n/iso* ratio of approximately one.

The reactivity of $[\{RhCl(CO)_2\}_2]$ in the presence of various amounts of added

tripod was also investigated. It was found that the presence of an excess of tripod had very little effect on the *n/iso* ratio of the aldehydes, with the maximum not exceeding 1.5 even with a Rh/tripod ratio of 1:4.

The activity and regioselectivity of **1** and **5** therefore contrast to those of monometal rhodium or ruthenium complexes, and the regioselectivity of complex **1** is particularly noteworthy. These results indicate that the active species uses some sort of bimetal cooperativity to effect high regioselectivities.

Any discussion of mechanisms should take into account the early work on cobalt-catalysed hydroformylation.[21] A monometal mechanism was proposed that has become the generally accepted pathway [22] for both cobalt and rhodium catalysts. A more speculative mechanism was also suggested involving an intermolecular hydride transfer from $[CoH(CO)_4]$ to $[Co(acyl)(CO)_4]$. Elimination

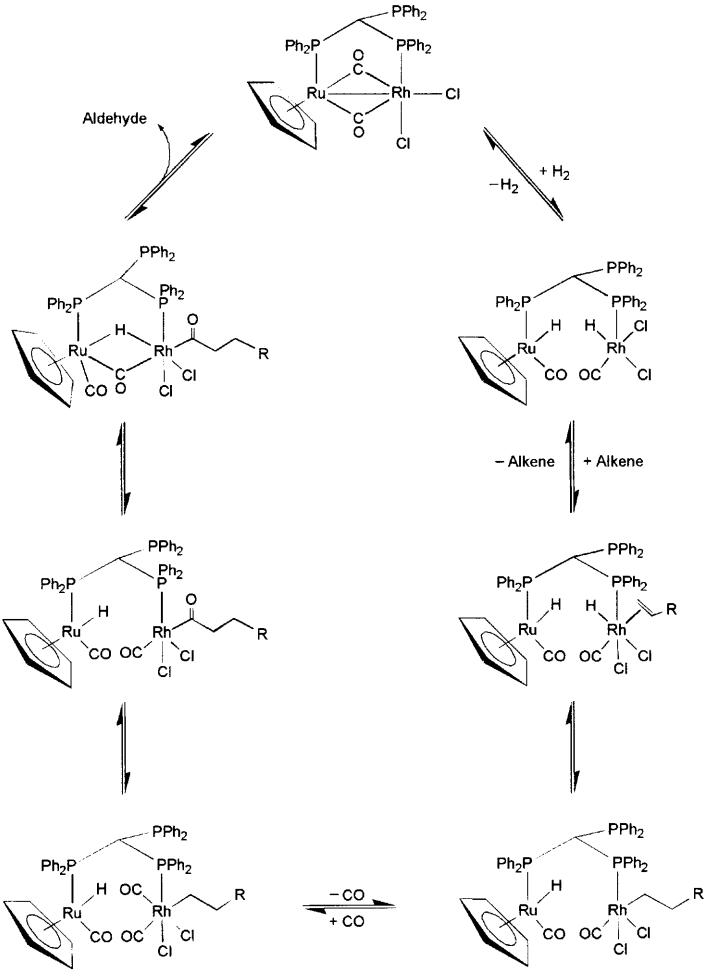

Figure 6 *Proposed mechanism for alkene hydroformylation with complex* **2** *as catalyst*

of the aldehyde product then produces $[Co_2(CO)_8]$, which reacts with H_2 to break the Co–Co bond to reform two $[CoH(CO)_4]$ molecules. This suggests an interesting mechanistic possibility for the heterobimetal catalysts **1** and **5**.

The constrained proximity of the two metal centres, held together by the tripod ligand, should increase the probability of an intramolecular hydride transfer. Thus a mechanism can be proposed (Figure 6) in which bimetal cooperativity, *via* an intramolecular hydride transfer, facilitates the elimination of aldehyde from the acyl intermediate.

The first steps in the proposed mechanism are essentially the same as those established for monometal Rh/PPh_3 catalysts, except that the proposed addition of H_2 oxidises two metal centres. In monometal systems, the final steps are the addition of H_2 to a rhodium(I) to produce a rhodium(III) dihydride species that can then eliminate aldehyde product. The ruthenium–rhodium intermediate avoids this problem by having a proximate Ru–H moiety, which can intramolecularly transfer a hydride to facilitate the aldehyde elimination. Thus the final steps of the mechanism are H and CO bridge formation between the

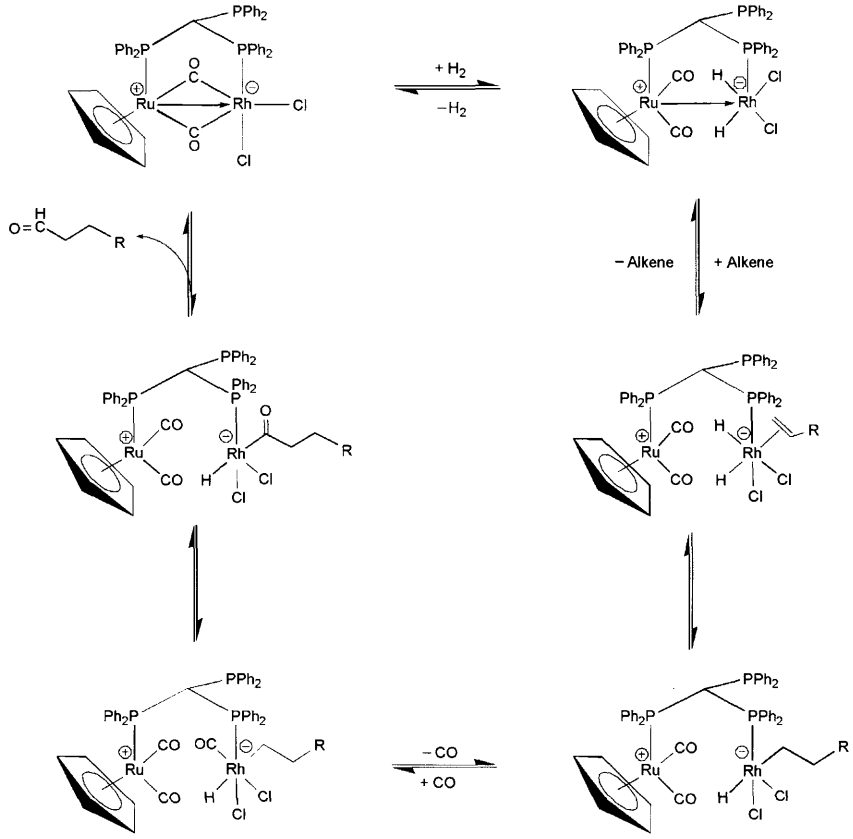

Figure 7 *Alternative mechanism for alkene hydroformylation using complex* **2** *as catalyst*

ruthenium and the rhodium atoms and then elimination of the aldehyde and reformation of **5**. A similar mechanism can be proposed for complex **1**.

The bimetal cooperativity in the proposed mechanism represents a very effective way of performing hydroformylation. The fundamental concept of a hydride transfer between two metal centres has been studied and shown to occur in stoichiometric model reactions by numerous groups.[23] Hidai and Matsuzaka[24] attributed the synergistic effect observed in the hydroformylation of olefins by the $[Co_2(CO)_8]$–$[Ru_3(CO)_{12}]$ bimetal system to a 'dinuclear reductive elimination of aldehydes from cobalt acyls and ruthenium hydride(s)'. $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2(PPh_3)_2]$ is another hydroformylation catalyst for which bimetal cooperativity has been proposed.[25] However, the reaction rates and regioselectivities of $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2(PPh_3)_2]$ very closely resemble those of Rh/PR_3 monometal catalysts, indicating that the active catalyst may be monometal in nature,[26] quite unlike **1** and **5**.

A mechanism in which the catalytic reaction takes place entirely at the rhodium atom, as shown in Figure 7, cannot however be discounted. In this case the cooperativity between the metal atoms arises from the ruthenium moiety acting as a labile ligand.

4 Conclusion

Bidentate or tridentate phosphine ligands that chelate to a metal atom to form a four-membered ring can undergo facile ring-opening reactions to produce heterobimetal complexes. Two of these complexes have been shown to be active and selective hydroformylation catalysts. The heterodinuclear complexes are recovered unchanged at the end of the reaction. Two possible mechanisms for the catalytic reaction have been proposed, one in which the initial addition of H_2 involves the formation of both Rh–H and Ru–H bonds, while the other mechanism involves oxidative addition of H_2 to the rhodium atom, with the ruthenium moiety playing the role of a labile ligand in the catalytic cycle. The bridging diphosphine or triphosphine ligands increase the selectivity of the reaction towards the linear aldehyde. Catalytic studies of possible monometal fragments from the bimetal complex indicate that these fragments are not the active species in the reaction. Further, *in situ*, studies will need to be carried out to determine the mechanistic pathway.

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Tethered Arene Complexes of Ruthenium

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1 Introduction

In this memorial volume devoted to one of the pioneers of modern coordination and organometallic chemistry, it is worth recalling that Joseph Chatt's classic papers in the 1950s dealing with the complexes of platinum(II) with alkenes and with tertiary phosphines appeared at about the same time as those of another great contemporary, Ronald (later Sir Ronald) Nyholm at University College London, on the closely related complexes of tertiary arsines with platinum(II) and the later transition elements.[1] Although Chatt and Nyholm worked independently during their careers, they were firm friends and exchanged information and ideas, especially during the early years of the development of the subject. There are other interesting historical similarities and connections between them. Both spent their formative childhood years in mineral-rich areas, Chatt in Cumberland, in the north west of England, Nyholm in Broken Hill, New South Wales, and their interest in minerals undoubtedly contributed to their interest in science.[2] The bidentate ligand *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4(AsMe_2)_2$, which Nyholm used to such good effect to stabilise unusual oxidation states and stereochemistries for the d-block elements, had been made first by Chatt in 1939 when he was a PhD student with F. G. Mann in Cambridge.[3] Nyholm inherited his interest in the coordination chemistry of tertiary arsines from the supervisor of his BSc. Honours project at the University of Sydney, G. J. Burrows. The latter had worked earlier with E. E. Turner who, like F. G. Mann, had been a Research Assistant at the University of Cambridge, working on organoarsenic chemistry with Sir William Jackson Pope.[4]

Potentially chelating ligands containing both alkene and tertiary phosphine or arsine donor centres were first synthesised in Nyholm's group in 1961 with the

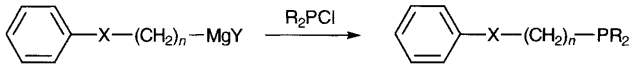
ideas of stabilising alkene coordination and studying the reactivity of the alkene when it was either coordinated to, or held in the vicinity of, a transition metal atom.[5,6] It was Chatt who first suggested that the anomalous platinum(IV) compounds that Nyholm's group had isolated from the addition of bromine to the platinum(II) complexes of (2-vinylphenyl)dimethylarsine, $[PtBr_2(o\text{-}Me_2AsC_6H_4CH{=}CH_2)_2]$, and (2-allylphenyl)dimethylarsine, $[PtBr_2(o\text{-}Me_2AsC_6H_4CH_2CH{=}CH_2)_2]$, contained a metal–carbon σ-bond in a chelate ring; this led to a rare joint publication by these two eminent chemists.[7]

Ligands containing both C- and classical N-, O-, P- or As-donors are now commonplace and have found extensive application in the study of 'strapped' or 'tethered' cyclopentadienyl complexes, for example.[8–10] Metal–arene complexes are less numerous and, in general, less stable than their metal–cyclopentadienyl counterparts, in part because the neutral arene is lost more easily from the coordination sphere. Thus, tethered arene complexes offer the possibility of stabilising arene coordination for a range of metals and oxidation states. Mirkin and co-workers[11–13] have shown that $Ph_2P(CH_2)_2XPh$ (X = CH_2 or O) form tethered arenerhodium(I) cations such as $[Rh\{\eta^1{:}\eta^6\text{-}Ph_2P(CH_2)_2XC_6H_5\}\{\eta^1\text{-}Ph_2P(CH_2)_2XC_6H_5\}]$, which undergo reversible electrochemical one-electron oxidation, presumably generating the corresponding arenerhodium(II) cations. These appear to be kinetically more stable than their unstrapped counterparts, but they have not so far been isolated.

Although complexes of the type $[RuX_2(PR_3)(\eta^6\text{-arene})]$ (X = Cl or Me) are known to undergo electrochemical one-electron oxidation,[14,15] the arene in the oxidised species is likely to be labile, rendering isolation difficult. One way to circumvent this problem is to use tethered arene-phosphine ligands, the idea being that dissociation of the arene from the higher-oxidation-state complex may be slow enough to allow the complex to be isolated. Similarly, chelating unsaturated tertiary amines and tertiary phosphines such as $o\text{-}CH_2{=}CHC_6H_4NMe_2$, $CH_2{=}CH(CH_2)_2PMe_2$ and $o\text{-}PhC{\equiv}CC_6H_4NMe_2$ have been used to generate chelation-stabilised complexes of bis(acetylacetonato)-ruthenium(II) and -ruthenium(III).[16,17]

2 Results and Discussion

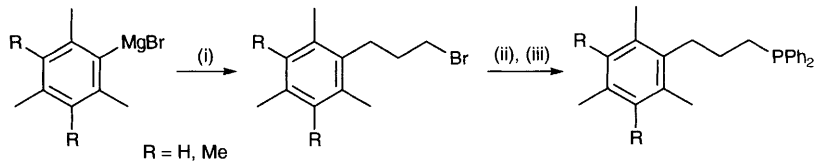
The ligands employed so far in our work are $C_6H_5(CH_2)_3PR_2$ (R = Ph or Me), $C_6Me_5(CH_2)_3PPh_2$, 2,4,6-$Me_3C_6H_2(CH_2)_3PPh_2$ and $C_6H_5SiMe_2CH_2PPh_2$. They have been made in yields of 40–80% by the standard methods outlined in Schemes 1 and 2. The reaction of Ph_2PCl with $C_6H_5SiMe_2CH_2MgCl$ gave some diphenylmethylphosphine as a result of Si–CH_2 bond cleavage; this was separated from $C_6H_5SiMe_2CH_2PPh_2$ by vacuum sublimation.



X = CH_2, n = 2, Y = Br
X = $SiMe_2$, n = 1, Y = Cl

X = CH_2, n = 2, R = Me or Ph
X = $SiMe_2$, n = 1, R = Ph

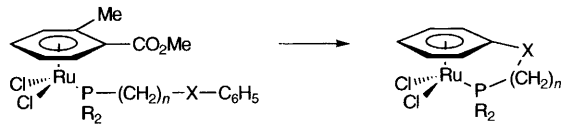
Scheme 1



Reagents: (i) $Br(CH_2)_3Br$, CuBr, hmpa/thf; (ii) Mg, thf; (iii) Ph_2PCl

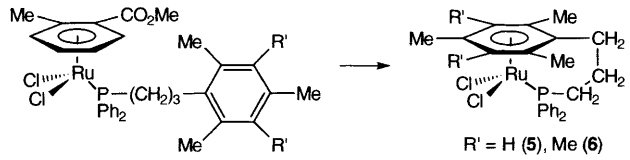
Scheme 2

The methyl *o*-toluate complex $[RuCl_2(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2Me)]_2$ (**1**) employed in earlier studies on planar chiral areneruthenium complexes[18] proved to be a suitably labile precursor to the tethered arene complexes. It reacts with the donors mentioned above in a 1:2 mol ratio in dichloromethane at room temperature to give quantitatively the corresponding P-bonded adducts $[RuCl_2(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2Me)(L)]$, which lose the methyl *o*-toluate on heating in dichloromethane or dichloromethane–thf at 120°C for 24–72 h. The resulting tethered complexes **2**–**6** can be isolated in the form of air-stable, orange, crystalline solids in yields ranging from 60–80% for $C_6H_5(CH_2)_3PR_2$ [R = Me (**2**) or Ph (**3**)] and $C_6H_5SiMe_2CH_2PPh_2$ (**4**), through *ca.* 18% for 2,4,6-$Me_2C_6H_3(CH_2)_3PPh_2$ (**5**), to *ca.* 7% for $C_6Me_5(CH_2)_3PPh_2$ (**6**) (Schemes 3 and 4). In the case of **6**, the yield can be increased to 35% by use of di-*n*-butyl ether in



X = CH_2, *n* = 2, R = Me (**2**)
X = CH_2, *n* = 2, R = Ph (**3**)
X = $SiMe_2$, *n* = 1, R = Ph (**4**)

Scheme 3



R' = H (**5**), Me (**6**)

Scheme 4

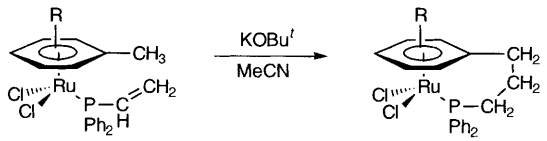
place of dichloromethane. The beneficial effect of ether solvents has also been observed in the synthesis of (η^6-arene)chromium tricarbonyls.[19,20] Attempts to form the tethered complexes **2** and **3** by UV-irradiation of solutions of the methyl *o*-toluate complexes at room temperature led only to decomposition. In the thermal reaction, the methyl *o*-toluate complex precursors of products **2**–**4** need not be isolated but can be generated *in situ* from solutions of complex **1** and the ligand.

Smith and Wright[21] have reported that complex **3** is formed in 50% yield by heating the *p*-cymene complex $[RuCl_2(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)$-

$\{Ph_2P(CH_2)_3C_6H_5\}]$ in chlorobenzene at 130°C and, in higher yield, by exhaustive anodic oxidation and subsequent spontaneous *in situ* reduction of the presumed labile ruthenium(III) species. However, we have consistently been unable to reproduce the thermal reaction, either under the stated conditions or in CH_2Cl_2/thf at 120°C. In refluxing chlorobenzene the *p*-cymene is displaced and we have obtained NMR spectroscopic evidence for the formation of a η^6-chlorobenzene complex, but attempts to isolate it failed.

Tethered areneruthenium(II) complexes similar to those described here have recently been investigated by several groups as catalyst precursors for ring-opening metathesis polymerisation and for cyclopropanation, so it is important to develop reliable syntheses. During the course of our work, two groups have reported independently[22,23] that tethered complexes such as $[RuCl_2\{\eta^1:\eta^6\text{-}Cy_2P(CH_2)_3C_6H_5\}]$ (Cy = cyclohexyl) can be obtained in 80–90% yield by heating the *p*-cymene P-donor adduct in chlorobenzene at 120–140°C. Possibly the formation of the tethered complex in this case is favoured by the bulky cyclohexyl groups on phosphorus, *cf.* the promotion of the formation of four-membered ring cyclometallated complexes by bulky substituents such as *t*-butyl on phosphorus.[24] Our results are, however, in agreement with those reported by Ward *et al.*[25–27] and Rieger *et al.*[28], who have used the more labile ruthenium(II) complex of an aromatic ester, ethyl benzoate, as a precursor to tethered areneruthenium(II) complexes containing the $CH_2CH_2PPh_2$ strap.

An alternative method of generating complexes containing a $(CH_2)_3PPh_2$ strap has recently been reported in which the diphenylvinylphosphine adduct of a (methylarene)ruthenium(II) complex undergoes an intramolecular base-promoted Michael addition reaction (Scheme 5).[29]



R = H, *p*-Me, *p*-$CHMe_2$, 3,5-Me_2 or Me_5

Scheme 5

The shifts to low frequency of the ^1H and ^{13}C NMR resonances associated with the arene ring in complexes **2–6** provide clear evidence for arene coordination and this has been confirmed by single crystal X-ray studies. The complexes show a typical half-sandwich structure with Ru–Cl distances of 2.40–2.42 Å and Ru–P distances of *ca.* 2.30 Å. The Ru–C(arene) distances *trans* to chloride (2.16–2.21 Å) are significantly less than those *trans* to the phosphorus donor (2.24–2.28 Å). These features are also evident in the structure of the non-tethered complex $[RuCl_2(PMePh_2)(\eta^6\text{-}C_6H_6)]$[30] and reflect the relative *trans*-influences of Cl and PR_3. In all the complexes containing $Ar(CH_2)_3PR_2$, the trimethylene strap allows simultaneously without strain an almost trigonal geometry for the $RuCl_2P$ fragment and coplanarity of the benzylic carbon atom with the arene

Table 1 *Electrochemical data*

Compound	$E_{1/2}$ V	ΔEp (mV s^{-1})
2	+ 1.26[a]	70
3	+ 1.32[a]	60
4	+ 1.34[a]	60
5	+ 1.20[b]	80
6	+ 1.10[b]	80

[a] Measured in 0.5 M $(Bu_4N)PF_6/CH_2Cl_2$ at 293 K with a scan rate of 100 mV s^{-1}, referenced to Ag/AgCl.
[b] Measured in 0.2 M $(Bu_4N)PF_6/CH_2Cl_2$ at 253 K with a scan rate of 100 mV s^{-1}, referenced to Ag/AgCl.

carbon atoms. In contrast, the two atom strap in complex **4** causes a bending of the Si–C(C_6H_5) bond out of the aromatic plane by *ca.* 14°.

As expected, the presence of the tether does hinder the release of the arene from the coordination sphere at the ruthenium(II) level. Thus, whereas benzene is displaced completely from the unstrapped complex $[RuCl_2(\eta^6\text{-}C_6H_6)\{\eta^1\text{-}Ph_2P(CH_2)_3Ph\}]$ in refluxing acetonitrile over 48 hours, displacement of the tethered arene in complex **3** does not proceed to completion, even after 11 days; in both cases, the product is a mixture of *cis*- and *trans*-isomers of $[RuCl\{\eta^1\text{-}Ph_2P(CH_2)_3Ph\}(NCMe)_4]Cl$.

All the tethered complexes show fully reversible, one-electron $Ru^{II/III}$ redox couples in CH_2Cl_2 (see Table 1). The $E_{1/2}$ values are in the range 1.34–1.10 V *vs.* Ag/AgCl, being reduced by increasing methyl substitution in the ring, as observed also for tethered arene-rhodium and non-tethered arene-ruthenium systems.[13,14] They are also reduced by replacement of PPh_2 by the more electron-donating PMe_2. The potentials appear to be consistently somewhat greater (*ca.* 200 mV) than the quasi-reversible potentials of 0.89–1.09 V (*vs.* SCE) reported for $[RuCl_2(\eta^6\text{-arene})(L)]$ complexes in acetonitrile,[14] indicating that the presence of the strap may slightly stabilise ruthenium(II) relative to ruthenium(III). Since the potentials of the tethered complexes are clearly too high to allow isolation of the presumed ruthenium(III) species, we are currently attempting to prepare strapped dimethylruthenium(II) derivatives, which are expected to oxidise at a lower potential. For example, treatment of complex **4** with dimethylzinc gives $[RuMe_2(\eta^1\text{:}\eta^6\text{-}Ph_2PCH_2SiMe_2C_6H_5)]$, identified tentatively on the basis of NMR data [δ(Ru-CH_3) − 0.32; δ(Ru-CH_3) − 4.75 ($^2J_{PC}$ = 17 Hz)]. We also plan to generate strapped areneruthenium(0) complexes in order to compare their C–H activation properties with those of their unstrapped counterparts.

3 Acknowledgements

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SECTION E:

Chemistry Related to Dinitrogen Complexes

The first complex of dinitrogen was announced in 1965, and despite the speculation that dinitrogen complexes analogous to the well known carbonyl complexes should exist, none had been hitherto forthcoming. Bert Allen announced the first, and that took some courage, since his evidence was primarily spectroscopic. Like many seminal discoveries, this was by chance (he was attempting to prepare $[Ru(NH_3)_6]^{2+}$*) but it is only the prepared and enquiring mind that is open to appreciate the significance of unexpected observations.*

After that dinitrogen complexes came thick and fast, and the Chatt group, with their sure foundation in phosphine chemistry, were ideally placed to exploit them. This is explained in the initial contribution from Richards. Inevitably the impetus of the Chatt group faded with the years and the group itself split up. Others took up the torch, and the beautiful work of Fryzuk, and the magnificent achievements of Floriani are reviewed here. Their work should be regarded as building on the foundations laid at the Unit of Nitrogen Fixation in Sussex.

Further developments from the same basis are detailed by Hidai and by Dilworth. Hidai was involved in the synthesis of one of the first dinitrogen complexes, and he spent some time working in Sussex. His account shows how many discoveries, initially quite unforeseeable, can arise from the same set of observations when they are analysed by the minds of different workers. The same is true of Dilworth, who obtained his D. Phil. in the Unit and who discovered there one of the first large groups of homologous dinitrogen complexes. Once he left the Unit, he exploited the ideas and principles he had absorbed there in his own individual way. His contribution is a summary of work that is yet another fruitful tree springing from the same seeds.

The reviews in this section provide a succinct summary of the Unit's dinitrogen chemistry, of some of the dinitrogen chemistry that sprang from it, and of the developments it helped to set in train. It represents a commendable legacy of the Unit of Nitrogen Fixation. The biological work of the Unit of Nitrogen Fixation and some of its influences are described in Section F.

Chemistry at the Unit of Nitrogen Fixation

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1 Introduction; The Early Years and the Search for Dinitrogen Complexes

I joined the Unit of Nitrogen Fixation (UNF) in 1964, actually taking up my post at the University of Sussex before the embryo UNF, then based in London at Queen Mary College (Chemistry) and the Royal Veterinary College (Biology), moved to Sussex. I joined directly from Manchester as a somewhat naive holder of a fresh PhD. As I left Manchester the then Head of Department, Jack Lewis, told me that Joseph Chatt had very high standards and joining him was a bit like jumping in at the deep end, but that I would benefit enormously from working with him. This proved to be entirely accurate. Although my original plan was to spend a short time at the UNF before moving on, I so much enjoyed the atmosphere and working ethos in the UNF that I remained there. I was to spend the next 16 years working with Joseph until his retirement in 1980 and this article is an account of the chemistry that developed during that period, with some indication of directions of progress after that date.

The UNF chemistry was set under way at Sussex by a small initial group consisting of myself, Brian Heaton, Rosemary Paske and David Newman, strengthened soon after by the arrival of Jeff Leigh and Mike Mingos. Joseph took a very close interest in all our projects. He had an impressive grasp of what we all were doing and a disconcertingly extensive memory for detail. He expected rigour in our work and kept us on our toes by recalling exactly what we told him in the previous discussion. We were immediately called to account if our discussions of progress lacked consistency! Nevertheless, Joseph's enthusiasm for chemistry was infectious and we all beavered away at our pet projects with enjoyment as well as care.

A major cloud was on our horizon, however. Although we knew from the emerging biochemistry that the action of nitrogenase must involve interaction of N_2 with iron or molybdenum or both, we had no routes to complex compounds that would establish this. In 1965, however, Allen in Toronto produced the first example of such an interaction[1] between Ru and N_2 in the complex ion $[Ru(NH_3)_5(N_2)]^{2+}$. This was followed by the preparations[2,3] of $[CoH(N_2)(PPh_3)_3]$ and $[IrCl(N_2)(PPh_3)_2]$ and although these discoveries were an encouragement in the sense that binding of dinitrogen in transition metal complexes appeared to be a general phenomenon, this was cold comfort since we had not been involved in making any of them!

The Ru compound was also reported (erroneously as it turned out) to give ammonia rather easily on treatment with sodium borohydride and at this stage it appeared that much of the chemistry required to understand the action of nitrogenase had been done. Indeed, I recall that at that time Joseph was considering what alternative project we might undertake; one that he was very interested in was C–H bond activation. He had in fact published a seminal, pioneering paper on this topic, also involving ruthenium chemistry.[4] I had read and re-read this paper and had been greatly impressed by the meticulous work and the techniques used in it, such as detailed use of isotope labelling, so that it proved inspirational for me, as it did for others who subsequently worked in C–H activation chemistry.[5]

However, what we decided to do was to broaden our strategy. As well as direct attempts to prepare dinitrogen complexes, which was proving difficult, (the above compounds had in any case been obtained by accident), we set out to examine the reactivity of the known dinitrogen complexes, develop the chemistry of metal complexes which might prove to be precursors of new dinitrogen compounds and also to look at the chemistry of dinitrogen analogues such as isocyanides, which might also be substrates of nitrogenase. This approach was typical of Joseph Chatt's management style, which led to so much success, in the following ways. First, the projects that were undertaken developed from group and interdisciplinary discussions in which we all took part, second we were encouraged to work around a topic following pathways that might have only an intuitive connection to our major interest, the only restriction being that the science should be of a good standard. This approach allowed us to follow hunches, kept us from becoming stale and in the end led to new chemistry of direct relevance to our remit of elucidating the function of nitrogenase.

For me particularly, the study of isocyanide complexes was a case in point. As well as competition in the chemical aspects of work at the UNF, there was strong competition in biochemical work. In particular, examination of alternative substrates for dinitrogen was in vogue and this had led to the seminal discovery by Mike Dilworth in Australia that nitrogenase would reduce acetylene to ethylene.[6] In an interdisciplnary effort which was to prove the hallmark of the UNF approach, the UNF biologists, John Postgate and Michael Kelly, and I demonstrated that MeNC was also a substrate and that the enzymatic reduction, to give methane and methylamine, could be mimicked if the MeNC was first coordinated to a metal.[7] More of this type of study later.

The dinitrogen complexes that had been prepared at this point carried phosphine co-ligands and it seemed reasonable for us to develop phosphine chemistry of the early transition metals, since this should lead to suitable sites to bind dinitrogen at biologically relevant metals such as iron and molybdenum. This approach also had an advantage for us in that we were building on the extensive background in such chemistry that had been built up by Joseph and his colleagues in his earlier career, particularly at ICI in the The Frythe laboratory.

A large range of complexes was prepared; in particular, halide–phosphine complexes in relatively high oxidation states provided the starting materials that eventually yielded dinitrogen-binding sites upon reductive elimination of halide.[8,9] Two examples are shown in Equations (1) and (2), each system giving an extended series of dinitrogen complexes.[10,11]

$$[OsX_3(PR_3)_3] + \tfrac{1}{2}Zn \xrightarrow[\text{thf, Hg}]{N_2} [OsX_2(N_2)(PR_3)_2] + \tfrac{1}{2}ZnX_2 \qquad (1)$$

(X = Cl or Br; R = alkyl or aryl)

$$[MCl_4(PR_3)_2] + 2PR_3 + (\text{excess})\ Na/Hg \xrightarrow[\text{thf}]{N_2} [M(N_2)_2(PR_3)_4] + 4NaCl \qquad (2)$$

(M = Mo or W; R = alkyl or aryl)

2 The Search for Reactions of Coordinated Dinitrogen

Other groups around the world were also producing dinitrogen complexes at a great rate and one of my interests was to try to produce ammonia from them by various means. Up to this point, as we reached the 1970s, it had turned out that none were capable of doing this by the methods we and others had used.[12]

Nevertheless, we were convinced that bound dinitrogen should be reactive towards attack by protons. Amongst other considerations, two pieces of chemistry stood out in supporting this view by demonstating that bound dinitrogen was weakly basic. The first was the observation that Allen's original dinitrogen complex, although not in fact able to produce ammonia, was able to bind a second $Ru(NH_3)_5^{2+}$ group to give the binuclear complex $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ [Equation (3)].[13]

$$[Ru(NH_3)_5(N_2)]^{2+} + [Ru(NH_3)_5(H_2O)]^{2+} \rightarrow$$
$$[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+} + H_2O \qquad (3)$$

The second was that the complex *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, prepared by Jon Dilworth during his D. Phil. work in the UNF,[14] was able to produce a whole range of adducts, such as shown in Equations (4) and (5).[15,16]

$$\textit{trans}\text{-}[ReCl(N_2)(PMe_2Ph)_4] + [CrCl_3(thf)_3] \rightarrow$$
$$[(PMe_2Ph)_4ClRe(N_2)CrCl_3(thf)_2] + thf \qquad (4)$$

$$2\ \textit{trans}\text{-}[ReCl(N_2)(PMePh)_4] + [MoCl_4(PPh_3)_2] \rightarrow$$
$$\textit{trans}\text{-}[MoCl_4\{(N_2)ReCl(PMePh)_4\}_2] + 2PPh_3 \quad (5)$$

Disappointingly, the rhenium complex also was not capable of producing ammonia. Most generally, protonation of dinitrogen complexes led to evolution of the dinitrogen as the gas, often with the production of metal hydrides, a not unexpected result in view of the electron-richness of the metal sites to which dinitrogen was bound. That we were eventually successful was due to a combination of factors, all important in research, as seasoned practitioners will know. These were persistence, preparedness and serendipity.

Because the metals important in nitrogenase were known to be molybdenum and iron, we had attempted to protonate some of the dinitrogen complexes known at that time. For example, on treatment with acids, the complex[17] *trans*-$[FeH(N_2)(PEt_2CH_2CH_2PEt_2)_2](BPh_4)$ evolved N_2 and the molybdenum compound *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $PPh_2CH_2CH_2PPh_2$) first prepared by Hidai,[18] gave a hydride, *trans*-$[MoH_2Cl_2(dppe)_2]$, on treatment with HCl,[19] and no appreciable amount of ammonia or hydrazine was observed. The last result was particularly perplexing because we had shown that the dinitrogen in the molybdenum complex is weakly basic, acting as a donor to $AlEt_3$.[20]

We appeared to have reached stalemate when Jeff Leigh and Graham Heath decided to look at the reactions of organic chlorides with *trans*-$[W(N_2)_2(dppe)_2]$. Instead of loss of N_2 with formation of W–C bonded species, they observed the formation of nitrogen–carbon bonds, as shown in Equation (6). The resulting acetyldiazenido-complex could be protonated reversibly to give a hydrazido(2 −) species.[21]

$$\textit{trans}\text{-}[W(N_2)_2(dppe)_2] + CH_3COCl \rightarrow$$
$$\textit{trans}\text{-}[WCl(N_2COCH_3)(dppe)_2] + N_2 \quad (6)$$

This led us immediately to re-examine our discouraging earlier work on the lack of protonation of dinitrogen in *trans*-$[Mo(N_2)_2(dppe)_2]$. We found that serendipity had worked in reverse, in that we had been correct in our approach, but had chosen the wrong metal to use with HCl as reagent and the wrong anion to use with *trans*-$[Mo(N_2)_2(dppe)_2]$ as reagent! Under the correct conditions, HCl gave *trans*-$[WCl(NNH_2)(dppe)_2]Cl$ from *trans*-$[W(N_2)_2(dppe)_2]$ and HBr gave *trans*-$[MoBr(NNH_2)(dppe)_2]Br$ from *trans*-$[Mo(N_2)_2(dppe)_2]$ [Equation (7)].[19,22]

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2HX \rightarrow$$
$$\textit{trans}\text{-}[MX(NNH_2)(dppe)_2]X + N_2 \quad (7)$$
$$(M = W, X = Cl; M = Mo, X = Br)$$

Thus we had reactivity of coordinated dinitrogen to make both N–H and N–C bonds, opening up the prospect of routes to ammonia, hydrazine and organonitrogen compounds using dinitrogen complexes as catalysts or catalyst precursors. For convenience, I will outline the advances made in the two areas separate-

ly, although they moved forward together of course, progress in one aiding that in the other.

3 Production of Ammonia and Search for a Catalytic System

Despite our demonstration of the partial reduction of coordinated N_2, outlined above, achieving the goal of ammonia production proved frustratingly slow. A lot of effort was expended in trying various ways of converting the NNH_2 ligand in the above complexes into ammonia, but without success. In these experiments we restricted ourselves to relatively mild conditions, bearing in mind that we wished to have some semblance of biological conditions.[22]

At that time Alan Pearman was working with me as a D. Phil. student and I set him the task of looking at the chemistry of the NNH_2 compounds. He examined their deprotonation to give NNH complexes and the displacement of the three-electron donor NNH ligand by the isoelectronic NO ligand to give nitrosyl complexes, as illustrated in Equations (8) and (9).[23]

$$\textit{trans}\text{-}[WF(NNH_2)(dppe)_2](BF_4) + NEt_3 \rightarrow$$
$$\textit{trans}\text{-}[WF(NNH)(dppe)_2] + (NEt_3H)(BF_4) \quad (8)$$

$$\textit{trans}\text{-}[WF(NNH)(dppe)_2] + NO \rightarrow \textit{trans}\text{-}[WF(NO)(dppe)_2] + \text{'HNO'} \quad (9)$$

He also rang the changes on the counter ions that could be used in the system, the aim being no more elevated than producing a good quantity of data for his thesis. This entailed both metathetical change of counter ion [Equation (10)] and use of various acids, including H_2SO_4.[23]

$$\textit{trans}\text{-}[MX(NNH_2)(dppe)_2]X + NaY \rightarrow$$
$$\textit{trans}\text{-}[MX(NNH_2)(dppe)_2]Y + NaX \quad (10)$$
$$(M = Mo \text{ or } W;\ X = Cl \text{ or } Br;\ Y = BPh_4,\ ClO_4 \text{ or } PF_6)$$

Having exhausted our enthusiasm for the dppe system, we decided to move on to monophosphine complexes, expecting to observe similar behaviour, perhaps with more lability in the products. It was our habit to run these reactions in sealed flasks and measure the gas evolved to give a mass balance.

Memorably, on a Friday afternoon in October 1974, we added H_2SO_4 to *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ in methanol and observed a rapid reaction to evolve a gas and deposit a blue solid. We were immediately very excited by this because it signified a different reaction pathway from those that we had seen before, and we set about measuring the amount of gas produced. With typical intuition Joseph came into the lab., to see how we were getting on, just as we found that only one mole of gas had been produced (we assumed correctly that it was N_2). We were all convinced that the remaining N_2 had been lost from the metal as ammonia or hydrazine, but we had to bite our nails until the following week, when the completed analysis of the system showed that we had indeed produced two moles

of ammonia per tungsten atom [Equation (11)]. We quickly showed that the Mo analogue also produced ammonia under the same conditions but with only about 0.7 moles of ammonia per Mo. Thus this success was a combination of serendipity in the matter of choosing the correct solvent and acid and sheer dogged persistence!

$$cis\text{-}[W(N_2)_2(PR_3)_4] \xrightarrow[H_2SO_4]{MeOH} N_2 + 2NH_3 + W^{VI} \text{ products} + 4(PHR_3)(HSO_4) \quad (11)$$

We confirmed this conversion by preparing *cis*-$[M(^{15}N_2)_2(PR_3)_4]$ and showing that it gave $^{15}NH_3$; then we published our preliminary results.[24] At around the same time other workers showed that ammonia could be obtained from the dppe system if rather more drastic conditions were used than the mild ones that we had employed.[25] In addition, it was also demonstrated around this time also that hydrazine and some ammonia could be obtained from complexes having dinitrogen bridging two metals (*e.g.* N_2H_4 from $[\{ZrCp^*_2(N_2)\}_2(N_2)]$)[26] ($Cp^* = C_5Me_5$) so the way seemed clear to using dinitrogen complexes in a catalytic, low-temperature system to produce ammonia and hydrazine on a commercial scale.

We now set out with high optimism first to characterise our system as far as possible, and then to use this knowledge to design a commercial catalyst, not realising at the time that attainment of a catalytic system that would work even under laboratory conditions was to prove elusive for some ten years.

Characterisation of the ammonia-producing reactions proved to be complex, and Richard Henderson in particular spent many hours in detailed kinetic studies of the various systems that we had studied. He demonstrated the different pathways that could be adopted, to give either hydrides, with or without dinitrogen loss, or to give hydrazides or ammonia, depending on the type of complex, the protic acid and the solvent used.[27] Nevertheless, the overall picture was for Joseph gratifyingly close to that which he had proposed for dinitrogen reduction at a single metal some years before.[12] We were able, by judicious choice of reagent and solvent, to isolate and fully characterise examples of the intermediate species MNNH, $MNNH_2$, $MNNH_3$, MN, MNH and MNH_2 from the ammonia-producing reactions, and also to observe their interconversion and degradation in reaction solutions by ^{15}N NMR spectroscopy and other techniques.[28–31] This led to the proposal of the cycle of reduction of N_2 to ammonia at a single metal site, shown in Scheme 1, which has been dubbed the 'Chatt cycle',[32] and the suggestion that it could be operative in nitrogenase if a single metal site is involved, which is still unclear.[33]

Using this chemistry as the basis, Chris Pickett and Jean Talarmin were later able to develop later an electrochemically-driven cycle for the reduction of N_2 to NH_3,[34] thus establishing in principle the vision that Joseph had held from early days in the UNF, that a low-technology electrochemical process for generating ammonia for agriculture could be achieved.

$$MoN_2 \xrightarrow[e^-]{H^+} MoNNH \xrightarrow[e^-]{H^+} MoNNH_2 \xrightarrow{H^+} MoNNH_3{}^+ \xrightarrow[e^-]{} MoN + NH_3$$

$$MoN \xrightarrow[e^-]{H^+} MoNH \xrightarrow[e^-]{H^+} MoNH_2 \xrightarrow[e^-]{H^+} Mo + NH_3 \xrightarrow{N_2} MoN_2$$

Scheme 1

4 The Formation of Nitrogen–Carbon Bonds

As pointed out above, the first formation of a nitrogen–carbon bond from a dinitrogen complex was achieved in 1972, [Equation (6)] and provided the stimulus for the protonation studies which lead to NH_3 formation. The work on N–C bond formation was not strictly in the remit of the UNF, whose members were supposed to devote their working hours to the study of nitrogenase, so this work was carried out by colleagues, directed by Joseph and Jeff Leigh, in an associated laboratory in the University of Sussex, the funding coming from sources outside the primary funding body of the UNF. Nevertheless, both groups kept a close interest in each other's work, scientific discussion was free and uninhibited and mutual benefit was enjoyed by all.

Initially it was thought that the mechanism of both protonation and alkylation would be the same, involving electrophilic attack by a proton or a carbocation such as RCO^+. It soon became clear, however, that the mechanism of N–C forming reactions was much more complicated. Moreover, several types of reaction were discovered.

Alkyl bromides and iodides were found to react with the *trans*-$[M(N_2)_2(dppe)_2]$ complexes to give diazenido-compounds; these could protonate at the terminal nitrogen to give hydrazido(2−)-complexes which reverted to the diazenido parents on treatment with base [Equation (12)].[35]

$$trans\text{-}[MX(N_2R)(dppe)_2] \underset{\text{Base}}{\overset{\text{HX}}{\rightleftharpoons}} trans\text{-}[MX(NNHR)(dppe)_2]X \qquad (12)$$

(M = Mo or W, X = Br or I)

The range of metals was also extended to include rhenium in the preparation of $[ReCl_2(N_2COR)(PMe_2Ph)_3]$ from $[ReCl(N_2)(PMe_2Ph)_4]$,[36] but other dinitrogen complexes proved resistant.

In the above reactions and related ones, such as the formation of $[MoCl(N_2COPh)(dppe)_2]$ from $[Mo(PhCN)(N_2)(dppe)_2]$, the halide of the attacking reagent was included in the complex product. However, the reaction of $[Mo(SCN)(N_2)(dppe)_2]^-$ with Bu^nI produced $[Mo(SCN)(N_2Bu^n)(dppe)_2]$, which suggested that the mechanism of the reaction must differ in detail from those of the previously described reactions.[37] The studies which led to a detailed understanding of the mechanism of N–C bond forming reactions are described below, but first the discovery of further types of complex will be described.

One type was essentially found by accident. When the complexes *trans*-$[M(N_2)_2(dppe)_2]$ were treated with MeBr in thf rather than benzene (the previous solvent of choice) instead of methyldiazenido-compounds, another type of

product was isolated. After some puzzlement, X-ray analysis proved the reaction products to be diazobutanol complexes, $[MBr\{N_2CH(CH_2)_3OH\}(dppe)_2]^+$ and other solvents such as tetrahydropyran and tetrahydrothiophene gave analogous materials.[38]

This reaction therefore gave a route to diazoalkane complexes by reaction of ligating dinitrogen and its discovery was particularly gratifying at the time, because attempts to produce such complexes directly by interaction of a diazoalkane with a metal complex generally caused decomposition of the diazoalkane.[39]

Once the diazoalkane products had been recognised, new routes were found to them. One involved a *gem*-dibromide as the reagent as shown in Equation (13).[40]

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + RR'CBr_2 \rightarrow [MBr(N_2CRR')(dppe)_2]Br + N_2 \quad (13)$$

$$(M = Mo \text{ or } W)$$

These complexes did not react with acids, but rather with nucleophilic reagents such as LiMe, to give diazenido-complexes [Equation (14)].

$$[MBr(N_2CRR')(dppe)_2]Br + LiMe \rightarrow [MBr(N_2CRR'Me)(dppe)_2] + LiBr \quad (14)$$

A more general reaction gave examples of diazoalkane complexes which could not be obtained from *gem*-dibromides and this involved the acid-catalysed condensation of hydrazido(2−) complexes with aldehydes or ketones.[41] The hydrazido(2−) complexes were obtained from protonation of dinitrogen complexes as described above. The condensation reaction was originally discovered by Masanobu Hidai, who had been involved in the discovery of the first molybdenum dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$, and in 1977 he was able to spend a year working at Sussex, where he extended the range of diazoalkane complexes by making use of the array of hydrazide complexes that we had amassed.[33,37,42] In particular, the use of the monophosphine precursors $[MX_2(NNH_2)(PMe_2Ph)_3]$ (X = halide, M = Mo or W) allowed access to the complexes $[MX_2(NNCMe_2)(PMe_2Ph)_3]$,[43] a useful way of accessing N–C bonds for the monophosphine series, since reaction of the complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ with alkyl halides generally leads to loss of all dinitrogen as the gas. The diazoalkane complexes also react with protic acids to give organonitrogen compounds, together with hydrazine, as shown for example in (15).[37]

$$[WBr_2(N_2CMe_2)(PMe_2Ph)_3] + HBr \rightarrow$$

$$[WBr_4(PMe_2Ph)_2] + [PMe_2PhH]Br + N_2H_4 + Me_2CNNCMe_2 \quad (15)$$

We conclude this survey of the types of reaction that were discovered by mentioning the variety of products obtained from reaction of α,ω-dibromides, $Br(CH_2)_nBr$, with *trans*-$[M(N_2)_2(dppe)_2]$, which depended on the value of n. As we have already noted, for $n = 1$, a diazoalkane complex was formed for M = Mo. However, for M = W the complex $[\{WBr(dppe)_2\}_2(\mu\text{-}N_2CH_2N_2)]$ was also isolated. In general, more than one type of complex was always formed, the long-chain diazenido-complexes evidently acting as alkyl bromides and attacking further dinitrogen complexes.[37,40]

This wide variety of reactions naturally raised questions as to the mechanism

of these reactions and detailed studies established that a wide range of substitution, exchange and alkylation reactions all proceeded at the same rate, and that, under pseudo first-order conditions, the reactions are first-order in the molybdenum complex. It also turned out that tungsten compounds showed similar behaviour, although irradiation is also necessary. Thus a common rate-controlling step is implied for these reactions, which can only be loss of dinitrogen as in (16).[44]

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] \rightleftharpoons [M(N_2)(dppe)_2] + N_2 \qquad (16)$$

$$(M = Mo \text{ or } W)$$

In substitution and exchange reactions there is competition between the new ligands and N_2 for the vacant site. Thus in all the alkylation reactions, the alkyl halide also competes with N_2, forming an unstable intermediate $[M(N_2)(XR)(dppe)_2]$, which homolyses to generate an M^I species, $[MX(N_2)(dppe)_2]$, and a radical $R^{\cdot}$, which for a dibromide can be a bromoalkyl radical $Br(CH_2)_{n-1}CH_2^{\cdot}$. If the radical is reasonably stable and the solvent is inert, then the radical appears to stay within the solvent cage containing both it and the M^I species, until it reacts with the remaining N_2 ligand as in (17).

$$[MX(N_2)(dppe)_2] + R^{\cdot} \rightarrow [MX(N_2R)(dppe)_2] \qquad (17)$$

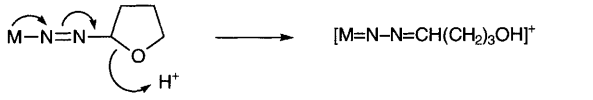
If the radical is too unstable (*e.g.* $BrCH_2CH_2^{\cdot}$) it will decompose before N–C bond formation. Alternatively, a radical which is too stable will not attack N_2. It appears that alkylation and acylation of coordinated dinitrogen have similar mechanisms.[44]

This mechanism is satisfying but not universal, as has been hinted at above. For example an alternative initiation step was discovered for the reaction of $[M(SCN)(N_2)(dppe)_2]^-$ with Bu^nI. The reaction was first-order in each reactant and the product, $[M(SCN)(N_2Bu^n)(dppe)_2]^-$ did not include the halogen from the alkyl halide. The mechanism shown in (18) was favoured on the grounds that the redox potential of $[M(SCN)(N_2)(dppe)_2]^-$ is about a volt more negative than that of $[M(N_2)_2(dppe)_2]$, so the anion is more likely to transfer an electron to the halide. Moreover, the electron transfer step would generate an M^I species plus a radical, which is exactly what results from metal-assisted homolysis of the alkyl halide.

$$[M(SCN)(N_2)(dppe)_2]^- + Bu^nI \rightarrow [M(SCN)(N_2)(dppe)_2]$$
$$+ C_4H_9^{\cdot} + I^- \rightarrow \text{products} \qquad (18)$$

It is clear from the products isolated from reactions in thf and related solvents discussed earlier, that as well as the alkylation reactions being a function of metal complex and halide, there is also a dependence upon solvent. If the solvent contains hydrogen atoms which are easily removed by radicals then attack on solvent might occur and the radical thereby generated can attack the M^I species thus yielding a diazenido-complex. This is the case, for example with thf as shown in (19), followed by a reversible reaction with protic acids to give a diazoalkane complex [Equation (20)].

(19)



(20)

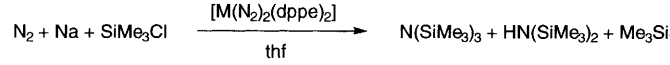
5 Formation of Amines

As might be expected from the parallel work on N_2 protonation, a major target of the N–C formation work was to develop a system to produce amines by a catalytic process involving an organic feedstock and N_2, *via* a dinitrogen complex intermediate. This concept was certainly established in principle by the above work, in that ligating dinitrogen had been transformed into an organic fragment at the metal. There still remained much to do if a catalytic system was to be viable, not least of which was the necessity to show that the metal-bound species could be removed from the metal, preferably by a mild hydrogenation step, so that the metal remained bound in a stable compound.

Although the removal of organic fragments was achieved, this was only at the expense of the metal complex, which was generally completely degraded because of the rather vigorous conditions that were necessary. Thus $[MoBr(N_2Bu^n)(dppe)_2]$ gave NH_3 and Bu^nNH_2 on treatment with $Na[BH_4]$ in a sealed tube at 100°C but no metal complex was isolated.[45] Hydrazido(2−) complexes were converted into anilines by various destructive methods, including treatment with sulfuric acid in propylene carbonate, reaction with $Li[AlH_4]$ and distillation from strong base;[46] diazoalkane complexes also gave amines on treatment with $Li[AlH_4]$.[43]

The potential for a cyclic system using electroreductive conditions was demonstrated by controlled potential electrolysis of $[MoBr\{NN\overline{(CH_2)_4CH_2}\}(dppe)_2]Br$, in thf under N_2, which gave *N*-aminopyrrolidine and the parent dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$.[47]

Work continued albeit at a lower pace after the above discoveries. For example the formation of N–Si bonds was established in the laboratory of Hidai and in this case a catalytic system was developed for formation of trimethylsilyl species from Me_3SiCl, using *trans*-$[Mo(N_2)_2(dppe)_2]$ and other dinitrogen complexes as catalysts (21).[48]



(21)

6 Reaction of Alternative Substrates

As I mentioned at the beginning of this article, from the early days at the UNF, the chemists were aware of the versatility of nitrogenase, in that a number of

substrates other than dinitrogen, such as CH_3NC (to CH_4 and NH_3),[7] cyanide ion (to CH_4 and NH_3)[49] and C_2H_2 (to C_2H_4), could be reduced by this enzyme.[6] These reactions and the observation that carbon monoxide inhibits the reduction of all substrates except the proton, established the organometallic nature of the enzyme. In the absence of any other substrate, protons are reduced to H_2; there is a corresponding reduction in the molecular yield of H_2 in the presence of substrate. The detailed biochemistry of these processes and their inter-relationships have been discussed in terms of an elegant kinetic study by the UNF biochemists Lowe and Thorneley and it is not my purpose to give an account of that work since it is well presented elsewhere,[50] but to emphasise the stimulus that the interaction with biochemists gave us to study the metal chemistry of dinitrogen and its alternative substrates. I will concentrate on only two aspects, since they illustrate the general approach, these being the reactivity of coordinating isocyanides and the behaviour of these ligands and of alkynes at dinitrogen-binding sites.[51,52]

Our first entry into the study of alternative substrates was the observation that MeNC was reduced by nitrogenase.[7] At that time there was still debate over whether or not a metal was involved in the enzyme action and it was a small triumph to be able to demonstrate that MeNC would only undergo reductive cleavage reactions to CH_4 and $MeNH_2$ after first binding a metal, otherwise the product of reduction was Me_2NH.[7] The work also lead us into some interesting organometallic chemistry. One of the metals we had used in our efforts to mimic nitrogenase action was platinum, and although its use was more inspired by Joseph's background in organometallic platinum chemistry than any biological consideration, we found that reductive cleavage of MeNC with reducing agents such as $Na[BH_4]$ did occur in platinum complexes. We never attempted to work out the detail of these reactions, but in some preliminary experiments our student Lisa Badley found that the ligating MeNC was succeptible to attack by reagents such as alcohols and amines to give carbene (alkylidene) complexes as shown in Equation (22), and this reaction proved to be general for a wide range of metals.[53,54]

$$\textit{cis}\text{-}[PtCl_2(R^1NC)(PR^2{}_3)] + HR^3 \rightarrow \textit{cis}\text{-}[PtCl_2\{C(NHR^1)R^3\}(PR^2{}_3)] \quad (22)$$

(R^1, R^2, and R^5 = alkyl or aryl; $R^3 = OR^4$ or NHR^5, R^4 = alkyl)

However, this work pre-dated the discovery of protonation of dinitrogen in the molybdenum and tungsten complexes and, once this had come to light, we turned our attention to the behaviour of isocyanides and alkynes at those sites that activated dinitrogen to reduction. For isocyanides, the first step was to bind these ligands in place of dinitrogen in the complexes *trans*-$[M(N_2)_2(dppe)_2]$, which was done by a displacement reaction [Equation (23)].[55]

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2RNC \rightarrow \textit{trans}\text{-}[M(RNC)_2(dppe)_2] + 2N_2 \quad (23)$$

(R = alkyl or aryl)

Immediately evident, from the pronounced lowering of the N–C stretching frequency of the isocyanides on binding, was the extent to which these sites are electron-releasing. This is of course the basis of the activation of N_2 at these sites towards protic attack at the position β to the metal, and together with Armando Pombeiro, then a graduate student, we were able to demonstrate a very similar pattern of protic attack on RNC at these sites, to give carbyne (alkylidyne) complexes,[52,56] as shown in Scheme 2; a similar reaction also occurs in *trans*-$[ReCl(RNC)(PMe_2Ph)_4]$.[52,57] Under appropriate conditions coupling of carbyne fragments can also occur to give alkyne complexes (Scheme 2).[58] Under similar conditions to those used to produce NH_3 from N_2 in *cis*-$[M(N_2)_2(PMe_2Ph)_4]$, RNC gives RNH_2, NH_3 and low yields of hydrocarbons from complexes of the type $[M(RNC)_2(PMe_2Ph)_4]$.[51]

$$\textit{trans}\text{-}[M(RNC)_2(dppe)_2] \xrightarrow{HX} [M(\equiv CNHR)(RNC)(dppe)_2]X \xrightarrow{HX}$$

$$[M(\equiv CNHR)_2(dppe)_2]X_2 \rightarrow [MX(\eta^2\text{-}MeHNC\equiv CNHMe)(dppe)_2]X$$

Scheme 2

The reactions of alkynes at these nitrogen-binding sites are complicated since a variety of pathways can be followed, including polymerisation, and although the work I shall now briefly describe was initiated while the UNF chemistry that concerns us here was being developed, the range of chemistry which flowed from it took many years to mature. Suffice to say that Scheme 3 shows one aspect of the chemistry of alkynes which relates closely to that shown by N_2 and RNC at these sites; the field has been reviewed.[59]

$$\textit{trans}\text{-}[W(N_2)_2(dppe)_2] \xrightarrow[-2N_2]{2HC\equiv CR} [W(\eta^2\text{-}HC\equiv CR)_2(dppe)_2]$$

$$\rightarrow [WH_2(C\equiv CR)_2(dppe)_2] \xrightarrow[-H_2]{HBF_4} [WF(\equiv CCH_2R)(dppe)_2]$$

$$\xrightarrow{HBF_4} [WF(=CHCH_2R)(dppe)_2](BF_4)$$

Scheme 3

The outcome of these studies was a reasonably coherent picture of reduction of dinitrogen and alternative substrates at a metal site, which appeared to relate at least in principle to nitrogenase action.

7 Further Developments

Here it is my purpose simply to point out the directions that 'UNF chemistry' took following the period covered by this review. Two major discoveries had great influence. The first was the demonstration, by genetic techniques, that alternative nitrogenases existed in which molybdenum is replaced by vanadium or iron.[60,61] This led to renewed interest in producing ammonia from iron

dinitrogen complexes[62] and the development of dinitrogen complexes of vanadium.[63,64] Much of the work involved phosphine co-ligands and could be seen as a further extension of the work begun at the UNF. However, because the metals in nitrogenase have a sulfur-ligand environment, efforts have been made to prepare complexes of dinitrogen at metal centres where the co-ligands have sulfur-donor atoms. This has proved to be a difficult task, although the number of sulfur-ligated dinitrogen complexes is increasing, notable examples being $[Re(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(N_2)(PPh_3)]$[65] and the most successful system in terms of binding N_2, the macrocyclic thioether complex *trans*-$[Mo(N_2)_2(Me_8[16]aneS_4)]$)].[66] Its dinitrogen ligands can be reduced, but the yields of ammonia are low and the susceptibility of the thioether ligand to degradation make an electrochemically-driven cycle for ammonia based on this system unlikely at present. Further developments in this area have involved the use of chelating thiolate ligands and are discussed in the article by Roger Sanders elsewhere in this book (p. 252).

The second major advance was the determination of the definitive X-ray crystal structure of nitrogenase, which showed the active centre of molybdenum nitrogenase to consist of an Mo–Fe–S cluster (FeMoco), which has a unique extended FeS-bridged structure and appears to be the centre at which the reduction of N_2 and related molecules occurs. The central Fe atoms in FeMoco are coordinated by three sulfides in an approximate planar environment and the molybdenum atom is also coordinated to three sulfurs, as well as two oxygens from homocitrate and one histidine nitrogen.[67] It is thought that the vanadium atom in vanadium nitrogenase and one iron atom in the 'iron-only' nitrogenase are in similar environments. This knowledge increased further the interest of chemists in iron–sulfur clusters, whose chemistry has been outstandingly developed by Holm, Coucouvanis and others.[68,69] The UNF and its later manifestations, by virtue of their multidisciplinary environment, were particularly well equipped to investigate the chemistry of FeMoco itself and the efforts of Barry Smith and his colleagues have led to detailed study of isolated FeMoco and demonstration of its ability to function outside the enzyme, to interact with CO, and to reduce protons.[70,71]

8 Conclusions

Joseph Chatt founded a laboratory with an environment that was multidisciplinary and flexible. It was an ideal place for a chemist such as myself to learn his trade and contribute towards the solution of a major problem, the function of nitrogenase. Certainly the work of the UNF chemists during the period that I have covered played a leading role in developing the area of dinitrogen chemistry. Whether that chemistry is indeed that chosen by nature remains to be established, as do catalytic processes based on it. I thoroughly enjoyed my time as a UNF chemist attempting to find such processes and I wish all success to current and future workers who attempt to complete the search. I also wish to thank all my colleagues during my time at the UNF for their help and friendship.

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Dinitrogen Activation by Early Transition Metal–Amido Phosphine Complexes

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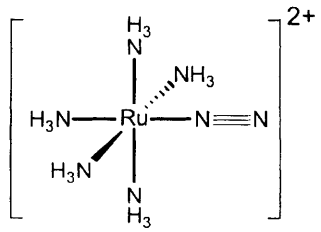
1 Preamble

The following describes work on dinitrogen activation by Group 4 and 5 complexes carried out at the University of British Columbia over the last decade or so in the Fryzuk group. While we are relative newcomers to this area, it is clear that our work builds on a strong foundation masterfully constructed by the Nitrogen Fixation Unit led by Professor Joseph Chatt while at Sussex University. There are also many other important contributors to the area of dinitrogen activation during the last 35 years, for example, the Hidai group from Japan, Schrock's group from MIT, and many others.[1] Before describing our contributions, I have included a short background section on how some of our work started.

2 Background

As a graduate student with Professor B. Bosnich at the University of Toronto during the period 1974–78, I had the pleasure of interacting with Professor A. D. Allen. During a graduate course, he recounted the story of the discovery[2] of the first ever dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$ **1** by his graduate student C. V. Senoff. It was fascinating, mainly because it went to the heart of scientific discovery through serendipity, curiosity, and insight.[3] A little later during my graduate career, in 1977, I attended a joint Chemical Institute of Canada–American Chemical Society conference in Montreal and there heard a fascinating lecture on zirconium hydrides by a young assistant professor from Caltech by the name of John Bercaw.[4] At the heart of this work was the dinuclear zirconium dinitrogen complex $[\{(Zr(N_2)Cp^*_2\}_2(\eta\text{-}N_2)]$ **2** ($Cp^* = C_5Me_5$) that

served as both a versatile starting material for Zr^{II} *via* displacement of coordinated N_2 but also for Zr^{IV} complexes by oxidative addition, for example, by dihydrogen.[5,6]



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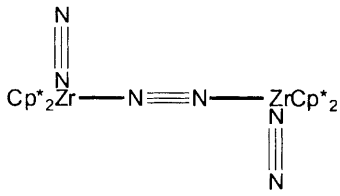
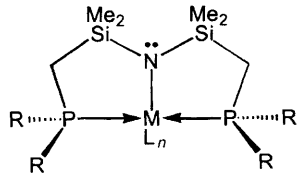


2 (Cp* = η^5-C_5Me_5)

I pretty much decided after that lecture that I wanted to learn more about early transition metal chemistry to augment my late transition metal background and applied to Bercaw for a postdoctoral position. I should point out that my graduate work was on the preparation of chiral diphosphine ligands (chiraphos and prophos) and their use in the asymmetric hydrogenation of amino acid precursors using rhodium(I) complexes. Bosnich was a fantastic supervisor who taught me the basics of ligand design, but more importantly showed me that chemistry was a craft.

Once I took up my independent career in 1979 at the University of British Columbia, dinitrogen chemistry was not one of my initial goals despite those early influences by pioneers in this area. I did have a fascination for early transition metal derivatives that I had picked up from the Bercaw experience but I also wanted to keep my fingers in the late transition metal area. To satisfy both cravings, I designed and synthesised a mixed-donor multidentate ligand that we subsequently called PNP.[7] However, it wasn't until 1988 that dinitrogen complexes were discovered in my laboratory. A general formula for a PNP complex is shown below.

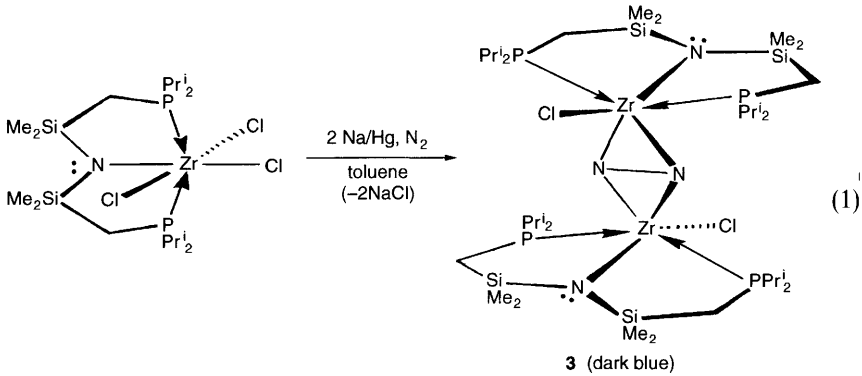


The design of the PNP amidodiphosphine ligand was based on the idea that the combination of both hard and soft donors should allow access to a variety of oxidation states for different transition metal complexes. For the late metals, the soft phosphine donors would serve to stabilise the hard amido-ligand bond while for the early transition elements, the amido donor would anchor the soft phos-

phine donors to these metals. In both cases, it was expected that the combination of mixed donors would facilitate changes in oxidation states and even allow for the preparation of uncommon oxidation levels for certain metals.

3 Our First Dinitrogen Complexes

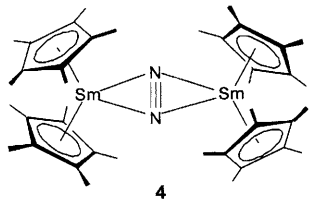
When Tim Haddad joined my group in 1985 his task was to examine the organometallic chemistry of Group 3 and Group 4 complexes stabilised by the PNP ligand. On one project, he examined the reaction of $[MCl_3\{N(SiMe_2CH_2PR_2)_2\}]$ (M = Zr or Hf; R = Me, Pr^i, or Bu^t) with 'magnesium butadiene' (MgC_4H_6·thf) to generate the Group 4 butadiene complexes $[M(C_4H_6)Cl\{N(SiMe_2CH_2PR_2)_2\}]$ (M = Zr or Hf). While these could be considered as Zr^{II} and Hf^{II} species, clearly this was a formalism. Tim also showed that these same complexes could be prepared by reductive techniques using Na/Hg and 1,3-butadiene. Unbeknownst to me, Tim also investigated the Na/Hg reduction of the zirconium(IV) precursors under dinitrogen. His first positive result was from the reduction of $[ZrCl_3\{N(SiMe_2CH_2PBu^t_2)_2\}]$ under N_2 from which he generated a deep green complex which he declared to be $[[\{(Bu^t_2PCH_2SiMe_2)_2N\}ZrCl]_2(\eta\text{-}N_2)]$. Unfortunately, he was never able to grow X-ray quality crystals of this material so its structure remains uncertain. Attempts to reduce the related complex with the smaller methyl substituents at phosphorus, $[ZrCl_3\{N(SiMe_2CH_2PMe_2)_2\}]$, failed completely; no colour changes were observed and recovery of starting material was generally achieved. He was pretty sure that he had a dinitrogen complex with the tertiary butyl derivative, but I remained sceptical. My input was to suggest changing the substituents at phosphorus to isopropyl, which I hoped would make things more crystalline. Fortunately, that lucky guess paid off and we did obtain deep blue single crystals of $[[\{(Pr^i_2PCH_2SiMe_2)_2N\}ZrCl]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ **3**, Reaction (1).



3 (dark blue) (1)

Complex **3** was a real surprise. It contained a side-on bound dinitrogen fragment bridging the two zirconium centres with a N–N bond distance of 1.548(7) Å, the longest N–N bond distance in a dinitrogen complex. When we

communicated this work in 1990,[8] it was only the second example of a side-on bound dinitrogen complex structurally characterised, the other being the dinuclear samarium derivative $[\{SmCp^*_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ **4**.[9]



4

What was intriguing about these two complexes was the very different N–N bond lengths for the coordinated dinitrogen unit; in contrast to the very long bond distance in our complex, the disamarium complex showed a rather short N–N bond length of 1.088(12) Å, virtually unchanged from that of free dinitrogen at 1.0947(5) Å. Another more obvious difference between our zirconium dinitrogen complex and the samarium derivative was that dinitrogen was irreversibly bound to the two Zr^{IV} centres whereas N_2 was easily lost from $[\{SmCp^*_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$. Given the long N–N bond length in **3**, it seemed reasonable to assign formal oxidation states such that the complex consisted of two Zr^{IV} centres and the bridging dinitrogen unit was N_2^{4-}. Addition of an excess of acid released exactly one equivalent of hydrazine, which supported this notion.[8] Also supportive of the presence of a highly reduced form of N_2 was the lack of reactivity with H_2; unlike the Bercaw dinitrogen complex **2** that reacts with H_2 to form $[ZrH_2Cp^*_2]$ with release of N_2, our side-on N_2 derivative **3** was impervious to H_2.

An obvious question that arose from this work was 'Why side-on bound dinitrogen rather than end-on?' We were able to show that the ancillary ligands play a major role in determining which orbitals on the metal centre are available to bind with the dinitrogen π^* orbitals; since the amide donor of the PNP ligand could overlap with one of the nonbonding d orbitals, this effectively removed one of the possible π-symmetry combinations found in the end-on mode of bonding. As a result the side-on mode became more favourable.[10] We were able to test this simple model by the preparation of related complexes, exemplified by the aryloxide complex $[[Zr\{(Pr^i_2PCH_2SiMe_2)_2N\}(O\text{-}2,6\text{-}Me_2C_6H_3)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ **5**, which was synthesised by M. Mylvaganam. This complex also showed a side-on bound N_2 unit with a very long bond length of 1.528(7) Å.[11] In collaboration with Thomas Loehr demonstrated that resonance Raman spectroscopy was extremely effective in distinguishing between the end-on and side-on modes of bonding for coordinated dinitrogen.[11,12]

Despite the fact that we had in our hands a strongly activated dinitrogen fragment and a relatively unexploited bonding mode for N_2, reactivity studies were hampered by the fact that the PNP ligand system was prone to phosphorus decoordination. Attempts to add HCl in a controlled fashion generally resulted

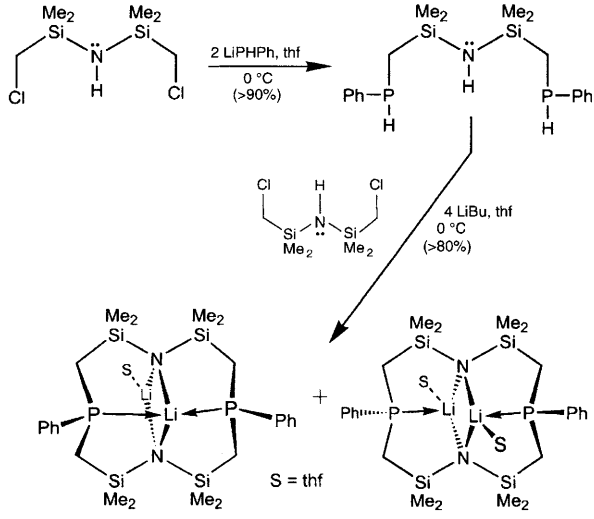
in complex mixtures from which no identifiable products could be obtained. In an effort to circumvent this phosphine dissociation problem, we redesigned our ancillary ligand.

4 The Macrocycle

If phosphorus decoordination were responsible for preventing clean, unique reactions of our dinitrogen complexes, then a strategy to prevent this process was necessary. One approach was to change from an acyclic tridentate ligand system to a tetradentate macrocyclic ligand that would mimic the PNPX ligand framework found for **3** (X = Cl) and **5** (X = OAr). The rationale was straightforward: incorporation of the phosphine donors into such an array would prevent dissociation since the macrocycle is rigid and not able to decoordinate any donor without the whole ligand being released. In 1995, a new postdoctoral fellow in my group, Jason Love, decided that he wanted to try and prepare the P_2N_2 macrocycle. At this point we had never successfully prepared a macrocycle containing phosphine donors and I reasoned that this might end up being a fairly arduous task. I cautioned Jason that this might be difficult and suggested that he use 'high dilution' conditions (what little I knew about macrocycles suggested that this might be prudent). He ignored me.

Jason's strategy was to prepare the P_2N_2 macrocycle by isolating the PNP intermediate and then to close the ring using the starting material for PNP, 1,3-bis(chloromethyl)tetramethyldisilazane, $HN(SiMe_2CH_2Cl)_2$. His first attempt was partially successful; the reaction of the intermediate $HN(SiMe_2CH_2PHPh)_2$ with one equivalent of $HN(SiMe_2CH_2Cl)_2$ and two equivalents of LiBu produced a small amount of crystalline material with a very unusual $^{31}P\{^1H\}$ NMR spectrum. Instead of the expected singlet(s) Jason observed 1:1:1:1 quartet patterns. When he showed this spectrum to me, I immediately realised what had happened; instead of isolating the expected neutral diamine macrocycle $PhP(CH_2SiMe_2NHSiMe_2CH_2)_2PPh$, he had clearly prepared the dilithio derivatives which were showing ^7Li coupling to the phosphorus nuclei. My suggestion to him was to repeat the reaction but add a total of four equivalents of LiBu; this worked amazingly well (yields were 80–90%). What was remarkable to me was that high dilution techniques were not necessary for the success of this reaction (Scheme 1). Our hypothesis still is that this reaction proceeds *via* lithium templating. There are some details that need to be included here; the reaction is both temperature- and solvent-dependent. Two forms of the macrocycle are generated because of the presence of the trigonal pyramidal phosphine donors. In thf, lower temperatures favoured the formation of the *anti* derivative whereas in Et_2O only the *syn* derivative was observed. As it turned out, the *syn* derivative was the most useful form for the preparation of early transition metal derivatives and so the use of diethyl ether is the method of choice in my group for the preparation of the P_2N_2 macrocyclic system.

Jason then turned his attention to the coordination chemistry of *syn*-



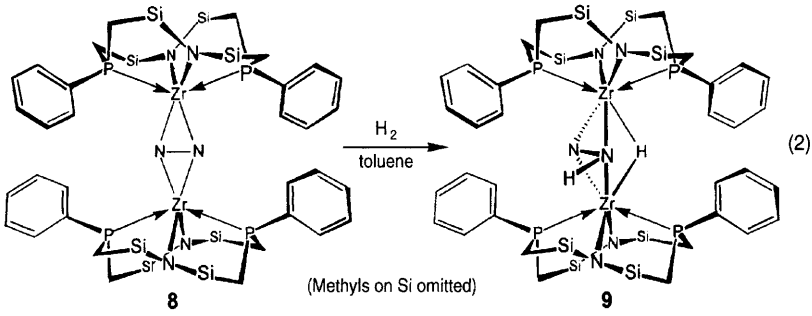
syn-$Li_2(thf)(P_2N_2)$ **6** *anti*-$Li_2(thf)_2(P_2N_2)$

Scheme 1

$Li_2(thf)(P_2N_2)$ **6** (P_2N_2 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$). One of his first reactions was with $[ZrCl_4(tht)_2]$ (tht = tetrahydrothiophene) to generate the Zr^{IV}-containing precursor $[ZrCl_2(P_2N_2)]$ **7**. The chemistry of this Zr^{IV} derivative is very extensive,[14] and it can also be reduced to generate the dinitrogen complex $[\{(P_2N_2)Zr\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ **8**. We were able to confirm that the change in ligand design had not dramatically affected the coordination mode of the N_2 unit as it was bound in a side-on manner.[15] However, the N–N bond length was only 1.43(1) Å, considerably shorter than the other side-on bound dinitrogen complexes that we had isolated thus far using the PNP ancillary ligand.

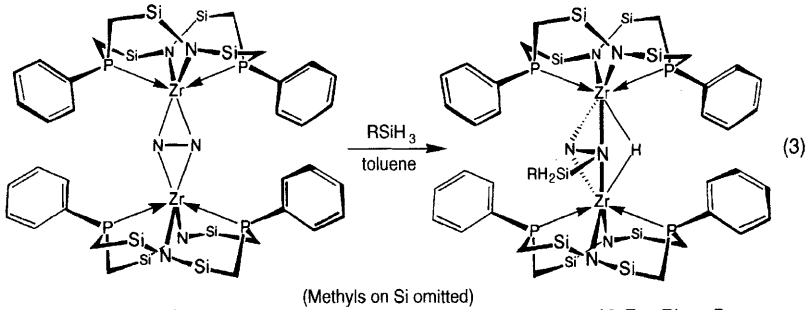
One of the first reactions we investigated was the reaction of **8** with dihydrogen. Now one might ask why this reaction should be pursued since our original dinitrogen complex **3** was unreactive to H_2. I guess the answer is that we thought that perhaps the shorter N–N bond length found in **8** might imply a less activated N_2 unit that might be displaced by H_2 like the Bercaw dinitrogen complex **2**. What in fact occurred was unexpected and certainly more remarkable than displacement of coordinated N_2. The reaction of H_2 with **8** resulted in the cleavage of H_2 and the formation of a N–H bond and a bridging hydride [Reaction (2)].

The evidence for this transformation was initially based on ^1H NMR spectroscopy. The formation of $[\{Zr(P_2N_2)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H)(\mu\text{-}H)]$ **9** was clearly evidenced by a loss of the deep blue-green colour of **8** to generate yellow-orange **9**. The solution ^1H NMR spectrum of **9** showed two new resonances at 5.53 ppm and at 2.07 ppm due to the N–H and the $Zr_2(\mu\text{-}H)$ units, respectively. These assignments were confirmed by ^{15}N and ^2H labelling. We also extended this reaction to silanes; the addition of phenyl- or butyl-silane ($RSiH_3$; R = Ph or Bu) to **8** resulted in the formation of the silylated analogues. One of these (R = Bu)



8 **9** (2)

was crystalline enough to confirm that the solid state structure was identical to that found in solution [Reaction (3)].



8 **10** R = Ph or Bu (3)

We were able to grow crystals of **9** and these were submitted to Victor G. Young, Jr., at the University of Minnesota for X-ray analysis using CCD detection and low-temperature data collection. The result was startling. Victor informed us that the structure had refined to indicate a coordinated dihydrogen unit bridging the two Zr centres and parallel to the side-on bound N_2 moiety. What this suggested was that in the solid state a different structure was present from that found in solution. In retrospect, we should have been much more circumspect, but the simplicity of this new bonding mode for dihydrogen found in the solid state structure dared us to over interpret this result. And unfortunately we did. Our report in *Science* in 1997 sparked a lot of interest and it didn't take too long before we had Thomas Koetzle and Alberto Albinati interested in collaborating to obtain a neutron structure of this crystalline material. Before Jason Love left my group to return to Sussex University, he grew some crystals of **9** but these weren't quite big enough for the neutron study. A new postdoctoral fellow in my group, Wolfram Seidel, was able to grow a variety of larger crystals of **9** suitable for transport to Grenoble. The result was pretty embarrassing. No bridging dihydrogen unit, just the same structure that we observed in solution. About the same time that we got this result, I attended an ACS meeting in Dallas, Texas where Djamaladdin Musaev, a research associate with Keiji Morokuma at Emory University, came up to me and told me how hard they had tried to model the bridging dihydrogen moiety from the low temperature X-ray structure

using DFT calculations but they found that it was unstable. I then recounted how we had just confirmed that the solution and solid state structures were in fact identical and did not involve a coordinated dihydrogen unit. As a result of this chance meeting, we published a joint paper with the results of the DFT calculations and the neutron structural analysis.[16] While the whole story did eventually get told, it was clear that my over-interpretation of the X-ray data was unfortunate, despite the happy ending.

5 Trying to Cleave the N–N Bond

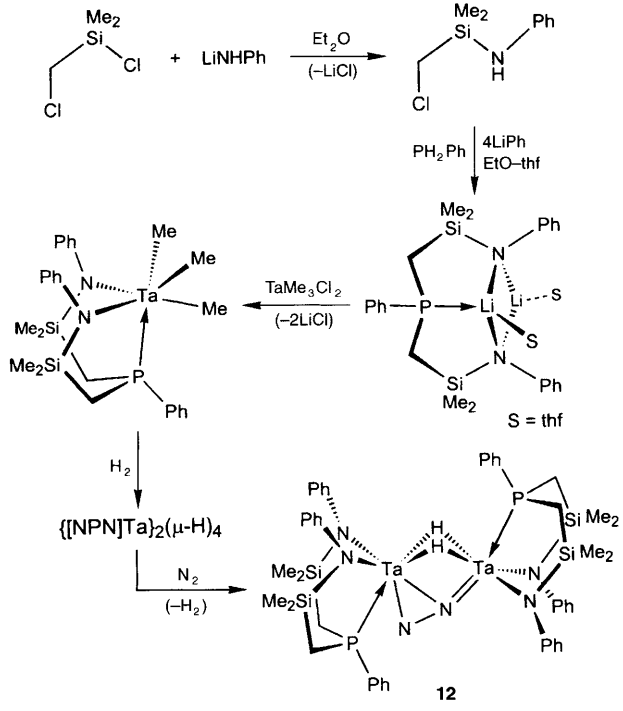
A drawback of the above dinuclear zirconium dinitrogen complexes is that one is limited to a total of four electrons that can be delivered to the dinitrogen fragment. In other words, even with the strongly activated dinitrogen fragments that we have been able to isolate, they still contain a N–N bond, albeit a single bond assuming the N_2^{4-} formalism. We have tried adding reducing agent (KC_8) to **3** in an effort to cleave the N–N bond, but we were unable to crystallise the product. One way to circumvent having to add the extra electrons at the end was to move to Group 5 and generate systems that might intrinsically be able to supply more electrons to the dinitrogen fragment. Our target molecule was the tantalum nitride complex, $[TaN(P_2N_2)]$, which might be accessible by formation of the tantalum(II) fragment $\{Ta(P_2N_2)\}$ and subsequent reaction with N_2. We hoped to mimic the dinitrogen cleavage discovered by the Cummins group at MIT using $[Mo(NRAr)_3]$.[17,18] Despite many attempts, our efforts have not met with success.

However, we have been able to prepare the dinuclear niobium complex $[\{Nb(P_2N_2)\}_2(\mu\text{-}N_2)]$ **11** by reduction of the niobium(III) precursor $[NbCl(P_2N_2)]$ with KC_8 under N_2;[19] complex **11** contains an essentially linear end-on bridging dinitrogen fragment. In this case each niobium centre is formally Nb^{IV} and contains one unpaired electron. Attempts to prepare the tantalum analogue of **11** have been completely unsuccessful, largely because of our inability to prepare a Ta^{III} precursor. While much new organometallic chemistry has been discovered using $[TaMe_3(P_2N_2)]$ as a starting material,[20,21] we could not find ways to access dinitrogen complexes of tantalum using P_2N_2 as an ancillary ligand. What we did find was that the P_2N_2 macrocycle tended to generate very unreactive complexes of tantalum, so we redesigned our ligand system.

Sam Johnson's PhD project was the ill-fated tantalum nitride synthesis described above. He struggled to generate reactive $Ta(P_2N_2)$ precursors and in every case was thwarted by the apparent coordinative saturation that the macrocyclic ligand engendered. He reasoned that a new ancillary ligand with fewer donors was necessary to generate more reactive tantalum precursors. He decided to prepare the NPN donor shown below. As it turns out, Jason Love and I were also talking about this same ligand system in the context of Group 4 chemistry and polymerisation catalysis. While the latter project never panned out (we got scooped by Schrock on this aspect), Sam's idea worked incredibly well, better than even I could have expected.

The tantalum(v) precursor $[TaMe_3(NPN)]$, prepared from $TaMe_3Cl_2$ and $(NPN)Li_2 \cdot thf$, reacts smoothly with H_2 to produce the dinuclear Ta^{IV} tetrahydride complex $[\{(NPN)Ta\}_2(\mu\text{-}H)_4]$, completely analogous to that found for the related $[TaMe_3(P_2N_2)]$ derivative. However, whereas the tetrahydride produced from the macrocyclic system is unreactive to ligand addition, exposure of $[\{(NPN)Ta\}_2(\mu\text{-}H)_4]$ to a dinitrogen atmosphere results in a colour change and the formation of the dinitrogen complex $[\{(NPN)Ta\}_2(\mu\text{-}\eta^2\text{-}\eta^1\text{-}N_2)(\mu\text{-}H)_2]$ **12** that displays a new bonding mode, [22] that of side-on and end-on as shown in Scheme 2.

While we still have some work to do to cleave the N–N bond, the fact that this change in ligand design allowed us to generate a dinitrogen complex of Group 5 is very encouraging. Work continues in our laboratory to probe the reactivity patterns of this side-on end-on bound N_2 unit, as well as examine the preparation of other dinitrogen complexes using these kinds of ligand designs.



Scheme 2

6 Conclusions

I remember reading in the Huheey texbook, *Inorganic Chemistry*,[23] about the headlines that travelled around the world after Joe Chatt showed that protona-

tion of Group 6 dinitrogen complexes generated ammonia stoichiometrically. The final headline of 'Basic life processes created in UK lab' that appeared here in Vancouver in the daily newspaper *The Province* in January of 1975 had certainly promised a lot. The whole area of nitrogen fixation, while vibrant in the 70s and 80s, seemed to lose some momentum in the late 80s. However, this topic would appear to be undergoing a renaissance in many different quarters. The report of the X-ray structure of the active site of the iron–molybdenum nitrogenase protein from Doug Rees' group,[24,25] the cleavage of the dinitrogen by transition metal complexes by a number of different groups, and the discovery of new reactivity patterns for coordinated dinitrogen, are all helping to fuel renewed interest in this important area of research. But it all comes back to a strong foundation. For that we owe a great debt to Joseph Chatt and the Nitrogen Fixation Unit. Without their commitment to curiosity-driven research, my own contributions would lack contextual substance.

7 Acknowledgements

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Metal–Dinitrogen Chemistry After Chatt

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1 Introduction

Reviewing the status of the art of dinitrogen activation is rather difficult, owing to the variety of widely spread results in the literature, and, generally speaking, to the prior lack of a methodological approach to the problem.[1] Even so, it is possible today to single out some major directions in the historical development of the field. Bearing in mind that we are still at the stage of acquiring fundamental knowledge before the dinitrogen molecule will become a useful chemical reagent, some of the objectives in the use of dinitrogen are: (i) to reduce and hydrogenate it under mild conditions; (ii) to functionalise organic substrates; (iii) to form metal–nitrido compounds analogous to metal–carbides in material science; (iv) to mimic the polymeric forms and the properties of metalla-acetylides. Then, the quite difficult move will be from stoichiometric to catalytic chemistry. We have to confess that the bio-oriented approach in the field, in terms of practical results, has so far been quite disappointing.[2] None of the claimed bio-inspired models[2] has been shown to be capable even to fix the dinitrogen molecule. Therefore, we will follow the historical development of biologically unrelated transition metal compounds devoted to dinitrogen activation. Three major advances can be singled out in the area, that have arisen since the discovery that a metal complex was able to bind dinitrogen.[3] They are: (i) coordinative dinitrogen binding; (ii) reductive dinitrogen binding; (iii) N–N triple bond cleavage to nitride.

2 Coordinative Dinitrogen Binding

The coordination of dinitrogen was initially pursued just for the pleasure of having such an inert molecule interact with a metal centre.[1] Then the perception

dawned that this aesthetic operation was chemically very important. Although isoelectronic with CO, the high-energy π^* antibonding orbitals of N_2 prevent good binding to an electron-rich metal, because of the very limited back donation. Although electron transfer to N_2 is rather weak because of the limited back donation, the binding to the metal has the important consequence of introducing a significant polarisation into the N_2 molecule, thus making accessible kinetic pathways for its reactivity. We should remember that in many cases thermodynamics are not the major problem for the chemical activation of dinitrogen, as is the case for CO_2, for example. The dinitrogen polarisation, which depends on the extent of the π back donation from the metal, has been proved by the quantitative study of the formation of acid–base adducts between metal-bonded dinitrogen and Lewis acids, in pioneering work by Chatt's school.[4] The elegant work by Sellmann[5] completed our understanding in this regard by transforming N_2 into Me–N=N–Me by a sequential reaction of an Mn–N_2 functionality with LiMe followed by MeX. These investigations revealed an electron-richness of the terminal nitrogen, which can be quantitatively related to the polarisation of the N_2 moiety in diazoalkanes,[6] opening perspectives in two major directions, namely the protonation[7] and the alkylation[1d,8] of N_2.

In the former case, the protonation appeared to be a quite complex reaction, with a major message: even in the absence of a significant electron-transfer from metal, the protonation can draw electrons from the metal, and the overall result is the formation of some NH_3 and N_2H_4.[7] Chatt's group provided a major contribution to this research domain. The protonation of the metal-bonded N_2 opened the door to its reaction with organic electrophiles,[1d,8] the beginning of the organic functionalisation using the metal-activated forms of N_2. The pioneering work by Chatt's group was actively pursued mainly by Hidai's group in Japan.[1d,8c] Using molybdenum and tungsten complexes having phosphines as ancillary ligands, this group demonstrated a variety of organic functionalisations employing both the protonation and the alkylation of metal-bonded dinitrogen.[1d,8]

3 Reductive Dinitrogen Binding

The historical move to early transition metals in rather high oxidation states and the use of σ- and π-donor ligands, contrary to what was observed in the late and low-oxidation-state transition metals, has been the preferred approach to achieve a real electron-transfer from the metal to the N_2 ligand. In this context, two major strategies have been particularly successful, namely the use of the ancillary ligands mentioned above and the macrocyclic effect.

Such an approach allows not only the pursuit of the two- but also the more important four-electron reduction of dinitrogen to a metalla-hydrazide.[9,10] In the case of early transition metals, the major strategy has been to take advantage of both the high energy of the filled d orbitals and the absence of the π-acceptor co-ligands around the metal. In this way, a much better matching has been achieved between the high energy of the π^* dinitrogen orbitals and the appropriate d orbitals of the metal. This can be exemplified by the end-on bridging

bonding modes of dinitrogen, moving from the form **a**, seen in the coordinative bonding mode, to **b** and **c** (Chart 1).[9d,11]

M–N≡N–M	M=N=N=M	M≡N–N≡M
a	**b**	**c**
M–C≡C–M	M=C=C=M	M≡C–C≡M

Chart 1

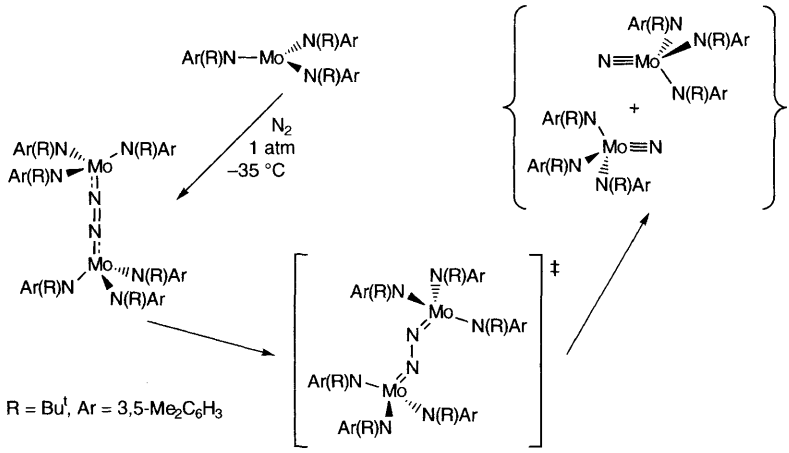
Such a move is associated with the electron-richness of the metal, the nature of the donor atoms and the set of the metal frontier orbitals, which should be preorganised to form one σ and one or two π bonds with a nitrogen atom of N_2. This is greatly enhanced by geometrical constraints, which have been provided mainly by a polydentate or macrocyclic ligand with nitrogen or oxygen donor atoms. A very significant example in the literature has been reported by Schrock with his class of trisamidoamine ligands.[9a,9b,9e,12] In the case of electron-rich early transition metals supported by conformationally very flexible monodentate or polydentate ligands, the electron transfer to dinitrogen takes place with side-on bonding modes to the metals.[11,13] Such a bonding mode sometimes makes the metal $\rightarrow N_2$ electron-transfer process more efficient, as revealed by the longest N–N bonds ($\sim$1.50 Å) found in the literature, even longer than in hydrazine derivatives and hydrazine itself.[13] The bonding modes shown in Chart 1 are full of implications for new perspectives in dinitrogen chemistry, particularly in the use of N_2 as the electronic equivalent of $[C{\equiv}C]^{2-}$.[14] The limiting forms reported in Chart 1 have also been reported for the dimetalla-acetylide derivatives. Monometalla-acetylides and dimetalla-acetylides are considered as the building blocks of metalla-cumulenes; their potential in material science is just now dawning.[15] Analogously, the metal–dinitrogen moiety can be considered as a potential building block for a variety of metal–dinitrogen polymers.[14]

4 N–N Triple Bond Cleavage to Nitride

N–N triple bond cleavage has always been assumed as a sort of a dream in dinitrogen activation, due to the major practical use of N_2 in producing ammonia, and to the fact that in the actual use of heterogeneous catalysts the formation of nitrides is unanimously considered as the intermediate step in the formation of NH_3 by dinitrogen hydrogenation.[16]

Nevertheless, N–N triple bond cleavage in the homogeneous phase, employing well-defined transition metal complexes, is an avenue in dinitrogen chemistry which is quite recent and there are as yet neither many nor diverse examples. Roughly speaking, the *a priori* requirements in order to achieve this goal are an early transition metal having a d^2 or d^3 configuration, ligands acting with σ-donor atoms without π-accepting properties, and the preorganised arrangement of the donor atoms expressed by macrocyclic or sterically hindered monodentate ligands. Under these conditions the form **c** (see Chart 1) of the metal–dinitrogen unit seems suitable to undergo a further two-electron reduction with the complete cleavage of the residual N–N single bond. Three examples

have appeared so far in the literature, with some of the common features mentioned above. Chronologically, the first one is the report by C. C. Cummins[17] on the spontaneous cleavage of the N–N triple bond occurring according to Scheme 1. Such a result has been achieved using sterically hindered amido groups assuming a trigonal planar geometry in binding to a Mo^{III} d^3 ion. The pathway leading to the formation of molybdenum-nitride from N_2 has also been accurately investigated. The latest report in the field is by Cloke,[18] who used a tridentate silylated diamidoamine ligand for supporting a vanadium(III)-d^2, chloride-bridged dimer. Its reduction with KC_8 under N_2 led to the formation of a dinuclear nitrido species.

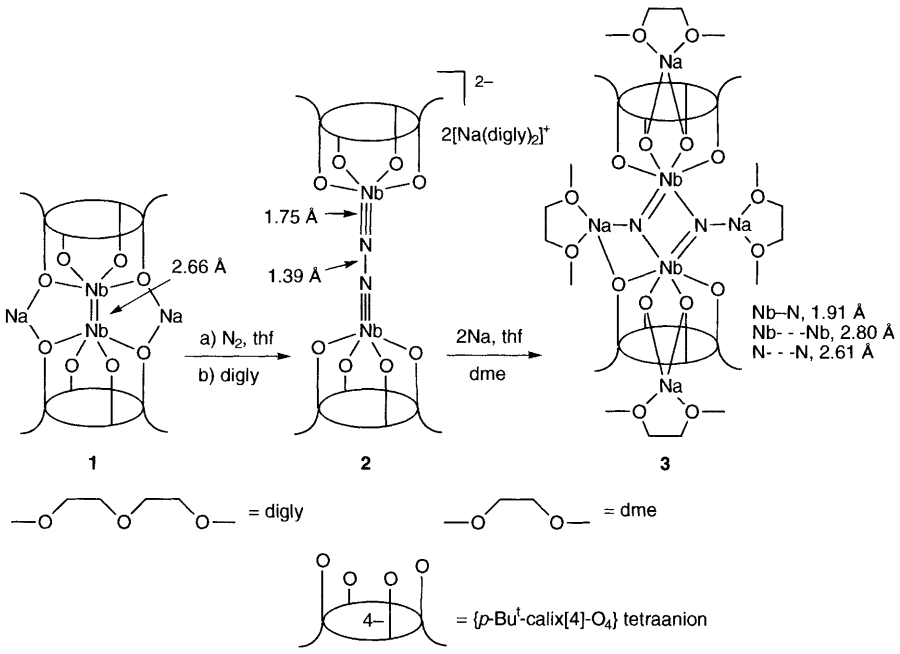


Scheme 1

A detailed account of extensive research by the author's group will be given here.[19] This includes numerous aspects of the problems related to metal-assisted N–N triple bond cleavage. The *a priori* choice has been a metal with high-energy d orbitals having either a d^2 or d^3 electronic configuration and capable of establishing a multiple bond in a well-defined direction. This has been achieved using a calix[4]arene moiety as an ancillary ligand. Such a choice introduces a number of unprecedented novelties. They are: (i) a set of oxygen donor atoms playing the role of σ- and π-donors: (ii) their arrangement in a quasi-planar geometry; (iii) a single reactive site accessible axially. In addition, by using a set of oxygen donor atoms which can exercise additional binding towards other metal ions, we took advantage of secondary thermodynamic driving forces derived from the solvation of alkali cations associated with the main structure in the ion-pair or ion-separated forms.

This rather complex strategic approach allowed us in this domain of chemical synthesis for the first time (i) to achieve the stepwise supply of electrons to dinitrogen up to the complete cleavage of the N–N triple bond; (ii) to understand how dinitrogen binding two metal ions rearranges its bonding mode, thus being ready to cleave to nitride; (iii) to mimic a metal-oxo surface; and (iv) highlight the relevance of the bifunctionality of the systems. A complete and very detailed

report on stepwise reduction of dinitrogen by the use of [Nb^{III}-calix[4]arene] dimer **1** has already been published.[19] The [Nb^{III})-calix[4]arene] (see complex **1** in Scheme 2) is a powerful reducing agent for N–N multiple bonds. The reaction of **1** with dinitrogen led to the formation of the dinuclear metalla-hydrazide, **2**, with four-electron reduction of N_2 (Scheme 2). This reaction is, however, strongly dependent on the nature of the solvent used, which should be either thf or dme. The complete cleavage of the residual N–N single bond in **2** is achieved when two electrons are provided to the system from the reaction with sodium metal (Scheme 2). It has been shown that this first step in the cleavage of N–N bonds can follow two different pathways, depending on the reaction solvents, which are summarised in Chart 2. The reduction in hydrocarbon solution (see below) follows a different pathway.



Scheme 2

Regardless of whether the solvent is thf or dme (dme = dimethoxyethane), the two electrons reduce the two Nb^V to Nb^{IV}, with the reduction of the Nb–N triple bond. At this stage, the Nb=N–N=Nb skeleton undergoes a *transoid* rearrangement (thf) followed by cleavage to the monomeric nitrido species, in equilibrium in solution with the corresponding dimer.[19] In the case of dme, the Nb=N–N=Nb skeleton undergoes a *cisoid* rearrangement followed by the formation of an Nb–Nb bond (Chart 2). Thus, the two electrons introduced in the system are temporarily stored in the metal–metal bond. At the same time, the N_2 molecule moves from an end-on to a side-on bonding mode, thus being preorganised for the cleavage to the dimeric nitrido species **3**, the latter occurring

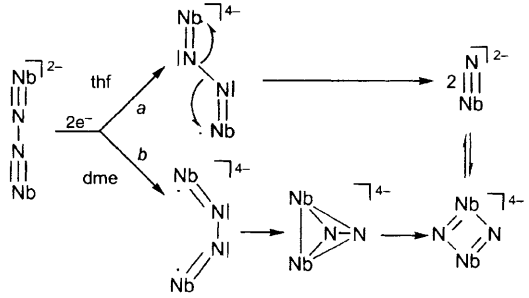
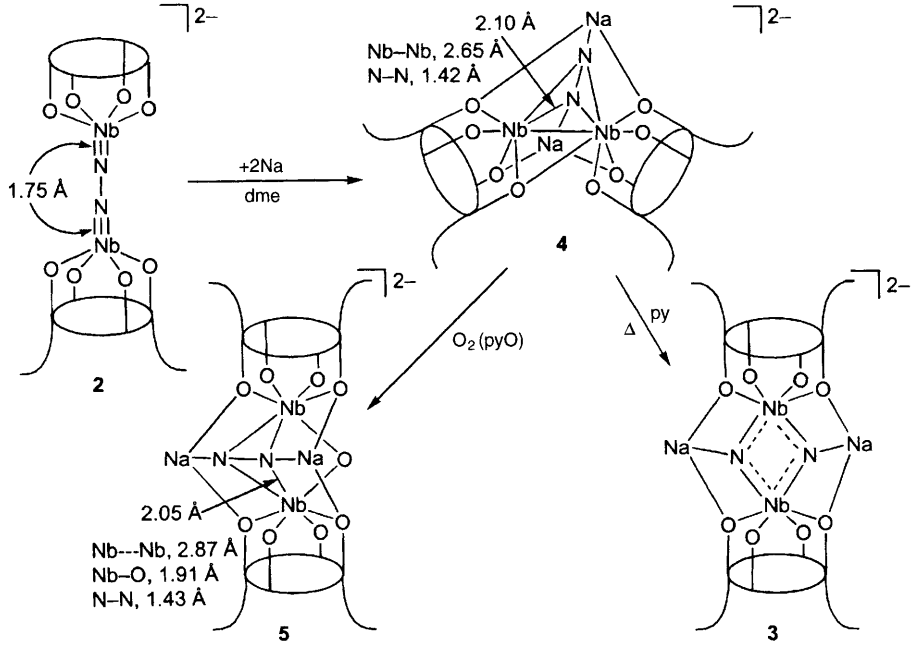


Chart 2

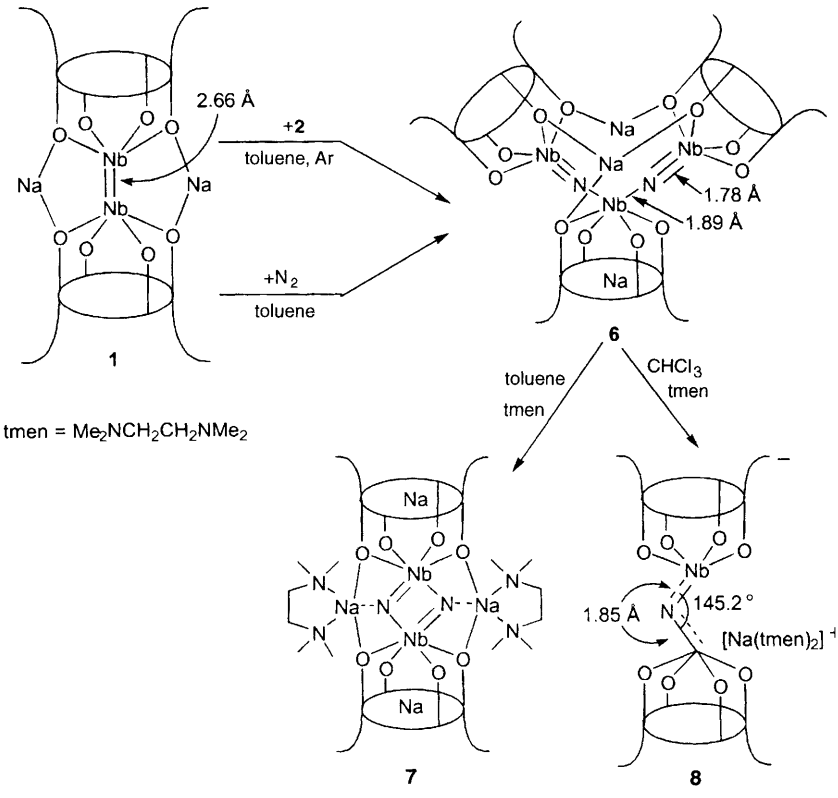
upon heating. The experimental sequence related to the pathway *b* in Chart 2 is shown in Scheme 3. The bonding rearrangement of N_2 does not affect its extent of reduction, the N–N bond remaining very long (1.43 Å). The isolation of **4** mimics not only the rearrangment of N_2 over a metal-oxo surface, but also raises the possibility of using the two electrons stored in the Nb–Nb bond for introducing a further functionality at metals close to the reduced N_2 moiety. The isolation of **5** with O_2 or pyridine-*N*-oxide (pyO) exemplifies this (Scheme 3).



Scheme 3

The active species {Nb=Nb}, **1**, can perform the six-electron reduction of N_2 without the addition of any further reducing agent when the reaction is carried out in toluene. The reaction leads to the trinuclear μ_2-bisnitrido species, which is rather labile in the presence of solvents binding alkali cations, leading to the compounds **7** and **8** (Scheme 4). A detailed report has been published on why the solvent can drastically affect the reduction pathway of N_2 mediated by metallacalix[4]arenes.[19] The bifunctionality of the complexes used is such that the solvation of the alkali cation can be an important driving force and at the same time the presence of tight-ion pair or separated-ion forms can affect the kinetic pathways (see Chart 3).

In conclusion, this section reports a number of novelties in the metal–dinitrogen chemistry scenario.[1] For the first time, it has been shown that the active species performing the reduction of N_2 is a very reactive M=M functionality, and that an ancillary ligand containing exclusively oxygen donor atoms can be successfully employed. The presence of alkali metal ions in the active bifunctional species reinforces the role of the solvent in dinitrogen reduction assisted by transition metal complexes. In particular, the solvent allows one to select either the four- (thf or dme) or the six-electron (toluene) reduction of dinitrogen to hydrazine or to ammonia, respectively. In the former case, a fine tuning of the



Scheme 4

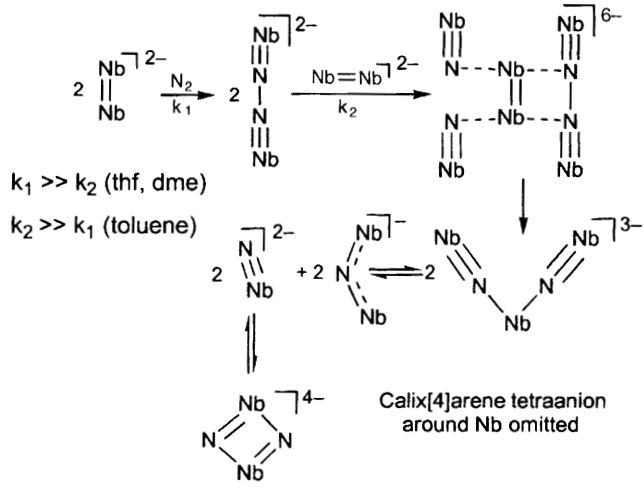


Chart 3

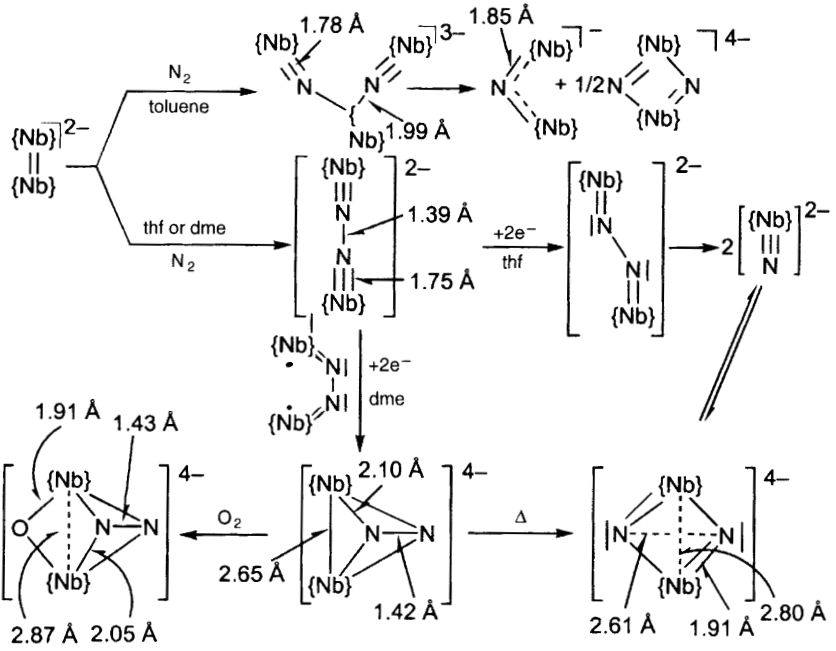


Chart 4

solvent (dme or thf) drives the ultimate two-electron reduction of N_2 to nitride *via* different intermediates. Particularly relevant in this context is the rearrangement of the bonding mode of dinitrogen from end-on to μ-η^2-η^2 over a metal-oxo surface modelled by the {Nb-calix[4]arene} fragment. A comprehensive sum-

mary of the different stepwise pathways leading to the reduction of dinitrogen to nitrides is given in Chart 4. The results presented here for a challenging area of research,[1,7,17,18] such as dinitrogen activation, show that, using appropriate model compounds, we were able to detect unprecedented pathways in dinitrogen reduction and to open up novel perspectives in the field.

5 Acknowledgements

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Novel Chemical Transformations at Diruthenium Centres Bridged by Thiolato Ligands

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1 Introduction

The transformation of small molecules on multimetal centres has received much attention because it is expected to lead to novel reactions which are rarely attainable at single metal centres. This might occur through the cooperative interaction of two or more adjacent metal atoms with a substrate molecule, or simultaneous activation of more than two substrates, or both. Indeed, unique and efficient chemical transformations are realised on sulfur-bridged multimetal active sites in metalloenzymes such as nitrogenase and hydrogenase. These well-designed biological multimetal systems inspired us to investigate the preparation of sulfur-bridged multimetal complexes and their reactivities towards nitrogenase substrates and related small molecules, such as hydrazines, CO, and alkynes. We have synthesised a series of thiolato-bridged diruthenium complexes with structural diversity, as outlined in our earlier review articles.[1] We summarise here our recent studies on the reactivities of these complexes.

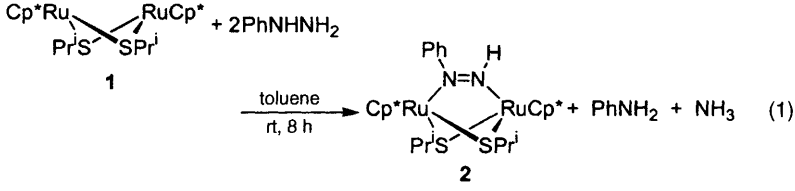
2 Reactions of Hydrazines at Thiolato-bridged Diruthenium Centres

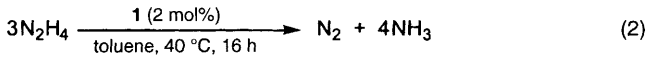
Crystallographic studies on nitrogenase have revealed that its active site, the

FeMo-cofactor, contains six coordinatively unsaturated, trigonal-planar Fe centres bridged by sulfido ligands.[2] This unique structural feature stimulated us to examine the reactions of the doubly coordinatively unsaturated diruthenium(II) complex $[Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*]$ **1** ($Cp^* = \eta^5\text{-}C_5Me_5$) with nitrogenous substrates. Complex **1** is inert toward molecular dinitrogen itself. However, treatment of **1** with phenylhydrazine affords the μ-phenyldiazene complex $[Cp^*Ru(\mu\text{-}\eta^1\text{:}\eta^1\text{-}PhN{=}NH)(\mu\text{-}SPr^i)_2RuCp^*]$ **2** with concurrent formation of aniline and ammonia (Equation 1).[3] The presence of the $\mu\text{-}\eta^1\text{:}\eta^1$-PhN=NH ligand in **2** was deduced by IR and ^1H NMR spectroscopy as well as by a preliminary X-ray diffraction study of the 2,4,6-triisopropylbenzenethiolato analogue of **2**, as depicted in Figure 1(a).[4]

Furthermore, the disproportionation reaction of hydrazine into ammonia and dinitrogen proceeds in toluene at 40 °C in the presence of a catalytic amount of **1**, according to the stoichiometry shown in Equation 2.[3] The ^1H NMR spectrum of the reaction mixtures revealed the presence of the diazene complex $[Cp^*Ru(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HN{=}NH)(\mu\text{-}SPr^i)_2RuCp^*]$ **3**, although isolation and full characterisation of **3** were unsuccessful. A plausible catalytic cycle based on these observations is depicted in Scheme 1. Considering that hydrazine and diazene species bound at the multimetal centre of the FeMo-cofactor have been proposed as important intermediate stages of the biological nitrogen fixation,[5] the dinuclear diazene complex **3**, which plays a key role in the N–N bond cleavage of hydrazine, is of special interest from the mechanistic point of view of nitrogenase.

On the other hand, the reactions of the cationic Ru^{III} complex $[Cp^*RuCl(\mu\text{-}SPr^i)_2Ru(OH_2)Cp^*](OTf)$ **4** ($OTf = CF_3SO_3$) with $RNHNH_2$ (R = Ph or H) result in the formation of the terminal hydrazine complexes $[Cp^*RuCl(\mu\text{-}SPr^i)_2Ru(NH_2NHR)Cp^*][OTf]$ **5**, which have been characterised spectroscopically as well as by a preliminary X-ray analysis for the phenylhydrazine complex **5a** (R = Ph; Figure 1(b)).[4] No disproportionation product has been detected in these reaction mixtures, in contrast to the reactions shown in Equations 1 and 2.





3 Transformations of Small Organic Molecules at Thiolato-bridged Diruthenium Centres

Various substrates other than those containing nitrogen have also been demon-

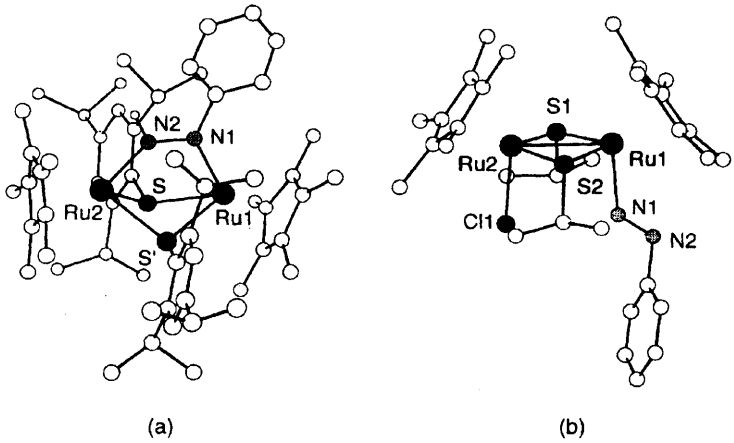
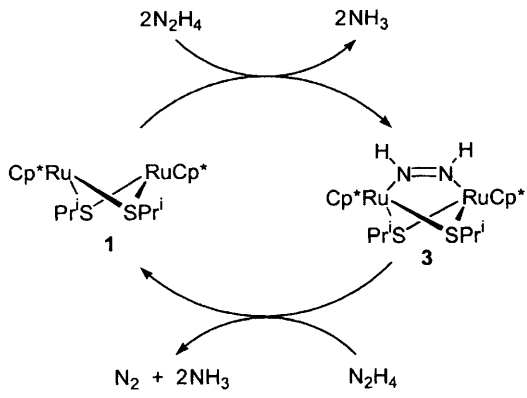


Figure 1 *Structures of* (a) *[Cp*Ru(μ-η¹:η¹-PhN=NH)(μ-SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$RuCp*] and* (b) *the cationic part of* **5a**



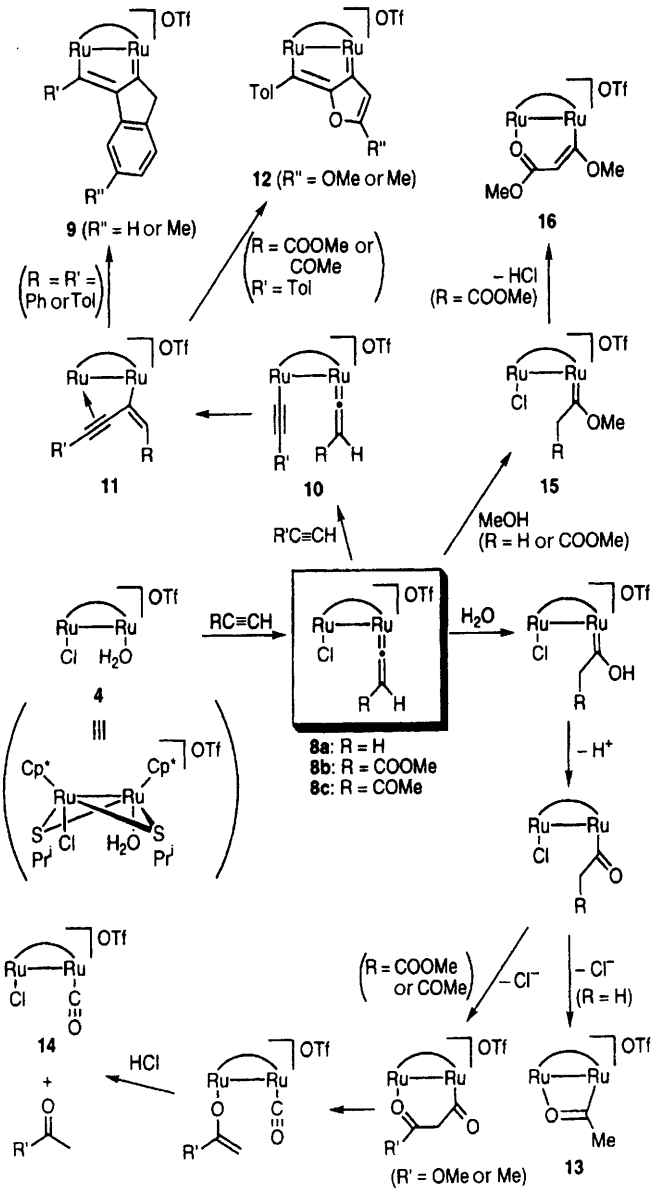
Scheme 1

strated to be activated and transformed on thiolato-bridged diruthenium complex such as **1**.[1] For example, we have isolated the bis(alkene)diruthenium complex [{Cp*Ru(H$_2$C=CHCN)(μ-SPr^i)}$_2$][6] as well as the butadiene complex [{Cp*Ru(μ-SFc)}$_2$(CH$_2$=CHCH=CH$_2$)] (Fc = ferrocenyl).[7] In this section, we describe the transformations of alkynes and other unsaturated organic molecules on the thiolato-bridged diruthenium complexes.

3.1 Stoichiometric Transformation of Alkynes

We have already found that the reactions of the coordinatively unsaturated diruthenium(II) complex **1** with alkynes result in unique coupling of the alkynes to afford a variety of ruthenacycles, depending significantly upon the substituent on the alkynes.[1] On the other hand, the corresponding reactions of the

Ru^{II}/Ru^{III} complex $[Cp^*Ru(\mu\text{-}SPr^i)_3RuCp^*]$ **6** give the bisalkynyl complexes $[Cp^*Ru(C{\equiv}CR)(\mu\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*]$ (R = aryl), which are further converted into diruthenacyclopentadienoindan complexes upon protonation.[1] Here we focus on the transformations of alkynes by the Ru^{III}/Ru^{III} complexes **4** and $[Cp^*RuCl(\mu\text{-}SR)_2RuClCp^*]$ **7** (R = Me or Et).



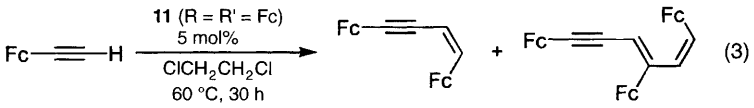
Scheme 2

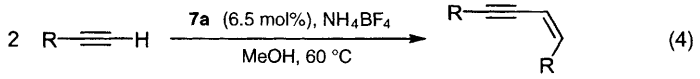
The reactions of the cationic complex **4** with acetylene or alkynes having electron-withdrawing substituents afford the terminal vinylidene complexes $[Cp^*RuCl(\mu\text{-}SPr^i)_2Ru(=C=CHR)Cp^*](OTf)$ **8** (R = H, COOMe, or COMe) as shown in Scheme 2.[8] When aromatic terminal alkynes are used, two molecules of the alkyne are incorporated into the diruthenium centre of **4** to give the cationic diruthenacycle complexes **9**, which are probably formed *via* the alkynyl–vinylidene and butenynyl intermediates **10** and **11** derived from **8**.[9] In fact, the butenynyl complex **11** (R = R′ = Fc) has been isolated from the reaction of **4** and ferrocenylacetylene.[10] Coupling of two different alkynes takes place in a similar manner to give the diruthenacycle complexes **12** when the vinylidene complexes **8b** and **8c** are treated with *p*-tolylacetylene.[8]

The vinylidene complexes **8** also react with nucleophiles such as water and methanol. Hydration of the unsubstituted vinylidene complex **8a** leads to the formation of the $\mu\text{-}\eta^1\text{:}\eta^1$-acetyl complex **13**, whereas the corresponding reactions of **8b** and **8c** result in the C–C bond cleavage, giving the cationic carbonyl complex **14** and organocarbonyl products R′COMe (R′ = OMe or Me).[8] On the other hand, the reactions of **8** with methanol afford the methoxycarbene complex **15** and the vinyl complex **16**, depending upon the substituent of the vinylidene complexes **8**. Intramolecular nucleophilic attack takes place in the reaction of **4** with 3-butyn-1-ol, giving the cyclic alkoxycarbene complex $[Cp^*RuCl(\mu\text{-}SPr^i)_2Ru\{=\overline{C(CH_2)_3O}\}Cp^*](OTf)$.[11]

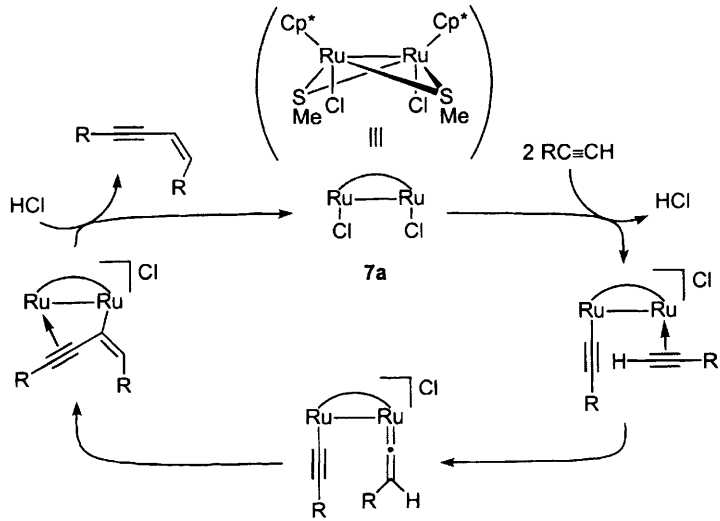
3.2 Catalytic Head-to-head *Z* Dimerisation of Terminal Alkynes

Interestingly, the butenynyl complex **11** (R = R′ = Fc) has been found to be an efficient catalyst for linear di- and trimerisation of ferrocenylacetylene (Equation 3).[10] Our subsequent investigations have led to the finding that the diruthenium(III) complex $[Cp^*RuCl(\mu\text{-}SMe)_2RuClCp^*]$ **7a** with bridging MeS ligands catalyses the head-to-head (*Z*)-dimerisation of various terminal alkynes stereoselectively (Equation 4).[12]





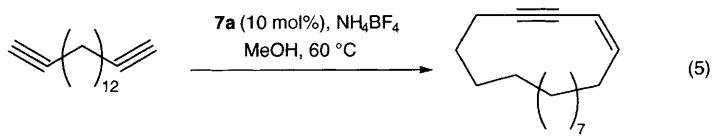
Even aliphatic alkynes with substituents such as chloro, hydroxy, and ester groups are effectively transformed into the corresponding head-to-head (*Z*)-dimers by **7a**. Noteworthy is the strong dependence of the catalytic activity



Scheme 3

upon the bridging thiolato ligands. Thus, the sterically hindered Pr^{i}S-bridged complex [Cp*RuCl(μ-SPr^i)$_2$RuClCp*] **7b** exhibits only marginal activity in contrast to the primary alkanethiolato complexes **7a** and [Cp*RuCl(μ-SR)$_2$RuClCp*] (R = Et or Pr^n). A plausible mechanism is shown in Scheme 3, which shows a butenynyl intermediate.

These dimerisation reactions of terminal alkynes have been further extended to the catalytic cyclisation of α,ω-diynes. For example, treatment of 1,15-hexadecadiyne with 10 mol% of **7a** affords the *endo*-macrocyclic product, (*Z*)-1-cyclohexadecen-3-yne with complete stereoselectivity (Equation 5).[13] This novel cyclisation is of particular utility, because synthetic routes to *endo*-cyclic (*Z*)-1-en-3-ynes are extremely limited. A related palladium-catalysed cyclisation of α,ω-diynes to give the corresponding *exo*-cyclic 1-en-3-ynes has been reported by Trost and co-workers.[14]

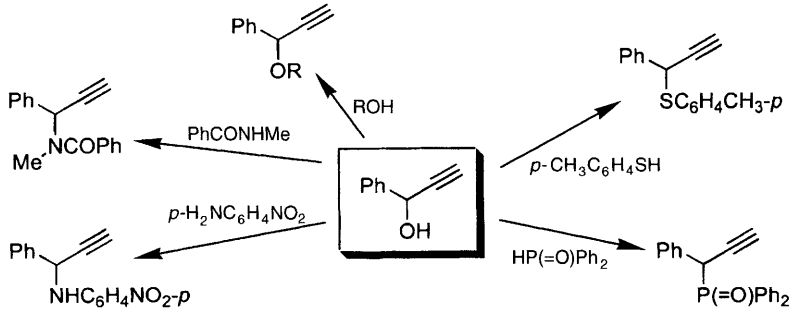


(5)

3.3 Transformation of Propargyl Alcohols

We have already revealed the unique coupling reactions of two moles of propargyl alcohols on the Ru^{II}/Ru^{III} complex **6**, which give two types of diruthenacycle complexes depending upon the substituents of the alcohols.[15] Formation of the terminal allenylidene complexes [Cp*RuCl(μ-SPr^i)$_2$Ru(=C=C=CR$_2$)Cp*](OTf) from the cationic diruthenium complex **4** and propargyl alcohols has also been

demonstrated.[9] On the basis of these findings, we have recently developed novel propargylic substitution reactions of propargyl alcohols catalysed by the thiolato-bridged diruthenium complex **7a** (Scheme 4).[16] These reactions enjoy several synthetic advantages. A variety of nucleophiles including alcohols, amines, amides, and thiols can be employed to realise the substitution at the propargylic position with complete regioselectivity. Allenic by-products, which



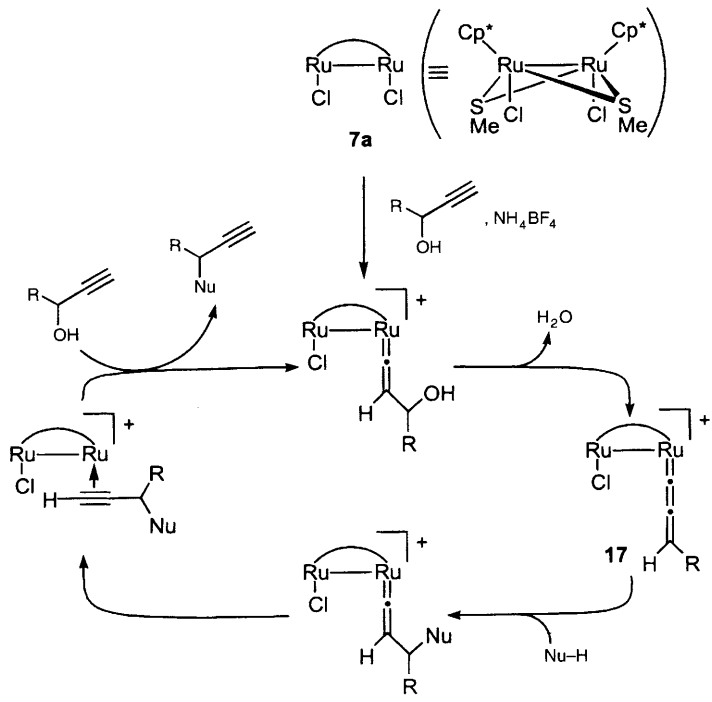
Scheme 4

are always produced by the classical propargylic substitutions, are not observed at all. In addition, easily available propargyl alcohols are used as the substrates without derivatisation to the corresponding halides or esters. The proposed reaction mechanism involves the attack of nucleophiles at the γ-carbon atom in an allenylidene intermediate **17** (Scheme 5). These catalytic reactions are in sharp contrast to the Nicholas reaction, in which a stoichiometric amount of $[Co_2(CO)_8]$ is used to achieve the propargylic substitution. It is also to be emphasised that these reactions provide some of the few examples of catalytic reactions *via* allenylidene intermediates.

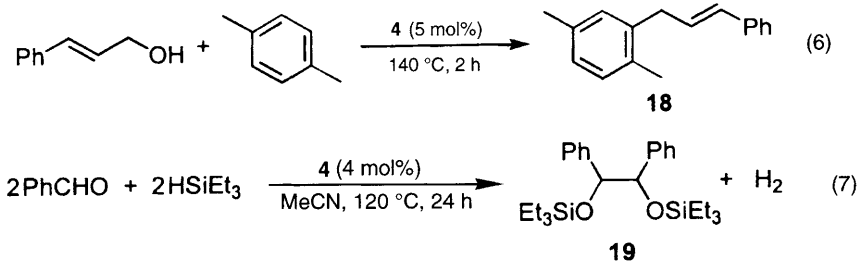
3.4 Other Catalytic Reactions

We have further examined the reactions of thiolato-bridged diruthenium complexes with other unsaturated organic substrates. When the cationic Ru^{III} complex **4** is treated with cinnamyl alcohol in *p*-xylene, the allylated aromatic compound **18** is obtained in good yield (Equation 6).[17] We assume a π-allyl intermediate because the reaction using 1-phenylprop-2-en-1-ol gives, instead of cinnamyl alcohol, the same product **18**; however, the detailed reaction mechanism is still obscure. This novel allylation reaction is halogen-free, and may replace the conventional Friedel–Crafts alkylation.

The cationic Ru^{III} complex **4** also promotes silylative dimerisation of aromatic aldehydes with hydrosilanes. For example, the reaction of benzaldehyde and triethylsilane in the presence of a catalytic amount of **4** affords the dimerisation product **19** along with a small amount of the hydrosilylation product $PhCH_2OSiEt_3$ (Equation 7).[18] This type of silylative dimerisation of aldehydes is relatively scarce in the literature; common ruthenium complexes such as $[RuCl_2(PPh_3)_3]$ and $[Ru_3(CO)_{12}]$ give only the hydrosilylation products.



Scheme 5



4 Concluding Remarks

We have shown that the thiolato-bridged diruthenium centres promote a variety of novel transformations of small molecules such as hydrazines and alkynes. Apparently, some of these transformations involve the cooperation of the two ruthenium atoms. Another important feature of these transformations is the strong dependence of the reactivities upon the oxidation states of the metals and the substituents on the bridging thiolato ligands. We believe that new types of reactions on multimetal centres will be further developed by designing metal frameworks and ancillary ligands.

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The Chemistry and Applications of Complexes with Sulfur Ligands

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1 Introduction

One of us (JRD) had the great good fortune to work under Joseph Chatt's supervision for some fifteen years at the then Unit of Nitrogen Fixation. It left an indelible impression. Joseph had a truly comprehensive grasp of the chemistry and periodicity of the elements and this was allied to an unerring instinct for where interesting coordination chemistry was to be found. The remit of the chemists in the Unit was of course to study nitrogen fixation, but the research scientists were allowed a substantial measure of freedom in the individual areas that were studied. Joseph believed firmly that an indirect approach often proves more fruitful than a direct frontal assault. Indeed the first genuinely extensive series of dinitrogen complexes (of rhenium) arose from a project directed to understand the mechanism of formation of nitrides from hydrazine.[1] Many of the early dinitrogen complexes contained tertiary phosphine co-ligands and the rational design of such dinitrogen-binding sites became feasible. Although these provided invaluable information on the mechanisms of dinitrogen reduction they were structurally far removed from the sulfur-ligated metals in the iron–molybdenum co-factor. This prompted a search that is still in progress to establish the factors that determine how a sulfur-ligated metal ion will bind dinitrogen. The initial work that we did in the Unit on metal–sulfur coordination chemistry stimulated my long-term research interest in the binding and activation of small molecules at metal–sulfur sites and the potential applications of such complexes in areas as diverse as catalysis and the treatment of cancer. This

review describes recent results on the coordination chemistry of a range of anionic and neutral sulfur ligands with metals in Groups 6–11. Appropriately perhaps this encompasses many of the elements, the chemistry of which Joseph was instrumental in opening up in the 1960s.

2 Sterically-hindered Thiolates

Our initial studies of small molecule activation by sulfur-ligated metals involved the use of sterically-hindered aromatic thiolates where the tendency for formation of inactive thiolate bridged species was minimised. The success of this strategy was illustrated by the isolation of stable complexes such as $[Mo(tipt)_3(CO)]^-$ (tipt = 2,4,6-triisopropylthiophenolate). This species has a trigonal bipyramidal structure with apical CO ligands.[2] The structure occurs throughout the chemistry of such ligands and was repeated in the 14-electron complex $[Re(tipt)_3(N_2)(PPh_3)]$,[3] still a very rare example of a metal thiolate species which binds N_2. We have recently been extending the reactions of bulky thiolates to Ru, Os, Rh and Ir with the objective of investigating their catalytic activity.

Square-planar mononuclear or binuclear complexes of the types $[M(SAr)(CO)(PPh_3)_2]$ and $[\{M(SAr)(CO)(PPh_3)\}_2]$ are obtained by the straightforward reaction of $[MX(CO)(PPh_3)_2]$ (M = Rh, X = F; M = Ir, X = Cl) with the free thiol, base being required for Ir. The size of the thiol and the ease of loss of a PPh_3 dictate whether a monomer of dimer is formed.[4] X-ray crystal structures of both monomeric (M = Ir, SAr = 2,6-$Cl_2C_6H_3S$) and dimeric forms (M = Rh, SAr = tipt) were reported. All the complexes were highly active for the hydroformylation of 1-heptene (comparable to rates for $[RhCl(PPh_3)_3]$ under the same conditions) and showed good regioselectivity for linear as opposed to branched aldehyde. More recently we have investigated the chemistry of ruthenium(II) with bulky aromatic thiolate ligands. There have been few systematic investigations of the chemistry of Ru^{II} with such ligands, and none of their catalytic activity. Reaction of 2,6-dichlorothiophenol (Hdct) with $[RuCl_2(PPh_3)_3]$ in methanol gave the complex $[Ru(dct)_2(PPh_3)_2]$ in high yield. An X-ray crystal structure (Figure 1) showed an octahedral structure with a chloro group on each thiolate interacting with the metal by electron-pair donation, conferring an overall 18-electron configuration. This contrasts with the structure of the analogous complex with pentafluorothiophenol where the electron deficiency of the metal centre is relieved by agostic interactions with phosphine phenyl hydrogens.[5] The difference reflects the greater electron-pair donating capability of chloride compared to fluoride. The bulky triphenylphosphine ligands in the dct complex are *cis*. The complex $[Ru(dct)_2(PPh_3)_2]$ is completely inactive for the hydrogenation of hex-1-ene, but shows approximately three times the activity of $[RuCl_2(PPh_3)_3]$ for the hydrosilylation of benzophenone to phenylethanol under comparable conditions. It appears that the Ru–Cl bonds are too strong to permit the metal to activate dihydrogen and/or bind the substrate. Electrospray mass spectrometry of solutions of the complex in MeCN identified species such as $[Ru(dct)(MeCN)_2(PPh_3)_2]^+$, suggesting that one thiolate ligand may be

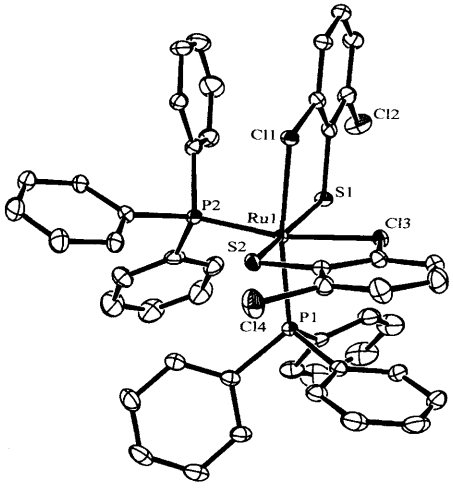


Figure 1 *The X-ray structure of* $[Ru(SC_6H_3Cl_2\text{-}2,3)(PPh_3)_2]$

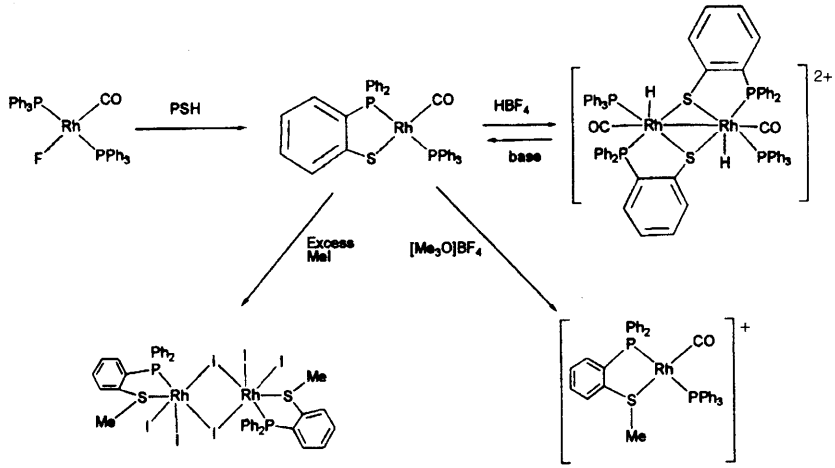
lost during the catalytic cycle. We are currently investigating the chemistry of other bulky thiols with a range of Ru^{II} precursors with tertiary phosphine and nitrogen donor ligands.

3 Phosphinothiolate and Related Ligands

In the course of our investigations of the chemistry of sterically encumbered thiolate ligands we observed several examples where the substituents on the aromatic group of the thiol were not mere spectator groups, but became coordinated to the metal. These interactions ranged from agostic hydrogen interactions in $[Re(dmt)_3(PPh_3)_3]$ (dmt = 2,6-dimethylthiophenolate) to η^6-bonding of an arene group in $[Mo\{(2\text{-}\eta^6\text{-}C_6H_5)C_6H_3S\text{-}1\text{-}Ph\text{-}6\}(SC_6H_3\text{-}2,6\text{-}Ph_2)(CO)]$.[6] The bonding interactions of the substituents with the metal range from weak to very strong, raising the possibilities of both hemi-labile and stable chelate behaviour for these classes of thiolate ligand. When starting our studies of catalysis by metal thiolate complexes we were concerned at the possibility of facile elimination of free thiol from possible thiolate hydride intermediates, and the strong binding characteristics of tertiary phosphine groups prompted us to initiate a study of phosphinothiolate proligands. We have recently published a comprehensive review of this area[7] which illustrates that such ligands chelate strongly to an extremely wide range of metals and non-metals, and that stable complexes can be formed even with elements that generally interact weakly with thiolate sulfur and tertiary phosphines. The three examples from our recent work below serve to illustrate the diversity of the coordination chemistry that is accessible.

We recently reported[4] the reactivity of the Rh^I complex $[Rh(PS)(CO)(PPh_3)]$ (PS = $2\text{-}Ph_2PC_6H_4S$) for oxidative addition reactions with a range of electrophilic reagents. These reactions are summarised in Scheme 1. The reversible

protonation of the precursor complex with HBF_4 provides a unique example of reversible formation of a dithiolate bridged system with an M–M bond (the X-ray crystal structure appears in Figure 2, with phosphine phenyl groups omitted for clarity).



Scheme 1

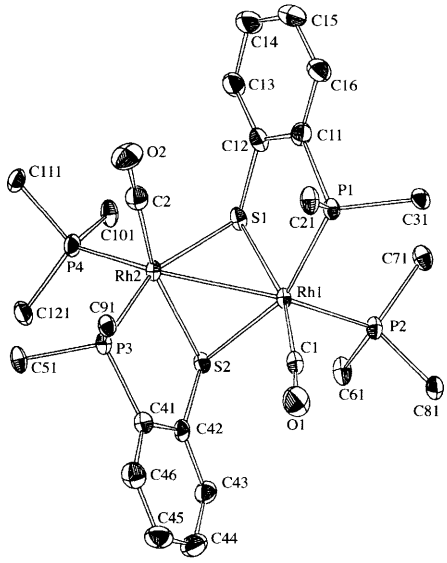
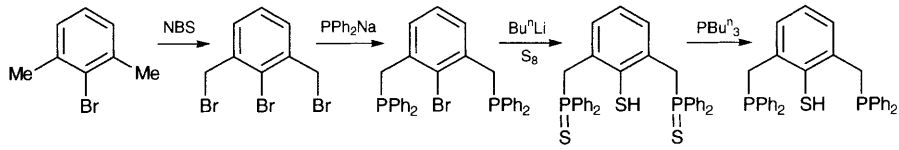


Figure 2 *The structure of* $[\{Rh(PS)(CO)(PPh_3)_2\}_2]^{2+}$, *anions and phosphine phenyls omitted*

Other electrophiles react at the sulfur of the PS ligand, showing that susceptibility to attack at the metal or sulfur is a delicate balance of steric and electronic effects. The quantitative formation of acetone by reaction with an excess of MeI (together with a triiodide bridged dimer, Scheme 1) also illustrates how the presence of anionic sulfur ligands can dramatically alter the course of a reaction ($[RhCl(CO)(PPh_3)_2]$ gives virtually no acetone under the same conditions) and augurs well for the possibility of thiolate-coordinated metal sites generating unique catalytic behaviour. We have also synthesised a binucleating phosphinothiolate proligand (HPSP) *via* a multistage synthesis starting from 2,6-dimethylbromobenzene[8] (Scheme 2). Such ligands support stable dinuclear structures as illustrated by the X-ray crystal structure of the Ir complex shown in Figure 3. Each Ir has a formal oxidation state of II, and there is a bridging CO group to complete a pseudo-octahedral geometry about each metal ion. We are currently investigating the catalytic activity of such complexes.

Phosphinothiolate ligands display a particularly varied and novel chemistry with gold.[9] Reaction of the potentially tridentate proligand $PhP(C_6H_4SH\text{-}2)_2$ (H_2PS_2) with $[AuCl_4]^-$ gave the square planar Au^{III} complex $[AuCl(PS_2)]$. The strong chelation of the PS_2 ligand inhibits reduction to Au^I with its preferred linear geometry. A second product from the reaction is an unusual dimeric species containing both Au^I and Au^{III} with an Au–Au bonding interaction (see Figure 4). An isomeric form of this complex was also structurally characterised, and this differed only in the orientation of the linear S–Au^I–S vector with respect to the planar Au^{III} unit. The use of the polydentate PS_n ligands ($n = 2$ or 3) with the Au unlikely to provide coordination numbers



Scheme 2

greater than four permits a variety of bridging structures supporting Au–Au bonding. The structure of one derived by using the potentially tetradentate PS_3 system is shown in Figure 5 and comprises two square planar Au^{III} units held in close proximity. There is some resemblance here to the well-known A-frame dimers, but with an additional carbon in the bridge. Gold–gold interactions are commonplace for Au^I but the Au^I–Au^{III} and Au^{III}–Au^{III} interactions seen here are comparatively rare.

It seemed plausible that if the thiolate sulfur were replaced by neutral thioether sulfur then the latter would be more weakly bound to the metal introducing the possibility of hemi-labile coordination. We have therefore investigated the chemistry of some related phosphinothioether complexes of Ru^{II} and Pd^{II}. The new ligand $2\text{-}MeSC_6H_4CH_2PPh_2$ (L) was prepared in reasonable yield in a three stage synthesis starting from 2-bromotoluene by bromination to 2-

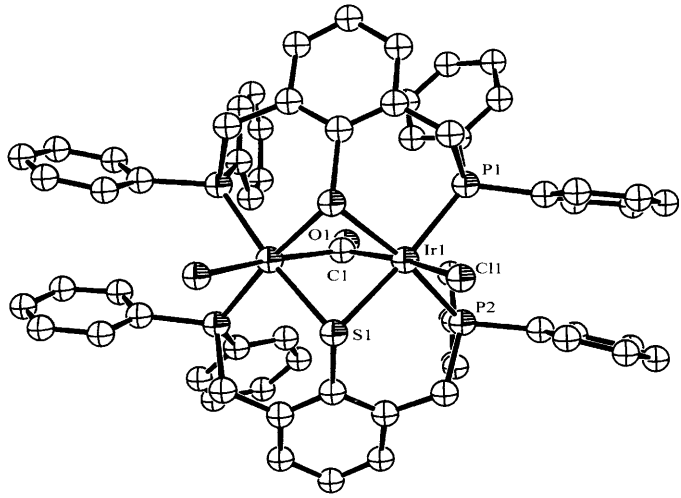


Figure 3 *The structure of* $[\{IrCl(PSP)\}_2(\mu\text{-}CO)]$

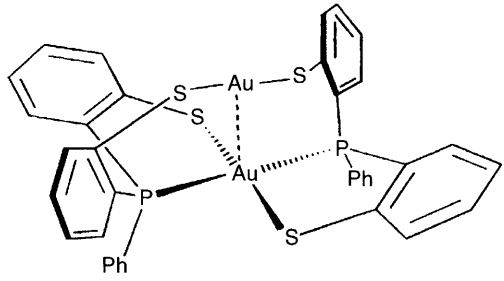


Figure 4 *The structure of* $[Au_2(PS_2)_2]$

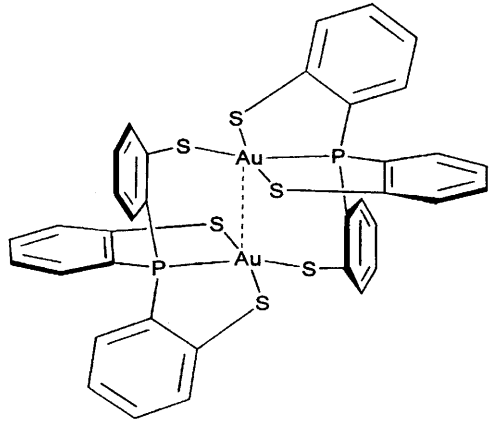


Figure 5 *The structure of* $[Au_2(PS_3)_2]$

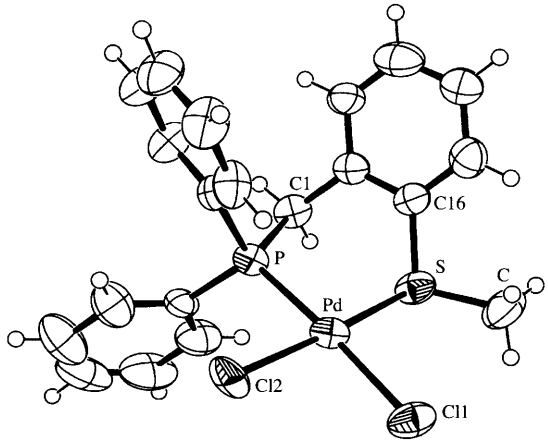


Figure 6 *The X-ray crystal structure of* $[PdCl_2(Ph_2PCH_2C_6H_4SMe)]$

$BrC_6H_4CH_2Br$ and successive reactions with $Na(Ph_2P)$ and $LiBu^n$/MeSSMe. The proligand L reacted readily with $RuCl_3 \cdot xH_2O$ in refluxing ethanol under N_2 to give the yellow complex $[RuCl_2(L)_2]$ in good yield. The X-ray crystal structure showed the expected pseudo-octahedral geometry with *cis* chloride ligands. The catalytic activity of this complex and that of the related 2-$Ph_2PC_6H_4SMe$ ligand are being investigated.

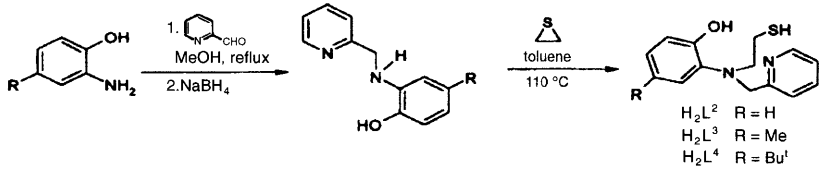
The complex $[PdCl_2(L)]$ was also prepared in a straightforward manner in good yield from $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) in dry acetone. The X-ray crystal structure of this complex is shown in Figure 6. The geometry about the Pd is essentially square planar with the PdPCCCS six-membered chelate ring having a boat-type configuration. This complex is one of the most active catalysts yet reported for the Heck coupling reaction of aryl halides with olefins, achieving turn-over numbers in excess of 10^6. The air-stability of the precursor means that the whole reaction can be carried out aerobically using reagent grade solvents. The stereochemistry of addition is almost exclusively *trans*, and unusually the system is active for both aryl bromides and iodides, and does not require the addition of co-catalysts such as silver salts to achieve very high activities. The exact mechanism remains unclear, but ^{31}P NMR spectroscopy shows that the precursor complex is essentially intact at the end of the cycle apart from exchange of the coordinated halide. This strongly suggests a cycle passing through Pd^{II} and Pd^{IV}, but detailed mechanistic studies remain to be done.

4 Polydentate *N,S* Donor Ligands

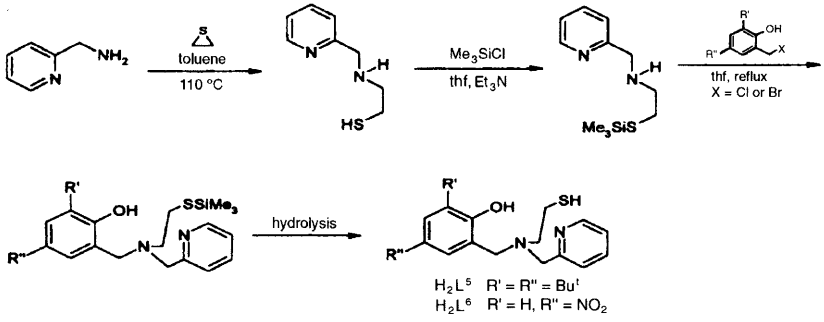
Mention has already been made of the Re complex $[Re(tipt)_3(N_2)(PPh_3)]$, and we wished to see if this trigonal bipyramidal motif could be extended to the activation of small molecules on other metals. We also wished to move away from tertiary phosphine ligands and we have embarked on a systematic study of asymmetric tripodal ligands with N_2S_2, N_2OS and NOS_2 donor sets with various backbone lengths. Symmetrical tetradentate N-capped ligands have

been investigated at great length and a recent series of elegant papers has described the chemistry of vanadium,[10] molybdenum[11], and iron[12] with $(N[CH_2CH_2S]_3)^{3-}$ and the binding of small molecules such as CO to the MNS_3 core. The tripodal triamido ligand $(N[CH_2CH_2NSiMe_3]_3)^{3-}$ has also been shown to form both the mononuclear complex $[Mo(NN_3)(N_2)]$[13] and the intriguing tetranuclear species $[Fe\{(N_2)Mo(NN_3)\}_3]$.[14] Asymmetric tripodal ligands represent a far greater synthetic challenge, and have been comparatively little explored,[15] despite the fact that certain of these can serve as models for the asymmetric coordination found in metalloenzymes such as nitrile hydratase. There have however been some reports of Mo^{VI} complexes of N_2S_2 tripodal ligands[16] and Mo^{V} complexes of NOS_2 ligands.[15d]

The methods used to synthesise the new compounds are summarised in Schemes 3 and 4 and permit multigram quantities of the proligands to be prepared with silica gel column purification of intermediates and the final product. The pyridylmethylaminodithiol $C_5H_4NCH_2N(CH_2CH_2SH)_2$ (H_2L^1) was prepared by a slight modification of the literature method.[17] These new compounds were initially allowed to react with $[MoO_2(acac)_2]$ (acac = pentane-2,4-dionate) or $[WO_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane) in methanol in the presence of triethylamine or KOH as base to give the yellow complexes $[MO_2L]$ (M = Mo or W, L = L^1 – L^6; see Schemes 3 and 4). The X-ray crystal structures of two of the complexes (M = Mo, L = L^1 or L^3) have been determined and a representation of the the first of these is shown in Figure 7. The overall geometry about the Mo is psuedo-octahedral with the two oxo-groups in the usual *cis* configuration. Despite the asymmetry of the coordination the bond distances are in the usual range found for Mo^{VI} dioxo-complexes. The five-membered chelate ring systems cause a bending of the NSO



Scheme 3



Scheme 4

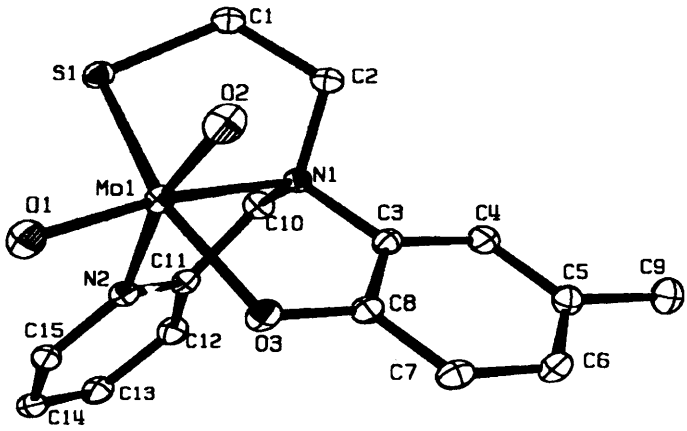
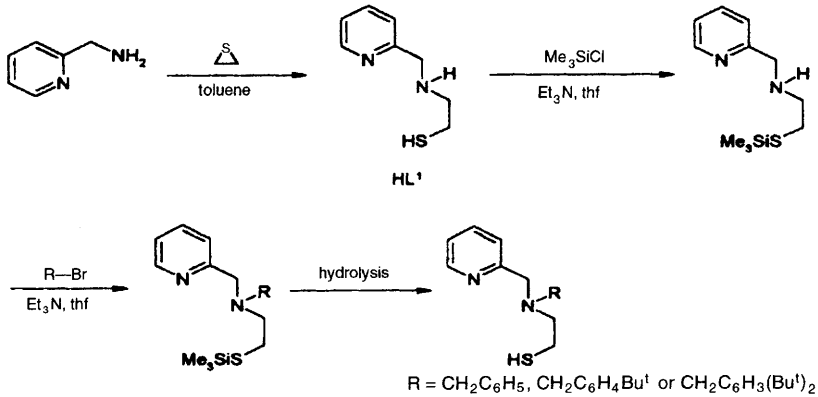


Figure 7 *The X-ray crystal structure of a Mo^{VI} complex of an asymmetric N_2SO ligand*

donor set away from the oxo-groups which have an O–Mo–O angle of close to 108°. We are currently investigating the chemistry and detailed electrochemistry of the dioxo-complexes and also reactions of the polydentate ligand systems with M^{II} and M^{IV} precursors. M^{VI} dioxo-complexes of molybdenum and tungsten have been investigated for their catalytic activity for reactions such as olefin oxidation[18] and epoxidation[19] and the results of our studies of catalysis with our complexes will be reported elsewhere.

In parallel we have investigated the coordination chemistry of a series of new tridentate HNNS proligands, the syntheses of which are summarised in Scheme 5. The use of the Me_3Si protecting group enables the alkylation of the amine nitrogen to be carried out in high yield. The di(amine)thiol proligands were obtained as colourless liquids in yields of around 50% following column chromatography. They deteriorate rapidly on standing, and are best freshly prepared. The proligands react readily with $[WO_2Cl_2(dme)]$ in methanol in the



Scheme 5

presence of base to give the new complexes of the type $[WO_2Cl(NNS)]$, isolated in high yield as yellow solids. These are reactive precursors for a wide range of chemistry exemplified by the replacement of the chloride ligands by both alkyl and aryl groups.

5 Thiosemicarbazone Ligands

Thiosemicarbazone ligands have been investigated extensively, the studies being largely driven by the biological activity of many of their metal complexes.[20] They are also of interest as they provide anionic sulfur donors with little tendency to form thiolate bridged dimers. Despite this there have been surprisingly few reports of their use in catalysis. A very rare example is the catalysis by a nickel bisthiosemicarbazone complex of the oxidation of CO to CO_2 by water.[21] We have therefore recently been exploring the catalytic potential of thiosemicarbazone complexes of Ru, Os, Rh and Ir.

5.1 Complexes of Ru, Rh and Ir

We have prepared a range of bidentate thiosemicarbazone compounds of the type $R^3{}_2NC(S)NHN{=}CR^1R^2$ ($R^1 = R^2 = R^3 = H$, alkyl or aryl). These react with $[RuCl_2(PPh_3)_3]$ in acetonitrile at room temperature to give complexes of the type $[RuL_2(PPh_3)_2]$ (HL = thiosemicarbazone). The X-ray crystal structure of the derivative for which $R^1 = H$, $R^2 = Ph$ and $R^3 = H$ is shown in Figure 8. It reveals an unusual bonding mode for the thiosemicarbazone ligands, each of which is N,S-bound and monoanionic, but each of the chelate rings contains four atoms rather than the five normally found. Since this work was done there have been two other reported examples of this type of bonding, also for Ru^{II}.[22] It has

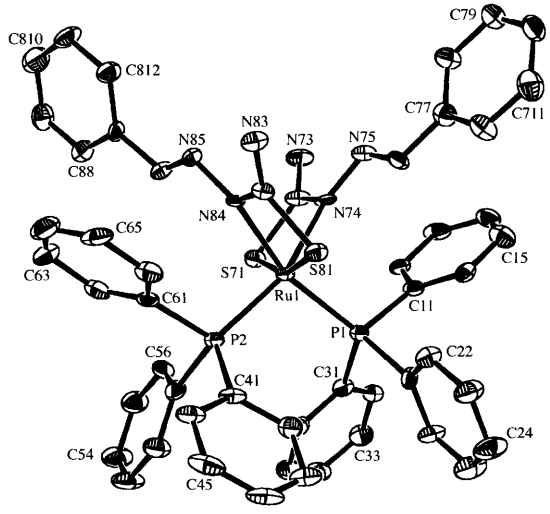


Figure 8 *The X-ray crystal structure of a Ru^{II} bis(thiosemicarbazonate) complex showing an unusual four-membered chelate ring*

been suggested that the ligand adopts this particular mode of coordination because of steric interactions of the metal with the thiosemicarbazone phenyl.[22] At a stoichiometry of 1:1 ligand-to-metal in acetonitrile the main products are the new Ru^{II} mono(thiosemicarbazonate) species $[Ru(L)(MeCN)_2(PPh_3)_2]Cl$. On the basis of ^1H and ^{31}P NMR spectra these are assigned a structure with the MeCN and PPh_3 groups in a *trans* configuration. Reaction of the mono-thiosemicarbazone cation (R^3 = H, R^2 = Ph, R^1 = Ph) with one equivalent of triethylamine as base in MeCN results in deposition of a deep red solid of the same stoichiometry, $[Ru(L)(MeCN)(PPh_3)_2]Cl$. This was recrystallised from dichloromethane–methanol and a representation of X-ray crystal structure appears in Figure 9. This shows that a phenyl substituent of the thiosemicarbazone has been *ortho*-metallated to give a planar tridentate ligand. The complex is interestingly still cationic (the chloride counter-anion is not shown in Figure 9) and the tridentate ligand still bears a charge of 1−. It is therefore in the thione form and, at least formally, a proton has been transferred from the phenyl group to a nitrogen of the thiosemicarbazonate ligand, which must be strongly basic. The thione form of bonding is reflected in the C–S bond lengths that are significantly shorter than those of the complex shown in Figure 8.

Initial investigations of the catalytic activity of the monohydrazone complexes for hydrosilylation have been encouraging with activities much higher than for $[RuCl_2(PPh_3)_3]$ under the same conditions. Reaction of the same thiosemicarbazones with $[MCl(CO)(PPh_3)_2]$ (M = Rh or Ir) gave complexes of the type $[M(L)(CO)(PPh_3)]$ which, on the basis of spectroscopic data, have square-planar structures with the thiosemicarbazone bonded as an anion. These are the first reported thiosemicarbazones of Ir, and their chemistry and catalytic activity will be reported elsewhere.

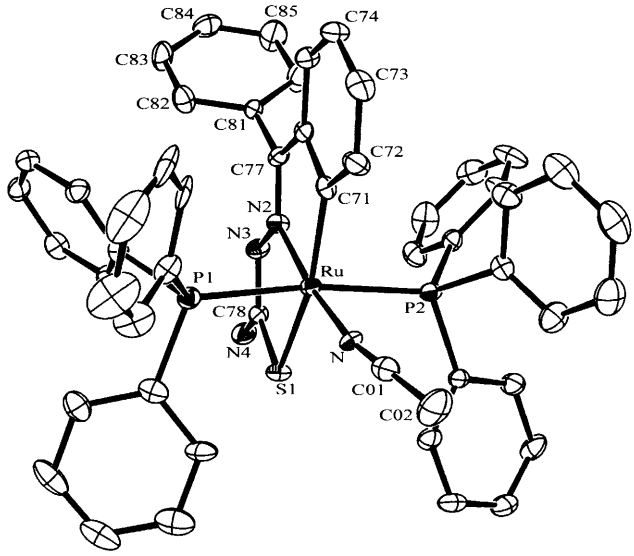
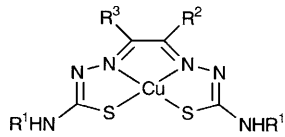


Figure 9 *The X-ray crystal structure of a Ru^{II} complex of a tridentate* o*-metallated thiosemicarbazone*

5.2 Copper Bisthiosemicarbazone Complexes as Hypoxic Selective Agents

There is currently great interest in the development of complexes of radioactive metals that can be specifically targeted to hypoxic tissue. Cancer cells, particularly those located inside actively growing tumours are hypoxic, due to a lack of blood supply. Such cells have significantly lower partial pressures of oxygen and are therefore less oxidising than normal cells. Many types of cells have enzymatic systems capable of reducing neutral metal complexes to anions, which are then trapped within the cell by virtue of the acquired negative charge. The tendency for the complex to be reoxidised to the neutral species, with consequent migration out of the cell by diffusion, will be significantly lower in hypoxic cells. Therefore if a neutral complex can be engineered to have a reduction potential within the range accessible within a cell, and a stable anion, it may well undergo selective retention in hypoxic tissue.

The copper(II) bisthiosemicarbazones defined in Figure 10 were initially prepared in the 1960s, but it was some twenty years before their potential as hypoxic selective agents was recognised through the work of Petering[23] and Fujibayashi.[24] These complexes have antitumour activity even with 'cold' copper, although the mechanism is largely unknown.[20] Copper has a number of medically useful radioactive isotopes such as ^{62}Cu and ^{64}Cu that are positron emitters and there is much interest in the possibility of using these for PET (positron emission tomography) imaging. Bisthiosemicarbazone complexes of these isotopes have been used to provide images of blood flow in the brain[25] and in tumours.[26] Our interest as inorganic chemists has been focussed on the remarkable dependence of the selectivity on the nature of the substituents on the ligand backbone. The complex with hydrogens on the C_2 backbone [Cu(gts)] shows no selective uptake in hypoxic cells whatsoever, and is irreversibly trapped in both oxic and hypoxic cells. However, the complexes with one or two methyl groups ([Cu(ptsm)] and [Cu(atsm)]) show high uptake selectivities for hypoxic cells. A study of the cyclic voltammetry of a series of Cu^{II} bisthiosemicarbazones showed that the most hypoxic selective complexes showed the most negative reduction potentials for formation of the Cu^{I} anion.[27] However, it was by no means clear if the redox potential was the principal factor in determining the selectivity for hypoxic cells. We have undertaken a detailed study of the redox chemistry of these systems with particular reference to the stability of the Cu^{I}



$R^1 = R^2 = R^3 = H$, gts
$R^2 = R^3 = Me$, $R^1 = H$, atsm
$R^2 = Me$, $R^3 = H$, $R^1 = Me$, ptsm

Figure 10 *Cu^{II} bisthiosemicarbazone complexes that show antitumour activity*

anion, using density functional calculations, the pH dependence of cyclic voltammetry and UV–visible spectroscopy.[28]

We found that for the hypoxic selective atsm and ptsm complexes the reduction process is reversible (Nernstian) and addition of small amounts of acid has little effect. By contrast [Cu(gts)] shows a very much less reversible reduction process which becomes completely irreversible on the addition of even traces of acid. This suggests strongly that the stability of the Cu^{I} state is crucial in determining the selectivity and that irreversibility is caused by protic attack on the anion. But the question of why backbone methylation should increase the stability of the Cu^{I} state has remained unanswered.

In an attempt to address this we have carried out calculations on the LUMO and HOMO orbitals of 13 Cu^{II} bisthiosemicarbazones using DF methods.[28] The complexes contain an unpaired electron and the calculations were done using the spin-unrestricted formalism. The first striking result was that the HOMO–LUMO gap was very small (around 0.05 eV) and was strongly substituent dependent. The overall effect is that for the atsm (hypoxic selective) complex the LUMO is metal-based whereas for the non-selective gts complex it is ligand-based. Addition of the electron to the gts system may therefore occur to give a formally triplet state. Since these ligand systems are planar and highly delocalised, and addition of an electron to porphyrin complexes is well known to occur often on the ligand to give radical anions, the formation of an analogous species in the Cu bisthiosemicarbazones is not unreasonable. We intend to carry out some low-temperature reduction/EPR experiments to try and obtain experimental evidence for the formation of a radical species.

6 Conclusions

There is some way to go before the chemistry of sulfur ligands rivals in its extent and applications that of the tertiary phosphines pioneered by Joseph Chatt. Nevertheless, we hope that this brief survey of our work in the area will serve to illustrate that sulfur-based ligands can generate unusual and novel chemistry in terms of structures and reactivities. This project started in the Unit with the remit of contributing to an understanding of nitrogenase with iron and molybdenum, but has ultimately led to applications as diverse as highly active catalysts and the development of metal complexes for imaging and therapy in medicine.

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SECTION F:

The Biological Work of the ARC Unit of Nitrogen Fixation at the University of Sussex, and Later Developments

The Unit of Nitrogen Fixation at the University of Sussex became the foremost laboratory in the world for the study of many aspects of the biological nitrogen fixation problem. Perhaps the areas most successfully exploited were the chemical (see Section E) and the genetic. However, the biological work was considerably broader than the genetical, and it says much for both Chatt and for his Deputy Director (and later Director of the Unit) that such a diverse research programme could be successfully carried out with such success.

In fact, it was the policy of the ARC to establish a Unit for the working lifetime of a particularly distinguished individual, but to wind up the work once that person had retired. When Chatt retired it was clear that it would have been an act intellectual vandalism to close the Unit, and the reputation of the Unit and its principal researchers continued to grow under Postgate's enlightened direction. Perhaps this owed much to the old-fashioned British attitude that informed the setting up of the Unit: find a good set of chaps and let them get on with it. Sadly, this kind of approach would not be acceptable today.

Included in this section is an account by Postgate of his time in the Unit and another by Sanders to show how the biological work influenced, and still influences, some related chemistry. There is also a contribution from Wedd, one of the many distinguished scholars who passed through the Unit in its formative days, and who is happy to acknowledge the influence it had upon him. The contribution by Lee shows how the problems originally tackled in the Unit are still giving rise to original and innovative research, and Garner, a Chatt Lecturer, describes some innovative work in the area of bioinorganic chemistry, a subject that the combined biological and chemical work in the Unit did much to stimulate.

Biological Nitrogen Fixation

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1 The Unit of Nitrogen Fixation

In 1963 Chatt became the first Director of the Agricultural Research Council's Unit of Nitrogen Fixation (UNF) and remained in the post until his retirement in 1980. The UNF comprised a multidisciplinary team of scientists whose research gained it a formidable reputation. That research involved not only chemistry but microbiology, biochemistry and molecular genetics, and the biological component grew to be the major part of the Unit's programme.

1.1 Nitrogen Fixation

The fixation of nitrogen is a process of transcendent importance in nature because it compensates for a net loss of nitrogen from the biosphere to the atmosphere which takes place during the normal breakdown and mineralisation of organic matter in soil and water, mediated by certain types of bacteria: a process called denitrification. Some natural non-biological processes, such as combustion, lightning and irradiation, lead to modest fixation of nitrogen as nitrogen oxides, which wash into soil and water as nitrates, but for many millennia the major input of new nitrogen into the biosphere has taken place by way of biological nitrogen fixation. During the twentieth century nitrogen fertiliser manufactured industrially from atmospheric dinitrogen has made a steadily increasing contribution. The biological process is a property of a heterogeneous group of bacteria called nitrogen-fixing bacteria, but of no other living things. Even in the present era of chemically-produced nitrogenous fertiliser, it provides over half of the global input of new nitrogen into soil and water. Nitrogen fixation and denitrification both form part of the planetary cycling of nitrogen, a complex of processes often formalised as the Nitrogen Cycle, of which Figure 1 is a representative example.

Thus nitrogen fixation is fundamental to the persistence of the biosphere as we know it today.[1–3] It is also fundamentally important to world agriculture and

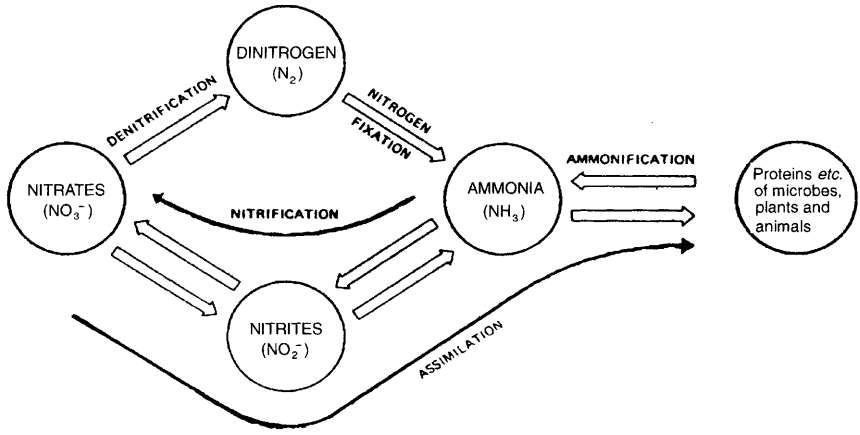

Figure 1 *A version of the nitrogen cycle, a diagram that illustrates the chemical transformations undergone by nitrogen atoms in the terrestrial biosphere. (After Reference 1)*

forestry, and primarily for this reason it has been the subject of intensive research in agriculturally-orientated Institutes and Universities throughout the world since the existence of the biological process was finally confirmed in 1886.

In 1960 a group of microbial biochemists in the Central Research Laboratories of the Dupont de Nemours Chemical Corporation, USA, broke through a barrier that had impeded researchers for at least two decades. They extracted from a species of nitrogen-fixing bacteria a solution containing the enzyme which is responsible for the activation of dinitrogen.[4] It was called nitrogenase, and, in appropriate conditions, it bound N_2 from the atmosphere and reduced it to ammonia.

Their extract was a highly impure proteinaceous solution obtained by disrupting the cells of a common soil bacterium, *Clostridium pasteurianum.* This organism belonged to the class of microbes called anaerobes: it would not grow in the presence of oxygen. Two features proved to have delayed earlier attempts to extract the enzyme: its nitrogen-fixing activity was irreversibly inactivated by exposure to dioxygen, and it functioned only when provided with pyruvate as the reducing agent. Within a couple of years the pyruvate was shown to have a dual function: it acted both as a reductant and as a source of ATP, both of which were essential for the biological conversion of N_2 into NH_3. The experimental achievement of the Dupont group lay largely in devising ways of extracting the material and handling it anoxically, but it opened up to biochemists the possibility of purifying nitrogenase and discovering how it bound and reduced the dinitrogen molecule.

Biological nitrogen fixation presented a chemical enigma. The two major industrial procedures employed to cause atmospheric dinitrogen to enter chemical combination, like the few available laboratory methods, required drastic conditions. The obsolete Birkeland–Eyde process required exposure of dinitro-

gen and dioxygen to an electric arc at some 2000 to 3000°C, followed by exceptionally rapid cooling and scrubbing of the nitrogen oxides so formed; and the widely-used Haber process required dinitrogen plus dihydrogen, catalysts, high pressures and temperatures, and the total absence of dioxygen and water. Yet nitrogen-fixing bacteria in soil brought dinitrogen into chemical combination at ordinary temperatures and pressures, in environments where both water and air were abundant: indeed, the genus *Azotobacter* would only grow and fix nitrogen in air.

One of the industrial processes used to fix nitrogen was oxidative, the other reductive. Both had provided models for speculation on the mechanism of biological nitrogen fixation, but Dupont's advance settled the matter: because the product was ammonia and because the least trace of dioxygen stopped the biological reaction, oxidative pathways needed no longer to be considered seriously as far as the biological process was concerned. Nevertheless, the details of how the enzyme actually bound and reduced dinitrogen were still a closed book.

1.2 The Unit's Origins

The historical circumstances surrounding the UNF's formation have been described in some detail elsewhere[5] and will be repeated here only in outline.

One of Dupont's commercial rivals, the multi-national petrochemical company Shell, was intrigued by the advance. Why was Dupont devoting a high quality research effort to so fundamental a scientific topic? To discover whether there was a possible industrial application that could be of interest, Shell commissioned the British microbiologist K. R. Butlin[6] to look into and report upon the state of the art in nitrogen fixation research, with special attention to chemical and biochemical aspects.

Butlin visited the four major centres of research on nitrogen fixation then operating in Britain, the USA's major research centre at the University of Wisconsin, Madison, and finally Dupont's Central Research Laboratories in Wilmington, Delaware, USA. There he talked freely with Dr Carnahan, the senior member of Dupont's team. Carnahan explained that it was good for the Corporation's public image to be seen to have advanced fundamental knowledge of a process so crucially important in agriculture; they had also hoped to learn enough about the enzyme to be able to imitate its action commercially, to patent procedures for making agricultural fertiliser more cheaply, or perhaps to develop new methods of making valuable nitrogen compounds directly from the atmosphere. However, they had already concluded that their discovery was unlikely to affect the fertiliser or fine chemicals industry in the short or medium term, and were planning to move closer to agriculture, into research on nitrogen-fixing bacteria that associate with plants.

Butlin did not agree; in his report he considered that a serious possibility still remained that understanding how nitrogenase worked would enable industrial chemists to mimic the process, or develop new processes, and he recommended Shell to make a substantial investment in biochemical research in this area. However, the Company also decided that the economic prospects of such

research were too remote to be of commercial interest, but considered that further research on the subject in a more open laboratory than Dupont's would be to their and everyone else's advantage. So they passed Butlin's report to the then Secretary of the Agricultural Research Council, Professor E. G. (later Sir Gordon) Cox FRS.

Cox, himself an inorganic chemist, was well aware of the perplexing chemical questions presented by the biological fixation of nitrogen. He also recognised that there was no centre in Britain with the combined biological and chemical expertise needed to pick up and extend the Dupont group's findings. So he urged the Council to set up a dedicated research Unit to study the problem. He wanted a research effort that would focus on the basic chemistry; he took the view that research on plants and/or other steps of the nitrogen cycle would be distracting. There had long been evidence that molybdenum was involved in some essential way in nitrogen fixation, perhaps in the actual catalytic process conducted by nitrogenase. It so happened that Joseph Chatt, already an FRS and distinguished for his research in metallo-organic complexes, had left Imperial Chemical Industries' Frythe Laboratory in 1962 and was considering posts in the USA. Chatt agreed to become Director of the Council's new Unit.

The Unit's remit would be to study the fundamental chemistry of biological nitrogen fixation. It would be multidisciplinary, involving microbiologists and biochemists as well as pure chemists, and would therefore be large. In the jargon of the day, its research would be strategic: it would study the basic science underlying a process of great practical importance. Its programme would definitely not be practically orientated: it would not involve itself in other steps of the nitrogen cycle, nor with associations with plants, nor yet with immediate problems in agriculture. Any useful fall-out of the new Unit's findings would be taken care of by other stations, university groups or research agencies.

In retrospect it was remarkably enlightened of the Council to approve and fund so basic a research project. In 1962–63 long-term strategic research was still the primary remit of the Research Councils, but the political climate was changing and pressure was already building up to shift their research programmes towards foreseeable practical objectives. Within a few years a fundamental initiative on that scale by a British Government research agency would become effectively impossible.

1.3 Earliest Days of the UNF

In 1963 the present writer was seeking a new research post. I had taken an honours degree in chemistry at Oxford before turning to microbiology, and had worked for nearly a decade in Butlin's group at Teddington, which specialised in Economic Microbiology, then briefly at the Microbiological Research Establishment on Salisbury Plain. With Butlin I had become a leading authority on sulfate-reducing bacteria, which play an important part in the planetary Sulfur Cycle as well as being of substantial economic importance.[7] Cox duly arranged for an interview with Chatt. I take up the story with an excerpt from a tribute I spoke at Chatt's funeral.

'So Joseph and I were put in touch and, one chilly morning in the Spring of that year, we met, in a distinctly austere room in the Abbey Hotel in New York City. Why there? Because we were both travelling scientists at the time; I was returning to the UK after a six-month visiting Professorship at the University of Illinois, Joseph was *en route* to a short sabbatical at Pennsylvania State University.

In the space of some 40 minutes he explained to me his plans for the new Unit. It would have ten research staff, half of them microbiologists – as he described them – with appropriate support staff; graduate students and post-docs would pass through. New laboratories would be built for it, but where was not yet clear; finding temporary lab. accommodation would be a priority on his return to the UK. I was impressed by his enthusiasm and shared his view of the need for basic research in that area, but it all seemed a little tentative.

I do not recall much more about the interview. It was low key and we parted thoughtfully.[1]

That last sentence glosses over the fact that we were each dubious about the other. I was unimpressed by Chatt's seemingly dismissive view of biological science (a not uncommon attitude among chemists in those days), and I learned much later that Chatt found me somewhat 'bohemian'. However, the meeting proved to be the beginning of nearly twenty years of very productive research collaboration. For despite my lack of experience of nitrogen-fixing bacteria, Cox and Chatt deemed my qualifications suitable – in the eyes of chemists someone who could handle sulfur ought to be able to cope with nitrogen; they are not far apart in the Periodic Table.[5] In that year I was appointed Assistant Director of the UNF-to-be, charged with planning and directing the biological side of the research. That autumn Chatt and I moved into the Agricultural Research Council's crowded headquarters in London, with a desk in the waiting room for me, and we set about planning a new laboratory, visiting possible sites, talking to architects, picking up ideas and, above all, telephoning fellow scientists for temporary laboratory space.

I discovered Chatt's remarkable tenacity and firmness of purpose, once he had decided what he wanted. I think the Council's planning staff was disconcerted by the juggernaut that had moved in among them, but they were admiring, too. Within a couple of months he had found temporary laboratory space for chemistry at Queen Mary College, and I had negotiated a conversion at the Royal Veterinary College, where I could get the microbiology started. We moved out of the Agricultural Research Council's HQ building in 1964, to their polite relief, and we worked separately for about a year, taking on a few staff. Finding a permanent home for the Unit was something of a problem; for some months Queen Mary College was the most probable host, but diverse practical considerations led to the University of Sussex being preferred and there the biological and chemical sides of the Unit came together, in temporary accommodation, early in 1965. Its own purpose-built laboratories at Sussex became available in 1967.

The Unit moved gradually into the forefront of its research area and gained a formidable reputation both nationally and internationally.[8] It became a para-

digm of successful interdisciplinary research: chemists, biochemists, physiologists and geneticists homing in on a central problem. Many of its senior staff became world leaders in their special research areas, while sustaining the principle of collaboration, both internal and external. Visiting workers came from all parts of the world and unanimously praised its collaborative atmosphere and effectiveness. By the time Chatt retired in 1980 it had grown from its intended 24 to some 80, including visiting workers. It forged links with the University, especially with its School of Molecular Sciences; its publications ranged from abstruse chemical kinetics to advanced molecular genetics – several opened up wholly new and exciting research areas.

As far as the biological side of the UNF's research is concerned, I should put on record a fact for which I am personally very grateful. Chatt planned and directed the chemical side of the UNF's research in considerable detail, but he left the planning and the directing of the biological programme entirely to me. A dichotomy between chemistry and biology was necessary at its outset, because the Unit's biological and chemical research thrusts were remote from each other – though naturally they shared the ultimate objective of understanding the mode of activation of the dinitrogen molecule by nitrogenase. Chatt and I were confident that the two prongs of the Unit's approach would in time converge and, with this end in mind, the Unit held regular internal seminars at which chemists and biologists would present, explain, and if appropriate justify, their research to each other. These meetings brought out early problems in communication: just as biologists would be bewildered by chemical jargon, such as talk of hard *versus* soft ligands, π-bonding, and charge states in metal complexes, so chemists would be bothered by casual use of biological acronyms such as ATP, ADP, NAD, not to mention that ghastly piece of biochemical jargon, 'reverse electron flow'. The experience was salutary for the linguistic discipline of both sides, and we gradually learned each other's languages and discarded imprecise terminology.

The UNF's biological research catalysed many important discoveries in other laboratories, as well as prompting re-thinks in general enzymology, microbial physiology, genetics and evolutionary theory. In the space available I can only touch upon a few highlights without detailed citations (see Section 6).

2 Biochemical Research

By the time the UNF had settled into its laboratories at the University of Sussex the Dupont group's break-through had been followed up and extended in several laboratories. In particular, the Charles Kettering Laboratory in the USA had extracted a particulate nitrogenase (*i.e.* one which sedimented in a regular high-speed centrifuge) from the aerobic nitrogen-fixing bacterium *Azotobacter vinelandii*. This had three valuable properties for research. Firstly, the particulate preparation was stable in air, provided it had no ATP and was therefore not functioning; secondly, *in vitro* it would function (anoxically and given ATP, of course) using sodium dithionite as an artificial reducing agent, to form ammonia from dinitrogen, plus gaseous dihydrogen (its activity with pyruvate was only

marginal); thirdly, in the absence of dinitrogen (*i.e.* under argon or helium) it generated exclusively dihydrogen. Manometric comparisons of the amounts of dihydrogen evolved under dinitrogen compared with argon were widely used in the mid 1950s as a quick and reliable measure of nitrogen fixation. Such findings opened up a route to rigid enzymological studies on nitrogenase.

2.1 Structural Analogues of Dinitrogen

In the 1960s the use of structural analogues of substrates to probe the kinetics of enzyme action had been commonplace for about two decades; sometimes they would be inhibitors of enzyme activity, competitive or non-competitive as the case might be, and sometimes they would be alternative substrates. Dinitrogen monoxide, azides and cyanides had been tested with intact nitrogen-fixing microbes and enzyme preparations and proved to be substrates alternative to dinitrogen. Carbon monoxide was not: it inhibited nitrogen fixation but the enzyme continued to form dihydrogen. Was a terminal nitrogen atom obligatory for interaction with the dinitrogen-binding site? One of the earliest collaborations between biologists and chemists within the UNF was the testing of methyl isocyanide, prepared by the chemists for the biologists, with our own nitrogenase preparation from *Azotobacter chroococcum*. It proved to be an alternative substrate that competed with N_2. It was reduced, not to dimethylamine but to methylamine plus methane (plus small amounts of C_2 products whose origin was the subject of now obsolete speculation); experiments in D_2O showed that the methane arose from the terminal C of the isocyanide, so the triple N–C bond had been split.[9] Chatt was intrigued by these findings, since they supported speculation that the substrate-binding site was a transition metal. He proposed a long-shot experiment: would xenon interfere with the N_2-binding site? A small but expensive cylinder of xenon was procured and an economical experiment designed, but no influence on N_2 reduction was detected.

Methyl isocyanide was reduced by living nitrogen-fixing bacteria, and this finding suggested that the reaction could be used as a versatile and quick assay for nitrogenase, since the methane produced could be quantitated readily by gas chromatography.[9] Indeed, it worked well with live bacteria or with nodules from nitrogen-fixing plant associations, as well as with enzyme preparations. However, fortunately for the progress of research in the world at large, because isocyanides are exceptionally unpleasant to work with, a more agreeable and equally versatile assay was developed almost simultaneously, jointly in Wisconsin and Australia, using acetylene, which nitrogenase also reduces, to yield ethylene.[10,11] The 'acetylene test' for nitrogen fixation is still widely used in the field as well as in laboratories.

2.2 Enzyme Studies

By 1965–66 research in the USA had shown that the nitrogenase in Dupont's original extract from *Clostridium pasteurianum*, which was a true solution, was composed of two distinct metalloproteins, both essential for activity, both irre-

versibly destroyed by exposure to dioxygen. The process needed magnesium ions as well as ATP, and the ATP was converted to ADP, which inhibited the reaction – in experimental work it had to be removed, or rather, recycled. The relatively dioxygen-tolerant but particulate nitrogenase preparation from *Azotobacter vinelandii* also consumed ATP and required Mg^{2+}; when disrupted it yielded two highly dioxygen-sensitive proteins very similar to those in the clostridial extract. Procedures for purifying the two nitrogenase proteins by anoxic ion-exchange chromatography were being developed. Facilities for the culture and harvesting of bacteria on a large scale were essential for work of this kind, and the UNF designed and developed its own all-glass culture facilities which served it satisfactorily for some twenty-five years.[12]

In the USA, the anaerobe *C. pasteurianum* and the aerobe *A. vinelandii* were the favoured bacteria for biochemical research on nitrogen fixation. In order that the UNF's research might be complementary to the research of others rather than competitive, it seemed logical to adopt different 'work horses'. I chose *Azotobacter chroococcum* as our aerobe. Preliminary tests with an anaerobe with which I was familiar from earlier years, *Desulfovibrio desulfuricans*, showed it to be unsuitable because it was difficult to culture routinely in large amounts (*Desulfovibrio* remained a secondary research subject for many years) and the more amenable *Klebsiella pneumoniae* became our 'pet' anaerobe. *K. pneumoniae* was not a true anaerobe; given fixed nitrogen as an ammonium salt it grew and multiplied vigorously in air, but it would fix nitrogen only in the absence of dioxygen. (The species name *pneumoniae* caused some consternation among our non-microbiologist colleagues until they were assured that ours was a harmless strain originally isolated from fermenting corn liquor.)

Nitrogenases were extracted from both microbes and proved also to be binary. We purified the two nitrogenase proteins from each organism: they were very similar to each other and to analogous proteins being reported from the USA. One was a large (MW $\sim$ 220 000) $\alpha_2\beta_2$ tetramer, and contained molybdenum plus much iron, the latter as iron–sulfur clusters; the other was γ_2 dimeric and contained only an iron–sulfur cluster. The former was termed the MoFe-protein and the latter the Fe-protein. They were duly characterised and detailed data published; comparable nitrogenase proteins from other genera and species of bacteria were purified and characterised, some by visiting workers who had come for that purpose, some by graduate students. They were very similar, and the similarities of nitrogenases from diverse bacteria extended to function: one could, for example, construct an active hybrid nitrogenase by mixing the larger MoFe-protein from *Klebsiella* with the smaller Fe-protein from *Azotobacter*.

2.3 Studies of Mechanism

By the early 1970s it had become possible to ask mechanistic questions. Did the two proteins act sequentially or as a complex? Where and in what order did N_2 and ATP bind? How was Mg involved? Were identifiable intermediates formed between dinitrogen and the end-product ammonia? Why was H_2 always evolved?

The UV–visible spectra of the MoFe- and Fe-proteins lacked exploitable features, but the behaviour of their electron paramagnetic resonance and Mössbauer spectra proved to be informative. For details of these studies, which occupied several years of research in various laboratories, specialised texts should be consulted. In outline, the Fe/S cluster in biologically active (*i.e.* not dioxygen-damaged) Fe-protein could exist in a reduced or an oxidised state. In the reduced protein it displayed a rhombic EPR signal which, in the presence of ATP and Mg ions, changed to axial, a change accompanied by a lowering of the protein's standard redox potential and changes in other physico-chemical properties. Native MoFe-protein displayed three redox states, observable in its Mössbauer spectra. It was normally isolated in the intermediate state, which also displayed a unique EPR signal (the other two states were EPR-silent). The most reduced, EPR-silent state appeared when the enzyme was actually functioning; the most oxidised state was probably physiologically irrelevant. Tests with substrate analogues gave hints that these influenced the spectra of the MoFe-protein. The upshot of experiments on these lines was that the MoFe-protein included the N_2-binding site, and that the Fe-protein bound and hydrolysed ATP, donating electrons to N_2 by way of FeS clusters in the MoFe-protein.[13] This view became accepted and a then contemporary suggestion from the USA that the Fe-protein bound dinitrogen was abandoned.

Conventional quantitative enzymology confirmed that dihydrogen evolution was an intrinsic part of biological dinitrogen reduction, and that the overall stoichiometry should be written as shown.

$$N_2 + 16MgATP + 8H_2O + 8e^- \longrightarrow 2NH_3 + 16MgADP + H_2 + 8OH^-$$

This involves a net transfer of eight electrons and the consumption of an unexpectedly large amount of ATP. This could hardly be a one-step reaction, and the questions regarding pathway and the existence of a nitrogenase complex remained.

High velocity sedimentation studies with mixtures of the separated proteins from *Klebsiella*, albeit unsatisfactory because of their sensitivity to air, suggested that the proteins associated readily, and steady-state kinetics suggested a stoichiometry of two Fe-protein molecules to one of MoFe-protein. For several years the UNF's consensus favoured a real rather than transient nitrogenase complex. However, proteins often associate *in vitro* and more convincing evidence bearing upon complex formation emerged from detailed kinetic studies on nitrogenase function.

Details of several years of UNF research exploiting rapid reaction, rapid quench and stopped flow kinetics are in the scientific literature and would be inappropriate here.[14] The upshot was a scheme which evolved over the period and, with later refinements, is now considered to be correct in all its major features. In brief, the obligatory evolution of dihydrogen is believed to arise from the formation of a metal–dihydride complex within the reduced MoFe-protein, a two-step process requiring the transfer of two electrons successively from the MgATP-activated Fe-protein coupled with two protonation steps and the hydrolyses of four molecules of ATP to ADP; N_2 is bound by displacement of two

hydrido groups as H_2 (precedents for this reaction exist in coordination chemistry); subsequent reduction of bound N_2 takes place by further sequential electron transfers from MgATP-activated Fe-protein molecules, with concomitant protonations and hydrolyses of another 12 molecules of MgATP; short-lived bound forms of N_2 in intermediate states of reduction precede the release of bound N as NH_3. Rate constants for many of the steps were estimated by computer modelling of the experimental data; they compelled the conclusion that no long-lived complex was formed; rather that a molecule of MoFe-protein charged with dinitrogen reacted with successive molecules of MgATP-activated Fe-protein. The rate of dissociation of the transient protein–protein associations determined the turnover time of the complete reaction. Following suggestions from the USA, the two nitrogenase proteins are now officially designated 'dinitrogenase' (the MoFe-protein), since it binds N_2, and 'dinitrogenase reductase' (the Fe-protein), since it donates electrons to dinitrogenase.

Parallel with this research, Chatt and his team were deeply involved in their exhaustive study of the chemistry of the dinitrogen complexes formed by various transition metals. In particular, their successful search for complexes in which the dinitrogen group could be protonated in mild conditions to yield ammonia (see the contribution by R. L. Richards in Section E) indicated that hydrazine was often formed instead of or alongside ammonia. It was logical for the UNF's biochemists to seek hydrazine as a biological intermediate, despite the fact that earlier isotope dilution experiments in the USA using ^{15}N-hydrazine had indicated none. Rapid quenching of nitrogenase, with acid or alkali, in the first few seconds of its functioning did indeed yield hydrazine, in amounts which peaked in the pre-steady state and became virtually undetectable in the steady state. Hence a bound species at the oxidation level of hydrazine was probably formed during nitrogenase function, which, being bound, did not exchange with isotopically labelled hydrazine.[15] By the later 1970s the Unit's chemistry and biochemistry were converging.

Everything pointed to the N_2-binding site being a metal atom in the MoFe-protein, probably Mo itself, but it remained elusive. Evidence that the site had to be sterically close to the Mo atom was in due course obtained using mutant bacteria (see Section 5, below).

3 Physiological Research

As soon as the enzymology of nitrogenase began to be resolved, no less that four obvious physiological questions arose. First, given their sensitivity to dioxygen, how did nitrogen-fixing bacteria protect the two nitrogenase proteins from denaturation in air? Secondly, how were electrons channelled from the cells' metabolism into the reduction of dinitrogen? Thirdly, how did the bacteria cope with the enzyme's substantial demand for ATP? Fourthly, nitrogenase activity was always accompanied by dihydrogen evolution; did this happen in nature? If not, why not?[16]

3.1 Dioxygen Exclusion

The first question arose with particular force from studies on bacteria belonging to the genus *Azotobacter*. These are very efficient and reliable nitrogen fixers yet they require dioxygen for growth; they neither multiply nor fix dinitrogen without it. The UNF approached the problem using continuous culture, which is a powerful tool for studying physiological questions in microbiology.[17] Imagine a microbial culture – a vessel in which a population of bacteria is multiplying – which is filled to the brim and fed continuously with fresh culture medium, the excess of medium being allowed to overflow. Imagine now that the medium contains an excess of everything the bacteria need to multiply but for one component, glucose, for example. The bacterial population in the vessel multiplies at a rate determined by how fast fresh medium is supplied and the population density is determined by the concentration of glucose in the influent medium. The bacteria comprising the population are said to be 'glucose-limited'. Once a population is in a steady state its density, multiplication rate and nutritional status remain constant for as long as the experimenter wishes and these parameters, as well as aeration and temperature, can be altered independently and the way the properties of the bacteria change can be examined.

(Parenthetically, much of the development work on continuous culture during the 1950s and 1960s, in which I had some involvement, had been carried out at the Microbiological Research Establishment, Porton Down, whose remit included work on defence against biological warfare. This information reached the University's student body during its militant 1960s, and the UNF was briefly picketed, suspected of secret bellicose research. Happily one of the editors of the present volume (GJL), more patient than either Chatt or me, explained to the demonstration's leaders the importance of nitrogen fixation to world nutrition, and it dispersed peacefully.)

Our continuous culture studies on *Azotobacter chroococcum* revealed that nitrogen-fixing, glucose-limited populations were unexpectedly sensitive to oxygenation: if aerated vigorously they ceased multiplying and fixing nitrogen. However, populations supplied with plenty of glucose were far from sensitive: they flourished not only in air but even in hyperbaric dioxygen. It transpired that they adjusted their respiration rate in proportion to the concentration of dissolved dioxygen; under high oxygenation the bacteria evinced the fastest respiration rates recorded for living things. But that adjustment took a little time; if they were abruptly exposed to a dioxygen stress, they would 'switch off' their nitrogen fixation and restore it rapidly when the stress was relieved (Figure 2).

Several years' research along these lines led to the conclusion that respiration, in addition to its normal function of generating energy, was exerting a protective action on nitrogenase simply by scavenging dioxygen, and that, if the dioxygen stress was greater than respiration could cope with immediately, the organism was able to protect the enzyme from oxygen damage, though it became nonfunctional in the protected state. We introduced the terms 'respiratory protection' and 'conformational protection' for these two processes. The latter term became obsolete in the 1980s when workers in the Netherlands demonstrated its

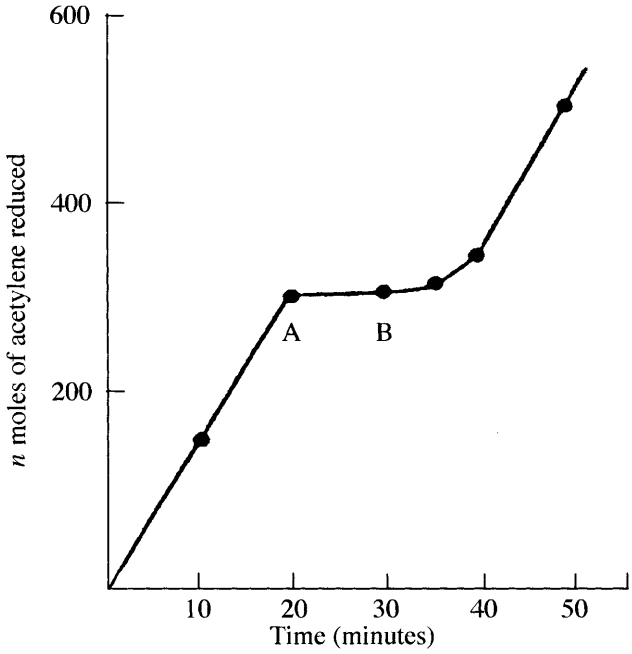

Figure 2 *'Switch on' and 'switch off' of nitrogenase in response to aeration levels. Live cells from a continuous culture of* Azotobacter chroococcum *were shaken gently in air while their nitrogen-fixing activity was measured using the acetylene test. Shaking, and therefore aeration, was intensified at A and returned to its original value at B. Notice the brief delay in reaching maximum activity again. (After Reference 1).*

mechanism: the bacteria possess a non-haem iron protein which, under dioxygen stress, forms a protected but enzymically inactive complex with the nitrogenase proteins; the complex dissociates as the dissolved dioxygen tension approaches zero.[18] However, the essential incompatibility of nitrogen fixation and dioxygen, which we had thus rationalised, influenced thinking in many laboratories and a variety of stratagems for evading oxygen damage were discovered among nitrogen-fixing systems, including respiration, compartmentation, 'switch on and off' processes, cooperative screening from dioxygen, and simple evasion. In addition, the number of recognised species of bacteria known to be able to fix nitrogen was multiplied several-fold over the next decade with the realisation that many were 'microaerobic' fixers: they were not good at respiratory protection and only functioned at low partial pressures of dioxygen. Dioxygen exclusion is now accepted as being fundamental to the physiology of both symbiotic and free-living nitrogen fixation.[16]

3.2 The Biological Reductant(s)

The standard redox potential of the Fe-protein is low, and it becomes even lower when it interacts with MgATP. A specific low-potential electron donor channels electrons from the cell's general metabolism to nitrogenase. In the anaerobe *Clostridium pasteurianum* it was known to be a ferredoxin; the UNF's particular contribution in this area was to show, in parallel with workers in the Netherlands, that the equivalent electron donor in *A. chroococcum* was a flavodoxin, shuttling between its reduced and semi-quinone forms.

3.3 The Demand for ATP

Nitrogenase consumes 16 molecules of ATP to fix one N_2 molecule, and more is consumed in synthesising and maintaining the enzyme itself. This is a significant drain on the cell's metabolic resources, and most nitrogen-fixing bacteria do not make nitrogenase if fixed nitrogen is available to them. In a continuous culture limited by a source of both carbon and energy, such as glucose, the population density is in effect being limited by the amounts of ATP the cells can divert into biosynthesis. Any metabolic process with a high ATP demand will thus lower the population density. By comparing steady-state glucose-limited populations of *K. pneumoniae* with and without fixed nitrogen (as ammonium ion), research in the UNF quantitated the energy cost of nitrogen fixation, quantitated the effect of ammonium ion as a repressor of nitrogenase synthesis, established quantitatively that dioxygen also repressed nitrogenase synthesis and, unexpectedly, demonstrated that *K. pneumoniae* could be coaxed into fixing nitrogen in an oxic atmosphere provided its respiratory activity kept the partial pressure of dissolved dioxygen vanishingly low: a marginal example of respiratory protection.

Details of the mechanisms of repression of nitrogenase synthesis by dioxygen or fixed nitrogen involved genetical research and are outined later in this article.

3.4 Dihydrogen Recycling

Bacteria such as *K. pneumoniae* and *C. pasteurianum* growing without air evolve dihydrogen as a normal product of their anaerobic metabolism whether they are fixing nitrogen or not, so the contribution made as a by-product of nitrogenase function is not easily assessed. However, azotobacters such as *A. chroococcum* evolve no dihydrogen, and continuous culture experiments analogous to those outlined in Section 3.1 showed that they were remarkably efficient in terms of substrate consumption, despite their need to sustain respiratory protection of nitrogenase. We discovered that acetylene caused the organisms to evolve dihydrogen; it acted by blocking an 'uptake hydrogenase', a type of enzyme which oxidised dihydrogen to water as it was formed. This enzyme enhanced respiratory protection and also provided energy to regenerate ATP; it significantly enhanced the efficiency of nitrogen fixation by these bacteria. These findings were consistent with concurrent research in the USA on hydrogen recycling in the symbiotic nitrogen-fixing bacteria *Bradyhizobium japonicum*.[18,19]

4 Genetical Research

The UNF was set up in order to study a problem in fundamental biological chemistry. In 1968 nothing whatever was known about the genetics of nitrogenase synthesis and it seemed to me that their study might open up a new approach. I privily undertook a few experiments myself, and rapidly realised that serious progress would only be made by someone with proper training. No staff position was available but I had funds to recruit a graduate student willing to try to open up the subject and, after an exacting period when we nearly gave up, he had success. Coincidentally and unknown to me, similar thoughts had occurred to Professor R. C. Valentine at the University of California, Davis, and he, too, could finance only a graduate student – who also had success. Again by coincidence, both of us were working with *K. pneumoniae*. Twenty years later the genetics of nitrogen fixation had become a major topic in molecular biology, demanding regular international conferences, and was occupying well over 300 research scientists in laboratories all over the world. It was all started by two graduate students.

4.1 The *nif* Genes

Earlier work in the UNF had shown that laboratory cultures of many kinds of bacteria could simulate nitrogen fixation by scavenging nitrogenous impurities from the atmosphere, from dust, or from components of culture media. Many scientists had been misled in earlier decades and as a result of our report (which editors were at first reluctant to accept because of its negative character) numerous putative nitrogen-fixing organisms were dismissed from the literature, including all those that were not bacteria.[20] But the examination of each isolate was laborious, and the advance of genetics depended absolutely on devising a quick, simple and reliable way of screening hundreds of bacterial colonies for fixation. Both students, in California and in Sussex, solved the problem and both prepared a few mutants of *K. pneumoniae* that were unable to fix nitrogen. Standard genetical techniques (transformation in the USA, plasmid-mediated conjugation in the UNF) were used to correct the mutations with DNA from the parent organism; prompted by the US work, we confirmed that the mutations lay close to genes coding for histidine biosynthesis in the bacterial chromosome.[21,22] The genetical shorthand *nif* was adopted for nitrogen fixation genes (and will be used henceforth here). The UNF's major break-through in this area, made in 1971, resulted from the manipulation of the *nif* genes of *K. pneumoniae* from the bacterial chromosome to a genetical element called a plasmid: a circle of DNA which carries genes which are not on the chromosome. The plasmid we used belonged to a class capable of transferring itself from one cell to another and, within limits, to other genera and species of bacteria. With it we were able to transfer the ability to fix nitrogen to *Escherischia coli*, a species of bacteria whose genetics was already substantially elucidated. In one of our hybrids, the *nif* genes had become incorporated into the *E. coli* chromosome: we had for the first time created an entirely new species of nitrogen-fixing bacteria. The exciting possibil-

ity thus arose that *nif* genes might be transferable to all sorts of creatures; the economic ramifications of this possibility, including that of creating self-fertilising plants for agriculture, caused something of a sensation and brought the UNF a brief spell of media attention.

The episode caught the Agricultural Research Council's administration napping. Chatt had realised that biological nitrogen fixation was a much more complex problem than we had suspected at the time of the UNF's formation and had accepted that genetics ought to form part of the biologists' approach. He had therefore sought an increase in staff, mentioning, among other evidence of good progress, the then unpublished transfer of *nif* to *E. coli*. But the Administration was unimpressed; his request was refused out of hand: no such increase was financially possible. However, once the press furore got under way, Chatt moved quickly; he arranged an interview in London with the Council itself, and they were sufficiently impressed to increase the UNF's senior staff by a third – from 10 to 15 – four of the new posts to reinforce the biological side of the programme, one to expand the chemical side. Thus his UNF became the largest autonomous research Unit in the Agricultural Research Council.

As far as research was concerned, the fundamental value of our gene transfer to *E. coli* was that a huge repertoire of well-defined mutants throughout the *E. coli* chromosome already existed and were available as backgrounds in which to study *nif* expression, and procedures were well established for mapping and characterising genes in *E. coli*. An additional bonus appeared within a year or so: in 1973 two scientists in the USA developed techniques for cutting up and manipulating DNA *in vitro* and inserting it into *E. coli*. The UNF's geneticists embarked upon a concerted programme of mapping the *nif* genes of *K. pneumoniae* using both traditional methods and new-style genetic manipulation and, where possible, establishing their functions. We were disconcerted when, in 1975, US scientists sparked a widespread panic about the dangers of genetic manipulation *in vitro*, with some bizarre political consequences,[24] but the agricultural potential of the UNF's use of the technique happily saved us from censure in the media.

We had originally expected klebsiella's *nif* to comprise about five genes; by the time Chatt retired we, along with a few other laboratories throughout the world, had discovered some fifteen (Table 1), all linked together as a chain of clusters of genes. (The final number, established in the late 1980s, when the complete DNA sequence of *nif* was published, was twenty.) A much improved *nif* plasmid was constructed, able to transfer itself to many genera of bacteria as well as being far more stable than the earliest *nif* plasmid.[25] Named pRD1 (earlier RP41), we made it available to laboratories throughout the world and it became the basic tool of most research on *nif* genetics. With it, several new species and genera of nitrogen-fixing bacteria were constructed in order to learn about the conditions and genetic backgrounds in which *nif* could be expressed. Many clones of DNA were prepared from it, some carrying all the *nif* genes at once, others carrying the clusters within *nif*, or carrying each of the known genes separately, and yet others with fragments of the genes, including their regulatory sites. Plasmids with mutated *nif* genes were also made.

Table 1 *The* nif *gene cluster of* Klebsiella pneumoniae *as it was known about 1980*

The individual genes clustered within *nif* were assigned capital letters (agreed among the research laboratories concerned); future research would reveal another five, and the nature and functions of most *nif* gene products would be established. The vertical arrows indicate subclusters of genes (called operons) which had been shown to be transcribed in concert, and the directions of their transcription.

hisD	this gene, involved in histidine biosynthesis, is attached to one end of the *nif* cluster and plays no part in *nif* function.
nifJ	codes for pyruvate oxido-reductase, which generates electrons from pyruvate.
nifH	codes for the peptide subunit of the Fe-protein of nitrogenase.
nifD	codes for the α subunit of the MoFe-protein of nitrogenase.
nifK	codes for the β subunit of that MoFe-protein.
nifE	function uncertain, see *nifN*.
nifN	suspected of involvement, with *nifE*, in the synthesis or insertion of the MoFe moiety in nitrogenase.
nifU	function unknown.
nifS	function unknown.
nifV	concerned with the specificity of the MoFe moiety.
nifM	probably concerned with the FeS moiety of the Fe-protein.
nifF	codes for the immediate electron donor to the Fe-protein.
nifA	codes for a peptide which activates all the groups of *nif* genes.
nifL	codes for a repressor which over-rides activation by the *nifA* product.
nifB	concerned with insertion of the MoFe moiety.
nifQ	concerned with mobilising Mo for nitrogenase synthesis.
shiA	this gene, concerned with shikemic acid synthesis, lies at the other end of *nif* and plays no part in its functioning.

The whole chain of operons was termed a regulon. It was activated by way of *nifA* and switched off by way of *nifL*. The fact that all the *nif* genes were linked into a single regulon in *Klebsiella* was fortunate for research; future studies would show that, in most nitrogen-fixing bacteria (including our *A. chroococcum*), comparable *nif* operons exist but they are dispersed about the genome.[1]

By the late 1970s, *nif* genetics had become a popular subject for research and, though we were leaders in this area, substantial advances were made in laboratories outside the UNF, as well as by visiting scientists working alongside the UNF's geneticists. By then, with the genetics of *K. pneumoniae nif* as a guide, we had started to investigate the genetics of nitrogen fixation in the aerobe *A.*

chroococcum, with special emphasis on its tolerance of oxygen and the fact that it did not evolve dihydrogen. When Chatt retired in 1980 dioxygen-sensitive mutants and mutants lacking hydrogenase had been obtained, despite operational difficulties in making mutants of this organism, but our major contributions to azotobacter genetics would be made later in the 1980s.

4.2 Regulation of *nif*

Gradually questions of how the expression of these genes was regulated arose: how did external factors such as ammonium ions or oxygen supply switch *nif* on or off? The emphasis of our research duly shifted from *nif* structure towards *nif* regulation. Plasmids were constructed bearing hybrid genes in which *nif* genes with their regulatory sites were fused to an alien gene (*lac*) whose product (β-galactosidase) gave a colour reaction with an appropriate substrate.[26] These were invaluable for studying the regulation of *nif* genes, because they would give a colour reaction when activated.

It was already clear that subclusters of genes within the *nif* cluster were transcribed independently, processes regulated by the products of *nifA* and *nifL* (Table 1). A complicated cascade of regulatory steps began to be revealed whereby ammonium ions prevented activation of *nifA* and thus blocked transcription of the whole of *nif*.[27] Studies with a construct in which the *nifH* gene was fused with *lac* proved that dioxygen repressed nitrogenase synthesis in a different way, seemingly by interacting directly with the *nifL* gene.[28] In due course the molecular details of these processes, and the nature of the stretches of DNA which interacted with regulatory substances, would become the major preoccupation of the UNF's geneticists.

5 Interdisciplinary Interactions

The Unit's research was essentially interactive and convergent. Just as convergent chemical and biochemical thinking led to the discovery of a bound intermediate at the oxidation level of hydrazine during N_2 reduction, so our biochemical and physiological research benefited from each other's progress, and our genetics grew out of both – and benefited both. For example, I mentioned in Section 2.3 that genetic mutants were recruited to prove that the FeMo-cluster of the molybdoprotein carried the site which bound dintrogen. The *nifB* (Table 1) mutant of *K. pneumoniae* made nitrogenase, but it was non-functional. If purified MoFe-protein from normal *K. pneumoniae* was treated with acid, a fragment of low molecular weight could be prepared which retained Mo, Fe and S as well as exhibiting that protein's characteristic EPR sprectrum. It was nicknamed 'FeMoco'; it was a very unstable molecule and was rapidly destroyed by dioxygen. When added to the defective *nifB* nitrogenase, FeMoco restored normal activity. A second mutant, *nifV*, also made a defective nitrogenase but its defect was different: it reduced acetylene but not N_2. A FeMoco preparation could be made from *nifV* nitrogenase, and when this material was added to defective *nifB*

nitrogenase, it converted it to a *nifV*-type enzyme: able to reduce acetylene but not N_2.

In later years studies on the chemical nature of FeMoco would involve detailed collaboration between our biochemists and our chemists. Again, on the physiological side, the *nifH-lac* fusion mentioned in Section 4.2 was exploited to study the quantitative kinetics of oxygen repression, and another *nif-lac* fusion was used to show that Mo had a regulatory effect on nitrogenase synthesis.

6 Envoi

The UNF was a multidisciplinary and cooperative research team; in addition, a great deal of work involved collaboration with other laboratories throughout the world. Moreover, the UNF was never without a few graduate students, short-term students, visiting scientists and postdoctoral researchers, whose contributions were often invaluable, sometimes ground-breaking. That is why I have here attributed all our scientific advances to the UNF; it has been impracticable to name names in this short chapter. The specific scientists involved were named as authors of the UNF's primary publications, most of which can be found in the bibliography of a textbook written at about the time of Chatt's retirement.[29]

Chatt was at times perceptibly bemused by the directions the biological research was taking and it says much for his understanding of the mechanics of research that he accepted the dedication of his biological staff and gave them their heads. The foregoing survey has given little more than a taste of the systematic biological research during his fifteen-year Directorship of the UNF, and further substantial advances were made in the years following his departure. None the less, my account illustrates how effective a focussed multidisciplinary project can be if the scientists participating are motivated to learn each other's languages and to interact cooperatively.

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Vanadium, Molybdenum and Iron Complexes Based on a Trithiolate Ligand

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1 Introduction – Phosphine and Thiolate Ligands

Joseph Chatt and his co-workers developed a functional model for nitrogenase action at the ARC Unit of Nitrogen Fixation at the University of Sussex in the 1960s and 1970s. This involved coordination and reduction of dinitrogen at Mo and W sites with monodentate and chelating phosphine co-ligands, and featured the isolation and structural characterisation[1] of several intermediate complexes in which the dinitrogen had been successively reduced to diazenide, hydrazide, imide and nitride ligands, leading to the formulation of chemical[2] and electrochemical[3] cycles of reduction. In the course of this work a great deal of new coordination chemistry of the metals Os, Re, Mo and W with ligands such as hydride, carbon monoxide, nitric oxide, cyanide and isocyanides (which act as inhibitors or alternative substrates for nitrogenase action) was developed. Subsequent research by Chatt's group at Sussex and by his many ex-students and collaborators contributed to the advance of coordination chemistry leftward across the Periodic Table into the vanadium group. This advance, along with his earlier discoveries in the field of platinum metals, has meant that one part of Chatt's legacy has been the establishment of the comparative coordination chemistry of the transition metals; another part has been subsequent generations of coordination chemists.

Concurrent studies on nitrogenases, including those carried out by biochemists in the Unit at Sussex,[4] revealed that they contain cofactors with significant quantities of molybdenum, iron and sulfur (later it was found that in some nitrogenases molybdenum is apparently replaced by vanadium or iron). Efforts were therefore made to develop the nitrogen chemistry of these metals with

co-ligands such as thiolates and thioethers rather than phosphines. Sulfur (unlike phosphorus) tends to bridge between metals; while this results in the formation of potentially very active cluster complexes, it means that the study of reactivity at single-metal sites is difficult. The strategy used to counter this tendency of sulfur to form bridges was to prepare compounds featuring sterically crowded ligands such as triisopropylthiophenolate or macrocyclic compounds such as trithiacyclononane. The chemistry of *S*-ligated metals such as iron, molybdenum and vanadium with co-ligands such as hydride, carbon monoxide, isocyanides and hydrazines was developed in this way,[5] though a comprehensive scheme of reduction of dinitrogen comparable to that on phosphine complexes was not achieved.

2 Recent Studies on Nitrogenase

The structure of the nitrogenase cofactor FeMoco[6] features an $MoFe_7S_9$ core (Figure 1). The Mo atom at one end of FeMoco is ligated by three core sulfurs, two oxygens in a homocitrate ligand and one nitrogen (from histidine in the protein). The iron at the other end is ligated by one cysteinyl sulfur and three core sulfur atoms, while the six iron atoms in the middle are each ligated by three sulfur atoms approximately in a plane, and apparently by no other ligands. On extraction from the protein the histidine and cysteine ligands are replaced by solvent, *e.g. N*-methylformamide.

There is still controversy about where on FeMoco dinitrogen, carbon monoxide and alternative substrates are bound and/or reduced. For example, it has been proposed on the basis of molecular modelling studies and experiments on structurally defined N_2 complexes[7] that the homocitrate ligand on the molybdenum could become monodentate leaving a vacant site which would be suitable for binding dinitrogen,[8] and on the basis of recent density functional theory calculations[9] M. C. Durrant of this laboratory has suggested that the molybdenum is the preferred site for N_2 binding. The interaction of CO with FeMoco has also been studied under turnover conditions by EPR[10] and by stopped-flow IR spectroscopy.[11] Using the latter technique, bands at 1906, 1936, 1958 and 1880 cm^{-1}, appearing under different partial pressures of CO, have been assigned to ν(CO). Bands in this region are also observed when FeMoco is electrochemically reduced in a thin layer cell under CO.[12] It has been inferred from these measurements that one CO molecule binds in a bridging mode between

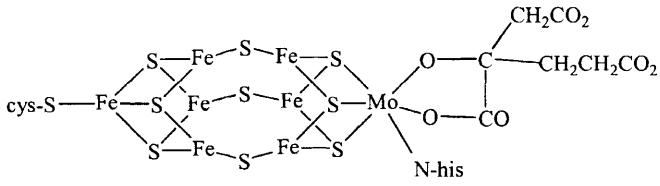

Figure 1 *The $\{MoFe_7S_9\}$ core of FeMoco*

two Fe atoms at low partial CO pressure, but that at higher partial pressure two CO molecules bind in a terminal mode on adjacent Fe atoms.[11]

Semi-reduced, isolated FeMoco has not been observed to interact with N_2, but kinetic studies have shown that it binds thiols and selenols (probably at the cysteinyl Fe), cyanide (at two sites, this Fe and the Mo) and protons (at the bridging sulfurs). Reduction of acetylene to ethylene and of protons to H_2 has also been demonstrated with various preparations of isolated FeMoco.[13]

3 Bulky Ligands and Tripodal Ligands

3.1 Ligands with Four-sulfur Donor Sets

The presence of sulfur groups in FeMoco has stimulated Sellman to prepare ligands such as A and B (Figure 2) that are derived from benzenedithiol. B reacts with iron(II) salts giving a sterically protected five-coordinate iron complex [$Fe^{II}B$] which binds CO and N_2H_4 (but not N_2) to form six-coordinate complexes. It also binds diazene N_2H_2 which is produced by oxidation of bound hydrazine in the dinuclear [$\{Fe^{II}B\}_2(\mu\text{-}N_2H_2)$].[14] This has led to a model for binding of diazene between two iron atoms in a form of FeMoco in which one of the central S bridges is lost and replaced by a bridging N_2, diazene or hydrazine. The two iron atoms in this opened-out FeMoco are assumed also to be ligated by neighbouring glutamine and histidine groups in the protein, and the structure is held together by N–H–S hydrogen bonds. A related bridging diazene complex is [$\{Ru^{II}A(PCy_3)\}_2(\mu\text{-}N_2H_2)$] (Cy = cyclohexyl) which catalyses the N_2-dependent HD formation by D_2/H^+ exchange,[15] a key feature of nitrogenase action.

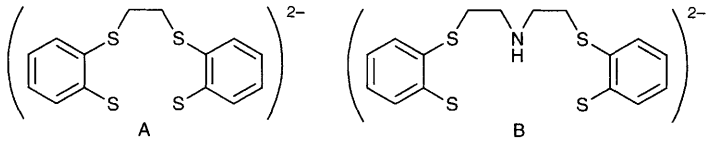

Figure 2 *The proligands* A^{2-} *and* B^{2-}

3.2 Ligands with Three-nitrogen Donor Sets

Two series of co-ligands used in syntheses of complexes that are able to react with and reduce dinitrogen feature bulky substituted amido groups. Cummins and co-workers have made [$Mo(NRAr)_3$] (R = *t*-butyl, Ar = 3,5-$Me_2C_6H_3$), a very crowded three-coordinate Mo^{III} compound that reacts with N_2 forming [$\{Mo(NRAr)_3\}_2(\mu\text{-}N_2)$] and ultimately [$MoN(NRAr)_3$].[16] Schrock and his colleagues have performed similar chemistry using trilithium salts of anions such as $([Me_3SiNCH_2CH_2]_3N)^{3-}$ $(NN_3)^{3-}$. This reacts with simple salts of V, Mo and Fe (among other metals) giving compounds in which the ligand binds in a

tetradentate manner, with an almost planar MN_3 set. The metal has three orbitals available to bind to one additional ligand; this facilitates the formation of a triple bond to ligands such as N_2 (for Mo and Fe) and the bulky trimethylsilyl group provides steric protection for transformations of these ligands.[17] Thus $[Mo(NN_3)Cl]$ is reduced in thf with Mg to $[\{Mo(NN_3)N{=}N\}_2Mg(thf)_2]$ and this reacts with $FeCl_2$ giving trigonal planar $[\{Mo(NN_3)(N{=}N)\}_3Fe]$.[18]

3.3 Ligands with Three-sulfur Donor Sets

Seeking to combine the geometry of a ligand that provides a trigonal environment at a single metal site with the presence of sulfur donor atoms to mimic as far as possible the coordination sphere of FeMoco, Power and co-workers synthesised an iron(II) complex anion $[Fe(SC_6H_2\text{-}2,4,6\text{-}Bu^t)_3]^-$ with very bulky sulfur ligands,[19] but its interaction with small molecules such as N_2 and CO was not reported. Other chemists have synthesised tripodal tetradentate ligands with the three arms terminating in thiolate rather than amine groups. For example Koch has used the ligands $(P[C_6H_4\text{-}2\text{-}S]_3)^{3-}$,[20] $(P[C_6H_3\text{-}2\text{-}S\text{-}3\text{-}Ph]_3)^{3-}$ [21] and $(N[CH_2C_6H_4\text{-}2\text{-}S]_3)^{3-}$ [22] to stabilise a series of complexes of iron and nickel in supporting ligands such as CO and CN, and George has made Fe^{IV} complexes using the ligand $(P[C_6H_3\text{-}2\text{-}S\text{-}3\text{-}Me_3Si]_3)^{3-}$.[23]

4 A Simple Tripodal Ligand

4.1 Introduction to the NS_3 Site

We have explored the chemistry of the simple tripodal ligand $(N[CH_2CH_2\text{-}S]_3)^{3-}$ $(NS_3)^{3-}$ with V, Mo and Fe, with respect to the binding of N_2, nitrogen species such as hydrazine, and other small molecules such as CO, CNMe, CN^- and NO. We have made this ligand on a large scale by adaptation of literature syntheses,[24] taking stringent safety precautions in handling the vesicant tris(chloroethylamine) hydrochloride. Our results are presented in the remainder of this review and illustrate the several different types of bonding exhibited in complexes of NS_3.

4.2 Vanadium and Molybdenum Complexes of NS_3

We have studied the reactions of $H_3(NS_3)$ with vanadium more thoroughly than those with any other metal,[25] starting from the known $[V(O)(NS_3)]$.[26] Figure 3 shows that the $V(NS_3)$ site will support imide, hydrazido, hydrazine, ammonia and nitride ligands, forming multiple bonds to nitrogen species that may be involved in the later stages of reduction of N_2. Several of these complexes are

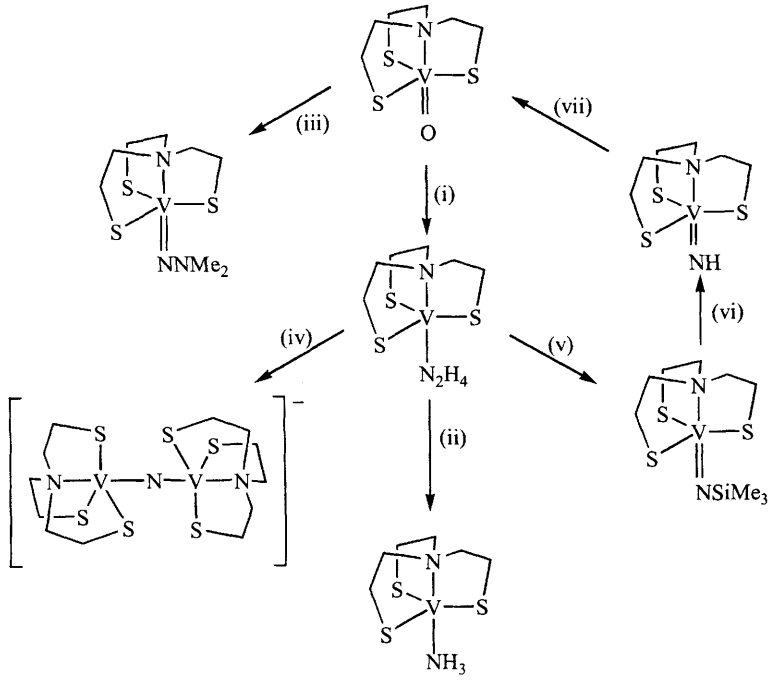

Figure 3 *Transformations of $V(NS_3)$ compounds. Reagents (i) N_2H_4; (ii) thf, 60 °C; (iii) $Me_3SiNHNMe_2$; (iv) NaN_3; (v) N_3SiMe_3; (vi) H_2O; (vii) $(NMe_4)OH$*

interconvertible. The site does not bind N_2, H_2 or CO in stable complexes, though we have evidence for the transient formation of an unstable dinuclear dinitrogen complex $[\{V(NS_3)\}_2(\mu\text{-}N_2)]$, formed in the initial stages of the reaction of $[V(O)(NS_3)]$ with hydrazine. It is noticeable that the $V(NN_3)$ site also does not bind N_2, despite the steric protection of the vanadium inside the pocket formed by the bulky substituents on the NN_3 ligands.

The compounds shown in Figure 3 have all been characterised crystallographically. The bridging nitride anion $[\{V(NS_3)\}_2(\mu\text{-}N)]^-$ features the first structurally characterised linear symmetrical V–N–V bridge.[27] There is no direct bonding between the two vanadium(IV) atoms. There are no compounds with a single-atom bridge between two metal atoms in NN_3 chemistry, where close approach of the $M(NN_3)$ sites is prevented by the bulky substituents on the NN_3 ligands.

We have made several other V^{III} complexes by displacing the hydrazine ligand in $[V(N_2H_4)(NS_3)]$ with Cl^-, N_3^-, CN^-, MeCN or $CNBu^t$, and have prepared a series of imido-complexes $[V(NAr)(NS_3)]$ (Ar = various substituted phenyl groups), and of hydrazido-complexes $[V(NNR^1R^2)(NS_3)]$ (R^1, R^2 = methyl or phenyl) from reactions of $[V(O)(NS_3)]$ with aryl isocyanates or 1,1-disubstituted hydrazines, respectively. Structural studies on several of these compounds always reveal trigonal bipyramidal coordination about the V atom. The V–N distance in the $V(NS_3)$ system, as a result of the shape of the NS_3, is sensitive to

the *trans*-influence of the other ligand. The range of compounds $[VZ(NS_3)]$ allows comparisons of *trans*-influence within two series of complexes, paramagnetic $[V^{III}Z^1(NS_3)]$ and diamagnetic $[V^{V}Z^2(NS_3)]$. For the first series, the V–N distances in the $M(NS_3)$ system *trans* to Z^1 give an order of *trans*-influence of $Cl^- > NH_3 > N_2H_4 >$ MeCN, and for the second series the order is $O > NSiMe_3 > NH > NC_6H_4Cl\text{-}4 > NNMe_2 = NNMePh$. The V–N distances in the latter are consistently higher than those in the former, reflecting the higher *trans* influence of the multiply bonded Z^2 ligands (despite the smaller ionic radius of V^V compared with that of V^{III}).

We have not studied the $Mo(NS_3)$ site as extensively as that of the vanadium analogue,[28] but it is evident that the pattern of reactivity of molybdenum with NS_3 is similar. Structurally characterised five-coordinate Mo^{IV} compounds, prepared starting from $[MoO_2(acac)_2]$ (acac = pentane-2,4-dionate), include $[Mo(NO)(NS_3)]$, $[Mo(NNR)(NS_3)]$, $[Mo(NNR_2)(NS_3)](BF_4)$ (R = Me or Ph) and $[\{Mo(NS_3)\}_2(\mu\text{-}S)]$ as a minor product. However, treatment of $[\{Mo(\mu\text{-}Br)Br(CO)_4\}_2]$ or of $[WI_2(CO)_3(MeCN)_2]$ with $H_3(NS_3)$ gives $[\{M^{IV}(NS_3)\}_2\{\mu\text{-}SCH_2CH_2N(CH_2CH_2SH)_2\text{-}S\}_2]$ (M = Mo or W), which feature two bridging diprotonated NS_3 ligands. Thus the NS_3 chemistry of both vanadium and molybdenum is characterised by multiple bonding between the metal and the ligand *trans* to the NS_3 ligand, and by the absence (so far) of any compounds in which the metal atom has an oxidation state lower than III.

4.3 Iron Chemistry of NS_3-Carbonyl, Nitrosyl and Isocyanide Complexes

Reaction of the very soluble $[Fe(acac)_3]$ with $(Et_4N)Cl$ and $H_3(NS_3)$ in MeCN gives $(Et_4N)[Fe(NS_3)Cl]$ (high-spin iron(III), S = 5/2). Unlike its vanadium counterpart, this is reduced (Figure 4) by sodium amalgam in MeCN, giving a yellow solution. This solution does not react with dinitrogen or with dihydrogen, but addition of CO gives the green $(Et_4N)[Fe(NS_3)(CO)]$, with ν(CO) at 1910 cm^{-1}. This is one of three five-coordinate iron(II) carbonyl compounds discovered recently; all have magnetic moments at 20°C characteristic of an S = 1 state.[29,30,21]

The $Fe(NS_3)$ site is the only one of the three $M(NS_3)$ sites that we have studied which appears to be capable of binding carbon monoxide. In order to understand better the characteristics of this binding, we have carried out quantum calculations on $[Fe(NS_3)Cl]^-$ and $[Fe(NS_3)(CO)]^-$, using density functional theory. The calculations correctly predict the ground states of the anions, give the ν(CO) of the carbonyl anion as 1926 cm^{-1} (close to the experimental value of 1910 cm^{-1}) and give good agreement between calculated and observed bond distances and angles in the $Fe(NS_3)$ system. They also predict the CO binding energy in the carbonyl anion to be -102 kJ mol^{-1}. We have carried out similar calculations on the hypothetical $[Fe(NS_3)(N_2)]^-$; these show that the ground state has S = 2, that ν(NN) is 2222 cm^{-1} and that the N_2 binding energy is -29 kJ mol^{-1}. The dinitrogen, unlike the carbonyl, is not a strong enough ligand

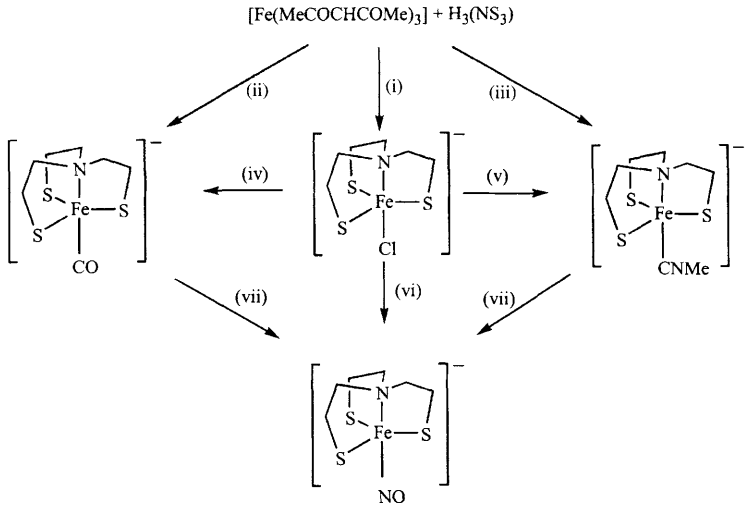

Figure 4 *Transformations of $Fe(NS_3)$ compounds. Reagents; (i) $(Et_4N)Cl$; (ii) $(Et_4N)OAc + CO$; (iii) $(Et_4N)OAc + CNMe$; (iv) $Na/Hg + CO$; (v) $Na/Hg + CNMe$; (vi) $Na/Hg + NO$; (vii) NO*

to enforce spin-pairing and the dinitrogen complex is too labile to be isolated. The results show that if the trigonal iron sites in FeMoco are similar to the $Fe(NS_3)$ site then CO binding at the former is entirely plausible, but that N_2 binding is, at best, transient.

$(Et_4N)[Fe(NS_3)(CO)]$ is also formed (Figure 4) if $[Fe(acac)_3]$ is treated with $H_3(NS_3)$ in presence of tetraethylammonium acetate under an atmosphere of carbon monoxide, when the excess of $H_3(NS_3)$ acts as a reducing agent. If the tetraethylammonium acetate is omitted, a complex of stoichiometry $Fe_3(NS_3)_2(CO)_2$ and structure $[Fe\{Fe(NS_3)(CO)\}_2\text{-}S,S']$ (Figure 5) with a linear trinuclear Fe_3S_4 core is isolated. The value of ν(CO) in the spectrum of this trinuclear compound is 1938 cm^{-1}. The following equilibrium holds in methanol, and can be demonstrated by the reversible uptake of CO.

$$3(Et_4N)[Fe(NS_3)(CO)] + 3HBF_4 \rightleftharpoons [Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2] + CO + 3(Et_4N)(BF_4) + H_3(NS_3)$$

We found that the anion $[Fe(NS_3)(CO)]^-$ can also be transformed into the trinuclear compound $[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ by condensation with $FeCl_2$. This prompted us to search for analogues with other metals and we have made $[Co\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ and D. J. Evans in our laboratory has made $[Ni\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$, by starting from $CoCl_2$ and $NiCl_2$ respectively; these have structures almost identical to that of the all-iron trimer. However, reactions of the iron carbonyl anion with $CuCl_2$, $ZnCl_2$ and VCl_3 produce only the all-iron trimer.

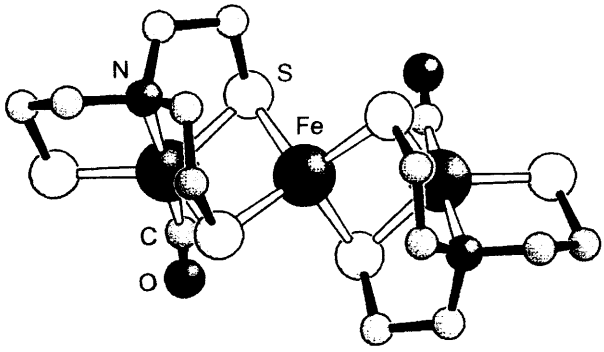

Figure 5 *Crystal structure of* $[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$

We have searched for interactions of the $Fe(NS_3)$ site with other small molecules able to function as alternative substrates for dinitrogen. In reactions which exactly parallelled those with carbon monoxide, we have obtained blue, mononuclear, terminal RNC complexes $(Et_4N)[Fe(NS_3)(CNR)]$ (R = Me, Bu^t or Cy) either by treatment of $[Fe(acac)_3]$ with RNC and $H_3(NS_3)$ in the presence of $(Et_4N)OAc$, or by reduction of $Et_4N[Fe(NS_3)Cl]$ in the presence of CNR.[31] They have NC stretching frequencies in the terminal range (2061–1940 cm^{-1}), values lower than those of the corresponding proligands (unlike in the case of the V^{III} compound $[V(NS_3)(CNBu^t)]$). By treating these isocyanide-containing anions with metal chlorides in MeCN we have made homo- and hetero-metallic cluster complexes $[M\{Fe(NS_3)(CNR)\text{-}S,S'\}_2]$ (M = Fe, Co, or Ni) with somewhat higher NC stretching frequencies than in the parent anions.

We have also prepared the nitrosyl compound $(Et_4N)[Fe(NS_3)(NO)]$ from the reaction of $[Fe(acac)_3]$ with $H_3(NS_3)$ in presence of Et_4NOAc and either NO gas or the NO source *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide.[32] The nitrosyl anion has ν(NO) at the relatively low frequency of 1621 cm^{-1}, a magnetic moment corresponding to a state S = 3/2 and a Fe–N–O angle of 154.4°. This nitrosyl anion also reacts with metal halides to make clusters $[M\{Fe(NS_3)(NO)\text{-}S,S'\}_2]$ (M = Fe, Co, or Ni), with rather higher values of ν(NO) than in the parent anion. The trinuclear carbonyl, isocyanide and nitrosyl complexes have subnormal magnetic moments at 20°C; variable-temperature magnetic measurements are underway.

We have been unable to isolate a complex with a simple monodentate cyanide ligand on the $Fe(NS_3)$ site but we have made an analogous complex of cobalt $(Et_4N)[Co(NS_3)(CN)]$ (ν(CN) 2100 cm^{-1}, spin S = 1) by the reaction of $[Co(acac)_3]$ with $(Et_4N)CN$ and $H_3(NS_3)$.[29]

The values of ν(CO) in our anionic (1910 cm^{-1}) and neutral (1938 cm^{-1}) carbonyls resemble those found (1906, 1936, 1958 and 1880 cm^{-1}) in the turnover reaction of FeMoco with CO,[11] reinforcing the idea that the central trigonally ligated iron atoms in FeMoco are those where CO binding occurs, and suggesting that such binding (even at low pressures of CO) is terminal rather

than bridging. Comparable IR data for CN^-, RNC and NO interactions with the enzyme are not yet available.

4.4 Models for Hydrogenases

In the trinuclear compounds with Fe_3S_4 clusters described above, two of the three sulfur atoms in each NS_3 ligand are used to make auxiliary bonds to the central metal atom. The individual ligation about each of the outer iron atoms is however still trigonal bipyramidal, but this is not true of all NS_3 compounds. Treatment (by D. J. Evans in our laboratory) of $(Et_4N)[Fe(NS_3)(CO)]$ under CO with $[NiCl_2(dppe)_2]$ (dppe = $Ph_2CH_2CH_2PPh_2$) gives the dinuclear complex $[\{Fe(NS_3)(CO)_2\text{-}S,S'\}NiCl(dppe)]$ in which the iron atom is octahedrally coordinated.[33] The core of this compound is dinuclear with nickel bound to iron by a bis(thiolate) bridge, and iron binding two CO molecules. This is as close a structural model as exists of the active site of the NiFe-hydrogenase from *Desulfovibrio gigas* which is a dinuclear thiolate-bridged nickel–iron complex in which the nickel atom is coordinated by four cysteinate-sulfur atoms, two of which bridge to a six-coordinate iron atom.[34] This hydrogenase model illustrates the use of metal–sulfur compounds in modelling cofactors of metal–sulfur enzymes other than nitrogenase, of which hydrogenases are outstanding examples. Related work by C. J. Pickett in our laboratory with the tridentate tripodal proligands $MeC(CH_2SH)_3$ and its monomethylated derivative $MeC(CH_2SH)_2(CH_2SMe)$ has led to modelling of the all-iron hydrogenase system.[35]

4.5 Dinuclear and Tetranuclear Iron-dinitrosyl Compounds

The possibility of sulfur bridging in our $Fe(NS_3)$ systems, together with the lack of steric protection of the metal atom afforded by bulky groups, makes isolation and study of complexes containing simple ligands on iron more difficult than when the $Fe(NN_3)$ site is used; on the other hand, these same properties give our complexes extra synthetic potential not available to $Fe(NN_3)$ systems. We have further exploited this synthetic potential using the iron dinitrosyl dimer $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$.[36] If this is treated with the anions $[Fe(NS_3)(L)]^-$ (L = CO, CNR or NO) described above, then semi-Roussin salts $[Fe(NO)_2\{Fe(NS_3)(L)\}\text{-}S,S']$, again with double-sulfur bridges, are formed. $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$ has also been treated with the yellow solution obtained from the reduction of the $[Fe(NS_3)Cl]^-$ anion (see above); this gives the tetranuclear $[\{Fe(NO)_2\text{-}\{Fe(NS_3)\}\text{-}S,S'\}_2S,S']$ (Figure 6) in which all the sulfur atoms of the NS_3 ligands form auxiliary bonds to other iron atoms. While these dinuclear and tetranuclear compounds are not obvious models for any metal–sulfur enzyme their further elaboration and the development of the use of the iron dinitrosyl iodide reagent present interesting synthetic challenges.

The NS_3 ligand thus displays different behaviour with iron from that with vanadium and molybdenum; this is largely dictated by the stability of the iron(II) oxidation state. The reactions of $H_3(NS_3)$ with iron compounds of very low

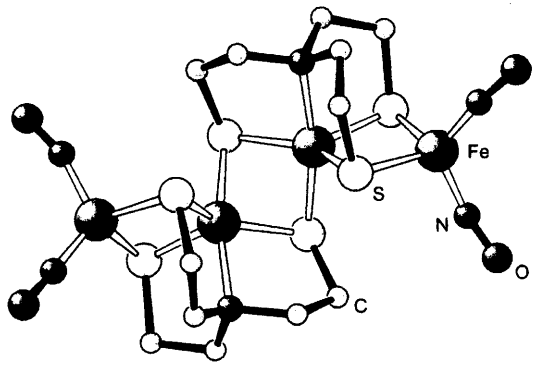

Figure 6 *Crystal structure of* $[Fe\{Fe(NO)_2\{Fe(NS_3)\}\text{-}S,S'\}_2S,S']$

oxidation state such as iron carbonyls have not yet been explored. Interesting chemistry may also be expected if one of the (CH_2CH_2SH) arms of $H_3(NS_3)$ is derivatised to make a mixed thiolate-thioether proligand such as $N(CH_2CH_2SH)_2\text{-}CH_2CH_2SMe$, similar to that in the all-iron hydrogenase model ligand described above.

5 Acknowledgements

I should like to thank my colleagues in the Unit, later the Nitrogen Fixation Laboratory, and now part of the Department of Biological Chemistry at the John Innes Centre in Norwich, who have helped me in this research and some of whose results I have presented here. Special thanks, in reverse order of age, go to Marcus Durrant, Dave Evans, Chris Pickett, David Hughes and Ray Richards.

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The Nature of Molybdenum and Tungsten Centres in Oxo-transfer Enzymes

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1 Introduction

In a perspective provided by structure of the Periodic Table, molybdenum and tungsten are distinct in being the only 4d- and 5d-transition metals that are required for the normal metabolism of biological systems. These metals play a vital role as the catalytic centres of a wide variety of enzymes.[1–3] Mo was first identified as an essential trace element in the 1930s, because of its role in nitrogen fixation;[4] this metal is now known to be the catalytic centre of over 50 enzymes. Evidence for the involvement of W in biological systems has been obtained only relatively recently, especially for enzymes of hyperthermophilic archea that thrive near 100 °C.[5]

There are (at least) two striking parallels between the nature and function of Mo and W centres in enzymes. First, the net effect of the catalysis effected by virtually all of these enzymes is the transfer of an oxygen atom to, or from, the substrate – with the metal undergoing a concomitant redox change from M^{VI} to M^{IV} or *vice versa* (1).

$$X + H_2O + M^{VI} \rightleftharpoons M^{IV} + 2H^+ + XO \quad (1)$$

Secondly, in each of the oxo-transfer enzymes, a single Mo or W atom is bound to one or two molecules of a special ligand, generally known as 'molybdopterin' (MPT).[6] This entity has been shown by a series of spectroscopic and degradative studies to be present in all of the Mo oxo-transfer enzymes. However, MPT was first structurally characterised by protein crystallography in a W enzyme, the aldehyde oxidoreductase from *Pyrococcus furiosus*.[7] Figure 1 shows the structure of MPT. It comprises a reduced pterin, fused to a pyran ring bearing a dithiolene group that chelates Mo or W.

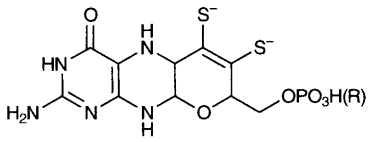

Figure 1 *Molybdopterin (MPT), one or two molecules of which ligate Mo (or W) in the Mo (or W) enzymes; the phosphate group may be bound to a nucleotide (R)*

Despite the above important common denominators, and the similar size and chemical properties of chemically equivalent W and Mo species,[8] important differences have evolved in the biological roles of these two metals. Two particular points highlight these differences: (i) the significance of these metals for nitrogen fixation; (ii) the prevalence of Mo over W as the catalytic centre of oxo-transfer enzymes.

(i) Protein crystallographic studies of the FeMo-protein of nitrogenase have identified Mo as an integral component of the Fe–Mo–S cluster that constitutes the catalytic centre.[9] Although the role that Mo plays in the catalytic process is not yet established, substitution of Mo by W leads to an inactive enzyme.[10] This difference is surprising because synthetic Fe–Mo–S and Fe–W–S clusters manifest quite similar chemical properties[11,12] and the elegant studies of Chatt *et al.*[13] clearly demonstrated the feasibility of reducing N_2 bound to a W^0 centre under ambient conditions.

(ii) Mo is a trace element that is required by *all* forms of life, from bacteria, through higher plants and animals to man,[1] whereas W has only been identified in a few primitive organisms.[2,3] Mo enzymes catalyse a wide variety of conversions, as illustrated in Figure 2, several of which are crucial to humans. Xanthine oxidase catalyses the oxidation of xanthine to uric acid and also oxidises a range of aromatic heterocycles and simple aldehydes.[14] Sulfite oxidases occur in animal and human livers and catalyse the oxidation of SO_3^{2-} to SO_4^{2-}, as the final step in the oxidative degradation of the sulfur-containing amino acids cysteine and methionine. Humans excrete *ca.* 1 g of SO_4^{2-} per day. Rare genetic deficiencies that lead to a lack of sulfite oxidase produce severe neurological abnormalities, mental retardation, and death in infancy.[15] Also, Mo is essential for both routes to fixed nitrogen in the biosphere: the nitrogenases that convert N_2 to NH_3 (see (i)) and the nitrate reductases that catalyse the first step in nitrogen assimilation, conver-

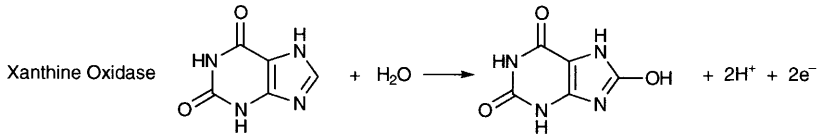

Figure 2 *Examples of reactions catalysed by Mo enzymes*

sion of NO_3^- to NO_2^- (prior to the reduction of NO_2^- to NH_3 by some nitrite reductases).[16]

In contrast to the Mo oxo-transfer enzymes, the majority of the W enzymes only catalyse aldehyde oxidation or its equivalent, *i.e.* oxygen atom transfer to a carbon,[2,3] with acetylene hydratase being a notable exception.[17] However, iso-enzymes, in which W is substituted for Mo – the metal normally incorporated by biology in these systems – have been identified[18–20] and these are extending the range of W oxo-transfer enzymes. Studies of the relative behaviours of these two metals at the same catalytic site are now beginning to reveal interesting differences in their kinetics and thermodynamics (see Section 3.2).

2 Nature of the Catalytic Centres of Mo and W Oxo-transfer Enzymes

2.1 Coordination of the Metal Atom

Several protein crystallographic investigations have been accomplished for Mo and W enzymes. The results of these structural studies have provided important details concerning the overall molecular architecture of the polypeptides involved and the nature and relative disposition of the corresponding reaction centres. Although proposed in advance of several of the protein crystallographic studies, the classification of the nature of Mo centres in oxo-transfer enzymes by Hille[1] (Figure 3) serves as a very useful, if still a provisional, means of subdividing this large group of enzymes.

Thus, in the oxidised forms of the enzymes:

- members of the xanthine oxidase family have one MPT group bound to a *fac*-$MoOS(H_2O)$ centre;
- members of the sulfite oxidase family involve one MPT group bound to a *cis*-MoO_2 unit;
- members of the DMSO reductase family possess two MPT groups bound to a *cis*-MoO(OSer) centre – this group of enzymes may also involve a Mo=S or a Mo=Se group in place of the Mo=O group and a Mo–SeCys group in place of the Mo–OSer group.

Several crystallographic studies of the Mo DMSO reductase (Mo-DMSOR) of *Rhodobacter capsulatus* and *Rhodobacter sphaeroides* have been accom-

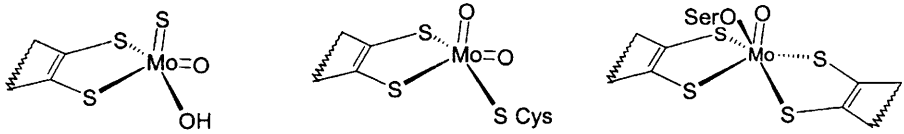

Figure 3 *Nature of the catalytic centres of some Mo enzymes*[1]

plished.[21–24] An important aspect of these structural studies has been a discussion concerning whether the oxidised enzyme has two or one 'oxo'-groups. The structure determination of *R. sphaeroides* DMSOR at 1.3 Å resolution[24] is significant in this context since it indicated that the enzyme, as crystallised, contains a disordered mixture of two types of Mo centre: one comprising a square pyramidal $[MoO_2(OSer)(MPT)]$ centre and the other a distorted trigonal prismatic $[MoO(OSer)(MPT)_2]$ centre. The present consensus favours the latter as the catalytic site.

The catalytic centres of W oxo-transfer enzymes appear to belong to the DMSOR family, as exemplified by the structure of the aldehyde oxidoreductase of *P. furiosus*.[7]

2.2 Function of the Metal Centre

The Mo centre of all of the Mo enzymes characterised to date is able to access the Mo^{VI}, Mo^{V}, and Mo^{IV} oxidation states. Spectroscopic studies of these enzymes, notably EPR investigations of the Mo^{V} state, have clearly demonstrated that the substrate interacts directly with the metal centre.[25] Bailey *et al.* have characterised the novel, pink form of DMSO reductase from *R. capsulatus*, produced by the addition of a large excess of DMS to the oxidised enzyme. This study revealed the presence of a complex with 'DMSO' bound to the Mo *via* its oxygen atom (Figure 4).[23] The oxidation state of the metal and the electronic structure of this centre have yet to be established. However, the clear implication of this structural investigation is that Mo-DMSOR catalyses the *direct* transfer of an oxygen atom from an Mo=O group to DMS. Microscopic reversibility means that the reduction of DMSO also involves direct transfer of an oxygen atom forming an Mo=O group. These conclusions are compatible with the observation that oxidation of the tertiary phosphine 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane by $DMS^{18}O$ mediated by *R. sphaeroides* DMSOR involves the transfer of ^{18}O from the sulfur to the phosphorus.[26] The presumption is that the reaction sequence is: $DMS^{18}O\text{–}Mo^{IV}$; $DMS\text{–}^{18}O\text{=}Mo^{VI}$; $R_3P\text{–}^{18}O\text{=}Mo^{VI}$; $R_3P\text{=}^{18}O\text{–}Mo^{IV}$.

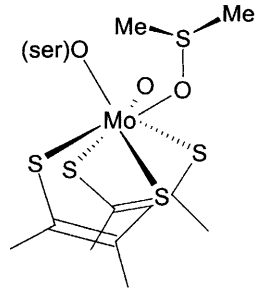

Figure 4 *The complex with 'DMSO' bound to the Mo* via *its oxygen atom at the heart of the DMSO reductase from* R. capsulatus[23]

The nature of the catalyses effected by Mo enzymes of the xanthine oxidase and sulfite oxidase families is not yet fully established, but it is clear that they do not function in the simple, direct, manner of the DMSO reductases.[1]

3 W-substituted DMSO Reductase

3.1 Production and Characterisation of W-DMSOR[20]

The periplasmic dimethylsulfoxide reductases (DMSORs) of the photosynthetic bacteria *R. capsulatus* and *R. sphaeroides* function in a respiratory chain with DMSO as the terminal electron acceptor and catalyse the environmentally important Reaction (2).[27,28]

$$DMSO + 2e^- + 2H^+ \rightleftharpoons DMS + H_2O \quad (2)$$

These enzymes have a high affinity for DMSO and will also catalyse the reduction of trimethylamine-*N*-oxide (TMAO) to trimethylamine (TMA).[29] The DMSORs are the simplest known Mo enzymes and are purified as monomers of molecular weight (M_r) *ca.* 85 000 Da that comprise a single polypeptide chain containing only one prosthetic group with an Mo atom bound to two pyranopterin guanine dinucleotides.

Stewart *et al.* have investigated whether the DMSOR of *R. capsulatus* is capable of utilising W in place of Mo.[20] Prior to this study, only limited comparisons between the nature and properties of a W enzyme and those of the corresponding Mo enzyme had been made.[18,19] Substitution of Mo by W was accomplished readily *via* natural uptake under $[WO_4]^{2-}$-rich, $[MoO_4]^{2-}$-depleted, conditions and W:Mo ratios of $> 99:1$ were produced. However, it is important and interesting to note that the presence of a low concentration (6 nM) of $Na_2[MoO_4]$ was essential for cell growth. In a separate experiment, involving a growth medium containing equal quantities of the two metals (3 μM $Na_2[MoO_4]$ plus 3 μM $Na_2[WO_4]$) the Mo:W ratio in the isolated DMSOR was *ca.* 1.5:1. Thus, the normal processes of metal uptake, delivery and/or incorporation lead to only a slight preference for Mo over W in the DMSOR of *R. capsulatus.*

In these investigations, the Mo- and W-grown cells were found to contain the same amount of DMSOR. This result is in contrast to that of Santini *et al.*, who observed that the amount of W-substituted TMAO reductase, produced from *E. coli* by genetic manipulation of the pathway for metal uptake, was *ca.* 15% of the level found with Mo.[30]

R. capsulatus W-DMSOR was obtained with the metal in the W^{VI} oxidation state.[20] Thus, the isolated enzyme exhibited no EPR signal and none could be induced by the addition of $K_3[Fe(CN)_6]$. However, an EPR signal, consistent with the presence of W^V, was obtained by incubation of the enzyme with dithionite for $\leqslant 10$ minutes; further such incubation extinguished the EPR signal, presumably because of the formation of W^{IV}. The nature of the super-hyperfine interaction observed in the EPR signal implies the presence of a

W^{V}–OH group and this appears to be the first identification of this moiety in a protein. The rhombicity, $[(g_1 - g_2)/(g_1 - g_3)]$, and the orientation of the W^{V} g-values were both very similar to those of the Mo^{V} 'high-g split' signal of Mo-DMSOR.[31] Also, the two EPR signals display a similar magnitude and orientation for metal–proton superhyperfine coupling tensors. Thus, the Mo^{V} and W(v) centres of *R. capsulatus* DMSOR appear to experience essentially the same ligand field. Furthermore, the UV–visible spectrum of oxidised W-DMSOR has a profile similar to that of its Mo counterpart,[23,27,28] with the λ_{max} values blue-shifted by *ca.* 150 nm (*i.e.* 3000–5000 cm^{-1}). The absorptions are considered to arise from ligand-to-metal charge-transfer transitions, from sulfur-based orbitals to a d^0 metal centre. Consistent with this view, the blue-shift observed is similar to that (*ca.* 4350 cm^{-1} from Mo to W) for the two lowest energy transitions of the $[MS_4]^{2-}$ (M = Mo or W) anions.[33] These spectrochemical differences indicate that W^{VI} is more difficult to reduce than Mo^{VI} (see Section 3.2), in this case by ligand-to-metal charge-transfer.

The structure of W-DMSOR from *R. capsulatus*[20] corresponds directly to the structure of the Mo-DMSOR isolated from this bacterium.[23] Thus, W-DMSOR comprises a single polypeptide chain that envelops the prosthetic group that comprises a WO(OSer) centre bound to two MPT groups, each covalently linked to a guanine dinucleotide (Figure 5). It is not clear whether there is a third oxygen atom bound to the W because of the possible ripples in the electron density in the vicinity of this heavy atom. However, the W L_{III}-edge EXAFS was satisfactorily interpreted by backscattering from two oxygen atoms, one at 1.76 Å (W=O) and another at 1.89 Å (W–OSer), plus a shell of four sulfur atoms at 2.44 Å from the metal.[20]

3.2 Assays of Mo- and W-DMSO Reductase Activity[20,37]

The activity of W-DMSOR has been measured, using procedures described

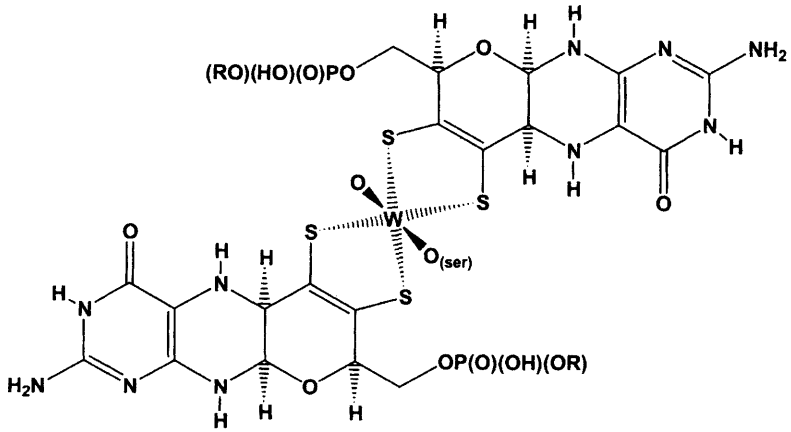

Figure 5 *Schematic representation of the nature of the metal centre of oxidised W-substituted DMSO reductase of* Rhodobacter capsulatus (*R = guanine dinucleotide*)[20]

previously for Mo-DMSOR.[34] With the dithionite-reduced dye, methyl viologen, as the electron donor, the steady-state rate of oxidation of the dye was found to be 52.8 ± 1.6 s^{-1} for Mo-DMSOR and 936 ± 20 s^{-1} for W-DMSOR. In the reverse assay, measuring the rate of DMS oxidation using 2,6-dichlorophenolindophenol (DCPIP) as the oxidant, the activities of Mo-DMSOR and W-DMSOR were found to be 8.5 ± 0.1 s^{-1} and $\leqslant 0.05$ s^{-1}, respectively. Thus, in these assays, W-DMSOR reduces DMSO some 17 times faster than the normal (Mo) enzyme but, in contrast to the behaviour of Mo-DMSOR, W-DMSOR displays no discernible ability to catalyse the oxidation of DMS.

^{1}H NMR spectroscopy provides a very convenient means of assaying the activity of enzymes in intact cells.[35,36] This technique has been used to monitor the rate of turnover of DMSO and the alternative substrate TMAO by DMSO reductase in *R. capsulatus* cells containing Mo-DMSOR or W-DMSOR.[37] In each experiment, the initial ^{1}H NMR spectrum was dominated by the DMSO (or TMAO) singlet, which decreased steadily in amplitude over time with a concomitant growth of the DMS (or TMA) signal. Plots of the concentration of substrate (or product) *vs.* time were essentially linear, indicating a zero-order process. The W-grown cells were found to reduce both DMSO and TMAO at *ca.* 9 and 22%, respectively, of the rate of Mo-grown cells. Nevertheless, these experiments showed that the W-grown cells are clearly capable of turnover, with either DMSO or TMAO acting as the terminal electron acceptor.

The lack of ability of the isolated W-DMSOR to catalyse the oxidation of DMS with DCPIP as the oxidant suggested that this enzyme might not be capable of physiological activity.[20] However, the ^{1}H NMR study of the performance of this enzyme in *R. capsulatus* cells[37] clearly demonstrated that W-DMSOR is physiologically competent. The apparent difference can be explained with reference to the relevant redox potential data. EPR potentiometric titrations[20] showed that the W^{VI}/W^{V} and W^{V}/W^{IV} couples of W-DMSOR have midpoint potentials of − 203 mV and − 105 mV (*vs.* SHE) with each potential being *ca.* 325 mV lower than that of the corresponding couple of Mo-DMSOR.[31] This difference defines the greater difficulty of reducing W^{VI} in the same enzyme environment as Mo^{VI} and rationalises why oxidised (isolated) Mo-DMSOR is reduced by DMS but oxidised (isolated) W-DMSOR is not. However, *in vivo*, the reduction of DMSOR by ubiquinol is mediated by the pentaheme *c*-type cytochrome DorC, with midpoint potentials of −34, −128, −184, −185, and −276 mV (*vs.* SHE).[38] Therefore, DorC is capable of reducing oxidised W-DMSOR, thereby allowing the protein to turnover inside a cell.

4 Chemistry Related to that of the Catalytic Centres of Mo and W Oxo-transfer Enzymes

4.1 Towards the Synthesis of Molybdopterin

A general strategy for the synthesis of asymmetrically substituted dithiolene ligands has been developed[39–41] (Figure 6), since MPT (Figure 1) is such an entity and virtually all dithiolene complexes previously investigated have involved symmetrical ligands. A wide range of Ar groups have been incorporated

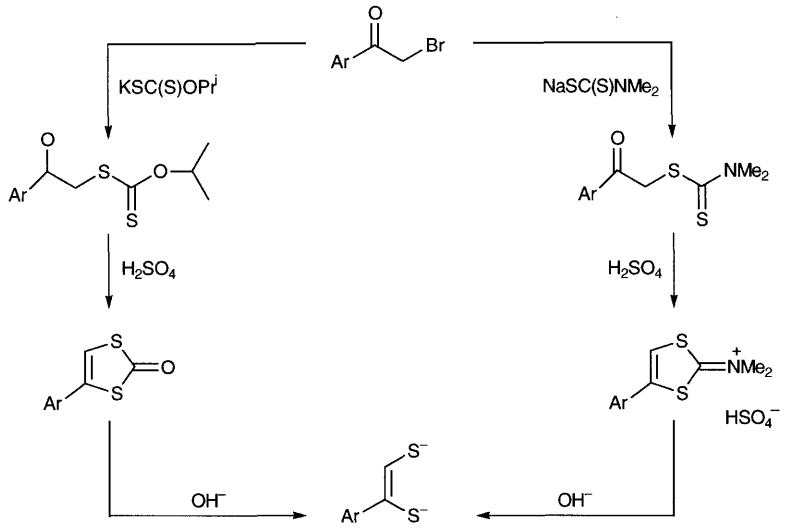

Figure 6 *General strategy for the synthesis of asymmetrically substituted dithiolenes*

into this synthetic procedure, including quinoxaline derivatives, in which the pyrazine ring has been reduced in a selective and controlled manner to produce a stereochemistry that matches that of the 'tetrahydro'-form present in the Mo and W oxo-transfer enzymes.[42] An important aspect of this strategy has been the formation of CpCo complexes to confirm the release of the dithiolene ligand from the proligand, *e.g.* Figure 7.[39,40,42] These investigations have been extended to substituted pteridine derivatives, involving substituents to ensure that the compounds were reasonably soluble in the organic reaction media employed.[43]

In addition to addressing directly the significant challenge presented by the synthesis of MPT using chemical procedures, these investigations are directed at improving the understanding of the role of MPT in the catalyses accomplished by the Mo and W oxo-transfer enzymes. One intriguing aspect is to consider a possible redox function for MPT. The protein crystallographic studies reported for Mo and W enzymes[7,20–24] indicate that the pyrazine ring is at a 'tetrahydro'-level. However, the presence of the fused pyran ring means that the level of oxidation of the pyrazine ring involved is actually equivalent to that of a dihydro-pyrazine. This consideration leads to the suggestion that the potential exists for a cooperation between the redox behaviour of Mo (or W) and that of MPT. Specifically, this would involve changing the oxidation level of the pyrazine ring by opening and closing the pyran ring (Figure 8).[44] This behaviour, when transmitted to the metal *via* the dithiolene group, could complement the redox changes of the metal that are required for the execution of catalysis.

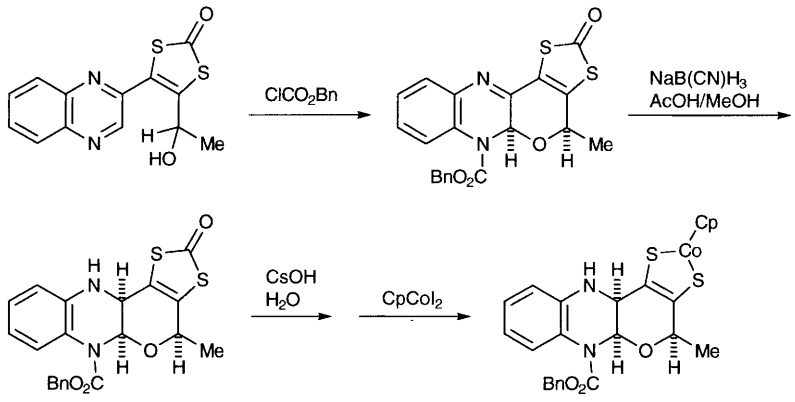

Figure 7 *Synthesis of a tricyclic compound, involving a CpCo centre bound to a dithiolene group substituted onto a tetrahydropyran ring*[42]

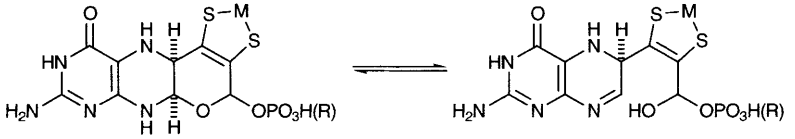

Figure 8 *Conversion of a 'tetrahydropterin' to a dihydro-state by opening of the pyran ring*[44]

4.2 Dithiolene Complexes

The general synthetic strategy that produces asymmetrically substituted dithiolenes (Figure 6) has been utilised to prepare a range of $[MO(dithiolene)_2]^{2-}$ (M = Mo or W) complexes (Figure 9).[45,46] The appropriate $K_4[MO_2(CN)_4]$ compound was employed as the starting material to prevent the synthesis of the tris(dithiolene) complex. Each of the $[MO(dithiolene)_2]^{2-}$ complexes has a square-pyramidal environment at the metal, as exemplified in Figure 10, and involves essentially identical dimensions for corresponding Mo and W systems (Table 1).

These complexes $[MO(sdt)_2]^{2-}$ (M = Mo or W) represent minimal structural analogues of the active sites of the Mo and W oxo-transfer enzymes of the DMSO reductase type (Figure 3). Furthermore, their redox properties show similarities to those of the Mo and W centres of the enzymes (Figure 11). Thus, each complex possesses a reversible $[MO(dithiolene)_2]^{-}/[MO(dithiolene)_2]^{2-}$ couple and the potential of each W^{V}/W^{IV} couple is *ca.* 225 mV lower than that of the equivalent Mo^{V}/Mo^{IV} couple; *cf.* the potential difference of *ca.* 325 mV observed for the Mo^{V}/Mo^{IV} and Mo^{VI}/Mo^{V} couples, with Mo > W, for the DMSO reductases of *R. capsulatus* (Section 3.2).[20] Also, these systems M^{IV} complexes are converted to their M^{VI} counterparts by oxygen-atom transfer from Me_3NO and the $[MO_2(dithiolene)_2]^{2-}$ complexes are reduced to the

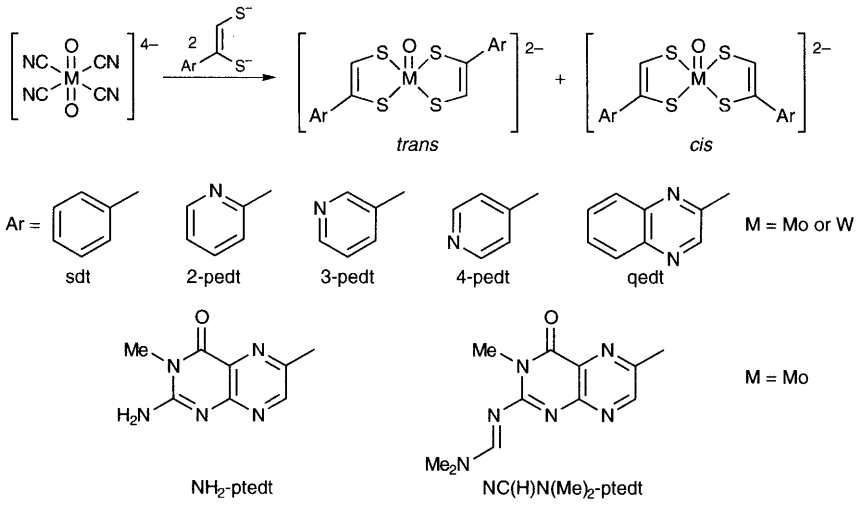

Figure 9 *Synthesis of* $[MO(dithiolene)_2]^{2-}$ *(M = Mo or W) complexes*[45,46]

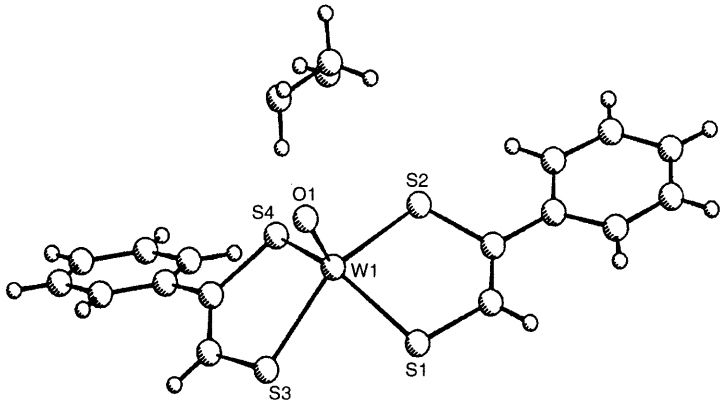

Figure 10 *Structure of the dianion in* $(PPh_4)_2[WO(sdt)_2].EtOH$ *(the nature of sdt is depicted in Figure 9); there is an H-bond between the W=O and EtOH groups*[46]

corresponding $[MO(dithiolene)_2]^{2-}$ by treatment with Ph_3P. The redox and spectroscopic properties of these systems are influenced by the nature of the substituent on the dithiolene group, implying electronic communication *via* the dithiolene group and that MPT could play a role in modulating the properties of the Mo or W centres of the oxo-transfer enzymes.

5 Conclusions

Based on the knowledge presently available, it is interesting to speculate on the different roles that have evolved for Mo and W in biological systems. A fundamental aspect is that, for an element to be involved in biology, it must be

Table 1 *A comparison of bond lengths (Å) and angles (°) for the* $[MO(sdt)_2]^{2-}$ *(M = Mo or W) anions in their* $(PPh_4)^+$ *salts.*[45,46] *There are no significant differences between the corresponding dimensions of the two anions*

	$[MoO(sdt)_2]^{2-}$	$[WO(sdt)_2]^{2-}$
M=O	1.700(5)	1.724(7)
M–S	2.366(2)–2.385(2)	2.362(3)–2.383(3)
C=C	1.325(9)–1.33(1)	1.32(2)
S–C	1.738(8)–1.774(7)	1.76(1)–1.79(1)
O–M–S	107.5(2)–110.7(2)	107.2(3)–110.5(3)
S–M–S	82.17(7)–86.92(7)	82.4(1)–87.2(1)

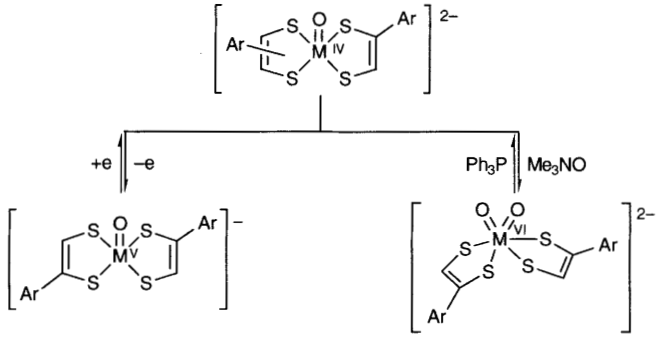

Figure 11 *Redox chemistry of complexes* $[MO(dithiolene)_2]^{2-}$ *(M=Mo or W)*[45,46]

available for incorporation. Starting from the premise that life evolved on this planet, it is relevant to observe that both Mo and W are present in the Earth's crust at a concentration of 1.5 ppm. Thus, both these elements are reasonably abundant, but less so than Cu (55 ppm), Zn (70 ppm) and Fe (50 000 ppm), metals that are widely employed in biology. Despite the extensive similarities between the chemistry of Mo and that of W, their geochemistry is quite different. Thus, Mo occurs in the Earth's crust primarily as molybdenite, MoS_2, whereas W occurs as scheelite, $CaWO_4$, and wolframite, (Fe, Mn)WO_4.[8]

Mo and W are generally taken up by organisms as the $[MO_4]^{2-}$ ion. Bacteria have efficient systems for $[MoO_4]^{2-}$ uptake and transport; the transport proteins bind these anions by a series of H-bonds to the polypeptide chain and the site is suitable for binding *both* $[MoO_4]^{2-}$ and $[WO_4]^{2-}$.[47] Therefore, the relative availability of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ will be an important factor in determining whether Mo or W is incorporated by an organism. Thus, *R. capsulatus* (Section 3.1) produces a physiologically competent enzyme with W replacing Mo under $[WO_4]^{2-}$-rich, $[MoO_4]^{2-}$-depleted conditions.[20,37] However, in a growth medium that contains an equal concentration of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$, *R. capsulatus* shows only a modest preference for incorporating Mo over W. One important caveat to emerge from this study was that a trace of Mo is required for cell growth;[20] the essential role that Mo is required to fulfil is

unknown, but it would appear that W is not capable of performing this function.

The significantly greater presence of Mo over W at the catalytic centre of enzymes can be understood by noting the relative concentrations of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ in seawater. Thus, $[MoO_4]^{2-}$ is present at the relatively high concentration of 1×10^{-2} mg dm^{-3}, *ca.* 100 × the concentration of $[WO_4]^{2-}$. Thus, when these metals are taken up from an aqueous medium where this concentration difference applies, $[MoO_4]^{2-}$ would be expected to be incorporated by an organism in preference to $[WO_4]^{2-}$. However, the 100-fold excess of $[MoO_4]^{2-}$ over $[WO_4]^{2-}$ in seawater has (probably) not always been the case. MoS_2 is insoluble in water and, therefore, it would appear that Mo was relatively unavailable for involvement in the early stages of evolution of life on Earth. However, in an oxidising atmosphere (*i.e.* post photosynthesis) MoS_2 is converted to $[MoO_4]^{2-}$ (3).

$$2MoS_2 + 7O_2 + 2H_2O \rightarrow 2[MoO_4]^{2-} + 4SO_2 + 4H^+ \qquad (3)$$

$[WO_4]^{2-}$, arising from the dissolution of oxide sources, has probably always been available in seawater.

These observations offer some rationalisation for the association of W with primitive organisms and the significantly greater involvement of Mo in biological systems currently observed. However, the differences in the chemical properties of Mo and W are likely to be important in determining the roles of these metals in biological systems. Given the similarities in the size of corresponding chemical systems of these two elements,[8] discrimination between them is likely to be achieved on the basis of redox potentials and/or bond strength considerations. Some such differences have emerged from the assays of the activity of Mo-DMSOR *vs.* W-DMSOR (Section 3.2). W-substituted *R. capsulatus* cells turn over at a *slower* rate than their Mo counterparts,[37] even though reduction of the substrate by the isolated enzymes proceeds at a significantly (*ca.* 17 times) *faster* rate for W-DMSOR than Mo-DMSOR.[20] Thus, for this system at least, reduction of the oxidised state (M^{VI}) to the reduced state (M^{IV}) would appear to contain the rate-determining step of the catalytic cycle employed by these enzymes (Figure 12). This latter aspect is consistent with the preference W > Mo for the VI oxidation state and the generalisation that W oxo-transfer enzymes catalyse reactions that have a low redox potential whereas Mo oxo-transfer enzymes operate at a higher redox potential.[1–3]

My involvement with this topic has spanned some thirty years. During this time, considerable progress has been made in the development of our understanding of the nature and function of the Mo and W oxo-transfer enzymes. However, many significant challenges remain and, to address these successfully, it will be necessary for the present pattern of interdisciplinary research to continue. Thus, geneticists, biologists, biochemists, chemists, and physicists need to maintain their synergic interactions that have long characterised this field. A major goal will be to define the coordination chemistry of the catalytic centres of these enzymes, to a standard that would be acceptable to Joseph Chatt – a formidable task!

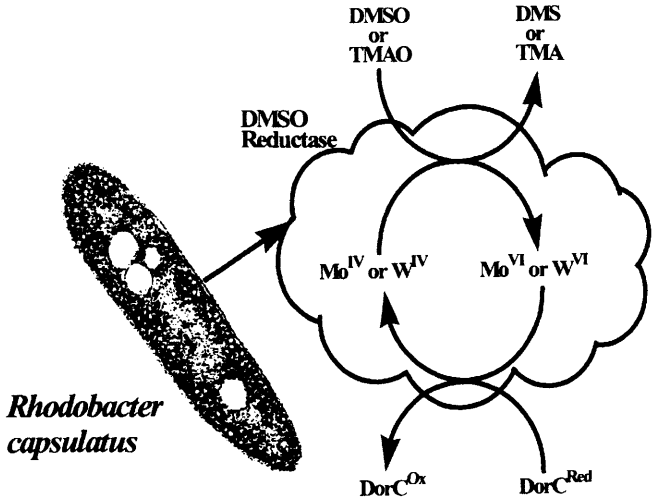

Figure 12 *Diagrammatic representation of the catalytic cycle of DMSO reductase in* Rhodobacter capsulatus, *with either Mo or W at the active site and DMSO or TMAO as the electron acceptor; reduction of the oxidized enzyme by ubiquinol is mediated by the pentaheme c-type cytochrome DorC*

6 Acknowledgements

I am very honoured by the award of the Joseph Chatt Medal and am pleased to be associated with this great scientist, who made so many significant contributions to coordination chemistry. In respect of the research described above, I wish to thank all of my colleagues who have made distinctive and important contributions. My interest and involvement with Mo and W chemistry has been sustained by stimulating collaborations of many friends, particularly David Collison, John Joule, Frank Mabbs (at Manchester), John Enemark (at Tucson) and Stephen Davies and Jon McMaster (at Nottingham). I gratefully acknowledge the important contributions to the research described in this article made by Professor Gareth Morris and Drs Elaine Armstrong, Michael Austerberry, Jacqui Birks, Ben Bradshaw, Stephen Boyde, Sue Bailey, John Charnock, Andrew Dinsmore, Arefa Docrat, Richard Ellis, David Rowe, Lisa Stewart and Clare Wilson.

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Iron–Imide Clusters and Nitrogenase: Abiological Chemistry of Biological Relevance?

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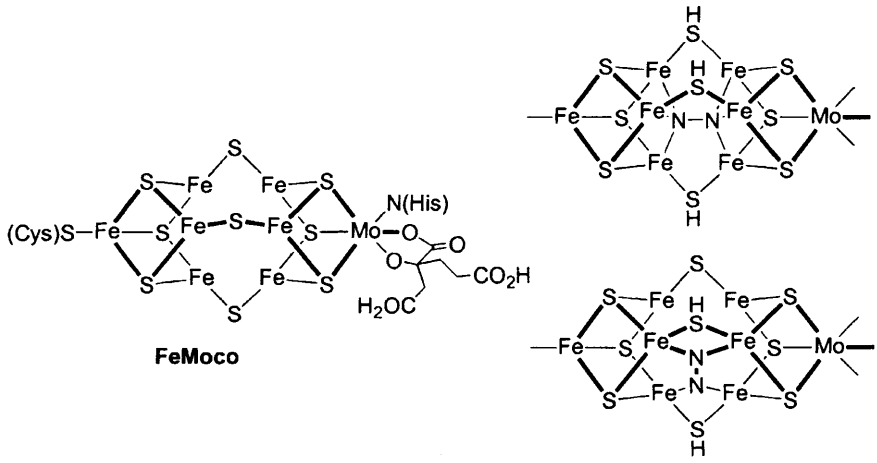
1 Nitrogenase: Problem and Approach

The biological reduction of dinitrogen to ammonia is accomplished by the nitrogenase enzymes through chemistry that, despite decades of study, continues to defy description at the atomic level.[1–5] The site of nitrogen reactivity within the enzyme is almost certainly an unusual iron–sulfur (Fe–S) cluster that can also contain a heterometal (either molybdenum or vanadium) depending on the enzyme variant. The Mo-containing enzymes are the best characterised, with macromolecular crystal structures of the Mo-nitrogenases providing the most detailed molecular visualisation to date of the catalytic metallocluster (the iron–molybdenum cofactor, FeMoco, Figure 1) in a resting state.[6–9]

The nitrogenase enzymes present formidable challenges to molecular understanding.[1–5] The enzyme cannot be studied in a poised 'ready' state; in the absence of dinitrogen substrate, protons from water are reduced to dihydrogen and the nature of the substrate-reducing form remains a mystery. Under turnover, the enzyme system undergoes a bewildering series of events: protein docking and release, electron transfer and storage, ATP hydrolysis, proton transfer and multisite substrate binding and release with the various enzyme states populated concurrently under experimental conditions; enzyme kinetics are therefore complex, and active enzyme intermediates (and inhibited forms) are generally ill-defined. FeMoco itself is structurally complex and unique in Fe–S chemistry; moreover, the resting state structure may not reflect important aspects of the reactive species. The cofactor cluster can be extracted intact from the



FeMoco

Figure 1 *Iron–molybdenum cofactor structures in resting (left) and hypothetical dinitrogen-bound states (right)*

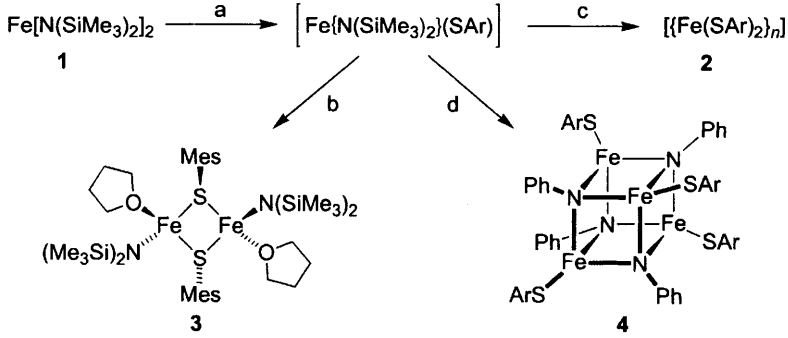
native protein, but in this condition shows only limited ligand substitution chemistry and no substrate reactivity.[10] Because of these (and other) constraints, oxidation state assignments for FeMoco remain contentious, the necessary reaction stoichiometry for substrate reduction is uncertain and the exact location of dinitrogen-binding is unknown.

The dearth of concrete molecular data has not discouraged mechanistic debate. The protein-derived FeMoco structure in particular has inspired speculation that dinitrogen is activated while bound as a bridging ligand to multiple iron centers (Figure 1).[7,11,12] This conjecture is drawn primarily from two observations: (1) the unusual structure of FeMoco, with six central iron sites that appear three-coordinate and anomalously unsaturated; and (2) the probable existence of an iron-only nitrogenase, indicating that the heterometal is unnecessary for dinitrogen activation. This hypothesis has been bolstered by computational models that also implicate dinitrogen interaction at the central iron positions, although the exact binding mode differs from study to study.[13–16] Experimental support for this proposal, however, is unavailable from either the enzyme system or from synthetic models.

We are investigating the fundamental cluster chemistry of the Fe–N bond to define possible interactions of iron and nitrogen during biological nitrogen fixation. Our strategy is loosely constrained; rather than seeking high-fidelity models, we focus instead on minimal complexes with key features congruent with those of the biological system. Thus, we have sought clusters of low-coordinate, weak-field/high-spin $Fe^{II/III}$ that incorporate nitrogen core ligands and/or mediate the multielectron reduction of N–N bonds. Through the study of these congruent complexes, we hope to establish chemistry equivalent to that which occurs, so far unobserved, in the natural system. Our initial progress using this approach is highlighted here.

2 Iron(II) Reduction of the N–N Bond

Hydrazine N–N bond reduction is a transformation that can lend insight into the final bond cleavage of nitrogen fixation. Under reducing conditions where hydrazines are neutral or protonated, simple iron–sulfur systems, including $[Fe_4S_4]$ cubanes, are unable to reduce the N–N bond, whereas heterometallic $[MFe_3S_4]$ cubanes (M = Mo or V) can.[17] This has led to the proposal that the final N–N bond reduction occurs at the molybdenum site in FeMoco.[17] However, the identities, and therefore protonation states, of various postulated intermediates during biological nitrogen fixation are unknown. A plausible alternative scenario could involve the multiple-bond reduction proceeding through anionic-forms of the partially reduced dinitrogen, for example, hydrazide(2−), with bond cleavage occurring prior to final protonation.



(a) 1 ArSH; (b) thf (Ar = mesityl); (c) 1 ArSH; (d) 0.5 PhN(H)–N(H)Ph

Scheme 1

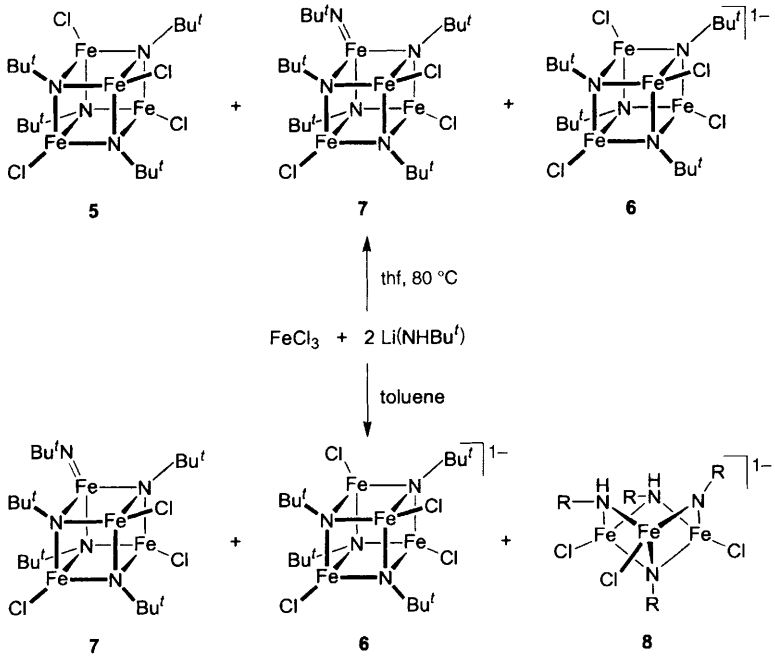
Our initial attempt to explore this possibility is outlined in Scheme 1.[18] Iron(II) bis(amide) precursor **1** serves as a synthetic starting point. The bis(trimethylsilyl)amide ligands perform two primary functions, providing steric control of the high-spin metal environment and acting as a strong latent base for protolytic metathesis chemistry; this last rôle allows incorporation of highly basic ligands such as hydrazide without the use of aggressive 'free' anions. Introduction of one equivalent of *ortho*-substituted aryl thiol allows the selective metathesis of amide for thiolate without disproportionation to bis(thiolate) **2** and starting bis(amide) **1**; the heteroleptic iron(II) dimer **3** can be isolated when this reaction is conducted in coordinating thf solvent. Addition of 0.5 equivalents of 1,2-diarylhydrazine to a solution of **3** results in the formation of the tetrameric imidoiron cluster **4** in good isolated yield. This cluster consists of four tetrahedral iron(III) centres, each terminally ligated by one thiolate and bridged through three μ_3-arylimide nitrogen atoms to form a heterocubane structure. Cluster **4** is paramagnetic with an S = 2 ground state; a high-spin iron(III) formulation for the tetrahedral iron sites was confirmed by Mössbauer measurement.

The formation of cubane **4** formally proceeds *via* the two-electron reduction of the hydrazine N–N bond coupled to concomitant one-electron oxidation of Fe^{II}

to Fe^{III} and cluster assembly. To our knowledge, this is the first example of a hydrazine cleavage mediated by Fe^{II}/Fe^{III} oxidation. With respect to proposed Fe-mediated nitrogenase mechanisms, this process offers a possible pathway for the final reduction of core-bound dinitrogen substrate prior to ammonia release, and therefore provides an opportunity to explore fundamental reaction chemistry of potential relevance to biological nitrogen fixation. The bridging core ligands in cluster **4** are readily accessible, the addition of free *p*-toluidine to **4** resulting in the rapid (minutes) exchange of core ligands with retention of cluster structure; in contrast, low-spin iron carbonyl imide clusters are essentially inert to the exchange of their imide bridges.[19] Detailed reactivity and mechanistic studies are in progress.

3 Iron–Imide Cluster Chemistry

The synthesis of the imidoiron cubane **4** and the possibility of cluster-bound imide ligands as intermediates during nitrogenase turnover has led us to a general exploration of weak-field iron–imide (Fe–NR) cluster chemistry. Our initial studies establish the existence of a rich reaction manifold that is readily accessible from simple iron(III) precursors.[20–22] A recent report from Fenske and co-workers describes additional synthetic routes to Fe–NR clusters,[23] further demonstrating the generality of the chemistry.



Scheme 2

Fe–NR clusters can be synthesised directly from anion metathesis reactions of iron(III) chloride and lithium *t*-butylamide, although reaction outcomes are complex and sensitive to minor changes in reaction conditions (Scheme 2). Thus, the reaction of $FeCl_3$ with two equivalents of $Li(NHBu^t)$ in thf at 80 °C results in the formation of three characterised species,[20] the major product being the reduced $1Fe^{II}/3Fe^{III}$ cubane **6**. Two neutral products are also isolated in limited yield, the all-iron(III) chloroimidocubane **5** and a C_{3v}, symmetric, site-differentiated cubane **7**. The latter cluster possesses three terminal chloride ligands and one terminal *t*-butylimide. (Figure 2). The terminal Fe=NR moiety is nearly linear (178.6(3)°) with an Fe–N distance (1.635(4) Å) characteristic of a multiple bond. The neutral cluster possesses formally an oxidized $3Fe^{III}/1Fe^{IV}$ core; zero-field Mössbauer analysis of polycrystalline material revealed a 3:1 ratio of valence-localised Fe^{III}/Fe^{IV} sites at −123 °C, firmly establishing the oxidation state assignment and therefore the presence of the terminal imide group in cluster **7**. This is the only example of a characterised terminal imide ligand on iron. In marked contrast to the well-studied, highly-reactive isoelectronic ferryl ($[Fe{=}O]^{2+}$) moiety, the terminal imide functionality in **7** is notable for surprising stability that probably arises from the steric shielding afforded by the *t*-butyl substituents; in addition, the potent nitrogen anion donors facilitate the stabilisation of high-oxidation state Fe^{IV}. Note that multiply-bonded metal–nitrogen groups (including the terminal metal–imide functionality) are essential intermediates in the classic Chatt nitrogen fixation cycle;[24] this pathway, formulated from studies of low-oxidation state mononuclear phosphine complexes of molybdenum and tungsten, represents yet another possible route for biological dinitrogen reduction.

When the self-assembly reaction is conducted in toluene, a different product distribution is obtained.[21] Neutral cluster products are still formed in low yields; however, terminal imide cluster **7** is now the predominant neutral species, with chlorocubane **5** virtually absent as judged by ^1H NMR spectroscopy. The

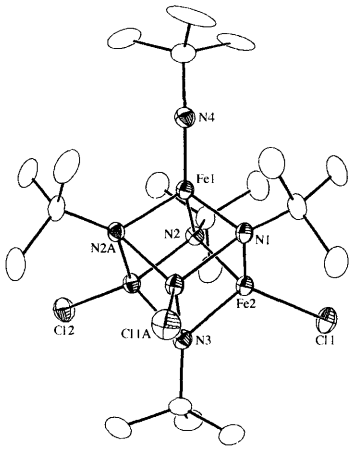


Figure 2 *The structure of* $[Fe_4(\mu_3\text{-}NBu^t)Cl_3]$, **7**

majority of the iron-containing reaction mass is divided equally between two anionic products, reduced cubane **6** and trinuclear cluster **8**. The structure of this new cluster is formally derived from cubane cluster **6** by removal of one iron(III) site (Figure 3); bond distances and nitrogen geometries reveal one μ-imide ligand, one μ_3-imide, and two μ-NR bridges protonated as amides. Although we do not yet understand the nature of the solvent effect on cluster formation, cluster **8** may be an intermediate in the assembly pathway of the cubane core.

We have also explored alternative synthetic routes to Fe–NR clusters using hindered iron(III) amide precursors and protolytic metathesis chemistry (Scheme 3).[22] Protolytic metathesis of the monomeric heteroleptic precursor **9** with one equivalent of *tert*-butylamine results in the self-assembly of neutral cubane **5** in modest (*ca.* 25%) yield. The equivalent reaction with aniline, however, produces more complex chemistry, with formation of the double cluster salt **10** and azobenzene. The cation structure in **10**, comprised of two facially bridged octahedral iron centres, has been reported previously as a diiron(II) monocation,[25] and we believe the same assignment is applicable here; the reduction to the iron(II) state is presumably linked to the oxidative coupling that generates azobenzene. This charge assignment dictates a 2− charge for the accompanying trinuclear cluster, which is formed from a linear array of edge-fused tetrahedral iron centres with μ-imide bridges. Formal oxidation states of $2Fe^{III}/1Fe^{IV}$ are required for the trinuclear dianion; we have isolated and structurally characterised the dilithium salt of this dianion (**11**, see below), providing support for the high oxidation state formulation.

The presence of lithium chloride alters the chemistry, presumably by coordination to intermediary species during cluster self-assembly. Thus, the addition of one equivalent of LiCl to **9** yields the chloride adduct **12**; further treatment with one equivalent of *t*-butylamine leads to neutral cubane **5**, but at a much reduced rate compared to the reaction without LiCl. The reaction with aniline is also retarded in the presence of LiCl, and the formation of azobenzene is significantly diminished. We have identified three products from this reaction

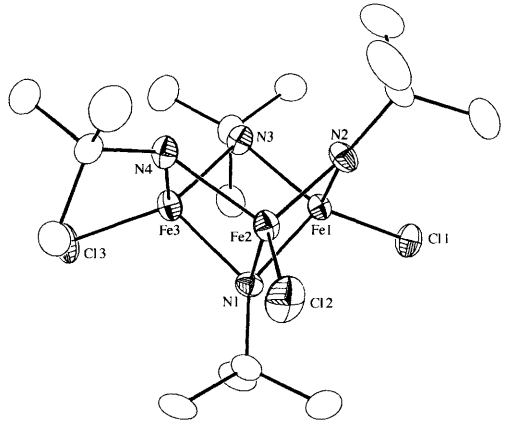
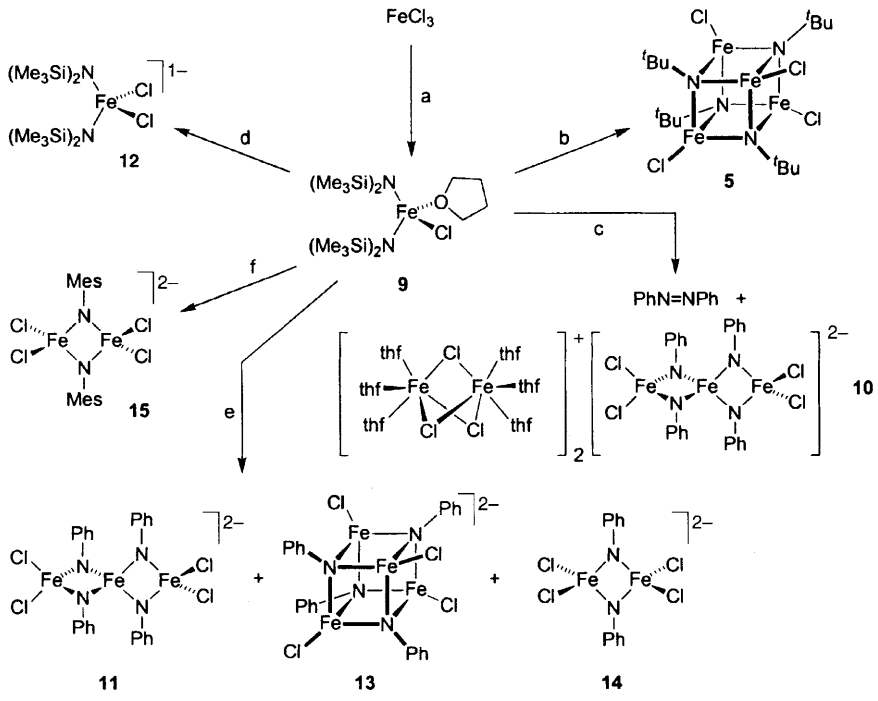


Figure 3 *The structure of* $[Fe_3(\mu\text{-}NHBu^t)_2(\mu\text{-}NBu^t)(\mu\text{-}NBu^t)Cl_3]^-$ **8**



(a) 2 Na[N(SiMe$_3$)$_2$]. thf; (b) 1 ^{t}BuNH$_2$, thf; (c) 1 PhNH$_2$, thf; (d) 1 LiCl, thf; (e) 1 LiCl, 1 PhNH$_2$, thf; (f) 1 LiCl, 1 MesNH$_2$, thf

Scheme 3

system, all of which are dianions: the linear trimeric cluster **11** noted previously; the phenylimidocubane **13**, with formal oxidation states of 2Fe^{II}/2Fe^{III}; and the dimer **14**, composed of edge-fused tetrahedral iron(III) centres bridged by imide ligands. The principal product of this reaction is diiron(III) **14**, which is consistent with the suppression of redox chemistry evident in the decreased azobenzene yield.

The nature of the imide substituent can also influence cluster assembly. For example, treatment of **9** with LiCl and mesidine (2,4,6-trimethylaniline, MesNH$_2$) leads cleanly to the synthesis of iron(III) dimer **15** in high yield without detectable formation of other clusters or of azomesitylene; the high selectivity in this case probably stems from the steric bulk of the aryl substituent which inhibits aggregation past the dimeric stage. In the absence of LiCl, the reaction with mesidine gives a complex product mixture including azomesitylene.

4 Analysis and Speculation

Our preliminary survey of Fe–NR cluster chemistry reveals strong parallels between imide and sulfide ligation on high-spin iron.[22] The dinuclear, trinuclear, and tetranuclear geometries found in imidoiron clusters all have structural counterparts in fundamental biologically-relevant Fe–S cluster motifs (Figure

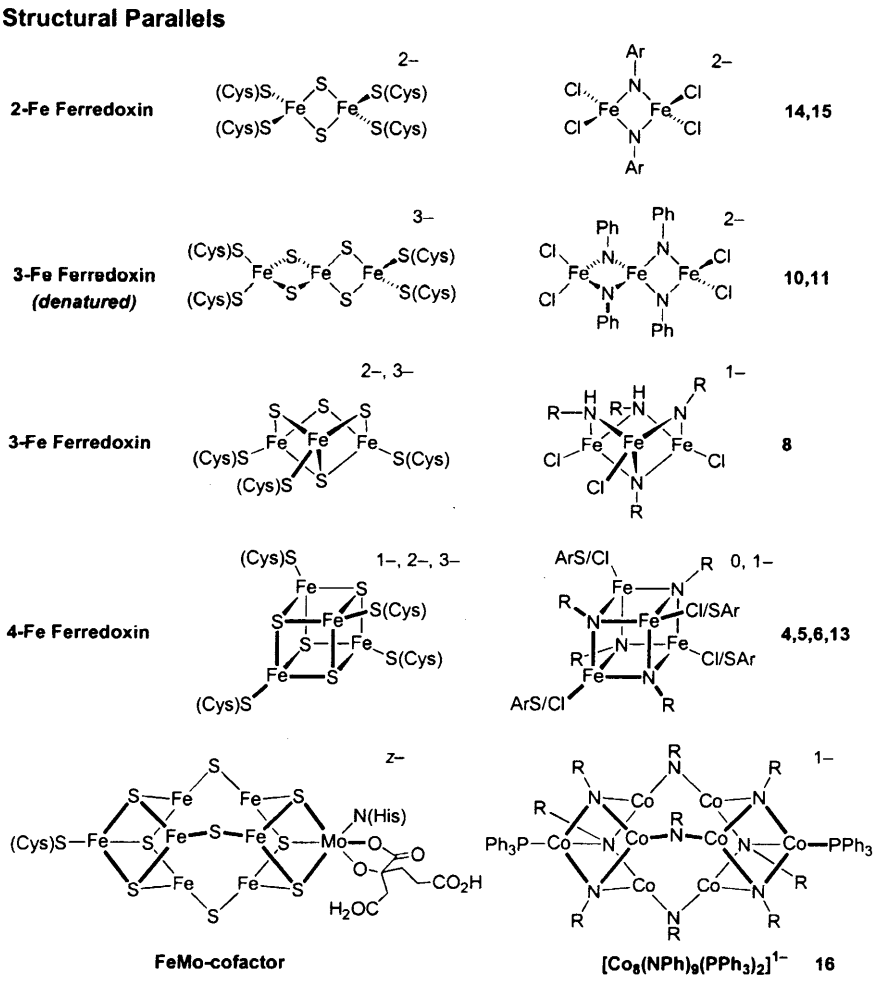


Figure 4 *Parallels between weak-field Fe–S and Fe(Co)–NR chemistry*

4).[26] The occurrence of protonated bridging amides in **8** may be analogous to the behaviour of three-iron ferredoxins that undergo protonation upon reduction, presumably at bridging sulfides.[27] The correspondence between Fe–NR and Fe–S chemistry extends to the redox activity of the core ligands, where the two-electron reduction of the N–N bond and the four-electron oxidative formation of the N=N bond are fully equivalent to sulfur-based half-reactions prevalent in

Fe–S chemistry (Figure 4, Equations 1–4).[28] Some differences are also evident, the most obvious being redox effects arising from the stronger donor ability of nitrogen anions; this is manifested in the generally higher mean oxidation states of Fe–NR clusters relative to their Fe–S analogues.

The relationship between imide and sulfide chemistry is reinforced by the imidocobalt cluster **16**, recently reported by Link and Fenske,[29] which is striking in its resemblance to FeMoco (Figure 4). For weak-field environments, metal–metal bonding and valence electron count are not thought to dictate cluster geometry; instead, properties such as oxidation state, ligand environment, and net charge are better indicators of structure. Thus, in weak-field metal–sulfur chemistry, Co^{II} is the prevalent oxidation state in tetrahedral geometries and structural homologues of Co–S and Fe–S clusters occur when mean oxidation states of II are approached.[22] Because of the parallel relationships between imide and sulfide, and between tetrahedral Co^{II} and Fe^{II}, we expect that an Fe–NR analogue of the FeMoco should exist as a predominantly iron(II) cluster; successful synthesis of this analogue cluster will advance our understanding of nitrogenase cofactor chemistry.

With respect to conjectured iron-mediated mechanisms of nitrogen fixation, our studies reveal the intrinsic chemistry of nitrogen anions in weak-field iron environments. High-spin, tetrahedral $Fe^{II/III}$ centres can mediate nitrogen redox chemistry at the N–N and N=N levels, and fully reduced, anionic nitrogen fragments are readily incorporated as accessible core ligands of clusters homologous to known Fe–S geometries. The possible convergence of this chemistry with equivalent, hypothetical events in nitrogenase offers an intriguing starting point for further inquiry.

5 Acknowledgements

I am grateful for the contributions of my co-workers whose names appear in the references. This work was made possible by the Beckman Foundation (Beckman Young Investigator Award) and the National Science Foundation (CAREER CHE-9984645).

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Determinants of the Reduction Potential in Rubredoxins, the Simplest Iron–Sulfur Electron-transfer Proteins

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1 Introduction

Professor Joseph Chatt guided one of us (AGW) during a postdoctoral period in 1970–71. As Director of the ARC Unit of Nitrogen Fixation, he emphasised the importance of connections across chemistry, biochemistry, microbiology and genetics. As a chemist, he taught that synthesis of simple species could illuminate the structure and reactivity of more complex systems and, in particular, the nitrogenase enzyme. His influence, and that of his associates Jeff Leigh and Ray Richards, upon the authors' approach to the chemistry of oxo-molybdenum centres has been outlined briefly.[1]

Recent developments in molecular genetics and chemical synthesis have brought a new sophistication to modelling of protein chemistry: *the biomolecule becomes its own model.* For example, variation of amino acid residues *via* site-directed mutagenesis allows variation of the ligands at a metal active site. Joe's eyes would have sparkled at the possibilities, especially that of rational design of synthetic proteins containing sites of desirable catalytic activity.[2,3] He would also have delighted in the continuing crucial role of experiment. For example, the nature of the blue copper centre is understood in exquisite detail[4] but attempts to construct an artificial blue copper site encountered a number of unanticipated experimental obstacles.[5] The resultant exploration indicated that the tetrahedral stereochemistry for Cu^{II} is achieved by destabilising the more favoured tetra-

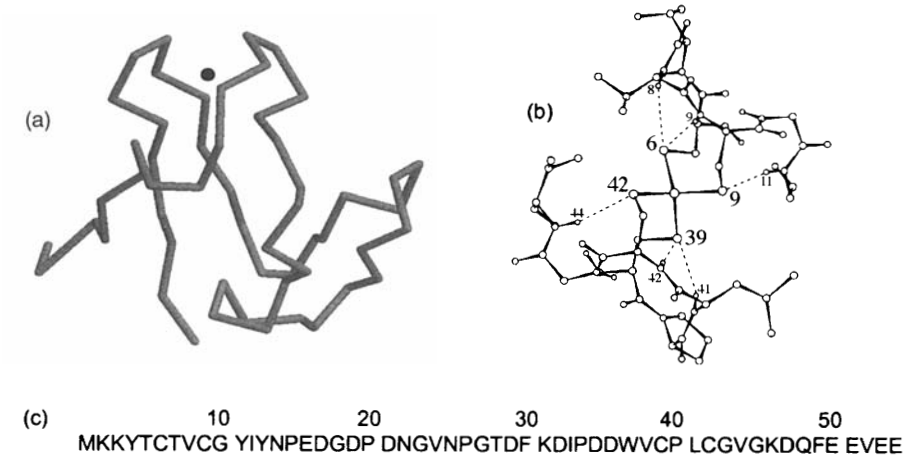

Figure 1 *Structural representations of the* Fe^{III}*-rubredoxin from* Clostridium pasteurianum.
(a) *Backbone (the Fe atom is represented by* •*). The pseudo-two-fold axis (see text) is in the plane of the page, passing though the Fe atom;* (b) *NH···S interactions* (- - - -) *around the* $Fe(S\text{–}Cys)_4$ *centre in Rd*Cp *(generated from the coordinates of pdb5rxn.ent in the Brookhaven Protein Databank). The pseudo-two-fold axis is now perpendicular to the page, passing though the Fe atom;* (c) *Amino acid sequence.*

gonal arrangement rather than by imposing peptide-induced 'strain'. Exclusion of solvent water is a key determinant.

A vigorous campaign is underway to understand the role of iron–sulfur proteins in all their beautiful structural manifestations.[6–8] The present contribution reviews factors that define the reduction potential of the simplest of the iron–sulfur electron transfer proteins, rubredoxin (Rd) which features an $Fe(S\text{–}Cys)_4$ site of tetrahedral geometry (Figure 1; residue numbering* is for Rd from *Clostridium pasteurianum*, Rd*Cp*, and the same numbering scheme for residues is applied to the other Rds discussed in the text). It has the advantages of being small ($\sim$6000 Da) and robust enough to endure substitution of both metal and ligands, as well as significant variation in the secondary coordination sphere.[9–13] This appears to be related to the presence of a hydrophobic core adjacent to the metal site plus 17 charged surface residues that ensure high solubility.

The structural parameters of the active site have been defined to good precision.[14–17] The active site forms a 'knuckle' sitting above the hydrophobic core of the protein (Figure 1(a)). The atoms of the β-loops of protein (residues 5–11, 38–44) which carry the cysteine ligands exhibit a *pseudo* two-fold symmetry which includes six NH···S interactions (Figure 1, (a) and (b)). The symmetry-related 'surface' ligands Cys9 and Cys42 are in a different environment from the

* For better readability, equivalent sequence positions for other Rds quoted in the text have been changed to those of Rd*Cp*

'interior' ligands Cys6 and Cys39. In addition, mutation at one residue, at its symmetry-related partner and, simultaneously, at both residues (the double mutant) provides *three* closely related mutant proteins for comparison with the native form.

2 Determinants of Reduction Potential

The reduction potential $E^{\circ\prime}$ of a protein active site P is defined by Equations (1)–(3). It is determined by its 'ionisation energy', IE, governed by electronic structure, and by its 'solvation energy', U, governed by reorganisation of the active site environment upon reduction [Equation (2)].[6]

$$P^x + ne^- \rightarrow P^{(x-n)} \tag{1}$$

$$\Delta G^{\circ\prime}{}_{rc} = -nFE^{\circ\prime} = \Delta H^{\circ\prime}{}_{rc} - T\Delta S^{\circ\prime}{}_{rc} \tag{2}$$

$$E^{\circ\prime} = IE + U \tag{3}$$

Note that Equations 2 and 3 each express $E^{\circ\prime}$ as a function of two variables. In general, both IE and U will contain enthalpic and entropic contributions.

Major determinants of IE are the geometry of the ligand field and the donor strength of the ligands that together determine the energy of the redox-active orbitals and define the effective nuclear charge, Z_{eff}. Low (negative) potentials would be expected for the Fe^{III}/Fe^{II} couples of tetrahedral alkyl thiolate complexes $[Fe(SR)_4]^{1-/2-}$ as the strongly electron-donating ligands preferentially stabilise the oxidised Fe^{III} state. However, their potentials are very low indeed (*e.g.* $[Fe(SEt)_4]^{1-/2-}$ in MeCN: $E^{\circ\prime}$, -1320 mV *versus* NHE).[18] This may be a consequence of strong spin polarisation in the d^5 configuration of the Fe^{III} form.[6]

The observed potentials of the native proteins of the family of simple rubredoxins in aqueous solution cover a range of about 140 mV: $+60$ to -80 mV *versus* NHE (Table 1). These are shifted positively by over one volt compared to the model complexes in MeCN solution. Decreased covalency in the Fe^{III}–S bonds of three Rds relative to the complex $[Fe\{o\text{-}C_6H_4(CH_2S)_2\}_2]^-$ was detected from the intensities of sulfur K-edge X-ray absorption spectra.[19] This is consistent with the presence of the six NH···S hydrogen bonds in the proteins (Figure 1(b)), lowering electron density on the ligands and causing an increase in Z_{eff}, IE and $E^{\circ\prime}$. However, differences in covalency among the three Rds examined did not follow the observed order of reduction potentials and it was concluded that the solvation energy term U also makes important contributions to the more positive potentials of the Rds.

A major contributor here is the low effective dielectric constant in protein sites ($\varepsilon \sim 5$–10 *versus* $\varepsilon \sim 38$ for MeCN and 80 for water) which reduces the difference in solvation energy between the oxidised and reduced states and increases $E^{\circ\prime}$. In addition, the geometry of the $Fe(S\text{–}Cys)_4$* site (including S–Fe–S bond angles) and the NH···S hydrogen bonding pattern is retained in all Rds that have been

* Formulations such as $Fe(S\text{–}Cys)_4$ are intended to imply direct bonds between iron and sulfur atoms of the cysteinyl residues and not from iron to sulfur and thence to cysteinyls.

Table 1 *Reduction potentials $E^{\circ\prime}$ for simple rubredoxins*[1]

Class	*Source*	$E^{\circ\prime}$, mV	*Ref.*
I (V44)	*Clostridium pasteurianum*	− 77, − 53	49, 53
	Chlorobium limicola[2]	− 61	54
	Butyribacterium methyltrophicum	− 40	55
	Heliobacillus mobilis	− 46	56
	Pyrococcus furiosus A44V	− 58	48
	Cp Pf chimeras[3]	− 46 to − 67	53
II (A44)	*Clostridium pasteurianum* V44A	− 24, + 31	49, 53
	Pyrococcus furiosus	0 to + 31	57, 58, 59
	Desulfovibrio vulgaris H[4]	0	50
	Desulfovibrio vulgaris M[5]	+ 5	60
	Desulfovibrio gigas	+ 6	61
	Megasphaera elsdenii	+ 23	62
	Cp Pf chimeras[3]	+ 63 to + 69	53

[1] *versus* NHE.
[2] f. sp. Thiosulfatophylum
[3] constructions of fused domains from *Clostridium pasteurianum* and *Pyrococcus furiosus*
[4] strain Hildenborough
[5] strain Miyazaki

characterised structurally. Consequently, the effects of changes in ligand geometry upon $E^{\circ\prime}$ would appear to be minimal, that is, the entatic state or rack mechanisms suggested for blue copper and other centres[4] do not appear to be relevant here.

The temperature-dependence of the potentials allows estimation of the contributions of the enthalpic ($-\Delta H^{\circ\prime}_{rc}/F = +170$ mV) and entropic ($T(\Delta S^{\circ\prime}_{rc}/F = -250$ mV) terms to $E^{\circ\prime}$ (Equation 2) for the Rd*Cp* couple.[21,22]

$$[Fe^{III}(S\text{–}Cys)_4]^- + e^- \rightarrow [Fe^{II}(S\text{–}Cys)_4]^{2-} \quad E^{\circ\prime} = -80(10)\,mV \qquad (4)$$

The enthalpy change $\Delta H^{\circ\prime}_{rc}$ is negative ($-\Delta H^{\circ\prime}_{rc}/F$ is positive), favouring the Fe^{II} oxidation state. The higher anionic charge of the $[Fe(S\text{–}Cys)_4]^{2-}$ centre seems to be compatible with the rather hydrophilic environment (including expected strengthening of the six NH···S hydrogen bonding interactions)[14] and solvent exposure of the two surface ligands Cys9 and Cys42 (Figure 1(b)). In addition, molecular dynamics calculations suggest that solvent access may be increased in the reduced state.[22] The entropy change is negative, favouring the Fe^{III} redox state. This will be determined by differences both in the flexibility of the protein chain and in the solvation properties between the two redox states.

The influence of the terms *IE* and *U* on the reduction potential for the 'simple' case of Rd (Equation 4) will now be assessed.

3 The Ionisation Energy Term, *IE*

Mutant forms of Rd*Cp* have been generated with the aim of replacing each of the four cysteine ligands, in turn, by serine.[23–25] These four proteins, C6S, C9S, C39S and C42S, would constitute four geometric isomers in which $FeOS_3$ centres are

orientated differently within the same protein chain. The total data confirm the presence of Fe^{III}–O–Ser bonds in the surface ligand mutants C9S and C42S and in the double mutant C9S/C42S.[21,25] The incorporation of the harder olate ligand[26,27] leads to large negative shifts of *ca.* − 200 and − 450 mV in $E^{\circ\prime}$ in the single and double mutants, respectively (Figure 2; Table 2). The protein has been converted from a weak reducing agent to a strong one. In addition, the potentials become dependent upon pH below characteristic pK_a values, interpreted as a consequence of protonation of the O–Ser ligands of the Fe^{II} centres. EXAFS data reveal an increase of 0.1–0.2 Å in the Fe–O bond length upon reduction. The data are consistent with the following couples ($x = 1$ or 2).

$$pH > pK_a: [Fe^{III}(S\text{–}Cys)_{4-x}(O\text{–}Ser)_x]^- + e^- = [Fe^{II}(S\text{–}Cys)_{4-x}(O\text{–}Ser)_x]^{2-} \quad (5)$$

$$pH < pK_a: [Fe^{III}(S\text{–}Cys)_{4-x}(O\text{–}Ser)_x]^- + H^+ + e^- = [Fe^{II}(S\text{–}Cys)_{4-x}(O\text{–}Ser)_{x-1}\{O(H)\text{–}Ser\}]^- \quad (6)$$

For pH values *above* the pK_a values, large increases in the reduction enthalpies are responsible for the dramatic lowering of $E^{\circ\prime}$ (Table 2). The new olate ligand is a stronger σ donor and decreases Z'_{eff}, stabilising the oxidised form. In addition, the structure of the Fe^{III}–C42S protein indicates that the smaller size of oxygen relative to sulfur leads to closer packing of atoms in the local surface region

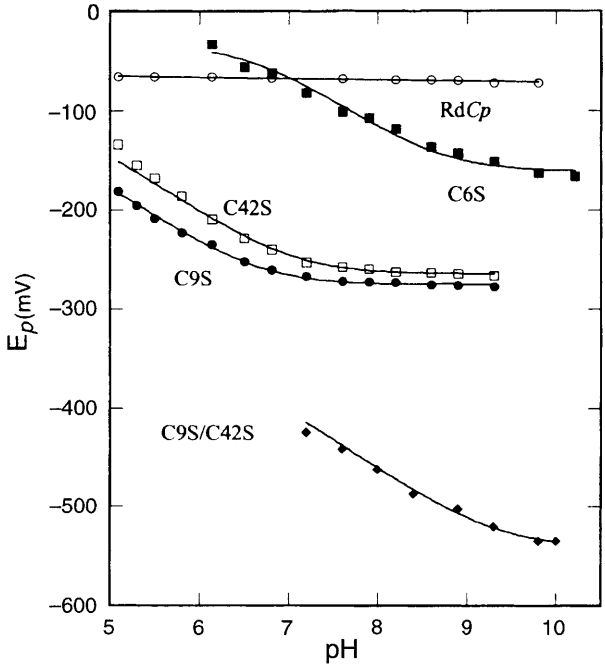

Figure 2 *Variation of peak potential* E_p *with pH for Rd*Cp *mutant proteins. Reproduced with permission of the publishers and authors of ref. 21*

Table 2 *Changes in the reduction thermodynamics of Rd*Cp *on Cys to Ser substitution*[a,b]

pH	*Mutant*	pK_a	$\Delta(-\Delta H^{\circ\prime}_{rc}/F)$[c] (*mV*)	$\Delta T(\Delta S^{\circ\prime}_{rc}/F)$[c] (*mV*)	$\Delta E^{\circ\prime}$[b] $(E^{\circ\prime}_{mut} - E^{\circ\prime}_{wt})$ (*mV*)
Above pK_a					
10	C6S	9	− 80	− 5	− 85
	C39S		(− 185)	(+ 80)	(− 105)
8	C9S	7	− 220	+ 10	− 210
	C42S	7	− 225	+ 35	− 190
10	C9S/C42S	$\geqslant$ 9.3	− 540	+ 85	− 455
Below pK_a					
8	C6S	9	+ 130	− 170	− 40
	C39S		(− 150)	(+ 70)	(− 80)
6	C9S	7	− 230	+ 60	− 170
	C42S	7	− 225	+ 105	− 120
8	C9S/C42S	$\geqslant$ 9.3	− 640	+ 250	− 390

[a] From ref. 21

[b] The data are relative to those of the recombinant form, averaged in the range pH 6–10

[c] Enthalpic and entropic contributions to $\Delta E^{\circ\prime}$ (see Equation 2). Differences of $\geqslant$ 50 mV are considered to be significant

around position 42, a closer approach of the polar peptide chain to the iron centre and loss of the NH···S-42 hydrogen bond.[25] This would modify interactions at the metal–protein interface (see below). The magnitude of the enthalpic contribution to $\Delta E^{\circ\prime}$ for the double surface mutant C9S/C42S is more than twice that for the single surface mutants, consistent with the presence of two O–Ser ligands. In contrast, the entropic contributions to $\Delta E^{\circ\prime}$ are minor in each mutant protein.

Relative changes at pH values *below* the pK_a^{red} of the single mutant proteins C9S and C42S show that the observed positive shifts in $E^{\circ\prime}$ from the pH dependence (Figure 2) are entirely due to increases in the entropic term $T(\Delta S^{\circ\prime}_{rc}/F)$. Structural changes induced by protonation of the Ser ligand appear to drive this change.

The environments of the interior ligands Cys6 and Cys39 differ from those of the surface ligands Cys9 and Cys42 (Figure 1). They are involved with two NH···S hydrogen bonds and are adjacent to the hydrophobic core of the protein. The C6S and C39S mutant proteins exhibit negative shifts in $E^{\circ\prime}$ which are only about one half of those seen for the surface single mutants (Table 2). The other properties of C39S are similar to those of the latter proteins and the primary reason for the difference in $E^{\circ\prime}$ appears to be a longer Fe–(O–Ser) link (about 0.03 Å) lessening the olate ligand donor strength in C39S.[25] A possible reason for the lengthening is that the protein chain carrying residue 39 may have lower conformational freedom as it is adjacent to the aromatic core of the protein.[14,15] However, two NH···S–Cys hydrogen bonds have been lost (as opposed to one for the surface ligand mutants, Figure 1(b)) and these are known to influence metal–ligand bond lengths.[28]

The thermodynamic parameters of the C6S protein below its $pK_a \sim 9$ are unique for Rd systems: a large positive $\Delta(-\Delta H^{\circ\prime}_{rc}/F)$ value is coupled to a large negative $\Delta(T\Delta S^{\circ\prime}_{rc}/F)$ value (Table 2). While the resonance Raman spectra of the C6S and C39S proteins are very similar, indicating the presence of a similar $Fe^{III}S_3O$ centre in each protein, a ν(Fe–OH) vibration of a Fe–OH_x ($x = 1$ or 2) fragment was detected at 617 cm^{-1} for C6S but not for C39S.[21] The weakness of a longer Fe^{III}–O(Ser) bond in C6S has led to its hydrolysis and the presence of a $[Fe^{III}(S\text{-}Cys)_3(OH)]^-$ centre and an unligated HO-Ser-6 residue.

The observed reversible electrochemistry and its pH dependence (Figure 2) may then be interpreted by the processes shown in Equations 7 and 8.

$$pH > pK_a: [Fe^{III}(S\text{–}Cys)_3(OH)]^- + e^- = [Fe^{II}(S\text{–}Cys)_3(OH)]^{2-} \quad (7)$$

$$pH < pK_a: [Fe^{III}(S\text{–}Cys)_3(OH)]^- + H^+ + e^- = [Fe^{II}(S\text{–}Cys)_3(OH)_2]^- \quad (8)$$

The more positive reduction potential for C6S relative to those of C9S and C42S is then attributable to the presence of a less-electron-donating HO^- ligand relative to Ser-O^-.

A more subtle approach to assess the influence of electronic factors on $E^{\circ\prime}$ addresses the conserved residue Tyr11 which is adjacent to the Fe(S–Cys)$_4$ site (Figure 3).[29,30] Its *p*-hydroxyl group is exposed to the solvent indicating that its substitution will have a minimal impact on protein structure. Substitution of -OH with -H, -F, -NO_2 and -CN in this position in Rd from *Pyrococcus furiosus* induced a 30 mV ($\sim$3 kJ) range in $E^{\circ\prime}$ and a correlation of 3 kJ per σ_p unit with the Hammett parameter for electron donation.[29] More electron-withdrawing groups on the ring induced more positive potentials (-NO_2, -CN) while more electron-donating groups induced more negative potentials (-H, -F, -OH). The possible interactions responsible for the modulation are remote from the substitution site. They are proposed to be either (a) an electrostatic interaction between the positively charged perimeter of the aromatic ring and the negatively charged ligand sulfur atom of Cys or (b) a perturbation of the 11-NH···S–Cys9 hydrogen bond (Figures 1 and 3).

4 The Solvation Energy Term, *U*

The effects upon $E^{\circ\prime}$ of the mutations discussed in the previous section were interpreted as consequences of changes primarily in the ionisation energy term *IE* of Equation 3. Similar assumptions are made in many literature discussions. The influence of the solvation energy term *U* is much more difficult to assess as it is determined by the reorganisation of the active site environment *upon reduction.* However, very few proteins have been characterised structurally in *both* oxidation states. Consequently, discussions of *U* must remain speculative. In the present case, we will proceed by assuming that, for each Fe(S–Cys)$_4$ site in the simple Rd proteins (Table 1), the background dielectric constant is the same and the intrinsic properties of the Fe–S bonds are the same. Then, differences in $E^{\circ\prime}$ due to U (Equation 3) can be attributed to differences in specific charge interactions in the vicinity of the active site as a result of varying amino acid sequence.

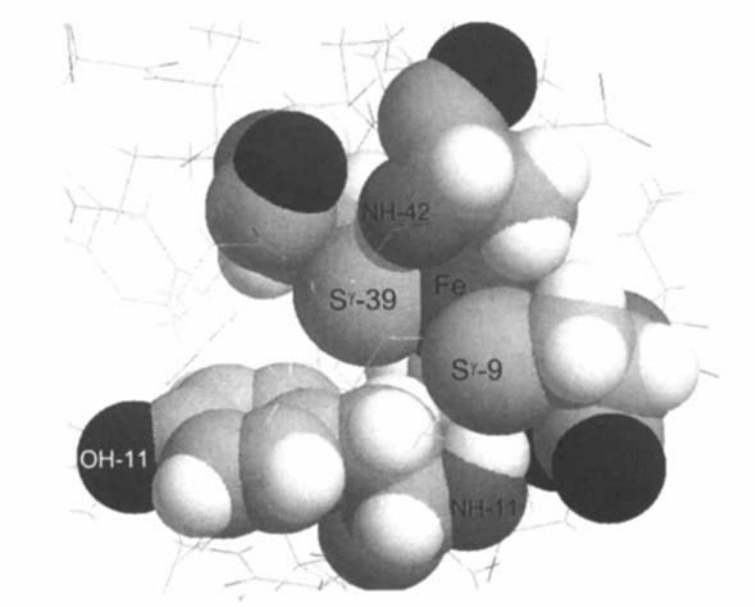

Figure 3 *Environment of the Tyr11 side-chain in rubredoxin*

Under this imperfect assumption, these interactions will be mono- or di-polar in nature and are listed below.

(1) Proximity of charged residues,
(2) proximity and orientation of dipoles (including NH···S hydrogen bonds),
(3) solvent access.

The challenge then is to devise experiments that will allow individual assessment of these factors, especially as they are interdependent and the potentials are very sensitive to small perturbations. The results of experiments designed to test factors (1)–(3) above will now be addressed in turn.

4.1 Proximity of Charged Residues

The high solubility of Rd*Cp* follows from its anionic charge of 9 units at pH 7. The amino acid sequence contains 13 carboxylate (Asp, Glu) and four ammonium (Lys) residues (Figure 1(c))[11] and their positioning relative to the active site must be assessed. The localised charges of these residues are all confined to the surface of the protein: none is buried in the interior. In addition, the surface adjacent to the $Fe^{III}(S\text{–}Cys)_4$ unit is, in fact, hydrophobic and the closest charged residues are Lys46 and Glu47 whose N^{ε} and O^{δ} atoms are, respectively, 8.0 and 7.7 Å from the S^{γ} ligand atom of Cys6. Such weak electrostatic effects could help tune the site to the observed $E^{\circ\prime}$ (Equation 4).

Altered surface charges influence $E^{\circ\prime}$ in some proteins and not in others. This appears to be related both to the distance of the charge from the active site and to the influence of solvating water in masking the effects of the charge.[7,31–34] For

example, changes in surface negative charge by up to five units did not significantly influence the reduction potential of an 8Fe–8S ferredoxin.[35]

Two alkyl side chains Val8 and Leu41 form part of the surface close to the $Fe(S\text{–}Cys)_4$ site of Rd*Cp* (Figure 1(b)). The influence of surface charge has been assessed by substituting these neutral residues with positively charged Arg and negatively charged Asp.[36] The potentials of the mutant proteins V8R and L41R showed increases of 40 and 58 mV, respectively, as expected if the positive charge stabilises the reduced $[Fe^{II}(S\text{–}Cys)_4]^{2-}$ member of the couple at distances of 7.0–8.5 Å. In addition, the effects were approximately additive as the shift for the double mutant V8R/L41R was +85 mV. However, the mutant proteins with negative charges in these positions, V8D and L41D *also* showed positive shifts and the conclusion was that the proximity of these charges alone could not be used to rationalise the observations. It was suggested that each mutation had induced an increase in effective access by the polar solvent water. Increased polarity would stabilise preferentially the reduced form with its higher anionic charge (see Section 4.3 below), assuming that the different charges on the side-chains were masked by solvation.

4.2 Proximity and Orientation of Dipoles (Including NH···S Hydrogen Bonds)

The idea that these dipolar interactions were important in tuning $E^{\circ\prime}$ values in proteins originated with Carter. He suggested that the differing numbers of backbone peptide NH···S hydrogen bonds determined which $Fe_4S_4(S\text{–}Cys)_4$ couple was employed by reductant ferredoxins ($[Fe_4S_4(S\text{–}Cys)_4]^{2-/3-}$) or by oxidant HiPIPs ($[Fe_4S_4(S\text{–}Cys)_4]^{1-/2-}$).[37] Spectroscopic support was supplied by Sanders-Loehr who also pointed out the hydrophobic nature of the HiPIP sites (Section 4.3 below).[38] Warshel and Stephens have laid emphasis on the number and orientations of backbone peptide amides surrounding active sites.[39,40]

Low and Hill have synthesised two backbone engineered analogues of the HiPIP from *Rhodocyclus tenuis*.[41] A peptide amide link is replaced by an ester, thereby removing an NH···S–Cys hydrogen bond to the $Fe_4S_4(S\text{–}Cys)_4$ cluster with apparently minor structural implications. The [O]-Val42 and [O]-Ala57 proteins showed negative shifts of −86 and −126 mV, respectively, consistent with the less polar environment favouring the oxidised state $[Fe_4S_4(S\text{–}Cys)_4]^{-}$ of lower anionic charge. In related work, the S79P mutant of the HiPIP from *Chromatium vinosum* was designed to reduce the partial positive charge on 79-NH, involved in one of the NH···S hydrogen bonds to the cluster.[42] NMR spectroscopy indicated that the overall protein folding and electron distribution in the cluster is little affected in the S79P mutant. $E^{\circ\prime}$ was again shifted negatively (−104 mV). Similar effects have been seen in other FeS systems and in model compounds.[43,44]

Careful structural monitoring is necessary when exploring the influence of mutations aimed to vary backbone peptide orientation. The amide groups near

the $Fe_4S_4(S\text{–}Cys)_4$ cluster were varied in ferredoxin I of *Azotobacter vinelandii*.[45] The P21G mutation alters the orientation of backbone amide relative to the cluster and $E^{\circ\prime}$ increased by 42 mV. The I40Q mutation inserts a new amide group near the cluster and $E^{\circ\prime}$ increased by 53 mV. Both results indicate a sensitivity of $E^{\circ\prime}$ to the proximity of amide dipoles and are consistent with theoretical predictions of contributions to enthalpy changes favouring the reduced form of the $[Fe_4S_4(S\text{–}Cys)_4]^{2-/3-}$ couple.

Two glycine residues adjacent to the cysteine ligands at positions 10 and 43 are conserved in all rubredoxins, consistent with the proposal that a β carbon substituent at these positions would eclipse adjacent peptide carbonyl groups and prevent formation of the 11-NH···S^{γ}-9 and 44-NH···S^{γ}-42 hydrogen bonds (Figure 1(b)).[46] Incorporation of valine at G10 causes the 9–10 peptide link to invert in the G10V/G43A double-mutant protein relieving steric interaction between C9 O and V10 C^{β}.[47] This drastic change in conformation is accompanied by other significant structural changes but the new conformation allows the 11-NH···S^{γ}-9 interaction to be maintained. The 9–10 peptide link now orients its negative pole towards the iron atom and the combined structural changes cause $E^{\circ\prime}$ to shift by at least -40 mV. One may speculate that inverted polarity of the 9–10 amide dipole dominates the shift: note that it is in the *opposite* sense (favouring the oxidised form) to that observed in the ferredoxin I system discussed above. In that work, the targetted amide directed its positive pole towards the active site.

For the V44A mutant of Rd*Cp*, $E^{\circ\prime}$ shifts by more than $+50$ mV while the complementary mutation A44V in the *Pyrococcus furiosus* protein produces a similar but negative shift.[48,49] The C^{β} atom of Ala 44 in V44A of Rd*Cp* lies very close to the position of the $C^{\gamma 2}$ atom of Val 44 in the native Rd (Figure 4). But the lower overall steric demand of A (Me) relative to V (Pr^{i}) allows the protein chain to move towards the iron site. The 44NH···S42 distance contracts by 0.4(1) Å, consistent with significant strengthening of the hydrogen bond. Consequently, a minor change in the steric requirements of a surface residue has been amplified to a positive shift in $E^{\circ\prime}$ of at least 50 mV by the strengthening of the NH···S hydrogen bond.

An Rd-like $Fe(S\text{–}Cys)_4$ centre identified in the 'as isolated' rubrerythrin from *Desulfovibrio vulgaris* exhibits an unusually high reduction potential ($E^{\circ\prime} = +230$ mV; *cf.* Table 1).[50] Recent structural data indicate that this centre features an unusually strong seventh NH···S–Cys bond in addition to the six NH···S–Cys bonds usually seen in Rd (Figure 1(b)).[28] The Fe–S distance involving this extra seventh NH···S–Cys bond appears to be lengthened significantly, consistent with relative stabilisation of the reduced form and the increase in $E^{\circ\prime}$.

4.3 Solvent Access

Although the protein surface close to the active site in Rd is hydrophobic, the S^{γ} ligand atoms of the two surface Cys ligands appear to have some contact with solvent. The Pr^{i} side chains of two adjacent valine residues, V8 and V44, define

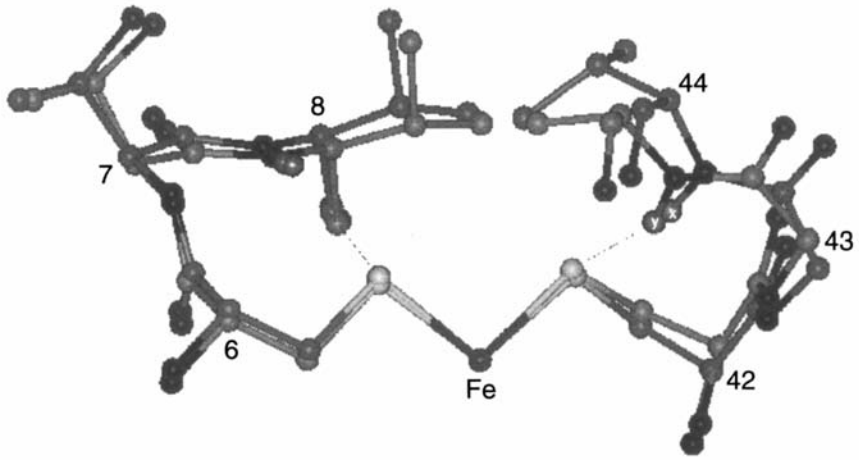

Figure 4 *Overlay of the structures of Rd*Cp *and the corresponding part of the V44A protein. The iron atom and residues 6–8 and 42–44 are shown. The modeled NH protons of residues 44 which are involved in the 44NH···S42 hydrogen bonds are labelled x in Rd*Cp *and y in V44A. The bond is 0.4(1) Å shorter in the V44A mutant protein than in Rd*Cp.
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the surface of the rubredoxin from *Clostridium pasteurianum* and control access to its $Fe(S\text{–}Cys)_4$ active site (Figure 1(b)). To assess the effect of systematic change of the steric bulk of the alkyl side chains, a number of single and double mutant proteins were isolated which vary G (H), A (Me), V (Pr^i), L (Bu^i) and I (Bu^{sec}) at those positions.[30,48,49]

At a superficial level, the increased potentials correlate with decreased side-chain volumes, consistent with increased solvent access (Table 3 and Figure 5). The double mutant V8G/V44G exhibits the most positive shift in potential (116 mV). This correlates with the absence of side-chains at positions 8 and 44, allowing maximum solvent penetration. On the other hand, the shift for the double mutant with larger alkyl side chains V8I/V44I (+22 mV) is essentially the sum of those of the single mutant constituents V8I (−4 mV) and V44I (+24 mV). Structural data for Fe^{III} forms of the V44A and V44I proteins are available to assist interpretation but conclusions must assume that no significant structural variation occurs upon reduction.

Ichiye and Scott have drawn attention to two classes of Rd proteins from bacterial sources.[33,48] The potentials of class I (*Cl*, *Hm*, *Bm*, *Po*) are negative and similar to that of Rd*Cp* (−77 mV) (Table 1). Those of class II (*Pf*, *Dv*H, *Dv*M, *Dg*) cluster around 0 mV. Ichiye observed that class I and II proteins have valine and alanine, respectively, at position 44. The amide NH of position 44 acts as a hydrogen bond donor to the S^γ atom of ligand C42 (Figures 1(b), 4). For Rd*Cp*, calculations predicted that the V44A mutant protein would show a positive shift in potential of about 40 mV, effectively converting it from class I to class II.[33] The lower steric demand of A (Me) compared to V (Pr^i) would drive an increase in

Table 3 *Peak potentials for V8 and V44 mutants of Rd*Cp

Protein	E_p mV	ΔE_p mV[b]
rRd	− 77	
V8G	− 7	+ 70
V8A	− 44	+ 33
V8L	− 82	− 5
V8I	− 81	− 4
V44G	0	+ 77
V44A	− 24	+ 53
V44L	− 87	− 10
V44I	− 53	+ 24
V8G/V44G	+ 39	+ 116
V8I/V44G	− 13	+ 73
V8I/V44I	− 55	+ 22

[a] From reference 49.
[b] Potential relative to rRd.

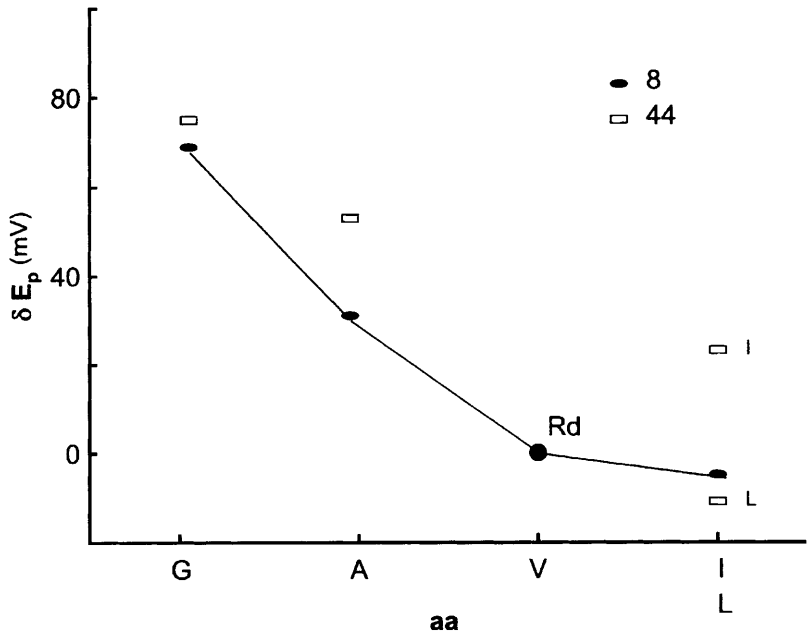

Figure 5 *Dependence of peak potentials E_p on the residue sidechain in V8 and V44 mutant Rd proteins.*
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polarity *via* a change in the conformation of the protein chain and its translation towards the iron atom. Solvent access effects would be less important.

The discussion of the structure of the V44A protein under Section 4.2 above provides some experimental support for this prediction.[48,49]

(i) The peak potential of V44A is $\geqslant 53$ mV more positive than that of rRd (Figure 5).
(ii) The backbone in the vicinity of residue 44 is shifted towards the iron site (Figure 4) and the 44N···S$^{\gamma}$42 distance is decreased significantly by 0.4(1) Å.

In addition, the solvent-accessible surface areas of the side-chains of the C9 and C42 ligands are increased by about 10% in the V44A mutant relative to rRd. Overall, the experimental results are consistent with a combination of backbone structural change and solvent access contributing to a more polar environment for the iron site in the V44A protein. Their relative contributions to the larger shifts of + 70 to + 116 mV seen for the V (Pr^{i}) to G (H) mutants (Figure 5; Table 2) must await further detailed structural information.

The difficulty in discriminating between these two influences is highlighted when examining the structure of the Rd from *Desulfovibrio desulfuricans*.[51] As its sequence is shorter than that of Rd*Cp* by seven residues (20–26), Rd*Dd* was not included in the analysis of Ichiye and Scott. Its potential is about 0 mV (class II) but it features valine at the position equivalent to 44 (class I). A number of separate structural features would appear to be at work here.

Estimation of the effects of solvent access has been the most difficult of the factors to assess. The best understood systems from this point of view are the HiPIP proteins where the aromatic core seems to stabilise the oxidised state $[Fe_4S_4(S\text{–}Cys)_4]^-$ of the buried site by restricting solvent access,[7,52] but this is, of course, negative evidence.

5 Acknowledgement

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SECTION G:

Patterns and Generalisations in Stability and Reactivity

During the twenties and thirties, immediately prior to the beginning of Chatt's research at Cambridge under the direction of F. G. Mann, the study of inorganic compounds was a relatively unfashionable area of chemical research. Even the early contributions of Werner were being overshadowed by developments in organic chemistry. This was, in part, associated with the largely descriptive nature of inorganic chemistry. Apart from some notable exceptions, such as the formulation of the periodic table of the elements and its rationalisation of chemical composition and Lewis' characterisation of the coordinate bond, there were few overarching generalisations which might permit the organisation of the vast body of data on inorganic compounds, the necessary precursor to a proper basis of fundamental understanding. Limitations in the physical and spectroscopic techniques available to investigate the synthesis, structure, bonding and reactivity of inorganic compounds made their study slow and difficult. The growth in inorganic, particularly coordination, chemistry which began after the Second World War, may be linked with the developments in structural and spectroscopic techniques, such as X-ray crystallography, IR and UV–visible spectroscopy and magnetic measurements, coupled with developments in crystal and ligand field theories, and associated models of metal–ligand bonding. It was inevitable that the relatively small number of those working in these areas should seek each other out to exchange ideas and to develop research collaborations. More surprising, perhaps, was the support given by ICI, Chatt's employers, to the arranging and hosting of such a meeting in 1951, later to be designated as the first International Conference on Coordination Chemistry. The meeting at The Frythe brought together names that will always be associated with the growth, contribution and impact of coordination chemistry in the latter half of the twentieth century.

*Chatt has recalled elsewhere his work on the synthesis of complexes of platinum(*II*) and the implications for structure arising from their stereoisomerism and the use of techniques such as the measurement of dipole moments to distinguish* cis *and* trans *isomeric forms. The extensive synthetic studies from the Russian school led by Chernyaev revealed the directing influence of ligands bound to metals in*

which groups in the trans *position were more readily substituted than those in the* cis *positions. The availability of a range of tractable materials, their ready and selective transformation and the availability of techniques able to monitor such reactions provided the stimulus for the study of the kinetics of these processes and proposals concerning their mechanisms. This permitted ideas to be formulated that sought to rationalise and explain the origins of this labilising effect. This topic is covered in the contribution from Professor Basolo, who has the distinction of being the Royal Society of Chemistry's first Chatt Lecturer in 1995–1996. Professor Basolo also reviews some of his work on platinum(*IV*) chemistry.*

Considering Chatt's contributions to synthetic and structural aspects of co-ordination chemistry and his interest in seeking associated patterns and rationalisations, it was natural that he would have been stimulated by evidence for stability trends for oxygen, nitrogen and halide donor atom ligands in coordination complexes in aqueous solution described by Irving at the 1951 meeting at the Frythe. This, and earlier summaries by Sidgwick in 1941, led him to study the stability of coordination complexes involving a range of acceptors and ligands with heavier donor atoms, such as sulfur, phosphorus, and arsenic. From an analysis of the available data, Chatt, with Ahrland and Davies, recognised two important generalisations: first, the significant difference between the affinities of donor atoms from the first and second periods of the Periodic Table, N and P, O and S, F and Cl and second, the existence of two classes of acceptor, those forming more stable complexes with the lighter ligating atoms, N, O and F, and those forming more stable complexes with the heavier ligating elements, P, As, S and Cl. These differences were characterised as representing class (a) or class (b) behaviour and were seen as a further manifestation of the role of metal–ligand π-bonding. The classifications (and those of others, most particularly of J.O. Edwards and G. Schwarzenbach) were to be later subsumed into Pearson's hard and soft acid and base (HSAB) description, as described by Professor Pearson in the first contribution in this section. In addition, Pearson also summarises later work, done in collaboration with R. G. Parr, which has sought to give a theoretical underpinning of the HSAB principle.

*Finally, the paper by S. Otto, S. N. Mzamane and A. Roodt, explores the consequences for reactivity of square planar rhodium(*I*) complexes towards oxidative addition and reductive elimination of changing a pair of P-donor ligands with As-donor analogues. Medium effects are also investigated.*

Hard and Soft Acids and Bases and Joe Chatt

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1 Introduction

I began my research career as a physical organic chemist. Very shortly, Fred Basolo introduced me to the chemistry of coordination compounds. As a result I knew a great deal of both organic and inorganic chemistry and could see the fundamental similarities. This led to an appreciation of G. N. Lewis and his concept of generalised acids and bases.

I realised that much of chemistry could be discussed in terms of the simple equation

$$A + B = A{:}B \tag{1}$$

Where A is an electron acceptor (acid), B is an electron donor (base) and A:B is an acid–base complex. The latter could be almost any chemical species. For example AgCl would be a combination of Ag^+ (acid), and Cl^- (base). CH_3OH would be $CH_3{}^+$ plus OH^-, and so on.

Clearly the strength of the coordinate bond in A:B was of the greatest importance in chemistry. Any empirical rules that could help to estimate ΔH of Reaction 1, even qualitatively, would be very useful. My thoughts on this subject were published in 1963 in a paper entitled 'Hard and Soft Acids and Bases'.[1] This paper has been identified by Current Contents as one of the most widely quoted in the scientific literature.

I would like to discuss next the people whose earlier work had a great influence on me, in the above connection. One of these was John Edwards, who was already expert in thinking of chemistry in terms of Reaction 1. He had published a paper noteworthy for several features.[2] First, he combined data on both organic reactions and metal ion complexation and secondly he combined both equilibrium data and rate data to draw his conclusions. He concluded that two properties of a base were important: one was the ordinary proton basicity and

the other was ease of electron donation. Also, different Lewis acids (serving as electrophilic centres) had different sensitivities to these two properties.

In 1961 Edwards spent some time at Northwestern University and we published a paper on nucleophilic reactivity that identified the kinds of electrophiles that would depend on proton basicity and those that would depend on electron donation. We also changed the emphasis to polarisability of the base, rather than ease of electron loss.[3]

We were very fortunate at this point in time because Harry Gray had collected a great deal of rate data on substitution reactions of platinum(II) complexes. This was my first exposure to the more noble of the transition metals. I soon had a great deal more because I was fortunate enough to be a collaborator with Joe Chatt on the kinetics of substitution reactions of a series of organometallic compounds of nickel(II), palladium(II) and platinum(II).[4]

This was a good piece of work because we pointed out the great difference in rates of reaction for the first, second and third transition series. The ratios were 5×10^6, 10^5, and 1, for Ni, Pd and Pt with compounds of the general formula $[MRCl(PR_3)_2]$ prepared by Bernard Shaw. Of even greater importance to me was the discovery of the stability of organometallic compounds of platinum(II) and palladium(II), compared to the great reactivity of compounds such as AlR_3 and RMgX or even nickel(II) analogues.

It will be recalled that the organometallic chemistry of the transition metals was in its infancy even in 1960. It had essentially begun only in 1951, with the discovery of ferrocene. By 1960 Chatt was arguably the foremost figure in this important field. Besides leading the way by making dozens of new compounds, he developed the guidelines for successful syntheses. He also made important contributions to the theory of bonding in these novel compounds.

In terms of what I was doing, his most important paper was published in 1958, with Sten Ahrland and Norman Davies.[5] This paper was entitled 'The Relative Affinities of Ligand Atoms for Acceptor Molecules and Ions.' The authors drew on a large basis set of data available to them. This included equilibrium data in aqueous solution and in the gas phase, but also data on the general stability and ease of preparation of the transition metal organometallics. This enabled them to add carbon donor ligands to the more common examples. Their acceptors included the metal atoms in various oxidation states and Lewis acids of the type $GaMe_3$ and BF_3.

Their conclusions pointed out two regularities: (1) there is usually a great difference in coordinating ability between the first and second element from each of the groups of the Periodic Table; (2) there are two classes of acceptor: (a) those that form their most stable complexes with the first ligand atom of each group, and (b) those which form their most stable complexes with the second or a subsequent ligand atom. These two classes were called (a) and (b), respectively, and a large number of acceptors (or Lewis acids) were classified as (a) or (b) in character.

In fact, something similar had been done even earlier by Gerold Schwarzenbach.[6] His paper, published in German, apparently attracted little attention. He was limited to metal ions in solution, in their normal oxidation states. Metal ions

with a rare gas outer configuration were called class A, and the ones with d^{10} configuration were called class B. Writing the donor atom of the ligands in order of decreasing electronegativity we find

$$F > O > N > Cl > Br > I > P \sim C > S \tag{2}$$

The class A metal ions form their most stable complexes with the left side of the order, and the class B with the right side.

The transition metal ions were classified as going from class A to class B, as the number of d electrons increased, except for Zn. The explanation for all of this was that ionic bonding was predominant in class A, and covalent bonding much more evident in class B. Zinc failed because of its low ionisation potential, which caused it to be more A in character.

2 Hard and Soft Acids and Bases (HSAB)

In the 1963 paper, Reaction 1 was actually discussed as the generalised nucleophilic displacement reaction:

$$A{:}B' + B = A{:}B + B' \tag{3}$$

The reason for this was partly because I was still using rates of reaction as input data and partly because in the laboratory it was Reaction 3 which was usually observed, and not Reaction 1. However B can be made constant and then (3) and (1) become equivalent for our purposes.

Apart from the kinetic data, the criteria of Ahrland, Chatt and Davies were used unchanged to categorise a large number of Lewis acids as either class (a) or class (b). Many examples other than metal ions or atoms were included, such as CH_3^+, RSO_2^+, RS^+ and I_2. Looking at the two classes, it was clear that class (a) acids were of low polarisability, and class (b) were of high polarisability. Since polarisation means the distortion of the electron cloud of a chemical system by an electric field, we can label class (a) systems as hard, and label class (b) systems as soft. Hardness means resistance to change or distortion.

Bases were classified according to the order (2). On the left side the donor atoms are of low polarisability, or hard, and on the right they are highly polarisable, or soft. We then can summarise the data used by the HSAB Principle, 'hard acids prefer to coordinate to hard bases and soft acids to soft bases.'

We could equally well have said that class (a) acids prefer class (a) bases and class (b) acids prefer class (b) bases. I had several good reasons for the name change, one being that the use of the comparative, or even the superlative, was easier. One acid being harder that another was easier to understand than one acid being more class (a) than another. Also hard and soft were simple, easily visualised descriptions of the key properties.

The original choices of A, or (a), and B, or (b), were related to the subgroup labels of the Periodic Table, IA *vs.* IB, and so on. Unfortunately, in the United States the labels A and B had become inverted from the convention in Europe, except for IA and B and IIA and B. This could lead to some confusion. At any rate, I decided to go with hard and soft, though I sometime regretted it.

It turned out that many scientists did not like the words hard and soft. They would be acceptable in private conversations, but not in serious scientific papers. Even today I find some people put quotes around 'hard' and 'soft.' When spoken aloud, as in a lecture, it is conventional to smile. Nevertheless, the terms have found their way into the literature, where they seem to fill a definite need.

Other work by Chatt was important to me in organising my thoughts on generalised acids and bases. One useful idea was his π-bonding theory.[7] The important feature, in his view, was the presence of loosely held outer d-electron in class (b) metal ions. These could form π-bonds by donation to empty orbitals in the ligands. These would include π-orbitals in CO or C_2H_4, and d orbitals in ligands with P, A, S and Se as donors. Class (a) metal ions would have only tightly held electrons in the valence shell and also empty orbitals, not too high in energy, on the metal. Basic atoms such as O and F could form π-bonds by electron donation from ligand to metal.

Of great importance was his realisation of the significance of oxidation state on the hardness.[5] Increased positive charge on the acceptor atom would lead to increased hardness, as a rule, though there were a few exceptions. A key conclusion was that metal atoms in the zero oxidation state would always be class (b) or soft. This would extend to bulk metals as well and led to an immediate understanding of poisoning in such catalysts.

The effect of other attached ligands was also understood by Chatt. For example BF_3 and BH_3 both had boron(III) as the acceptor atom. But in BF_3 it would be almost B^{3+} because of the high electronegativity of F. In BH_3 the bonding between B and H would be very covalent, and we would have B^0. Hence BF_3 is a hard acid and BH_3 is a soft acid. Klixbull Jørgensen systematised this effect and called it 'Symbiosis'.[8]

Armed with so much data, and new insights, it was easy to predict that RSO_2^+ would be a hard acid, and RS^+ would be a soft acid (the outer p electrons of sulfur take the place of the d electrons of the transition metals). Finding that RSO_2F was stable, while RSO_2I was almost impossible to make, and that RSSR disulfides were stable, while sulfenic esters, RSOR, were very unstable, simply confirmed the predictions.

The HSAB Principle is supposed to be a unifying concept which makes easier the remembering of a vast body of chemical facts, and which allows predictions of a limited nature. It is a summary of facts, and not a theory, though it is often called that. The reasoning seems to be that its validity is dubious, like that of a theory.

A common misconception is that HSAB says that only combination of hard acids with hard bases, or soft acids with soft bases, can be stable. This is certainly not the case in fact, nor is it implied in HSAB. Instead it only implies an extra stabilisation in hard–hard or soft–soft combinations. The overall stability of an A:B bond depends on the intrinsic strengths of A and B, determined by such factors as size, charge and polarity, for the most part.

For example, in the gas phase F^- always is a stronger base that I^- and forms stronger bonds to all metal ions. But in aqueous solution F^- is more strongly solvated than I^- by 53 kcal mol^{-1}. Both effects are due to size, and only the

difference in the heats of hydration enables I^- to compete with F^- for various metal ions in solution. For soft metal ions, like Hg^{2+}, I^- wins out. For hard ion such as H^+, F^- is the stronger base.

The really serious objection to the HSAB concept was that no exact definition of hardness or softness was given. There was an operational definition as given by Ahrland, Chatt and Davies, but it only put Lewis acids into one of two boxes. There was no way to rank-order within the boxes, though there were borderline cases. There was a rank-ordering of bases, given by (2), but it was only approximate and did not distinguish between all the bases with the same donor atom. Finally all that was done was to put bases into one of the two boxes labelled hard and soft.

An operational definition could be given using the equilibrium constant or reaction heat, for a reaction such as (3). This would rank-order a series of acids or bases with suitable choices for A: B. Many such definitions were suggested, but they failed because somewhat different orders were found, depending on the reference reactions chosen. Also, they lacked a theoretical basis linking them to accepted theory. Any numbers obtained were valid only for the chosen reference, and were not transferable.

One can certainly argue that ill-defined terms that cannot be measured and quantified have no place in exact science. But it can also be argued that the statement 'the substance is red' has some informational value, even though an absorption spectrum would usually be better. Saying that an acid is soft also has some value. The uses made of such statements are actually examples of 'fuzzy logic.' In spite of its name, this is a respected branch of mathematics. It is a method for making the best use of limited information.[10] It is widely used in technology, manufacturing and finance.

In spite of its limitations, the HSAB concept proved to be useful in almost all areas of chemistry, and related fields. This was more true for chemists actually working in the laboratory, trying to make definite compounds, or materials with certain properties. A good example is given by the work of Chatt and his co-workers. While probably not thinking in terms of hard and soft, they drew the same conclusions. It hardly needs to be said how successful this kind of thinking was.

Another area where the simple HSAB rules has been helpful is in the teaching (or learning) of chemistry. Students today are overwhelmed with vast quantities of material. Being introduced in high school and in the first year of general chemistry to the HSAB Principle, pupils can systematise much of their information. In my experience students always want a few simple rules that cover a lot of territory.

3 Chemical Hardness

The problem of an exact definition of hardness, and a valid experimental procedure to measure it, was solved for me in 1983. Bob Parr, the well-known theoretician, spent a sabbatical quarter in Santa Barbara. He had already used density functional theory to define the electronic chemical potential, μ.[11]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \cong -\left(\frac{I + A}{2}\right) = -\chi_M \tag{4}$$

In (4), E is the energy of any chemical system, N is the number of electrons, v is the potential given by the nuclei, I and A are the ionisation potential and electron affinity. These also define the Mulliken electronegativity, χ_M.

Density functional theory (DFT) is a branch of quantum mechanics that uses the electron density function, ρ, to describe a chemical system, rather than the more usual wave function. It had already been shown that the electron density contained all the necessary information to calculate the ground state energy and other properties. [12] It is much easier to work with than wave functions.

Parr asked me if the quantity $(\partial\mu/\partial N)_v$ was related to my ideas of hardness and softness. This showed great chemical insight on his part since within a few hours I was convinced that it was exactly what I meant by hardness. Within a few days we wrote a definitive paper.[13]

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v \cong \frac{I - A}{2} \tag{5}$$

Here η, the Greek letter h, is the hardness. The softness, σ, is simply the reciprocal of η.

The initial reason for my accepting (5) as the definition of hardness, was that the few values of I and A that I could easily find were in agreement with what I already knew. Class (a) metal ions did give large values of $(I - A)$, and class (b) ions gave low values. Other virtues of (5) quickly became apparent. It gave a procedure for calculating the hardness for any chemical system by simply measuring I and A. Fortunately, just at this time there was a great deal of new activity in measuring ionisation potentials and electron affinities. This could be done for atoms, molecules and positive ions, and tables of hardness values, as well as electronic chemical potentials, were made available.[14]

An important factor for me was that (5) gave η the meaning of resistance to change in the number of electrons, N. But this also implies that we can write

$$\eta = \frac{1}{2}\left(\frac{\delta \mu}{\delta \rho}\right)_v \tag{6}$$

where the symbol δ means the functional dependence of one variable upon another. This follows because ρ is a function of N. Equation 6 has the meaning of resistance to change, or deformation, of the electron cloud. But this was exactly the meaning that I had for hardness!

There was another reason why (5) is a good definition of hardness, though I was not aware of it in 1983. In molecular orbital theory, Koopman's theorem says that $(I - A)$ is the energy gap between the HOMO and the LUMO.[15] This energy gap is the difference in energy between the ground state and the lowest excited state of the same multiplicity. If this gap is small then it is easier to change the electron density, according to quantum mechanical perturbation theory. For example, a large gap means low polarisability and a small gap (η small) means

high polarisability. But these were just the properties that I had associated with hard and soft in the beginning.

The meaning of both μ and η is also seen in describing the initial interaction of two chemical systems, C and D. Since the electronic chemical potential of the combined systems must be constant everywhere, electrons will flow from the system of low electronegativity to that of higher electronegativity (see Equation 4). The number of electrons that are transferred is given by[13]

$$\Delta N = \left(\frac{\chi_C - \chi_D}{2(\eta_C + \eta_D)} \right) \tag{7}$$

This is a chemical form of Ohm's Law. The numerator gives the difference in potential and the denominator gives the resistance to electron flow.

Parr and I had originally called η the 'absolute' hardness. The reason was that it was a companion parameter to χ_M (or $-\mu$), called the 'absolute' electronegativity, because it had a sound basis in fundamental theory. While this made sense for μ, it seemed unnecessary for η. The other scientific use of the term hardness would be for physical or mechanical hardness. Thus the name 'chemical' hardness seems more appropriate for η.

The concepts of electronic chemical potential and chemical hardness have led to many new ways of looking at chemical reactions and other phenomena of interest to chemists. For example, the identification of hardness with the HOMO–LUMO gap leads to the 'Principle of Maximum Chemical Hardness.' There seems to be a rule of nature that molecules arrange themselves to be as hard as possible, that is, to have the largest gap between the occupied orbitals and the empty ones.[16]

This is not the place for a discussion of the many new uses of chemical hardness. A recent book gives a fairly detailed introduction and current summary.[14] Applications are given ranging from atoms to solids. The case of solids is particularly interesting because both μ and η have long been a part of solid state theory. Thus μ is the Fermi energy and η is the band gap. Physical hardness is an important property of solids and is related to chemical hardness.

Density functional theory is the basis for the definition and use of μ and η. DFT, of course, has revolutionised the whole theory of chemistry in the last twenty years. The Nobel Prize in Chemistry was given to Walter Kohn in 1998 for his contributions. These include the original concept and an efficient method for making energy calculations on molecules (and solids). But μ and η are concepts of DFT which are still new and where many more applications will undoubtedly be found.

At this point we seem to have come a long way from the chemistry of Joe Chatt. Is there really a connection between the stability of olefin complexes of platinum(II) and the semi-conducting properties of GaAs? In this short review I have tried to show that there is a direct relationship between the two. The class (a) and class (b) metal ions of Chatt and the two classes of electrophiles of Edwards clearly are the parents of the Principle of Hard and Soft Acids and Bases. The latter, in turn is one parent of Chemical Hardness, the other being

DFT. This puts hardness near the forefront of modern chemical theory. Hopefully, there will be many new uses for the concept. These, like myself, will owe a debt to the scientists who went before.

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Mechanisms of Platinum Reactions

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Professor Joseph Chatt was one of the truly outstanding inorganic chemists of the twentieth century.

I wish to begin by thanking the editors, G. J. Leigh and N. Winterton for asking me to write a chapter in this book honouring my professional and personal friend, Professor Joseph Chatt. He and I met for the first time in 1955 when my wife and I were on our initial tour of England. We drove making unannounced stops at bed and breakfast places; starting from St Andrews where I played a round of golf at the Royal and Ancient golf course, where the game was first played. We continued to drive south, again making unannounced stops at various universities where I wanted to meet some particular inorganic chemists, whom I knew from their publications, and who knew me for the same reason. One place I wanted finally to reach was The Frythe to meet Joseph, because I had read most of his papers, and I felt his research problems were well designed to get reliable information that answered important questions of fundamental concern. Furthermore, it was clear from his publications that the experimental work was done with great care, and that his interpretation of the experimental results was almost always on target.

Not only did I get to meet Joseph, but my wife Mary met his wife Ethel. We all had a friendly visit together, after which they took us to see some Roman (archaeological) digs nearby. They asked us to be their house guests overnight, which we gladly accepted. After a delightful dinner, we talked about personal matters, but no chemistry. We learned they had two children, a girl and a boy; we had the same but ours were a little younger. This way our families became acquainted, and we developed a friendship that has lasted all these years – see the end of this chapter for some of the friendly exchanges between Joseph and me.

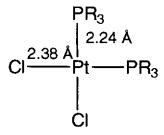
1 Chemistry of Platinum(II) Complexes

Immediately when chemists think of platinum(II) complexes, they know it will almost certainly involve Chatt chemistry. He could rightly be called the 'Father of Platinum(II) Coordination Chemistry in the UK,' because the scientific literature abounds with his publications on important aspects of platinum(II) chemistry. I do believe that his fundamental seminal research on these systems is second to none.

In 1996, *Coordination Chemistry Reviews* (CCR) dedicated one of its issues to the memory of Joseph Chatt. I published an article in that issue entitled, 'Recollections of early studies on platinum(II) complexes related to Chatt's contributions to coordination chemistry'.[1] For this reason, and because some authors will discuss platinum(II) chemistry in other chapters, I will devote most of this paper to our research on the kinetics and mechanisms of platinum(II) ligand displacement, and to the chemistry of platinum(IV) complexes. Since Joseph did little research on platinum(IV) chemistry, it seems appropriate that I review our work on it. Following this, I will briefly describe another area we worked on that interested Chatt although he was not involved in such research. This was that of making use of reaction mechanisms to help design the synthesis of metal complexes.

2 Kinetics and Mechanisms of Ligand Substitution Reactions of Platinum(II) Complexes

We have published many papers on the kinetics and mechanisms of platinum(II) reactions, and the publications on this aspect of our research are reviewed in the Basolo and Pearson book.[2] It seems appropriate to summarise some of our work on this topic, because it differs from the *extrakinetic trans effect* properties of platinum(II) complexes studied extensively by Chatt. This means that he and his research group investigated mostly the static properties of platinum(II) complexes. Instead our work is on the dynamics of the reactions of platinum(II) complexes, and we chose to call this the *kinetic trans effect*. Thus, Chatt and his research group considered measurements on the complexes' stabilities, dipole moments, infrared spectra, nuclear magnetic resonance (NMR) and platinum(II)-ligand bond distances measured by X-ray crystallography. They also noted the qualitative rates of ligand substitution, and further observed that this reaction occurs without stereochemical change. For example, these experimental observations resulted in data such as the bond distances (Å) of *cis*- and *trans*-$[PtCl_2(PR_3)_2]$ (**1** and **2**).



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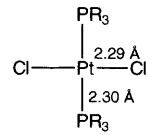

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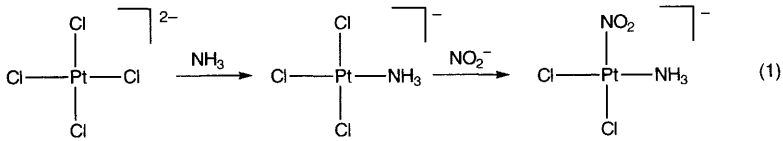
Table 1 *Dipole moments of* trans-$[PtLCl(PEt_3)_2]$ *complexes in benzene at 25°C*[3]

L	*Debye units*
H	4.2
CH_3	3.4
C_6H_5	2.6
p-ClC_6H_4	1.1
Cl	0.0

This shows that the Pt–Cl bond distance is greater if it is *trans* to PR_3 (**1**) than if it is *trans* to Cl^- (**2**). Such results are in accord with the fact that the greater rate of Cl^- displacement is that of the Cl^- *trans* to PR_3. Another approach used by Chatt to obtain information on the nature of ligands *trans* to the ligand being replaced was to measure the dipole moments of a group of analogous compounds. The net dipole moment of a complex will depend on the polarity and the geometry of the four groups surrounding the metal. Data of interest in this discussion are shown in Table 1 for the compounds *trans*-$[PtLCl(PEt_3)_2]$.

For changes in L, the dipole moments decrease in the order $H > CH_3 > C_6H_5 > p\text{–}ClC_6H_4 > Cl$, which is the same as the order of decreasing *trans*-effect for these ligands. The results suggest there is a larger transfer of electrons from H^-, CH_3^-, $C_6H_5^-$ and $p\text{–}ClC_6H_4^-$ toward platinum(II). Therefore, the Pt–Cl bond is more polar and presumably weaker in H–Pt–Cl than in Cl–Pt–Cl. This agrees with the bond distances derived from X-ray crystallography and these results are consistent with the qualitative observations that the reactivity of these complexes depends on the nature of the ligand in the *trans* position.

The Russian School, particularly Chernyaev, did much of the early research on platinum(II) chemistry. This arose from the large platinum resources in some of their natural minerals. So important was the availability of platinum to them that they had an Institute devoted in large part to the chemistry of platinum. Most of their research dealt with the syntheses and reactions of platinum complexes. Their primary goal seemed to have been to enhance the extraction of platinum from its mineral source. As early as 1926, Chernyaev[4] reported that certain ligands in the position *trans* to the leaving group of square-planar platinum(II) complexes have a marked effect on its replacement substitution. He used this with considerable success in the preparation of desired platinum(II) complexes. For example, he was able to prepare *cis*-$[PtCl_2(NO_2)(NH_3)]^-$ by the reactions shown in (1).



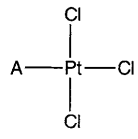
(1)

Chernyaev designed this synthesis, knowing that Cl^- has a greater *trans effect*

than does NH_3. Therefore, the NO_2^- will replace a Cl^- opposite a Cl^- ligand, whereas, if NH_3 had the greater *trans effect* the NO_2^- group would replace the Cl^- *trans* to the NH_3. The Russian School attributed this to the activating group being the more polarisable; thus, in the reactions above Cl^- is more polarisable than NH_3. During some 30 years that followed, ligands such as CO, NO and C_2H_4 were found to have among the highest *trans effects*. This could not be explained by the Russian ideas concerning the importance of polarisability of the *trans* ligands.

It is of interest to note that as early as 1828, a Danish pharmacist, Zeise, prepared the stable compound $K[PtCl_3(C_2H_4)]$, commonly called Zeise's salt. Some 125 years later, the chemical bonding of ethylene (C_2H_4) to platinum(II) was finally understood. There is very little doubt that the unsaturated ligand $H_2C{=}CH_2$ coordinated to platinum(II) is held to the metal by a double bond, where the π-bonding electrons from the organic molecule form a coordinate bond. The metal in turn donates a pair of *d* electrons to the organic molecule through a π bond. This description of the bonding was proposed by Chatt[5a] and Dewar[6] and is generally known as the Dewar–Chatt–Duncanson model. The bonding type is very important in organometallic chemistry.

Again, I feel certain that other authors will give a more detailed account in this book of the above π-bonding description. Therefore, returning to the very high *trans effect* of ligands such as C_2H_4, CO, and NO, Chatt proceeded to explain how the π concept could be used to account for the bonding of C_2H_4 to platinum in Zeise's salt. He wrote,[5b] 'The operation of the rapid and readily reversible elimination of groups *trans* to ligands **A** (**3**) of high *trans-effect* (*i.e.* high double-bonding capacity) is readily explained if we suppose that *trans*-substitution occurs by an S_N2 (bimolecular) mechanism. Increasing double bonding by **A** increases the electron affinity of the metal atom and hence the ease of nucleophilic attack. Also, because the electron withdrawal occasioned by **A** occurs from the antinodes from **A** of the d_{xz}-orbital, the attack takes place there, preferentially displacing the ligand *trans* to **A**.'



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As stated by Chatt and co-workers, their early speculation on the role of *trans*-π bonding groups in ligand substitution of platinum(II) complexes was based on the assumption that the reactions proceed by an S_N2 mechanism. However, at the time (1955) most of the observations reported on such reactions were qualitative and little had been done to use detailed kinetic studies in attempts to elucidate the mechanism of ligand substitution.[7] Since the valence bond theory in use then assigned dsp^2 hybridisation to the square-planar platinum(II) complexes, coordination chemists believed an entering nucleophile would readily attack the low energy vacant *p* orbital on the metal and substitution would take place by an S_N2 mechanism. Furthermore, a coordination

number of four means little or no steric hindrance in going to coordination number five. Many kinetic studies now support the S_N2 mechanism, so much so that when Romeo[8a] and co-workers[8b,8c] discovered S_N1 reactions of platinum(II) complexes, the referees delayed publication because of the strong belief that 'all platinum(II) substitutions are S_N2 as appears in Basolo's and Pearson's book'.

It was clear in the 1950s that there was a need for detailed kinetic studies of ligand substitution reactions of platinum(II) complexes, and our laboratory was prepared to do this because it was engaged in such studies of octahedral substitution. However, only a brief account of our studies is given in this article. At about this time Martin[9] and his students initiated their investigations of aquation reactions of chloroammineplatinum(II) complexes.

There is now much kinetic data on substitution reactions of square-planar complexes[2] all of which are explained in terms of a bimolecular (S_N2) displacement mechanism. For reactions such as

$$[MA_3X]^{n+} + Y^- \xrightarrow{H_2O} [MA_3Y]^{n+} + X^- \tag{2}$$

in water solution, a two-term rate law

$$\text{Rate} = k_1[MA_3X^{n+}] + k_2[MA_3X^{n+}][Y] \tag{3}$$

is generally followed, where k_1 and k_2 are first-order and second-order rate constants, respectively. Under pseudo-first-order conditions with an excess of Y^-, the experimental first-order rate constant, k_{obs}, is related to the individual rate constants as shown by the equation

$$k_{obs} = k_1 + k_2[Y] \tag{4}$$

This requires that a plot of k_{obs} *versus* [Y] be linear with an intercept of k_1 for the reagent-independent path and a slope of k_2 for the reagent path. Plots of this type are common for substitution reactions of square-planar complexes. Such a plot is shown in Figure 2 for the reaction *trans*-$[PtCl_2(py)_2]$ (py = pyridine) with a variety of different reagents.

The results shown in Figure 2 are consistent with Chatt's classification that a polarisable ligand atom such as S of SCN^- is a much better nucleophile towards a polarisable metal such as platinum(II) forming Pt–SCN.[10] His classification refers to these metals as class (b) metals. Such metals do not interact strongly with much less polarisable ligands. The other class of metals, (a), are much less polarisable and interact more strongly with the much less polarisable ligand atoms as would be the case for Al–F. My former colleague Pearson[11] has proposed the nomenclature 'soft' for highly polarisable metals and ligand atoms, and 'hard' for the less polarisable metals and ligands. Like Chatt, Pearson also states that 'soft/soft' or 'hard/hard' interactions are more stable than are 'soft/hard' systems. Both Chatt and Pearson would be the first to agree that this classification is qualitative, albeit useful. I do recall that the first time Pearson told me about his 'hard/soft' classes, my response was 'so what else is new?' I was aware of Chatt's (a) and (b) classes, as well as the work on the stabilities of metal

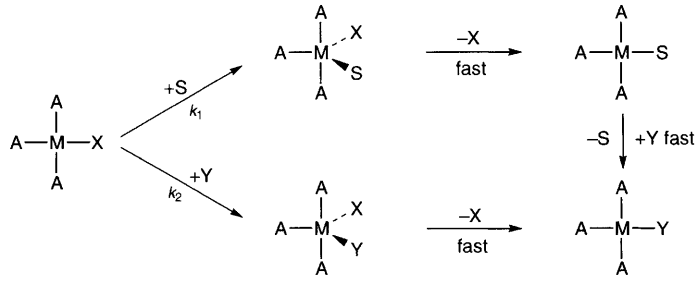

Figure 1 *General S_N2 mechanisms of ligand substitution reactions of square-planar metal complexes, such as platinum*(II) *compounds, where S is solvent and Y is entering nucleophile*

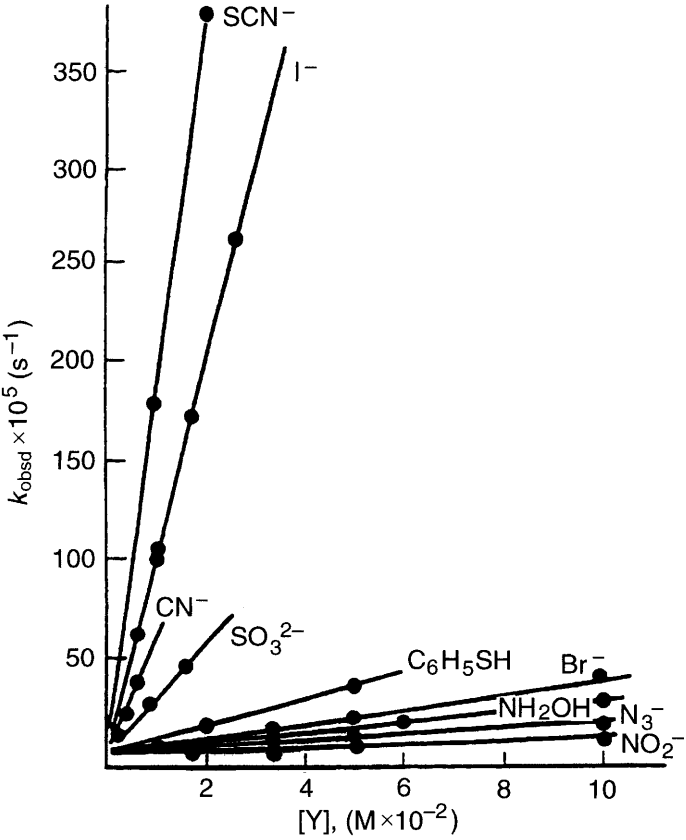

Figure 2 *Rates of reaction of* trans-$[PtCl_2(py)_2]$, *with different nucleophiles in CH_3OH solvent at 30°C.*

complexes by Jannik Bjerrum and Gerold Schwarzenbach. I even knew about the Swedish chemist Jons Jacob Berzelius (1779–1848) who had discovered the elements selenium, silicon, thorium and zirconium. I am told he made the point that certain metals are found on the Earth's crust as sulfides (HgS), others as oxides (Al_2O_3). However, the names 'soft' and 'hard' have a real meaning, readily understood, and this acid/base concept is even in elementary chemistry text books, and in undergraduate courses in inorganic chemistry.

Physical organic chemists for years attempted to evaluate and quantify the strengths of nucleophiles in S_N2 reactions towards carbon. One approach that met with some success was that reported by Swain and Scott.[12] They determined a large number of nucleophilic reactivity constants n_c using CH_3Br as a standard. Although this proved reasonably satisfactory for nucleophilic displacement reactions at carbon, it is well known that no one scale of nucleophilicity exists and that the substrate is important in any determination of nucleophilic strengths. Quantitative evaluation of the nucleophilic properties of various reagents generally brings in their basicities toward the proton and a characteristic which may be loosely defined as polarisability or electronegativity. The nature of the electrophilic substrate determines which of the properties makes the greatest contribution.

Although Edwards has had success with the use of electrode potentials to estimate[13] nucleophilic strengths, one disadvantage is that E^0 values are not known for many common reagents. Other attempts to quantify nucleophilicities towards metals were less successful, so finally Belluco *et al.*[14] decided to use the rate constants for Cl^- displacement from *trans*-$[PtCl_2(py)_2]$ by different nucleophiles as standards. The procedure followed was essentially that used by organic chemists[17] to standardise reactivities towards CH_3Br.

The nucleophilic reactivity constants $n^0{}_{Pt}$ were defined by

$$\log(k_Y/k_s)^0 = n^0{}_{Pt} \tag{5}$$

where k_Y and k_s refer to the constants for reactions of *trans*-$[PtCl_2(py)_2]$ in CH_3OH at 30 °C.

$$\textit{trans}\text{-}[PtCl_2(py)_2] + Y^{-/0} \xrightarrow[30\,^\circ C]{CH_3OH} \textit{trans}\text{-}[PtClY(py)_2]^{0/+} + Cl^- \tag{6}$$

Table 2 gives values of $n^0{}_{Pt}$ for several nucleophilic reagents. A plot of log k_Y for other platinum complexes against $n^0{}_{Pt}$ gives reasonably good straight lines (Figure 3), which supports the linear free energy relationship

$$\log k_Y = Dn^0{}_{Pt} + \log k_s \tag{7}$$

The intercepts of plots such as Figure 3 are close to the values of k_s for each substrate, and the constant D is dependent on the nature of the substrate. It is a nucleophile discrimination factor, and a large value of D means the complex is very sensitive to changes in the nature of the nucleophilic reagent. Finally the most significant point that can be made from values of $n^0{}_{Pt}$ (Table 2) is that platinum(II) is a class (b) or soft metal. The strongest protonic base CH_3O^- in

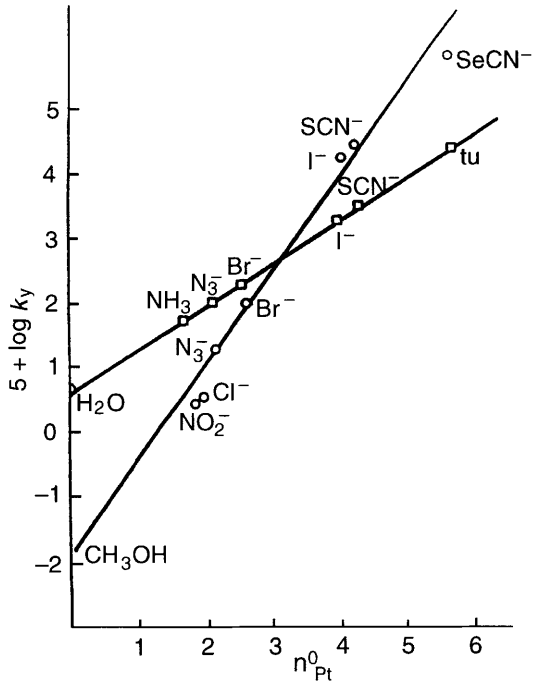

Figure 3 *Correlation of the rates of reaction of platinum*(II) *complexes with* n^0_{Pt} *for various nucleophiles*: ○, trans-$[PtCl_2(py)_2]$ *in methanol at 30 °C*, □, $[PtCl_2(en)]$ *in water at 35 °C.*

Table 2 *Values of* n^0_{Pt} *and of* pK_a *of some nucleophiles*

Nucleophile	n^0_{Pt}	pK_a
CH_3O^-	< 2.4	15.8
Cl^-	3.04	− 5.74
NH_3	3.06	9.25
NO_2^-	3.22	3.33
I^-	5.42	− 10.7
SCN^-	6.65	− 1.8
$S{=}C(NH_2)_2$	7.17	− 0.96
$S_2O_3^{2-}$	7.34	1.9
PPh_3	8.39	2.61

CH_3OH solvent has the smallest n^0_{Pt}, whereas some of the weakest protonic bases which are highly polarisable (I^-, $S{=}C(NH_2)_2$, $S_2O_3^{2-}$) have the largest n^0_{Pt} values. This came as no surprise, but it was important to quantify the fact and to have a standard for values of nucleophilic strengths of reagents towards platinum(II) complexes.

3 Collaborative Research with Chatt on the Kinetic *Trans Effect* of the Nickel Triad Metal Complexes

By the late 1950s, Chatt and Bernard Shaw[3] had succeeded in preparing several alkyl-, aryl- and hydrido-metal complexes of the nickel triad. Because of our mutual interest in the *kinetic trans effect* of platinum(II) complexes, Chatt and I decided to examine the rates of ligand substitution of these new organometallics. Shaw prepared the compounds and Harry Gray did the kinetic studies. Years later Chatt gave the following account of why the research was so rapidly accomplished.

'Shaw said, "that man Gray must be an absolute glutton for work. I did not know it was possible to do kinetics so fast; as soon as I get a compound out of the lab., the result is in and he is waiting for another. I cannot keep up with him". When I met Fred Basolo at our next conference, he told me Gray said "that guy Shaw's a worker. He nearly drives me mad, the compounds come so fast; as soon as I have done one the next compound is waiting".' Joseph and I laughed, saying if this competition continues, we will very soon have enough for a publication.

The results of this joint venture were reported for reaction (8) in ethanol solution between pyridine and several planar compounds of the general formula indicated.

$$\textit{trans}\text{-}[MClL(PEt_3)_2] + py \rightarrow \textit{trans}\text{-}[MLpy(PEt_3)_2]^+ + Cl^- \qquad (8)$$

(M = Ni, Pd, or Pt; L = alkyl, aryl, or hydride)

The relative rates of reaction *trans*-[M(*o*-tolyl)Cl$(PEt_3)_2$] are approximately 5×10^6 for Ni, 1×10^5 for Pd, and 1 for Pt. The large difference in lability between platinum(II) and nickel(II) is in accord with a mechanism where ligands above and below the plane move in to displace Cl^-, since nickel(II) more readily expands its coordination number than does platinum(II). In further support is the observation that *trans*-[Ni(mesityl)Cl$(PEt_3)_2$] reacts only about 2×10^4 times faster than the corresponding platinum(II) compound, because the mesityl ligand blocks the coordination sites above and below the plane and retards the reaction of nickel(II) more than of platinum(II). In fact, the differences in rates for the mesityl systems resemble those between octahedral cobalt(III) and rhodium(III) complexes.

The results of this study further show that the *trans*-labilising ability of the ligands L decrease in the order $PMe_3 > H > Me >$ phenyl $\approx p$ methoxyphenyl $\approx p$-chlorophenyl $>$ biphenyl $> o$-tolyl $>$ mesityl $\approx$ Cl.

As mentioned above, there are two main hypotheses used to account for the *trans effect*. One is that of the Russian School[4,7] which considers it to be mostly electrostatic in origin, depending largely on the polarisability of the ligand: the more polarisable the ligand, the greater its *trans effect*. The second hypothesis is that of the English School[5] which suggests that large *trans effects* are produced by ligands able to π back-bond to the metal. This π back-bonding lowers the electron density on the metal which enhances nucleophilic attack on the metal and/or stabilises a five-coordinate transition state for reaction. The results of our

study with Chatt further support there being two types of ligand that have high *kinetic trans effects*: those that seem to function *via* the polarisation theory and those that involve π bonding. For example, the relative rates of reaction of compounds with the *trans* ligands H, Me, phenyl, and Cl are approximately 100 000: 200: 30: 1. Since π back-bonding is of no importance for these ligands, it follows that this rapid rate decrease must be mainly electrostatic in origin. This is supported by the large decrease in dipole moment for changes in the *trans*-ligand L = H (4.2 D), Me (3.4 D), phenyl (2.6 D), and Cl (0 D). However, good π bonding ligands such as C_2H_4 and CO do not have this polarisation effect, but they do have a large *kinetic trans effect* best explained by the π back-bonding concept. This study was also the first to get rate data on the ligand substitution reactions of homologous complexes of metals of the nickel triad, and to determine the *kinetic trans effects* of many different ligands.

4 The Kinetics and Mechanisms of Ligand Displacement Reactions of Platinum(IV) Complexes

All of the research we and others had done on ligand substitution reactions of six-coordinate octahedral complexes showed them to react by a dissociative S_N1 mechanism. Instead, four-coordinate square-planar metal complexes react by an S_N2 process, because of the ease with which their coordination numbers can increase, and because of a low energy *p*-orbital for attack by the entering ligand. Furthermore, all studies on the analogous d^2sp^3 six-coordinate cobalt(III) complexes react by an S_N1 mechanism. Why then would we want to investigate the substitution reactions of *trans*-$[PtCl_2(NH_3)_4]^{2+}$? Our reasoning was that the higher oxidation state of platinum(IV) might make it more electrophilic than cobalt(III), and result in the platinum(IV) complexes being more susceptible to an S_N2 nucleophilic attack. We were not wrong about this but, as is now to be seen, we also found some other more interesting chemistry of platinum(IV) complexes.

There is a considerable amount of information on the preparations and reactions of platinum(IV) complexes, largely done by Russian chemists. In spite of this, there seems to have been only one quantitative kinetic study reported on substitution reactions on these systems. Unfortunately, as is pointed out later, the results of this investigation are difficult to interpret because of the complications due to photosensitivity and platinum(II) catalysis of these reactions. Thus the correlations attempted by the Russian workers[7] for the series of complexes they investigated should be viewed with some caution.

We followed spectrophotometrically Reaction (9).

$$\textit{trans}\text{-}[PtBr_2(en)_2]^{2+} + Cl^- \rightarrow [PtBrCl(en)_2]^{2+} + Br^- \qquad (9)$$

It was observed that this reaction is photocatalysed so that all studies were then made on reaction mixtures which were kept in the dark. Using an excess of hydrochloric acid, the data were found to give good pseudo-first-order plots and the rates showed a first-order dependence on the concentration of chloride ion. However, different preparations of *trans*-$[PtBr_2(en)_2]Br_2$ (en = 1,2-

diaminoethane), all identical in analysis, gave quite different rate constants. Recrystallisation of a particular sample also gave fractions which differed in their reactivity.

From the work of Taube and King,[15] it was suspected that the different reactivities of these presumably identical compounds were caused by catalytic amounts of $[Pt(en)_2]^{2+}$. This was confirmed[16] both by the addition of the catalyst and also by the addition of cerium(IV) to destroy the catalyst. Addition of five mole per cent $[Pt(en)_2]^{2+}$ results in complete reaction within five minutes of a complex which would otherwise react in the dark at 25°C with $t_{\frac{1}{2}} = 44$ min. This same complex in the presence of cerium(IV) showed no detectable reaction under these conditions over a period of 24 h.

The extremely slow exchange of chloride ion in *trans*-$[PtCl_2(en)_2]^{2+}$ is catalysed by $[Pt(en)_2]^{2+}$ with the attendant rate law (10).

$$\text{Rate} = k\,[PtCl_2(en)_2{}^{2+}][Pt(en)_2{}^{2+}]\,[Cl^-] \tag{10}$$

However, the results can be explained in terms of the *inner-sphere* mechanism [Equations (11) and (12)].

$$\underset{\mathbf{4}}{[Pt(en)_2]^{2+}} + Cl^- \xrightarrow{\text{fast}} [Pt(en)_2]^{2+}, Cl^- \tag{11}$$

$$[Pt(en)_2]^{2+}, Cl + \textit{trans}\text{-}[PtCl_2(en)_2]^{2+} \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \underset{\mathbf{5}}{[Cl(en)_2Pt\text{-}Cl\text{-}Pt(en)_2Cl]^{3+}} \downarrow \text{fast} \tag{12}$$

$$[Pt(en)_2]^{2+}, Cl^- + [PtCl_2(en)_2]^{2+}$$

There is now a good deal of evidence[2] for the addition of other groups to square-planar complexes such as **4**. There is also X-ray evidence[2] for the existence of bridged platinum(II)–X–platinum(IV) halogen complexes of the type **5** postulated in Equation (12). Furthermore, there is ample evidence to support the view that certain oxidation–reduction reactions proceed by an atom-transfer mechanism through a bridged intermediate analogous to **5**. Such a halogen atom-transfer mechanism is applicable to a one-electron redox process,[17] but not to a two-electron process of the type described here for the platinum(II)–platinum(IV) system. In this case, where the bridged intermediate involves only one halogen, the net effect requires a halogenium ion transfer.

It follows from the proposed mechanism of chloride ion exchange in this system that platinum exchange between the platinum(II)–platinum(IV) species should proceed at the same rate as does the chloride ion exchange.[18] Another way of observing the same thing would be to start with ^{195}Pt in one of the complexes and follow the rate at which it is distributed between the two different oxidation states of platinum. These experiments[19] have been done and support the proposed mechanism.

Finally, it should also be pointed out that the ligand which adds to platinum(II) as in Equation (11) need not be of the same kind as those attached to platinum(IV) Therefore, it follows that there may be a very common mechanism for the syntheses of platinum(IV) complexes involving platinum(II) catalysis. For

example, the method of preparation of *trans*-$[PtX_2(NH_3)_4]X_2$ is the oxidation of $[Pt(NH_3)_4]^{2+}$, as shown by Equation (13).

$$[Pt(NH_3)_4]^{2+} + \underset{-X_2}{\overset{+X_2}{\rightleftharpoons}} \textit{trans}\text{-}[PtX_2(NH_3)_4]^{2+} \qquad (13)$$

Having prepared *trans*-$[PtX_2(NH_3)_4]^{2+}$, it can be allowed to react with a solution of $[Pt(NH_3)_4]^{2+}$ plus Y^- to form the desired *trans*-$[PtY_2(NH_3)_4]^{2+}$. This method was used successfully[20] to prepare *trans*-$[Pt(SCN)_2(NH_3)_4]^{2+}$.

Also, the Russians were able to allow solutions of $[PtCl(NH_3)_5]Cl_3$ in aqueous HCl to react under mild conditions to give quantitative yields of *trans*-$[PtCl_2(NH_3)_4]Cl_2$. This puzzled them, because they knew that NH_3 should not be displaced by Cl^- under the experimental conditions used. Now we can be certain that the reaction proceeded rapidly to give quantitative yields of the desired product due to the presence of catalytic amounts of $[Pt(NH_3)_4]^{2+}$.

5 The Application of Reaction Mechanisms for the Synthesis of Metal Complexes

Joseph was interested in our research on the application of reaction mechanisms to design the syntheses of new metal complexes and of known compounds. He was naturally more concerned with platinum compounds, but as our work was mostly with cobalt complexes, he would also listen to me tell him about our research on these compounds.

One example will suffice to show the value of making use of reaction mechanisms in syntheses. This approach allowed us to prepare the new nitrito (M–ONO) complexes $[M(ONO)(NH_3)_5]^{2+}$ of rhodium(III) and of iridium(III), although their nitro (M–NO_2) compounds had been known for about a century. The success we had with this started with our detailed kinetic study[21] of the apparently simple Reaction (14).

$$[CoCl(NH_3)_5]^{2+} + NO_2^- \xrightarrow{\Delta} [Co(NO_2)(NH_3)_5]^{2+} + Cl^- \qquad (14)$$

We found the reaction to be anything but simple. The following five steps appear to be involved.

$$[CoCl(NH_3)_5]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{3+} + Cl^- \qquad (15)$$

$$[Co(NH_3)_5(OH_2)]^{3+} + H_2O \rightarrow [Co(OH)(NH_3)_5]^{2+} + H_3O^+ \qquad (16)$$

$$2HNO_2 \rightarrow N_2O_3 + H_2O \qquad (17)$$

$$[(NH_3)_5Co\text{–}OH]^{2+} \xrightarrow{N_2O_3} \left[\begin{array}{c}(NH_3)_5Co\text{–}O \text{ - - - } H \\ \quad\quad\quad\quad | \\ \quad\quad\quad O\text{–}N \text{ - - } NO_2\end{array}\right]^{2+} \rightarrow [(NH_3)_5Co\text{–}ONO]^{2+} + HNO_2 \qquad (18)$$

$$[Co(ONO)NH_3)_5]^{2+} \rightarrow [Co(NO_2)(NH_3)_5]^{2+} \quad (19)$$

Of particular significance in this reaction scheme is the *O*-nitrosation step (18), which suggests that the Co–O bond is not cleaved and that the kinetic product is therefore the unstable nitrito (Co–ONO) isomer. This then rearranges to the stable nitro (Co–NO_2) linkage isomer. Oxygen-18 labelling experiments of Murmann and Taube[22] later confirmed that there is no rupture of the Co–O bond during this process.

This mechanistic concept for the formation of nitrito-complexes of cobalt(III) suggests that other analogous metal systems should yield similar materials. However, the corresponding nitrito-complexes of rhodium(III) and of iridium(III) were not known. One reason that previous investigators had not been successful in preparing these is that the platinum group metal complexes are usually very slow to react and rather drastic reaction conditions had been used. As a result, the stable nitro-product rather than the kinetic nitrito-product was isolated. Since the formation of M–ONO does not involve M–O bond cleavage, the reaction as shown in (18) is expected to occur even under rather mild experimental conditions. This was found to be the case and salts of the new complexes $[M(ONO)(NH_3)_5]^{n+}$ where M = rhodium(III), iridium(III) or platinum(IV) have been prepared.[23]

Sometimes amusing things happen when dealing with graduate students doing PhD research. That occurred in this case. After I talked about this problem to Geneva Hammaker, one of our few female graduate students at the time, she went to the library to get directions for the preparations of the two starting materials. In a few days she returned asking for a new problem because she read that an attempt had been made to prepare $[Rh(ONO)(NH_3)_5]^{2+}$, but that it had failed. I asked about the conditions of the experiments, and was told the reaction mixture was kept at 100°C for a few hours and the product isolated was the nitro-complex $[Rh(NO_2)(NH_3)_5]^{2+}$. I explained to her that this was to be expected, because under those conditions one gets the thermodynamically stable nitro-compound. She was almost in tears. Rather than suggesting a different problem, I described to her in detail why I felt this preparation should work, because the metal–oxygen bond was not broken. This indicates that the metal may only have a small effect so the reaction to give the desired nitrito kinetic product should take place under mild conditions. She reluctantly agreed to try it. A few days later she came to my office and was a different person – all smiles and joyous with the satisfaction that she had been able to make a new compound, $[Rh(ONO)(NH_3)_5]Cl_2$. She then proceeded to prepare the corresponding iridium and platinum complexes. She followed this by investigating the rates of rearrangement of each to the thermodynamic nitro complexes, $[M(NO_2)(NH_3)_5]^{2+}$.

Her paper was submitted to the new journal. *Inorganic Chemistry*, and has the honour of being its first paper with the reference that I can easily remember, *Inorg. Chem.*, 1962, **1**, 1.

6 Joseph Chatt the Person

I have always considered Joseph a friend, one with whom I could always discuss chemistry and family. I am so very pleased that the Royal Society of Chemistry and the British inorganic chemists are paying him the honour he justly deserves. It is my opinion that he should be considered, 'the Father of platinum(II) chemistry.'

I think the first time Joseph came to the US was in the late 1950s when we invited him to give a lecture at the Gordon Research Conference. He took that occasion to visit me at our department and give a seminar. In England, he is called Joseph – in the US, Joe. I know of no other chemist who conducts his research with greater care. Research scientists say, 'If a scientist does not want to make a mistake, albeit minor, he should not do research.' To my knowledge, Joe, by his careful research, proved this statement to be false.

The seminar he gave was on some elegant pioneering work on the syntheses, reactions, and properties of some new complexes. Joe was very likeable and pleasant, but formal. Therefore, it surprised me when he started his lecture by telling this story:

> On a commuter train to London there were two passengers who always caught the train at the same time, and who often sat across from one another. One of the passengers had a pad of paper and kept throwing a sheet out the window during the ride. After some days of seeing this, the other passenger asked, "Why are you doing this?" His answer was "To keep the lions away." The questioner said, "But there are no lions in England," and the response was, "Yes, so you see it works."

Joe wanted to make the point that in basic science it is not enough to know it works, but one also needs to know why it works. He then proceeded to illustrate the point in the talk about his elegant research.

Joseph and I began to see less of one another after our retirements. However, each Christmas we exchanged news letters about our doings during the year. His letter was always much longer than mine, as he told me about his coin collection and his and Ethel's holiday cruises. I miss getting his letter each year, but I think of him often during the season of Christmas and the New Year.

I am humble but very honoured to have received the first Joseph Chatt Medal from the Royal Society of Chemistry.

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Tuning Rhodium(I) Metal Centre Accessibility in Iodomethane Oxidative Addition to Vaska-type Complexes by Interchanging Tertiary Phosphine for Arsine and Stibine

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1 Introduction

The complex, *trans*-[IrCl(CO)$(PPh)_3)_2$], which was first reported by Angoletta[1] and later correctly formulated by Vaska,[2] is one of the best known early organometallic complexes exhibiting catalytic activity. Interestingly enough, at that time the rhodium analogue was already known[3] and had been investigated to some extent.[4]

These complexes are typical of those studied by Chatt, which enabled bonding theories and their applications to be developed,[5] and were soon recognised as important model systems for studies on homogeneous catalysis. These d^8 square-planar systems thus undergo a range of reactions, such as oxidative addition, with different substrates.[6] Ironically, today complexes with the general formula *trans*-[$MCl(CO)(L)_2$] (M = Rh or Ir; X = halide or pseudo halide; L = neutral ligand) are still in many instances known as analogues of Vaska's complex,[6,7] in spite of important earlier contributions by Chatt and co-workers.

The rhodium complexes are more resistant towards oxidative addition than their iridium counterparts and this is believed to be linked to steric crowding, especially when employing bulky tertiary phosphine ligands. Work by Wilkinson[8-10] explored several aspects of the steric and electronic properties of the rhodium(I) analogues, but definite crystal structural confirmation of the reaction

products could not be achieved. In this paper we address several of these aspects[11] and outline steric implications of analogous Group 15 donor ligands (P, As and Sb) – including the incorporation of methyl substituents on the phenyl rings of these ligands, which results in interesting isomorphic structures.

2 Experimental

For experimental procedures utilised in this work, *i.e.* synthetic,[12,13] UV–vis spectrophotometry,[14] kinetic analyses,[15] IR/NMR spectroscopy[16] and X-Ray crystallography,[11,17] the reader is referred to earlier work.[14] The data for the crystal structures reported herein were solved using standard techniques and details have been reported.[18–21]

3 Reaction Scheme

The general stoichiometry of the reaction is shown in Scheme 1. The equilibrium reaction defining the first step (forward = oxidative addition; reverse = reductive elimination) was verified previously.[10,14] Figure 1 illustrates the oxidative addition of MeI to $[RhCl(CO)\{Y(p\text{-}Tol)_3\}_2]$.

$$[RhCl(CO)\{Y(p\text{-}Tol)_3\}_2] + CH_3I \underset{k_{RE}}{\overset{k_{OA},\ K_{OA}}{\rightleftharpoons}} [Rh(CH_3)Cl(I)(CO)\{Y(p\text{-}Tol)_3\}_2]$$

$$k_{CI} \downarrow \uparrow k_{-CI}$$

$$[Rh(COCH_3)Cl(I)\{Y(p\text{-}Tol)_3\}_2]$$

Scheme 1 *General reaction pathway for the iodomethane oxidative addition and successive migratory CO insertion reactions in Vaska-type compounds (Y=P (1), As (2))*

The slow transformation of the *trans*-$[RhCl(CO)\{As(p\text{-}Tol)_3\}_2]$ complex, **2**, (Figure 2) (ν(CO) = 1973 cm^{-1}), and the clean conversion to the intermediate

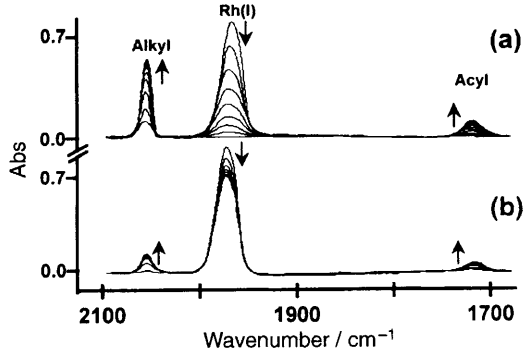

Figure 1 *Infrared spectra (25 °C; 10 min intervals) of iodomethane oxidative addition to* (a) *[RhCl(CO){As(p-Tol)$_3$}$_2$] (2) and* (b) *[RhCl(CO){P(p-Tol)$_3$}$_2$] (1), illustrating the formation of the rhodium(III)-alkyl and rhodium(III)-acyl species; $CHCl_3$, [Rh] = 0.02 M; $[CH_3I]$ = 3 M*

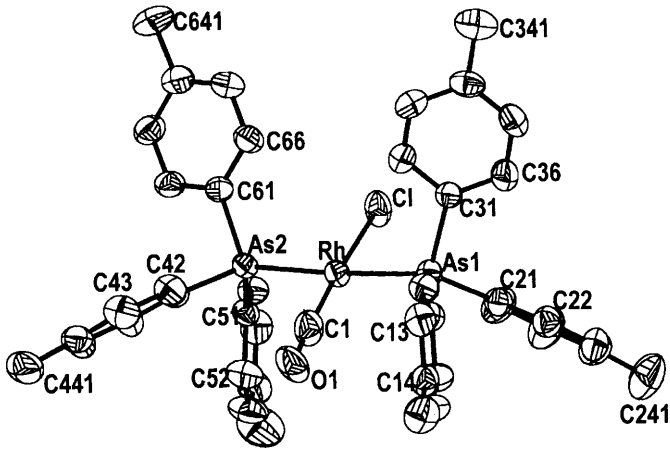

Figure 2 *Ortep drawing of trans-*[*RhCl*(*CO*){*As*(p-*Tol*)$_3$}$_2$] (**2**) (*50% probability ellipsoids; hydrogen atoms omitted for clarity*) *showing the numbering scheme. The first digit of the carbon atom numbering corresponds to the phenyl ring number and the second to the atom in the ring*

alkyl species (ν(CO) = 2050 cm^{-1}), is apparent. However, in the case of the *trans*-[RhCl(CO){P(*p*-Tol)$_3$}$_2$] complex, **1**, it is clear that under identical conditions the reactant is converted to the intermediate alkyl species only to a small extent, thus confirming its thermodynamic unfavourability. This probably also explains why the intermediate P-alkyl complex could not be isolated, compared to the corresponding As species, which has indeed been obtained in the solid state and structurally characterised (see Figure 3).

4 Structural Aspects

The reactants as well as the intermediate alkyl species in this reaction have been characterised. Thus, the difficulty associated with interpreting NMR spectra of As and Sb complexes (arising from the unfavourable properties of the nuclei) has been partially circumvented by X-ray structural analysis.

4.1 Rhodium(I) Complexes

The molecular structure of **2**, shown in Figure 2, is isomorphous and thus virtually identical to the P(*p*-Tol)$_3$ analogue.[11] **1** and **2** are compared in Table 1.

As shown in Table 1, the As–Rh–As moiety in **2** (4.824(1) Å) is significantly longer than that of P–Rh–P in **1** (4.665(1) Å). This in turn means there is a larger 'cavity' for entering nucleophiles in the arsine Vaska-type complex compared to the sterically more hindered phosphine analogue.

The increase in the length of Rh–Cl bonds from complex **1** and **2** suggests more electron density on the Rh-centre in complex **2**. The Rh-C(1) and C≡O bond distances in the isomorphous complexes **1** and **2** do not differ significantly.

Table 1 *Selected interatomic bond lengths (Å) and angles (°) in complexes* **1**, **2** *and* **3**

	1 $L = P(p\text{-}Tol)_3$[a]	**2** $L = As(p\text{-}Tol)_3$	**3** $L = As(p\text{-}Tol)_3$
Rh-C(1)	1.798(5)	1.817(5)	1.841(13)
Rh-Cl	2.358(2)	2.393(2)	2.403(3)
Rh-L(1)	2.334(2)	2.4181(4)	2.4664(11)
Rh-L(2)	2.331(2)	2.4169(4)	2.4727(11)
$L(1)\text{-}C(n1)_{av}$	1.821(5)	1.940(5)	1.944(9)
$L(2)\text{-}C(n1)_{av}$	1.823(5)	1.942(5)	1.942(9)
C(1)-O(1)	1.139(6)	1.082(5)	1.174(14)
Rh-C(2)	–	–	2.280(8)
Rh-I	–	–	2.7860(11)
L(1)-L(2)	4.665(5)	4.835(1)	4.939(2)
L(1)-Rh-L(2)	175.67(4)	175.91(2)	176.66(4)
C(1)-Rh-Cl	173.11(19)	174.2(2)	178.9(5)
C(1)-Rh-L(1)	90.64(15)	90.77(13)	91.0(4)
C(1)-Rh-L(2)	91.77(15)	92.11(13)	90.6(4)
Cl-Rh-L(1)	89.84(4)	89.14(3)	89.59(6)
Cl-Rh-L(2)	88.19(4)	88.29(3)	88.76(6)
O(1)-C(1)-Rh	177.3(10)	174.4(5)	174.8(15)
C(1)-Rh-I	–	–	80.7(5)
As(1)-Rh-I	–	–	93.53(4)
Cl-Rh-I	–	–	100.32(7)
C(2)-Rh-I	–	–	165.6(2)
As(2)-Rh-I	–	–	89.62(4)

[a] Ref 11

These compounds are some of the few structurally characterised Vaska-type complexes not showing a disorder along the carbonyl/chloro axis. The L(1)–Rh–L(2) bond angles for these are 175.91(2)° and 175.67(4)° for L = As(*p*-Tol)$_3$ and P(*p*-Tol)$_3$ respectively, which, being significantly smaller than 180°, enables them to crystallise in the non-centrosymmetric space group, $Pna2_1$. The Flack parameters are zero within experimental error, indicating that the correct stereochemical isomer was refined.

As indicated[11,17] and compared in Table 2, not only are **1** and **2** isomorphous with one another, they are also isomorphous with *trans*-[IrCl(CO){P(*p*-Tol)$_3$}$_2$],[11] *trans*-[Pt(CH$_3$)Cl{As(*p*-Tol)$_3$}$_2$][22] and *trans*-[Ir(CH$_3$)(CO){P(*p*-Tol)$_3$}$_2$].[23] This range of metal centres, oxidation states, donor atoms and combinations of *trans* ligands is thus quite novel. It seems that incorporation of the 4-methyl substituents on the aryl rings of the Group 15 L tertiary ligand causes such space demands that, during crystallisation, the space requirements of the halide, CO *etc.* moieties are overridden. Similar isomorphism is not observed in the case of the corresponding [RhCl(CO)(YPh$_3$)$_2$] complexes (Y = P, As or Sb).[24]

Of further interest is the fact that the Rh–P and Ir–P bond lengths in the structures listed in Table 2 are virtually identical. However, changing the Group 15 donor atom results in significant increases in the Rh–L bond length {from 2.33

Table 2 *Comparison of bond data and spectroscopic properties in* trans-$[MX(CO)L_n]$ (M = *Rh or Ir*; X = *Cl or* $C(O)CH_3$; n = 2 *or* 3)

Complex	*M–L* (Å)	*M–X* (Å)	*ν(CO)*[a] (cm^{-1})	*M–CO* (Å)	*C–O* (Å)	*L–M–L* (°)	*Ref*
$[RhCl(CO)(PPh_3)_2]$	2.322(1)	2.382(1)	1979	1.77(1)	1.140(2)	180.0(1)	25
$[RhCl(CO)(PCy_3)_2]$	2.3491(7)	2.388(2)	1943	1.748(8)	1.163(7)	180	26
$[RhCl(CO)(PPh_2Fc)_2]$	2.3344(14)	2.415(7)	1970	1.814(14)	1.056(14)	180	27
$[RhCl(CO)\{P(NMe_2)_3\}_2]$	2.3426(7)	2.443(7)	1964	1.731(9)	1.15(2)	180	27
$[RhCl(CO)\{P(p\text{-}Tol)_3\}_2]$	2.333(2)	2.3581(12)	1976	1.798(5)	1.139(6)	175.67(4)	11
$[RhCl(CO)\{As(p\text{-}Tol)_3\}_2]$	2.4175(4)	2.393(2)	1973	1.817(5)	1.082(5)	175.91(2)	b
$[RhCl(CO)(AsPh_3)_2]$	2.4226(4)	2.3538(14)	1975	2.017(7)	0.717(7)	175.97(6)	27
$[RhCl(CO)(SbPh_3)_2]$	2.5655(2)	2.315(3)	1971	1.797(13)	1.175(13)	180	27
$[RhCl(CO)(SbPh_3)_3]$	2.5981(5)	2.4094(18)	1971	1.875(7)	1.035(6)	119.97(2)	27
$[Rh(COCH_3)(CO)(SbPh_3)_3]$	2.568(2)	–	1710	1.911(20)	1.121(25)	120.0(1)	28
$[IrCl(CO)(PPh_3)_2]$	2.330(1)	2.382(3)	1950	1.791(13)	–	–	29,30
$[IrCl(CO)\{P(p\text{-}Tol)_3\}_2]$	2.331(2)	2.364(2)	c	1.817(8)	1.134(10)	175.19(2)	31
$[IrCl(CO)(PCy_3)_2]$	2.345(2)	2.398(7)	1934	1.78(2)	1.10(2)	180	32

[a] Dichloromethane solution
[b] This work
[c] Not reported

(P) to 2.42 (As) to 2.58 Å (Sb)}. The relatively easy formation of five-coordinate stibine-containing complexes[27,24] may be a consequence of these changes.

In Table 2, comparisons between the complexes investigated in this study and a few other relevant iso-structural complexes from the literature suggest that the introduction of ligands with heavier donor atoms, such as arsines and stibines, leads to reduced steric crowding at the metal, creating more space for entering moieties in reactions such as oxidative addition.

To further illustrate the steric effects induced by these tertiary Group 15 ligands, we have calculated the Tolman angles[33] (θ_T, using 2.28 Å for standardised Ni–P bonds) and the effective cone angles (θ_E, using true bond distances).[34] $\theta_T = 140$ and 133° and $\theta_E = 140$ and 132° for $AsPh_3$ and $SbPh_3$, respectively. These values are more than 10° less than the corresponding values for PPh_3 (we assume that *para* substitution has negligible effect on the cone angle). The increase in P–C, As–C and Sb–C bond lengths (Table 1) from 1.82 to 1.94 to 2.10 Å[27] and reduction in the C–L–C angles for the Group 15 elements, 116, 109, 102 and 97° for N to Sb, respectively,[35] result in an increased ability of the ligand to 'fold back' from the metal.

Whether the decrease in the Rh–Cl bond length in $[RhCl(CO)(YPh_3)_2]$ (Y = P, As, Sb; Table 2) is a result of the decrease in electron density at the metal centre or arises from the decrease in steric crowding of the Group 15 donor ligand as discussed above is, however, not clear at this point.

As the electron-donating ability of the Group 15 donor L ligand decreases, the electron density on the metal decreases, resulting in a weaker M–CO bond, a stronger C≡O bond and a small but significant increase in ν(CO) (in dichloromethane). The net change in electron density is further illustrated by the reactivity change of the complexes towards oxidative addition (Table 3).

4.2 Rhodium(III) Alkyl Complexes

The molecular structure of the intermediate alkyl complex, *trans*-$[Rh(CH_3)Cl(I)(CO)\{As(p\text{-}Tol)_3\}_2]$ **3** (Figure 3), clearly shows that *trans* addition of iodomethane has occurred, as has been found previously[14] in systems with sterically congested and electron-rich metal centres.

Complex **3** represents one of the very few characterised arsine complexes of this type, and of interest is the fact that the Rh–As bonds were lengthened by almost 0.05 Å compared to its precursor, **2**, increasing the As–Rh–As distance from 4.835(1) to 4.959(2) Å. The Rh–Cl bond stayed virtually unaffected. The increase in the Rh–CO bond length, while of borderline statistical significance, is consistent with the higher ν(CO) value of 2050 cm^{-1}.

The rhodium(III)–I bond distance in **3** (*trans* to Me) is longer than those (*trans* to PPh_3) in $[Rh(CH_3)I(CO)(PPh_3)(cupf)]$ (Hcupf = cupferron; *N*-nitrosophenylhydroxylamine)[36] and $[Rh(CH_3)I(CO)(PPh_3)(quin)]$ (Hquin = 2-quinolinecarboxylic acid)[37] (from the *cis* addition of iodomethane), though it is significantly shorter than for other *trans*-CH_3-Rh-I moieties, such as the average value of 2.803(1) Å in $[Rh(CH_3)I(CO)(PPh_3)(oxin)]$ (Hoxin = 8-hydroxyquinoline)[38] and 2.849(1) Å in $[Rh(CH_3)I(CO)(PPh_3)(dmavk)]$ (Hdmavk = dimethyl β-

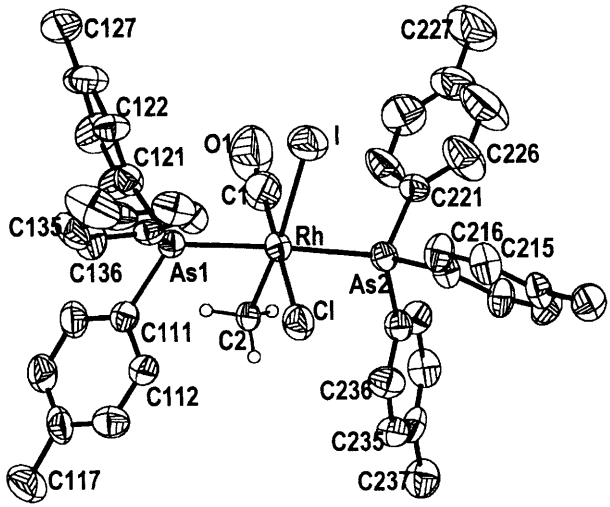

Figure 3 *Ortep drawing of* trans-$[Rh(CH_3)Cl(I)(CO)\{As(p\text{-}Tol)_3\}_2]$ **(3)** *(50% probability ellipsoids; hydrogen atoms omitted for clarity) showing the numbering scheme. The first digit of the carbon atom numbering corresponds to the As atom, the second to the ring and the third to the atom in the ring*

aminovinylketone).[39] The metal centres in the latter examples display high reactivity toward iodomethane, with half-lives (for $[CH_3I] = 1$ M) in the second range. The slower kinetics observed for iodomethane oxidative addition to **2** and the shorter Rh–I bond length in **3** may be related.

5 Rate Laws for Reaction

Iodomethane oxidative addition to rhodium(I) complexes proceeds according to the general mechanism[10,14] given in Scheme 1, followed by a migratory carbonyl insertion. The reverse of the first step represents reductive elimination. The observed pseudo-first-order rate constant ($[CH_3I] \gg [Rh]$) for the first step in Scheme 1 is defined by Equation 1.

$$(k_{obs})_{OA} = k_{OA}[CH_3I] + k_{RE} \quad (1)$$

The kinetic constants k_{OA} and k_{RE} refer to the rates of the oxidative addition and reductive elimination reactions, respectively. The equilibrium constant for the first step is given by Equation 2.

$$K_{OA} = k_{OA}/k_{RE} \quad (2)$$

Oxidative addition and reductive elimination were studied in a range of solvents and different CH_3I concentrations at three different temperatures using different kinetic techniques (IR and UV–vis). The rate of rhodium(III)-alkyl formation shows a direct relationship of the pseudo-first-order rate constant on $[CH_3I]$, as illustrated in Figure 4.

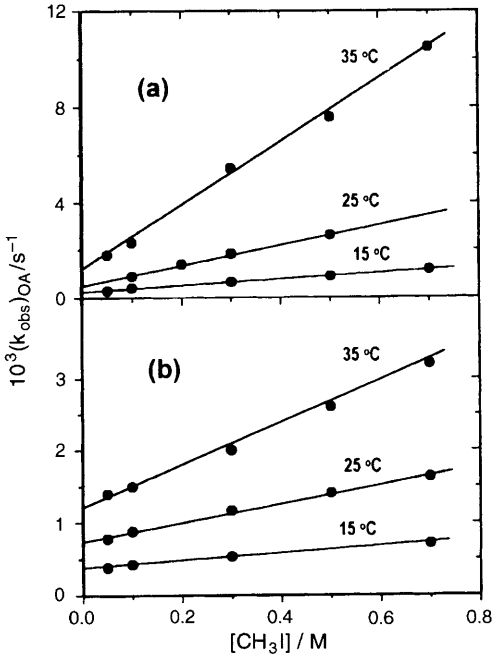

Figure 4 *$[CH_3I]$ and temperature dependence of the pseudo-first-order rate constant for the iodomethane oxidative addition to*: (a) trans-*$[RhCl(CO)\{As(p\text{-}Tol)_3\}_2]$ and* (b) trans-*$[RhCl(CO)\{P(p\text{-}Tol)_3\}_2]$ in acetone*

These results are also supported by time-resolved IR spectroscopy studied under identical conditions (Figure 1). The conversion to the alkyl species from **1** is clearly less favoured than that from **2**. In the latter case the reaction proceeds quite efficiently to the alkyl species (ν(CO) = 2050 cm^{-1}), while the conversion of $[RhCl(CO)\{P(p\text{-}Tol)_3\}_2]$ to the rhodium(III)-alkyl complex is thermodynamically less favoured.

An aim of this study was to investigate the effect of structural aspects on the reactivity of the two Vaska-type complexes. It was shown crystallographically that **2** is less sterically crowded than **1**, since introduction of the larger arsenic atom enlarges the 'cavity' in the complex to accommodate entering moieties, such as in oxidative addition of iodomethane. This increase in 'cavity' size is expected to shift the equilibrium more toward the intermediate, resulting in a larger K_{OA} for **2** than for **1** as shown in Table 3. Of interest is the fact that oxidative addition is thermodynamically favoured for **2** compared to **1** in both dichloromethane (K_{OA} 9 *vs.* 1.7 M^{-1}) and acetone (15 *vs.* 2.3 M^{-1}). However, in ethyl acetate and toluene values of K_{OA} are, strangely enough, quite similar though of lower precision.

The expression for the observed rate constant for the formation of the rhodium(III)-acyl species *via* migratory carbonyl insertion ($[CH_3I] \gg [Rh]$), as

Table 3 *Temperature and solvent dependence of rate constants (Scheme 1) for the oxidative addition of* CH_3I *to* trans-$[RhCl(CO)\{Y(p\text{-}Tol)_3\}_2]$ *(Y = P, As and Sb*[a]*; AC = acetone, EA = ethyl acetate, DCM = dichloromethane, TOL = toluene)*

Constant	Temp (°C)	$P(p\text{-}Tol)_3$				$As(p\text{-}Tol)_3$			
		AC	*EA*	*DCM*	*TOL*	*AC*	*EA*	*DCM*	*TOL*
ε[b]		20.7	6.0	8.9	2.38	20.7	6.0	8.9	2.38
D_N[c]		17.0	17.1	4[d]	0.1[e]	17.0	17.1	4[d]	0.1[e]
$10^3 k_{OA}(M^{-1}s^{-1})$	5	–	0.08(4)	–	–	–	–	–	–
	15	0.5(2)	0.09(3)	0.56(1)	–	1.32(5)	0.11(4)	0.22(1)	–
	25	1.30(6)	0.24(2)	2.90(9)	0.20(1)	4.2(2)	0.84(4)	0.60(1)	0.05(2)
	35	2.78(8)	–	6.86(6)	–	13.3(4)	3.8(1)	2.03(9)	–
$\Delta H^{\ddagger}_{k_{OA}}$ (kJ mol^{-1})	–	58(3)	–	72(12)	–	85(1)	115(5)	87(6)	–
$\Delta S^{\ddagger}_{k_{OA}}$(JK^{-1} mol^{-1})	–	−100(9)	–	−48(30)	–	−1(4)	86(15)	−8(18)	–
$10^3\, k_{RE}$ (s^{-1})	5	–	0.20(1)	–	–	–	–	–	–
	15	0.366(9)	0.362(4)	0.54(1)	–	0.25(2)	1.13(1)	0.029(4)	–
	25	0.75(2)	0.880(3)	1.27(4)	1.63(1)	0.52(6)	5.11(1)	0.041(4)	0.445(2)
	35	1.22(3)	–	1.61(4)	–	1.1(2)	15.1(6)	0.10(4)	–
$\Delta H^{\ddagger}_{k_{RE}}$ (kJ mol^{-1})	–	39(4)	–	30(12)	–	53(1)	83(6)	–	–
$\Delta S^{\ddagger}_{k_{RE}}$(J K^{-1} mol^{-1})	–	−167(14)	–	−193(40)	–	−123(5)	−3(18)	–	–
K_{OA} (M^{-1})[f]	25	1.7(1)	0.27(2)	2.3(1)	0.12(1)	9(1)	0.16(1)	15(1)	0.11(4)
K_{OA} (M^{-1})[f,g]	25	1.8(3)	0.28(6)	2.5(5)	–	9(2)	0.17(3)	14(3)	–

[a] Ref 27. In neat CH_3I at 25°C, estimated values for $SbPh_3$ complex: k_{OA} *ca.* 3×10^{-4} $M^{-1}s^{-1}$; $K_{OA} > 100$ M^{-1}
[b] Ref 40
[c] Ref 41
[d] Estimated from chloroform
[e] Estimated from benzene
[f] From Equation (2)
[g] Average of three temperatures

illustrated in Scheme 1, is shown in Equation (3), where k_{Cl} and k_{-Cl} represent the rate constants for the forward and reverse steps for the migratory carbonyl insertion reaction, respectively.

$$(k_{obs})_{Cl} = (k_{Cl}K_{OA}[CH_3I])/(1 + K_{OA}[CH_3I]) + k_{-Cl} \quad (3)$$

The formation of the final rhodium(III)-acyl species has been observed and identified (Figure 1), though was not studied in detail.

6 Reactivity and Activation Parameters for Iodomethane Oxidative Addition

Depending on the solvent, the relative reactivities of **1** and **2** (as well as of $[RhCl(CO)(SbPh_3)_2]$) towards the oxidative addition and reductive elimination span ranges of up to two orders-of-magnitude (Table 3). The half-lives for the reaction at ambient temperature and $[CH_3I] = 1$ M, range from a few minutes to hours, and are comparable with those observed for $[RhCl(CO)(YPh_3)_2]$ (Y = P or As).[10]

1 is more reactive in the less polar/coordinating solvents dichloromethane and toluene, but the reaction is thermodynamically less favoured. In the more polar and coordinating acetone and ethyl acetate the As complex is actually a factor of 4–5 more reactive than the P analogue, which suggests increased solvent contribution in the As complex (see discussion below).

The fact that the $[RhCl(CO)(SbPh_3)_2]$ complex shows comparable reactivity to **2** suggests similar electron density on the Rh-centre in both. However, the Sb complex shows a significant increased reactivity toward solvents, which is attributed to the smaller steric demand at the metal centre.[27]

The formation of the rhodium(III)-acyl species (see Figure 1) was not studied in any detail. However, at low $[CH_3I]$, it follows from Equation 3 that the rate of formation of the acyl species is first-order in $[CH_3I]$, and directly proportional to the equilibrium constant K_{OA}. Thus, in the case of **1**, the effective rate of formation of the acyl species is decreased (by at least a factor of five), as the conversion of **1** to the intermediate $[Rh(CH_3)Cl(I)(CO)\{P(p\text{-}Tol)_3\}_2]$ species is thermodynamically less favoured.

The activation parameters (Table 3) are characterized by positive values of $\Delta H^{\ddagger}_{k_{OA}}$ and negative values of $\Delta S^{\ddagger}_{k_{OA}}$ and indicate that bond-formation plays an important role in forming the transition state. This is in agreement with previous work which showed that oxidative addition proceeds *via* an associative mechanism.[42] For **2** in ethyl acetate, the oxidative addition rate constants could not be determined accurately, but k_{RE} could be used for the calculation of the activation parameters. The values suggest less ordered transition states in which significant solvent interaction may occur, but it is clear that additional research is still required.

7 Solvent Effects

The arsine complex, **2**, shows a two orders-of-magnitude variation in the k_{OA}, k_{RE} and K_{OA} values in the four solvents studied. The P analogue, **1**, however, shows only *ca.* one order-of-magnitude variation in these constants, with a two-fold variation in k_{RE} in the four solvents.

An increase in solvent polarity (as manifested in the dielectric constant, ε) for solvents with roughly similar solvent donicity (from the donor number D_N), that is, comparing ethyl acetate to acetone and toluene to dichloromethane, results in an increase in both k_{OA} and K_{OA} for both **1** and **2**. However, k_{RE} for **1** shows very little solvent dependence (a decrease of only *ca.* 1.2-fold is observed from ethyl acetate to acetone, and 1.5-fold from toluene to dichloromethane) whereas for k_{RE} for **2** a one order-of-magnitude increase is observed. We conclude that the reductive elimination is inhibited in solvents of increased polarity, whereas oxidative addition is favoured. As a result K_{OA} for **2** spans a larger range of values compared to **1**.

Increasing the coordinating ability of the solvent (*i.e.* dichloromethane to ethyl acetate) with relative constant polarity increases k_{RE} in the As complex by two orders-of-magnitude, while leaving k_{OA} virtually unaffected. In the P complex, however, a change in the donicity of the solvent has a quite significant effect on the values of k_{OA} (about 15-fold increase), compared to that of k_{RE} (only a *ca.* two-fold increase). This might be indicative of competition between the CH_3I and the solvent in complex **2** where there is less steric congestion at the metal centre. The different steps in the reaction sequence are thus apparently influenced differently in the two complexes, but the net effect on K_{OA} is the same. Moreover, it cannot be excluded that the intercept in the equivalent to Figure 4(b) for ethyl acetate (so large compared to the other rate constants in general) actually incorporates contributions from both the reductive elimination as well as a possible parallel solvent pathway.

8 Concluding Remarks

It was shown that these Vaska-type complexes of rhodium(I) are excellent model complexes to study basic effects, including the use of molecular structure information to explain solution effects on reaction mechanisms. However, additional research is still required to aid in understanding solution behaviour of these systems.

9 Acknowledgements

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2; Emp. formula $C_{43}H_{42}As_2ClORh$; FW. 862.97; crystal system Orthorhombic; space group *Pna2*$_1$; *a* 21.8704(10); *b* 10.6662(5); *c* 16.8577(8) Å; *V*/Å^3 3932.5(3); *Z* 4; D_c/g.cm^{-3} 1.458; μ/mm^{-1} 2.203; *T*max/*T*min 0.681/0.804; *F*(000) 1744; crystal size/mm 0.68 × 0.54 × 0.34; θ limit/° 1.86 to 28.27; index ranges $-12 \leq h \leq 28$; $-12 \leq k \leq 12$; $-21 \leq l \leq 22$; collected refl. 16086; independent refl. 7961; R_{int} 0.0217; Obs. refl.[$I > 2\sigma(I)$] 7161; data/restr./param. 7960/1/440; goodness of fit 1.088; *R*/w*R* ($I > 4(\sigma)I$) 0.0289; 0.0590; *R*/w*R* (all data) 0.0361; 0.0629; Flack parameter 0.017(7); $\Delta\rho_{max}$; $\Delta\rho_{min}$/ e.Å^{-3} 0.466; −0.403.
3; Emp. formula $C_{44}H_{45}As_2ClIORh$; FW. 1004.90; crystal system Triclinic; space group $P\bar{1}$; *a* 11.1449(6); *b* 12.5765(7); *c* 17.4452(10) Å; α 75.795(1); β 87.296(1); γ 75.042(1)°; *V*/Å^3 2289.8(2); *Z* 2; D_c/g cm^{-3} 1.458; μ/mm^{-1} 2.568; *T*max/*T*min

0.458/0.861; F(000) 996; crystal size/mm 0.36 × 0.10 × 0.06; θ limit/° 1.20 to 25.03; index ranges $-13 \leq h \leq 12$; $-14 \leq k \leq 14$; $-20 \leq l \leq 14$; collected refl. 12107; independent refl. 7669; R_{int} 0.0241; obs. refl.[$I > 2\sigma(I$] 6085; data/restr./param. 7669/0/459; goodness of fit 1.213; R/wR ($I > 4(\sigma)I$) 0.0712; 0.1347; R/wR (all data) 0.0885; 0.1431; $\Delta\rho_{max}$; $\Delta\rho_{min}$/e.Å^{-3} 1.648; −1.459.

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SECTION H:

Other Papers Presented at the 34th International Conference on Coordination Chemistry, Edinburgh, Scotland, July 2000

The health and dynamism of contemporary coordination chemistry is well exemplified in the many and varied lectures and posters presented at the 34th ICCC. This would have pleased Joseph Chatt. He would also have been gratified to see his own contributions recognised in the session in his honour.

Papers presented in the 'Joe Chatt Chemistry' session illustrate the breadth of his contributions and their continuing legacy as well as the new directions, approaches and techniques, unanticipated by Chatt, but which would have excited his interest. Authors include many of Chatt's co-workers, collaborators and former students as well as those acknowledging a scientific debt to his pioneering work. It is sad to recall that we had hoped that Luigi Venanzi would have been among them but his illness and later passing prevented this.

Of the 22 plenary and invited lectures presented in the Joe Chatt Chemistry session at Edinburgh, 18 are included in this volume, some in amended and expanded form. Three of these papers we believe to be sufficiently distinctive for it to be inappropriate for them to be assigned to one of the earlier sections. These concern the use of electrospray mass spectrometry to study the processes of elimination from carbonyl clusters of ruthenium and iridium described by J. S. McIndoe and co-workers, the synthesis and characterisation of complexes containing the $\{Pt_2S_2\}$ *core (also reporting the use of electrospray mass spectrometry) reported by T. S. A. Hor and colleagues and of squarate coordination complexes, described by F. Dumitru and colleagues.*

Formaldehyde Elimination from Methoxylated Transition Metal Carbonyl Clusters

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Joseph Chatt's interests in organometallic chemistry were wide-ranging, from bonding theories to nitrogen fixation. While these areas may not seem of immediate relevance to either carbonyl cluster chemistry or to electrospray mass spectrometry (both of which play a major role in the work described herein), the chemistry that is discussed broadly overlaps with Chatt's contributions in metal hydride, metal phosphine and low-oxidation-state chemistry.

The following work describes our investigation into some unexpected chemistry resulting from our interest in unsaturated metal clusters.[1] We study such systems primarily by mass spectrometry, and to assist these investigations we developed the new data presentation technique of energy-dependent electrospray mass spectrometry (EDESI-MS). One of the first systems studied was that of alkoxylated transition metal carbonyl clusters, which display loss of formaldehyde in their electrospray ionisation fragmentation process. We have been able to correlate this behaviour with macroscopic chemical properties of these clusters.

1 Alkoxylation of Carbonyl Ligands

A well-known reaction in transition metal carbonyl chemistry is nucleophilic

attack of alkoxide ions, RO^-, on the electropositive carbon atom of a carbonyl ligand, affording an anionic alkoxycarbonyl species (Equation 1).

(1)

Alkoxylation occurs very rapidly and the product is thermodynamically favoured.[2] The reaction between alkoxide ions and transition metal carbonyl clusters, $[M_n(CO)_m]$, generates anionic species of general formula $[M_n(COOR)(CO)_{m-1}]^-$. A number have been isolated and crystallographically characterised, including $[Ir_6(COOMe)(CO)_{15}]^-$,[3] $[Os_5C(COOEt)H(CO)_{14}]^-$ and $[Os_5C(COOMe)I(CO)_{14}]^-$,[4] $[Ir_4(COOMe)(CO)_{11}]^-$[5] and $[Rh_6(COOMe)(CO)_{15}]^-$.[6]

2 Chemical Derivatisation

The alkoxylation reaction has been exploited in the *in situ* derivatisation of neutral metal carbonyl complexes for analysis by electrospray ionisation mass spectrometry (ESI–MS).[7] ESI is a relatively new ionisation technique which involves spraying a solution from a charged capillary into a strong electric field. Tiny droplets are formed from which the solvent is evaporated by means of a warm bath gas. Acquisition of charge by the target molecule usually takes place by chemical ionisation, frequently addition of H^+ from a protic solvent (typically acetonitrile/water). However, neutral metal carbonyl compounds do not readily undergo protonation as they are insufficiently basic. Derivatisation by alkoxide ion was subsequently found to be a convenient method for chemically generating $[M + OR]^-$ ions.[8] Charged organometallic species are readily analysed by electrospray mass spectrometry,[9] and typically just a single envelope of peaks corresponding to the parent is observed in the mass spectrum. In ESI-MS, fragmentation is considerably reduced compared to more conventional ionisation techniques, such as electron impact.[10] The alkoxide derivatisation method works equally successfully for clusters, and, despite the presence of multiple reaction sites, double alkoxylation giving $[M + 2(OMe)]^{2-}$ ions has never been observed by ESI-MS. Such a reaction is, however, not without precedent, as a double alkoxylation product was recently isolated from the reaction between NaOMe and $[Ir_6(CO)_{16}]$ in methanol and the solid-state structure of the product $[Ir_6(COOMe)_2(CO)_{14}]^{2-}$ was determined.[11] The two methoxycarbonyl fragments are on adjacent metal vertices of the octahedral framework.

3 Energy-dependent Electrospray Mass Spectrometry

While fragmentation tends to be minimal for electrospray ionisation under normal conditions, it can be increased very conveniently by changing the voltage applied at the skimmer cones. Essentially, increasing the cone voltage causes

collision-induced dissociation (CID) before the ions are directed into the mass analyser. Analysis of the resulting fragmentation pattern can yield interesting information on the compound in question, and we have been able to correlate the information gained from the mass spectrometric studies with the compounds' macroscopic chemical behaviour.

The conventional method of displaying fragmentation data from ESI-MS is to stack a series of spectra gathered at different cone voltages.[12] Such an approach is illustrated in Figure 1, which shows the negative-ion ESI mass spectra of $[Ir_4(COOMe)(CO)_{11}]^-$ **1** recorded at cone voltage settings of 25, 75 and 150 V.

Each spectrum provides a snapshot of the ligand stripping process as a function of increasing cone voltage, and presentation of all the possible data sets in this fashion is clearly not practical. However, the entire fragmentation pattern can be easily visualised using energy-dependent electrospray ionisation mass spectrometry (EDESI-MS). This technique has recently been shown to be useful for the analysis of fragmentation processes of cluster compounds, demonstrated using $[Rh_6(COOMe)(CO)_{15}]^-$ **2**.[13] A very large amount of data is generated in such studies as a different spectrum is obtained at each increment. EDESI-MS

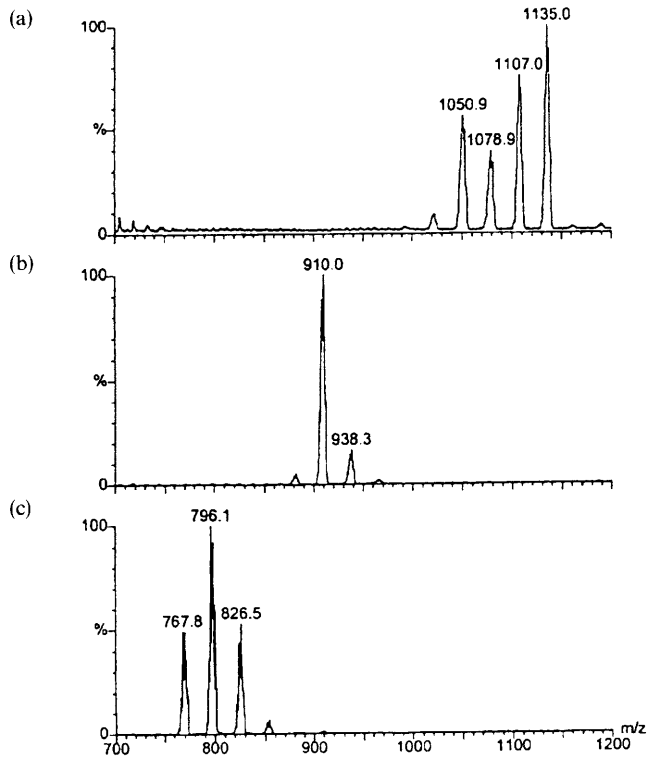

Figure 1 *Negative-ion ESI mass spectra of* $[Ir_4(COOMe)(CO)_{11}]^-$ **1**, *showing the effect of the cone voltage setting on the fragmentation patterns*; (a) *25 V*, (b) *75 V*; (c) *150 V*

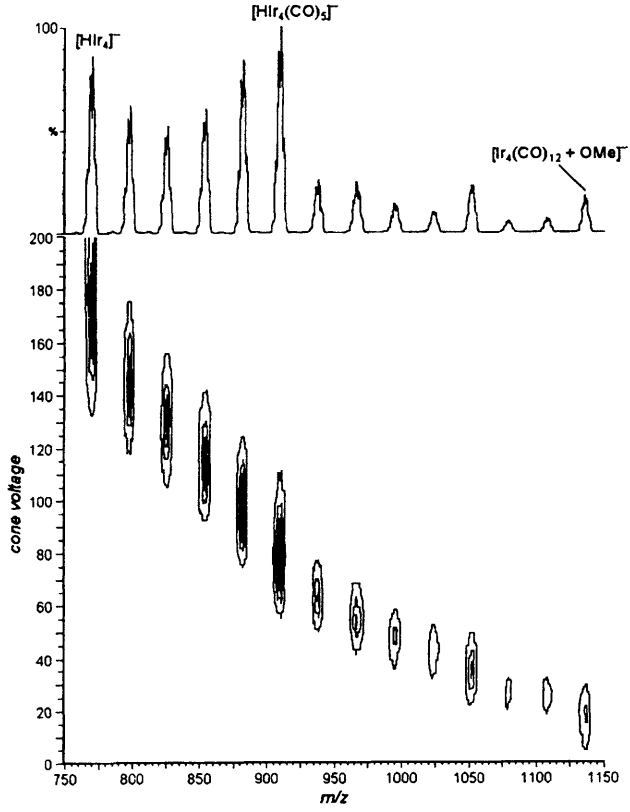

Figure 2 *The two-dimensional EDESI-MS map generated from 201 negative-ion ESI-MS spectra of* $[Ir_4(COOMe)(CO)_{11}]^-$ **1** *at cone voltage settings of 0–200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together*

involves plotting this huge amount of data (up to 201 spectra) in a two-dimensional format, generating a map (with mass-to-charge ratio on the horizontal axis and cone voltage on the vertical axis), the contours of which describe the entire fragmentation pattern of the compound in question. An additional feature is a spectrum generated by summing all the spectra used in the map; this spectrum appears at the top of the map. Each cross peak in the EDESI map represents a particular fragment ion, the most intense and/or long-lived of which are generally regarded as having particular stability. For transition metal carbonyl clusters, the primary fragmentation route is *via* loss of the carbonyl ligands as carbon monoxide.

Figure 2 shows the composite 1D/2D EDESI mass spectrum for **1**. Due to the timespan of the experiment, good signal-to-noise is obtained at the expense of resolution.

The fragment peaks in the spectrum correspond to consecutive loss of CO from the central Ir_4 core. A formaldehyde molecule, HCHO, is also lost. From the EDESI-MS spectrum shown in Figure 2 it is not immediately clear where the

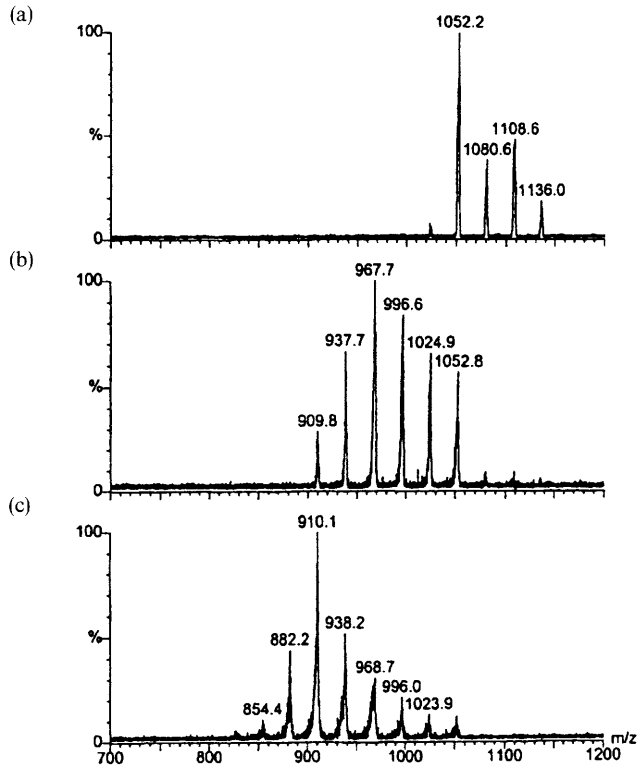

Figure 3 *Negative-ion ESI-MS/MS spectra of* $[Ir_4(COOMe)(CO)_{11}]^-$ **1**, *showing the effect of the collision voltage setting on the fragmentation patterns*; (a) *25 V*, (b) *75 V*; (c) *150 V*

HCHO loss (*m/z* 30) channel occurs relative to the CO loss (*m/z* 28) channel, but careful inspection reveals that the discontinuity probably occurs at *m/z* 969, *i.e.* $[Ir_4(CO)_6 + OMe]^-$ loses HCHO to form the $[Ir_4H(CO)_6]^-$ at *m/z* 939. Unequivocal confirmation of formaldehyde loss is provided by acquiring a conventional high-resolution mass spectrum at the appropriate cone voltage.

4 Energy-dependent Electrospray Tandem Mass Spectrometry

Alternatively, the recent introduction of EDESI-MS/MS provides another useful tool for analysing such systems.[14] Tandem mass spectrometry (MS/MS) allows selection of a single ion using one mass analyser then introducing it to a collision cell. Energetic collisions with an inert gas in this cell cause fragmentation of the ion and a daughter ion spectrum is obtained. MS/MS techniques are especially useful for the analysis of complex mixtures, but their application to molecules

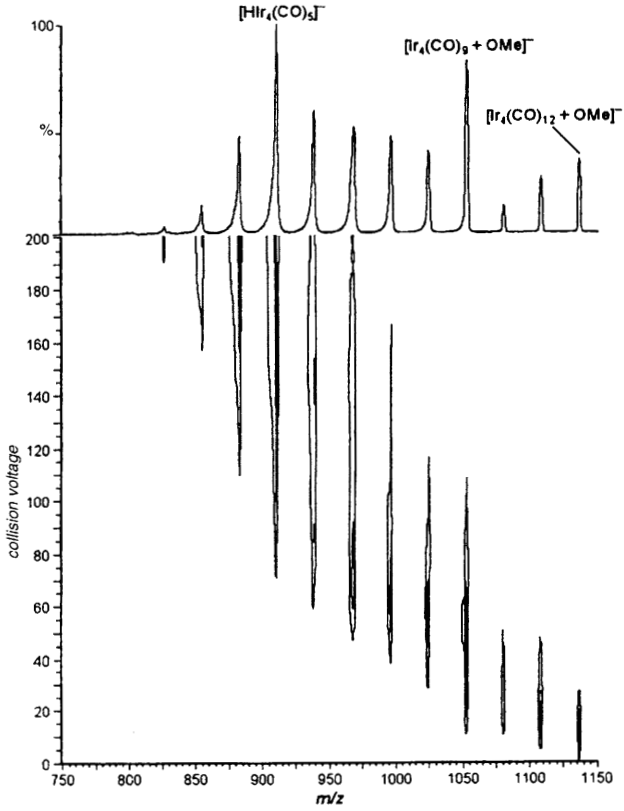

Figure 4 *The two-dimensional EDESI-MS/MS map generated from 201 negative-ion daughter ion ESI-MS/MS spectra of* $[Ir_4(COOMe)(CO)_{11}]^-$ **1** *at collision voltage settings of 0–200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together*

with complicated isotopomer envelopes is also useful, as instead of a broad, near-Gaussian distribution of peaks for each ion, a single peak is produced instead. This feature of MS/MS spectra is illustrated in Figure 3, which shows negative-ion daughter ion ESI-MS/MS of $[Ir_4(COOMe)(CO)_{11}]^-$, recorded at collision voltage settings of 25, 75 and 150 V.

The principal difference between these spectra and those shown in Figure 1 is the disappearance of the isotopomer envelopes; instead, a single peak is observed for each ion. An EDESI-MS/MS map for $[Ir_4(COOMe)(CO)_{11}]^-$ can be generated by stacking all the spectra, collected at collision voltages of 0–200 V, in an entirely analogous way to that in EDESI-MS (Figure 4).

Comparison between the two EDESI maps reveals the expected similarities, but also some marked differences. In particular, the ability to fragment the parent ion within the collision cell is markedly less than that achieved at the skimmer cone. The EDESI map shows that the ion $[Ir_4H]^-$ (in which all CO

ligands have been removed) makes its first appearance at a cone voltage of 132 V, and by 175 V is the only ion present. In contrast, the most heavily fragmented ion in the EDESI-MS/MS is $[Ir_4H(CO)_2]^-$, which only just appears at a high collision voltage of 190 V. The same ion in the EDESI-MS map appears at 105 V and disappears by 158 V. Despite this behaviour at high voltages, at low voltages fragmentation is induced more readily in the collision cell, as a comparison of the two maps at 20 V makes clear. In the EDESI-MS map, only the intact parent ion $[Ir_4(COOMe)(CO)_{11}]^-$ is present, whereas in the EDESI-MS/MS map, the fragment ions $[Ir_4(COOMe)(CO)_n]^-$ ($n = 8$–10) are already evident in significant intensity. It should be noted that fragmentation in the collision cell can, however, be increased by the simple expedient of using argon instead of dinitrogen as the collision gas.

Apart from the differences in fragmentation power, overall the EDESI-MS and EDESI-MS/MS maps are qualitatively similar. Essentially the same pattern of intensities for each daughter ion is observed, best represented by the summed spectrum at the top of each map. This feature is not surprising given that the mechanism for fragmentation is collision-induced dissociation by N_2 gas in both cases. An advantage of the selection of a single ion is apparent in the EDESI-MS/MS approach in that identification of the point at which HCHO loss *versus* CO loss takes place is more straightforward.

5 Formaldehyde Elimination

We have studied a number of different anionic methoxycarbonyl clusters, and found them all to undergo loss of HCHO at some point during their fragmentation processes. In some cases, we have correlated differences in fragmentation patterns between the various clusters with their macroscopic chemical properties. Confirmation of peak assignments was carried out in some cases using Fourier transform ion cyclotron resonance (FTICR).

The elimination of an aldehyde or ketone from a coordinated alkoxide is a well known process in coordination chemistry. For example, treatment of metal halide complexes with alcoholic base is a standard method for the preparation of metal hydride complexes (Equation 2).[15] Labelling experiments have shown that the α hydrogen is transformed into the hydride ligand.[16]

$$M\text{-}X + R_2CHO^- \rightarrow M\text{-}H + R_2CO + X^- \qquad (2)$$

This process has also been observed in cluster chemistry. For example, the cluster anion $[Ru_3IrH(OMe)(CO)_{12}]^-$ eliminates HCHO under carbonyl loss conditions (prolonged heating) to generate the cluster anion $[Ru_3IrH_2(CO)_{12}]^-$.[17] Because fragmentation in the mass spectrometer also involves carbonyl loss, it seems plausible that such a process might be simulated under EDESI-MS conditions.

Methoxylation of the hexaruthenium carbide cluster $[Ru_6C(CO)_{17}]$ generates the stable anionic cluster $[Ru_6C(COOMe)(CO)_{16}]^-$ (**3a**), the negative-ion EDESI mass spectrum of which is shown in Figure 5.[18]

As seen for **1** and **2**, at the lowest cone voltages, the only peak observed is that

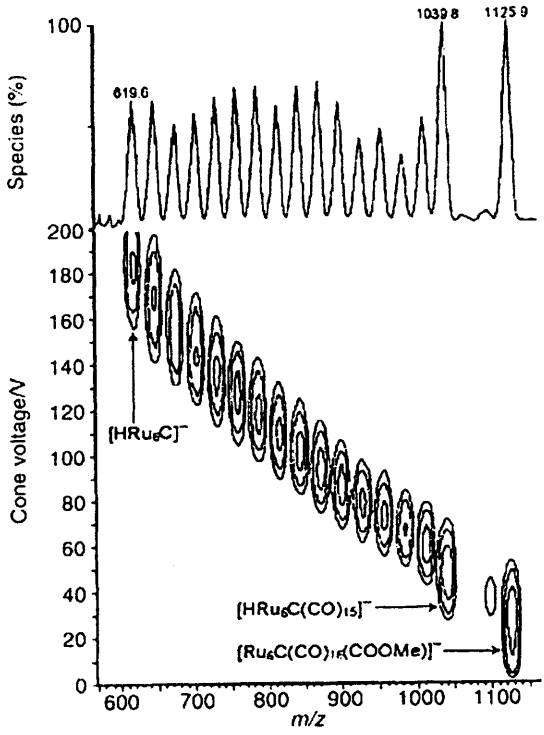

Figure 5 *The negative-ion EDESI mass spectrum of* $[Ru_6C(COOMe)(CO)_{16}]^-$ **3a**

of the intact parent ion. Upon increasing the fragmentation energy, two CO ligands are lost, and the ions $[Ru_6C(COOMe)(CO)_n]^-$ ($n = 14$ or 15) appear in the EDESI-MS map at very low intensity. The structure of these ions is not obvious because the CO ligands may be lost from either the cluster shell or from the methoxycarbonyl ligand. The third neutral molecule to be lost from the cluster is HCHO rather than a CO ligand, to generate the hydride cluster $[Ru_6C(H)(CO)_{15}]^-$. The remaining fifteen cross peaks correspond to the series $[Ru_6C(H)(CO)_x]^-$ ($x = 0$–14), and have roughly equal intensity, leading ultimately to $[Ru_6C(H)]^-$. The closely related anion $[Ru_6C(COOEt)(CO)_{16}]^-$ (**3b**) undergoes an analogous fragmentation sequence, except that CH_3CHO is eliminated instead of HCHO. As expected, $[Ru_6C(COOPh)(CO)_{16}]^-$ (**3c**) does not display similar behaviour, as the phenyl ring prevents formation of an exocyclic C=O bond. The CO ligands are progressively stripped in the case of **3c**, with complex fragmentation occurring at the highest cone voltages.

Compound **3a** is quite stable and we have isolated $(Ph_2PNPPh_2)[Ru_6C(COOMe)(CO)_{16}]$ and established its solid-state structure (see Figure 6 for the structure of the anion);[18] the structure of **2** is known.[6] The phosphine-substituted derivative of **3a**, $[Ru_6C(COOMe)(CO)_{15}(PPh_3)]^-$ (**4**) was prepared by treatment of $[Ru_6C(CO)_{16}(PPh_3)]$ with sodium methoxide. The EDESI mass spectra of **4** is

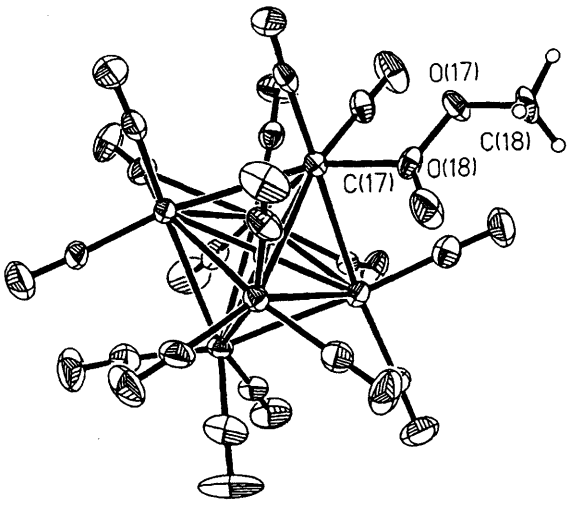

Figure 6 *The molecular structure of the anion* $[Ru_6C(COOMe)(CO)_{16}]^-$ **3a**

shown in Figure 7.

The spectrum of **4** is very similar to that of **3a**. The PPh_3 is clearly lost first, as shown by the large space between cross peaks in the EDESI map, followed by a single CO ligand and then rapid loss of HCHO. The remainder of the pattern involves straightforward CO stripping, from $[Ru_6C(H)(CO)_{15}]^-$ down to the $[Ru_6C(H)]^-$ core, as for **3a**.

While caution must be applied to any direct comparisons between fragmentation patterns observed in the gas phase and chemical properties observed in solution, in this case there is an obvious correlation. The early loss of formaldehyde from **3a** (and **4**) compared to **2** during the fragmentation process equates to the differences in chemical reduction of the two clusters. Treatment of $[Ru_6C(CO)_{17}]$ with methanolic KOH provides $[Ru_6C(CO)_{16}]^{2-}$ cleanly[19] whereas reduction of $[Rh_6(CO)_{16}]$ requires stronger reducing agents such as Na/Hg to produce the dianion. The hexaruthenium dianion $[Ru_6C(CO)_{16}]^{2-}$ is a widely-used precursor in cluster chemistry[20] and the mechanism of its formation presumably commences similarly to the reaction with NaOMe. Treatment of $[Ru_6C(COOMe)(CO)_{16}]^-$ with OH^- quantitatively yields $[Ru_6C(CO)_{16}]^{2-}$.[12c] Based on the EDESI data, we would also expect that treating $[Ru_6C(CO)_{16}(PPh_3)]$ with OH^- should yield $[Ru_6C(CO)_{15}(PPh_3)]^{2-}$, and preliminary synthetic results show that this seems to be the case (though some $[Ru_6C(CO)_{16}]^{2-}$ is also formed).

It is reasonable to assume that the -COOMe group rearranges to form a relatively strong multicentre bonding interaction, probably driven, in the first instance, by the loss of a CO ligand (Scheme 1). Formation of an -OMe ligand is likely to be the step prior to elimination of formaldehyde, and as already mentioned, the cluster anion $[Ru_3Ir(H)(OMe)(CO)_{12}]^-$ is known to eliminate

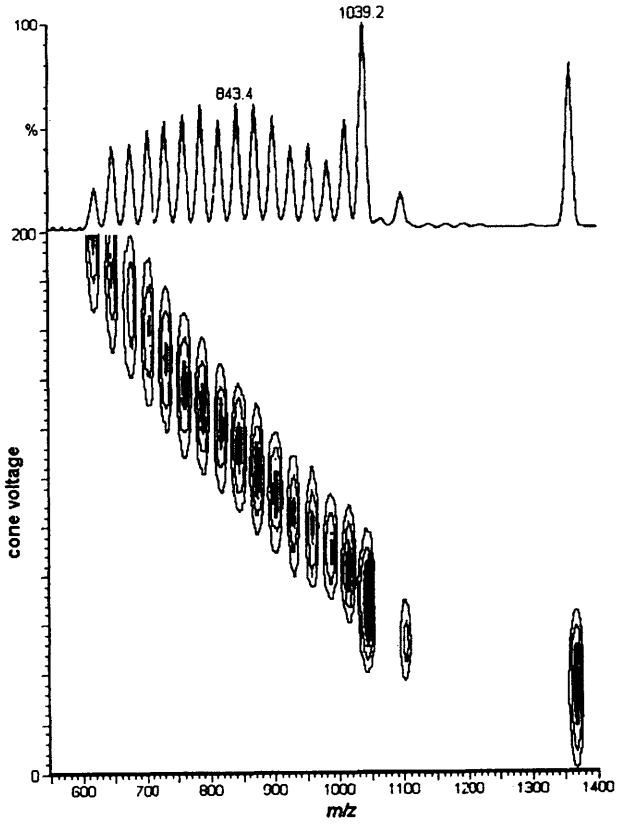

Figure 7 *The negative-ion EDESI mass spectrum of* $[Ru_6C(COOMe)(CO)_{15}(PPh_3)]^-$ **4**

HCHO under carbonyl loss conditions (prolonged heating) to generate the cluster anion $[Ru_3IrH_2(CO)_{12}]^-$. The hydride ligand is likely to be abstracted from the cluster by OH^- (this step, of course, is not observed in the mass spectrometer). The resulting cluster will be short of one CO ligand, but as two have been lost, there will be plenty of CO present in solution for the unsaturated cluster to pick up.

This HCHO elimination mechanism is different from one proposed earlier for the reduction of $[Ru_6C(CO)_{17}]$, involving nucleophilic addition of OH^- to a CO ligand to form a ^-COOH intermediate, followed by expulsion of CO_2 and then removal of H^+ by OH^- to form $[Ru_6C(CO)_{16}]^{2-}$.[21] Further experiments are in progress to confirm the mechanism.

6 Acknowledgements

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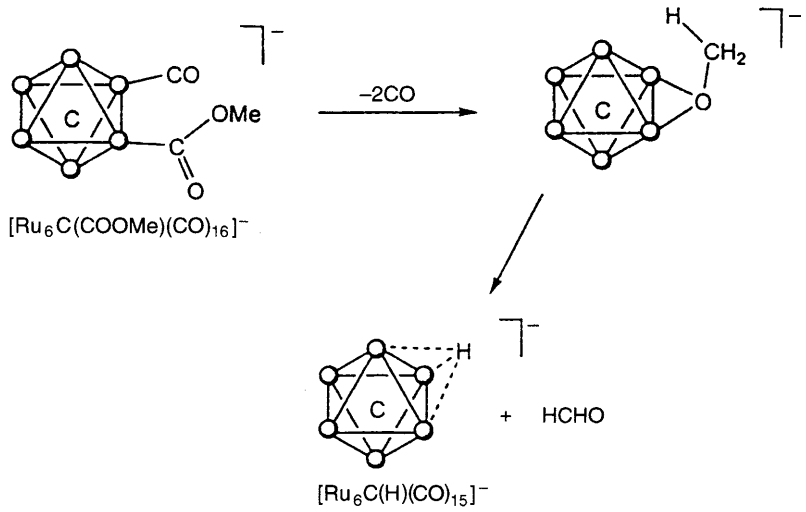

$[Ru_6C(COOMe)(CO)_{16}]^-$

$[Ru_6C(H)(CO)_{15}]^-$

Scheme 1

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Exploring New Structures Based on Chatt's $\{Pt_2S_2\}$ Core for Nucleation of Intermetallic Growth

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1 Historical Perspective

The development of the chemistry of platinum sulfide complexes can be traced to the early work of Chatt.[1,2] Among his complexes in this field, those having a significant impact on modern cluster chemistry are probably $[\{Pt(PR_3)_2\}_2(\mu\text{-}S)_2]$ (**1**). These compounds were synthesised independently by Chatt (PR_3 = $PPhMe_2$)[2] and Ugo (PR_3 = PPh_3)[3] in the early 1970s. The triphenylphosphine complex can be easily prepared in good yields but it is practically insoluble in all common organic solvents, except $CHCl_3$ and CH_2Cl_2 in which it decomposes readily.[1,2,4–6]

The methylated derivative $[Pt_2(PR_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]PF_6$[3] was among the earliest crystallographically-characterised derivatives whereas the protonated analogue $[Pt_2(PR_3)_4(\mu\text{-}S)(\mu\text{-}SH)]PF_6$ (Figure 1) has been isolated and characterised only very recently.[7]

Although the related trinuclear derivative $[Pt_3(PR_3)_6(\mu_3\text{-}S)_2]^{2+}$ was synthesised by Chatt and Mingos in their earlier work,[2] its synthetic relationship with **1** was not established until the work particularly of Mingos who explored a series of metallation reactions using **1**, R = Ph as a metalloligand.[8–10] This has led to an exponential growth of medium- to high-nuclearity aggregates over the past two decades.[9–12] To date, the metalloligand **1**, R = Ph probably accounts

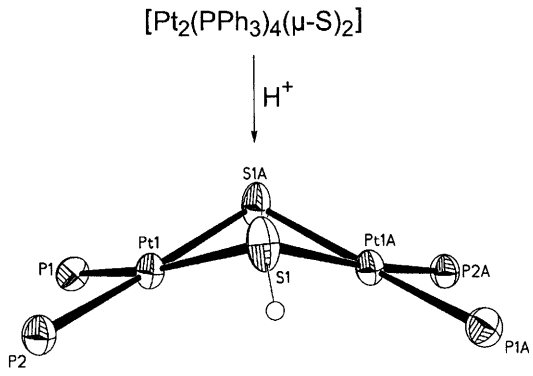

Figure 1 *Structure of* $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SH)]PF_6$ *(For clarity, the* PF_6^- *counter-anion is omitted)*

not just for the largest number of heterometal aggregates, but also the largest permutation of different heterometals.[13–15] Its ligating abilities towards *p*-, *d*- and *f*-block, hard and soft metals, as well as late and early transition metals have been demonstrated. Two significant predecessors are the pentanuclear $[Pt_4Pd(PPh_3)_8(\mu_3\text{-}S)_4](BF_4)_2$[9] and hexanuclear $[Pt_4Ag_2(PPh_3)_8(\mu_3\text{-}S)_4](BF_4)_2$.[10] They proved conclusively that two $\{Pt_2S_2\}$ units can be brought together by 'naked' metals, and that in doing so, they can support M–M bonding, as shown in the latter. This finding prompted a vigorous exploration of other metal aggregates with different nuclearities, with or without M–M bonds. This is summarised in our recent review.[16]

Over the years, there have been three major milestones that mark the development of this work (Figure 2):

(i) *Capping of a single metal atom on the* $\{Pt_2S_2\}$ *core* – This is best exemplified in the isolation of $[Pt_2Tl(PPh_3)_4(\mu_3\text{-}S)_2](PF_6)$.[13] It highlights the ability of this metalloligand to support and stabilise coordinatively and electronically unsaturated metal centres and, in some cases, to promote heterometal M–M interactions.

(ii) *Aggregate to cluster conversion* – A range of aggregates has been made using this methodology but the majority of them do not have M–M bonds. However, a facile reduction process of $[Pt_2M(PPh_3)_4(\mu_3\text{-}S)_2]X$ (M = Cu or Ag) to $[Pt_2MX(PPh_3)_3(CO)(\mu_3\text{-}S)]$ (X = halide) by CO raises the possibility of converting these aggregates to a new class of cluster compounds.[14] It is remarkable that these reduction and desulfurisation processes can be achieved in a single step by such a mild reductant with no intractable by-products.

(iii) *Tandem migration of a metal fragment across the S–S bridge* – This is best illustrated in $[Pt_2Au(PPh_3)_4(\mu_3\text{-}S)_2]^+$ which displays an interesting dynamic process with the metal moving across the sulfur sites with a low energy barrier between an intermediate and two transition states.[17] This metal migration complements a ligand migration process that we reported earlier in a similar M_3 core.[18]

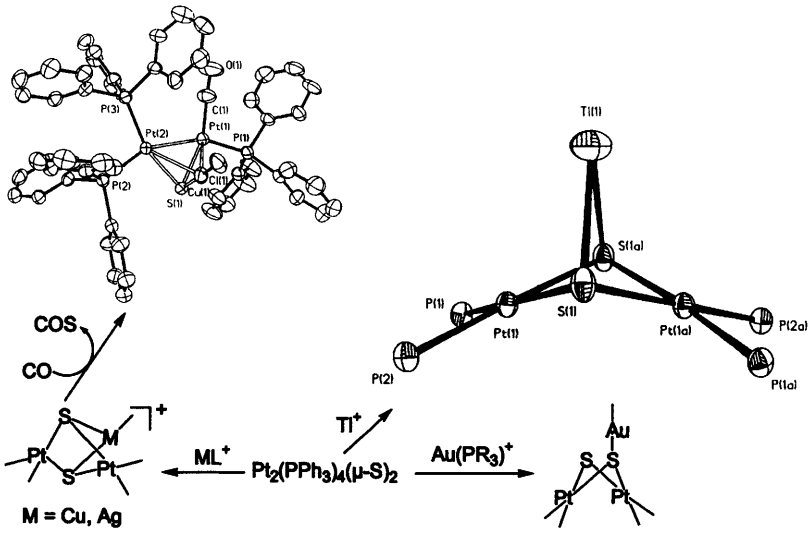

Figure 2 *Major developments in the field of* $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ *chemistry*

To date, we have extensively studied the metallation chemistry of the $\{Pt_2S_2\}$ core. Our immediate aim was to explore the materials chemistry of these aggregates. The use of these aggregates as precursors to electronic and magnetic materials is an interesting prospect. This system is especially suitable for such development because of the almost infinite possibilities arising from combining different metals and ligands. In doing so, we are able to tune the chemical and physical properties to suit desired applications.

2 Current Perspectives

2.1 Stereochemical Changes

The $\{Pt_2S_2\}$ plane in the parent complexes is usually flat whereas in the metallated derivatives it is commonly hinged. There are however several notable exceptions, one of which is $[Pt_2Hg_2(NO_3)_2(PPh_3)_4(\mu_3\text{-}S)_2]^{2+}$ which has a flat $\{Pt_2S_2\}$ core (Figure 3). In this stereoconfiguration, metal addition takes place both above and below the $\{Pt_2S_2\}$ plane, thus resembling the growth in 'one-dimensional' coordination polymers. In a folded configuration, metallation can occur at the apical positions of both sulfur sites, with or without M–M bonding. With a careful choice of metal and supporting ligands, one can envisage the development of metallocycles with different stereochemistry and cavity sizes. An example is found in $[Pt_2Hg_2(PPh_3)_6(\mu_3\text{-}S)_2(\mu\text{-}Cl)_2]^{2+}$.

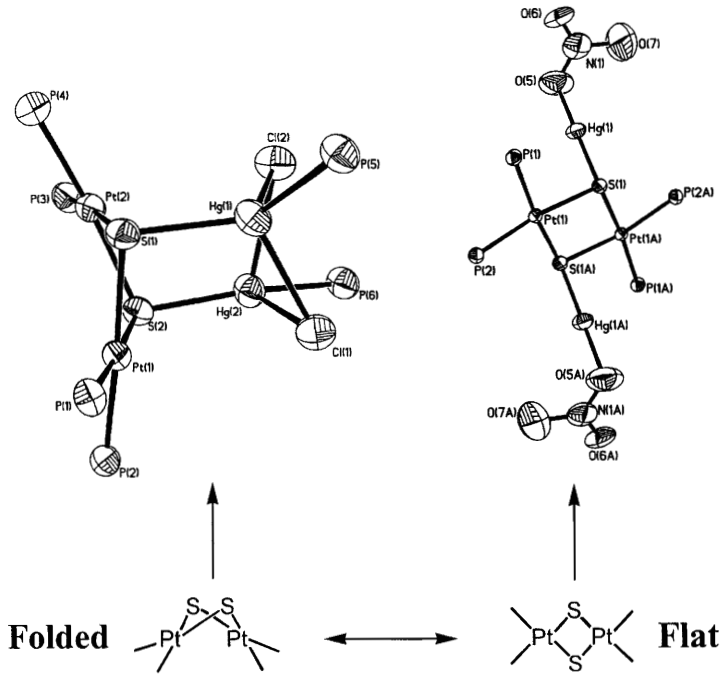

Figure 3 *Different stereochemistry of the $\{Pt_2S_2\}$ core*

2.2 Different Degrees of Site-anchoring

Although the $\{Pt_2S_2\}$ core undergoes simple single-site derivatisation easily, *e.g.* to give $[Pt_2(PPh_3)_4(\mu\text{-S})(\mu\text{-SMe})]^+$ and $[Pt_2Au(PPh_3)_5(\mu_3\text{-S})_2]^+$, there are examples which show that, under certain conditions, both sulfurs can be metallated. When this happens, they can support a single heterometal atom, *e.g.* $[Pt_2Hg(C_6H_5)(PPh_3)_4(\mu_3\text{-S})_2]^+$ or two metals anchoring in close proximity *e.g.* $[Pt_2Hg_2(C_2H_5)_2(PPh_3)_4(\mu_3\text{-S})_2]^{2+}$ (Figure 4). This versatility gives an additional degree of freedom to materials-growth based on the $\{Pt_2S_2\}$ core.

2.3 Bifacial Addition and Dissociation

In a chelating mode, the metalloligand can exhibit different modes of adduct formation. Addition of a binary compound gives rise to a neutral addition compound, *e.g.* $[Pt_2HgCl_2(PPh_3)_4(\mu_3\text{-S})_2]$ (Figure 5). Halide dissociation would give rise to ionic adduct, *e.g.* $[Pt_2Hg(PPh_3)_5(\mu_3\text{-S})_2]^{2+}$. A 2:1 addition would lead to a bifacial attack and formation of a bis(chelate) configuration, *e.g.* $[Pt_4Hg(PPh_3)_8(\mu_3\text{-S})_4]^{2+}$.

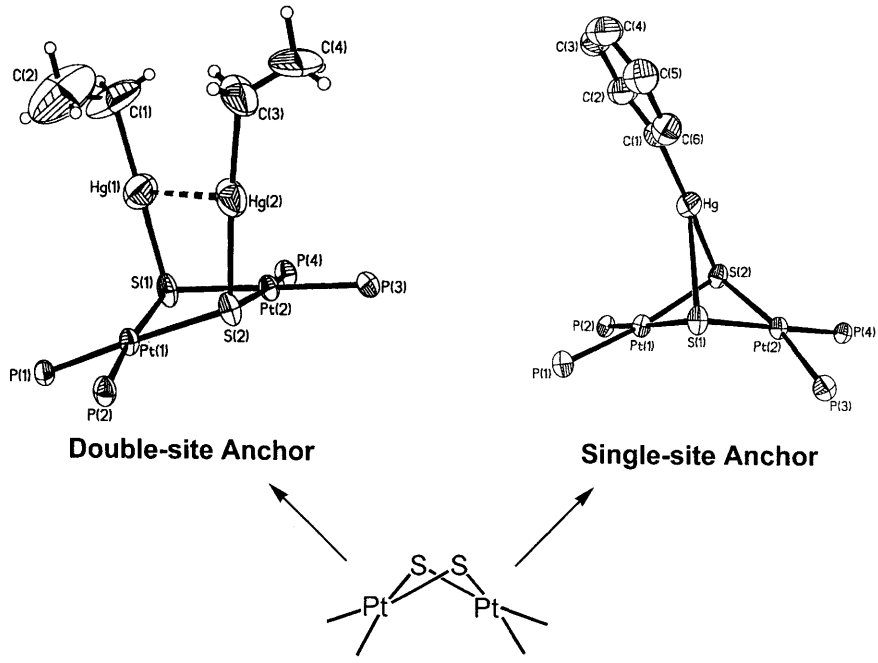

Figure 4 *Different degrees of site-anchoring on the* $\{Pt_2S_2\}$ *core*

2.4 Formation of Bimetal Complexes from Early and Late Transition Metals

Most of the documented examples of aggregate formation with the $\{Pt_2S_2\}$ core are addition reactions involving metals from the middle and late transition series. These are generally Lewis acidic systems that complement the basic character of the metalloligand. In most cases, the soft ligating behaviour of the sulfur donors also matches the softer character of the late metals. Our recent efforts have been directed to the synthesis of late/early bimetal systems, a typical example of which is the synthesis of $[Pt_2VO(OCH_3)_2(PPh_3)_4(\mu_3\text{-}S)_2]^+$ from NH_4VO_3. The lack of acidity of the vanadate substrate is remedied by a methanolysis process (Figure 6).

2.5 Introduction of an Unsaturated Functionality

The $\{Pt_2S_2\}$ core is formally coordinatively and electronically saturated since the 16-electron d^8 centre is effectively stable to addition reactions. However, upon metallation, it is possible to introduce unsaturation to the system when the metal carries along a labile ligand such as cycloocta-1,5-diene (cod). This is exemplified in the synthesis of $[Pt_3(cod)(PPh_3)_4(\mu_3\text{-}S)_2]^{2+}$ and $[Pt_2Pb(NO_3)_2(PPh_3)_4(\mu_3\text{-}S)_2]$. This transformation from a Lewis basic to a Lewis acidic complex is accompanied by alteration of its chemical reactivity and coordination

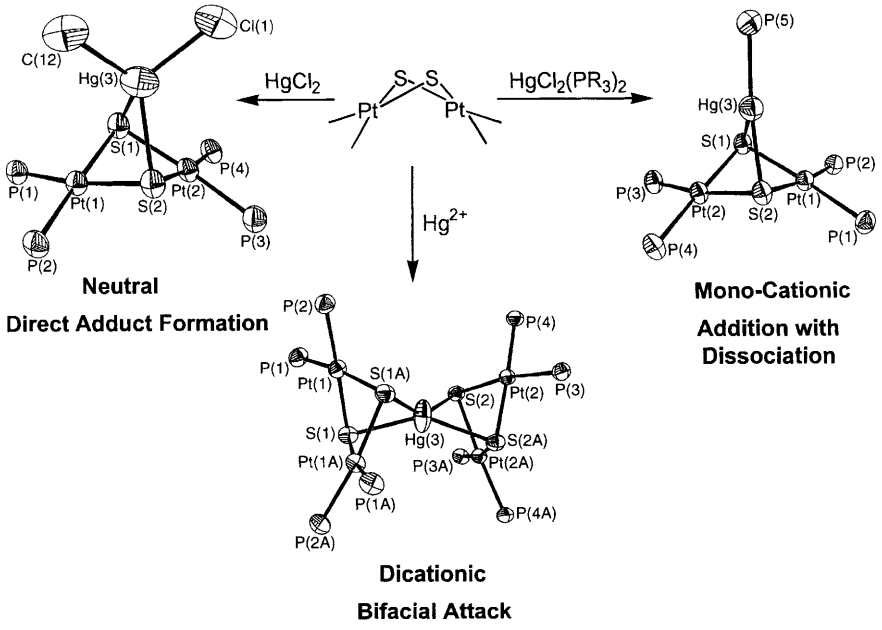

Figure 5 *Different modes of adduct formation exhibited by* $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$

behaviour. When a 'naked' metal such as Tl^+ is introduced, as in $[Pt_2Tl(PPh_3)_4(\mu_3\text{-}S)_2]^+$, the unsaturated behaviour is significantly enhanced.

2.6 Enhancing Electrochemical Activity

The electrochemical activity of some heterometallic aggregates has been reported.[19] When different metals are in close proximity within a cluster core, and especially when sulfide is a connecting ligand, electronic communication becomes a clear possibility. When each metal carries an electroactive ligand such as the ferrocenyl group, in principle the complex becomes a multi-centred redox system. The level of electrochemical activity, as well as M–M and M–L communication, can be tuned easily by fitting the appropriate ligands and metals to this core. This represents a relatively simple yet powerful approach to synthesise electroactive aggregates, *e.g.* $[Pt_2Hg(Fc)(PPh_3)_4(\mu_3\text{-}S)_2]^+$ (Fc = (C_5H_5)-(C_5H_4)Fe) and $[Pt_2Tl(dppf)_2(\mu_3\text{-}S)_2]^+$ [dppf = $Fe(C_5H_4PPh_2)_2$].

2.7 Electrospray Mass Spectrometry (ESMS) Analysis

In view of the powerful nature of the $\{Pt_2S_2\}$ core to couple to virtually all metals in the Periodic Table, and because different metals can carry a range of functionalities, there is an infinite number of possible permutations that one can attempt. It is therefore important to develop a combinatorial-like tool which can be used

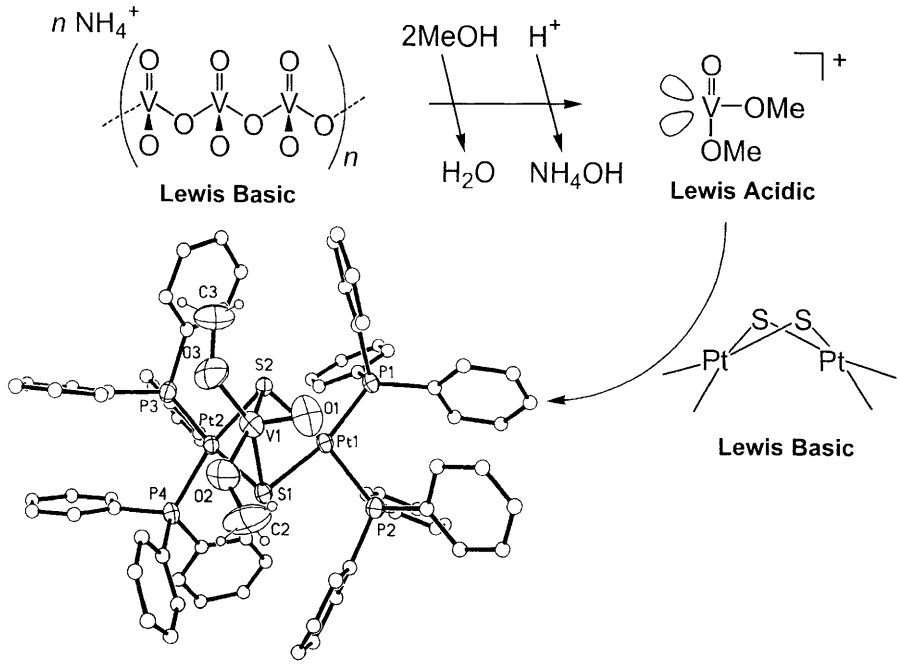

Figure 6 *Formation of* $[Pt_2VO(OCH_3)_2(PPh_3)_4(\mu_3\text{-}S)_2]^+$, *an example of the introduction of an early transition metal to the heterometal system*

to screen for positive reactions and to identify potentially stable and isolable products. When such information is fed into the design and synthesis process, one can maximise the productivity of synthetic experimentation. We have developed ESMS as such a combinatorial tool. It permits '*in situ*' observation of possible products when the substrates are mixed in solution. A good example is illustrated in our study of the mercury(II) systems in which a number of Hg/Pt aggregates were detected and subsequently synthesised.[7] (Figures 7, 8 and 9) When this technique is applied to the V/Pt system, we observed metal-assisted ligand transformation in these aggregates at different cone voltages. In addition, the methanolysis process shown in Figure 6 for a reaction involving **1** and a vanadium(V) system can be followed conveniently by ESMS. When this technique is be applied to a molybdenum(VI) system, using $[MoO_4]^{2-}$ as a substrate in a reaction with **1**, R = Ph, one could also detect cyclometallation activity.

What started as a project involving simple Lewis acid/base addition reactions has emerged into one that traverses materials synthesis to the development of a technique that could change our approach to inorganic synthesis in general. The contributions of Chatt in the early 1970s, Mingos in the 1980s and other researchers in the past two decades[1–5,7–14] made this evolution possible. Our work in the past two decades proved that the $\{Pt_2S_2\}$ system is probably the most powerful, convenient and general synthetic precursor to heterometal aggre-

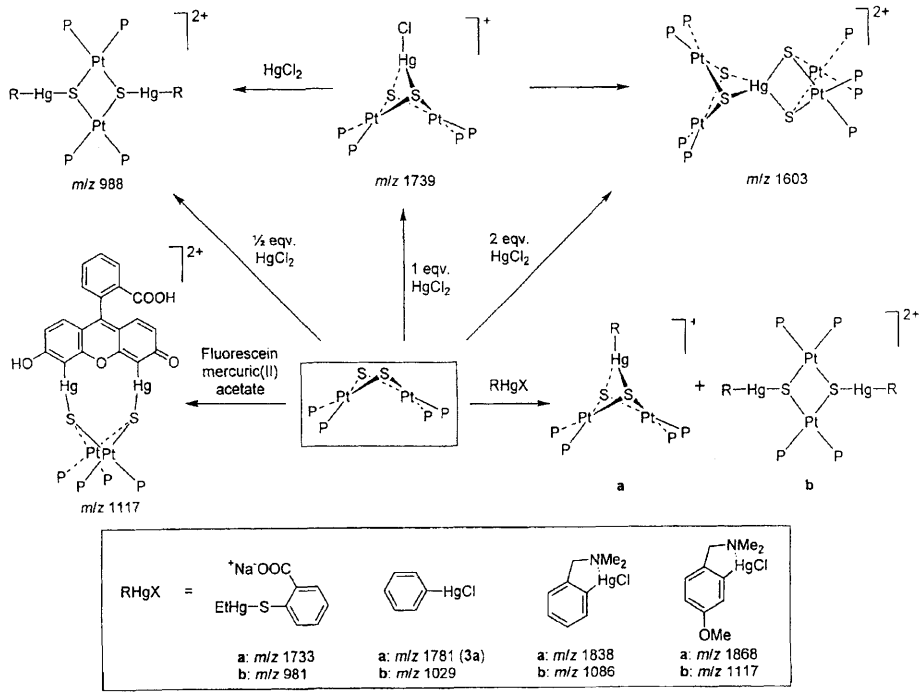

Figure 7 *ESMS observed species in mixtures containing* $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ *and various mercury(II) species*

gates and clusters. The materials, chemical and dynamic properties of a large portion of these heterometal complexes remain largely unexplored. This is a subject of our future investigations.

3 Acknowledgements

T. S. A. H. thanks D. M. P. Mingos (who started this research under the guidance of J. Chatt) for introducing him to this fruitful area of research. We are grateful for funding support from the National University of Singapore and the University of Waikato and to J. J. Vittal for X-ray structural characterisation of some compounds. Technical assistance in the preparation of this manuscript from Tengku Tjendekrawan is acknowledged.

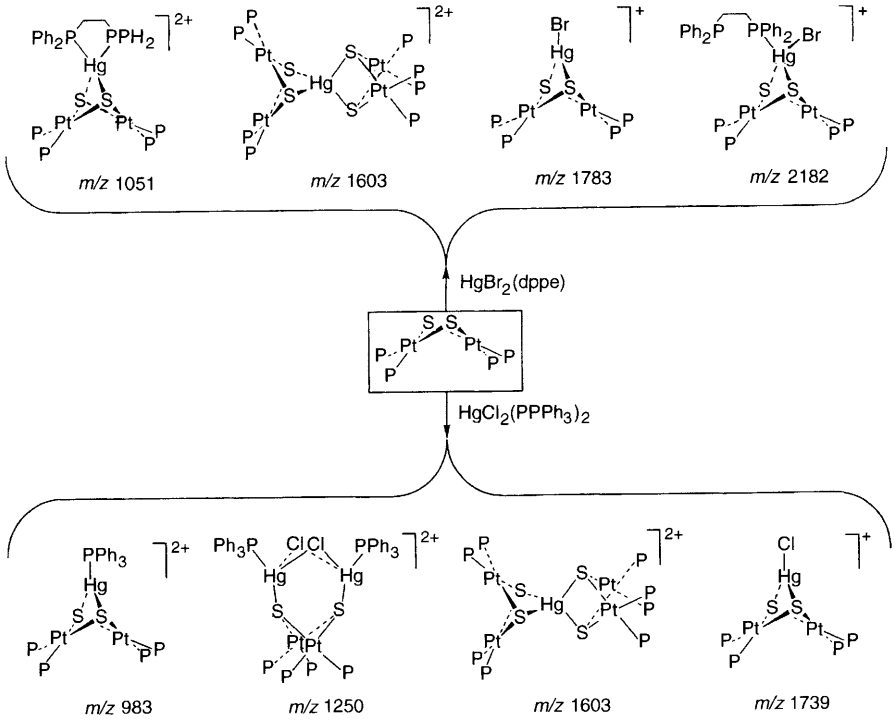

Figure 8 *Major species observed in the mixtures of* $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ *and mercury–phosphine complexes under ESMS conditions*

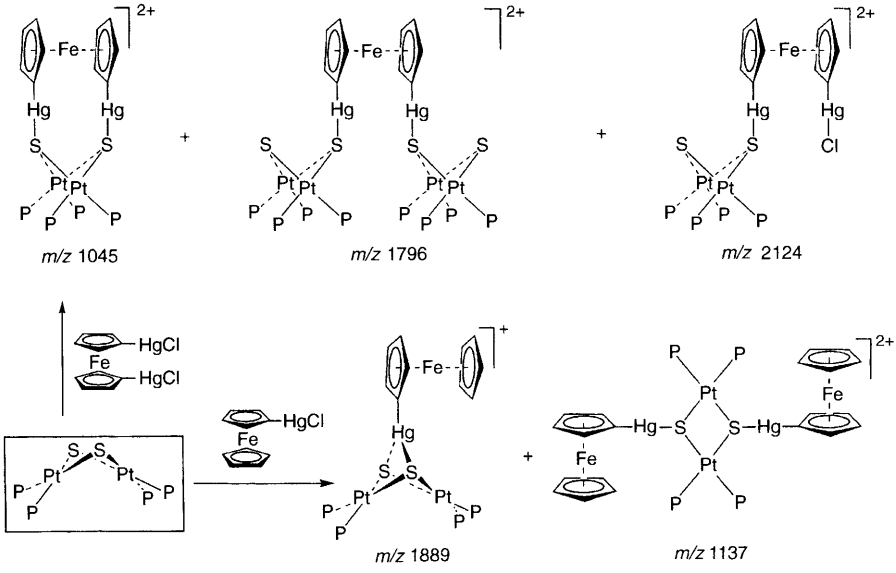

Figure 9 *Major species observed in the mixtures of* $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ *and mercury–ferrocenyl complexes under ESMS conditions*

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A Rational Design of Heteropolynuclear Squarate Complexes

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1 Introduction

The synthesis of the first divalent metal complexes of squarate ion $(C_4O_4)^{2-}$ by West and Niu[1] in 1963, has constituted the starting point for many researches of the coordination chemistry of squarate dianion.

In their pioneering work, West and Niu[1] assumed that the squarate complexes of divalent cations Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} form an isostructural series (Figure 1). They suggested a bis-chelating coordination mode for the squarate dianion in all the squarate complexes, but their proposed structure does not correspond to the actual coordination mode of squarate.

In the light of the structures of squarate–metal complexes reported so far it is clear that chelation by this ligand is limited to some alkaline- and rare-earth metal cations.[2–7] This behaviour is explained by the large bite parameter of squarate dianion.

X. Solans and co-workers,[8] attempting to answer the question: 'does squarate act in a bidentate manner?', calculated the value of the bite parameter ($b = d_2/d_1 = d(O–O)/d(M–O)$, Figure 2) for the squarate ligand in a series of copper complexes of formula $[Cu(C_4O_4)L]$, where L represents an *N*,*N*-bidentate ligand.

They estimated the bite parameter for a bidentate squarate ligand to be 1.70 Å and d_1 to be 2.47 Å (using the value of the bite parameter of the oxalate and the d_2 bite for squarate). From this they concluded that the squarate should act as a

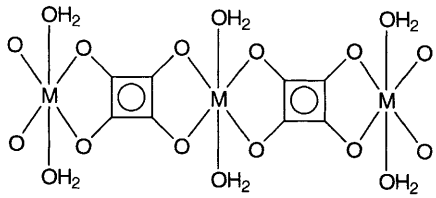


Figure 1 *Structure for divalent metal–squarate complexes (M = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn)*

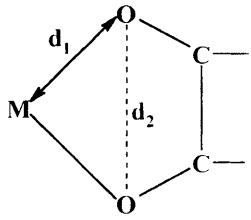


Figure 2 *The bite parameter, d_2/d_1, of the squarate ion*

bidentate ligand in either an asymmetric manner or in a symmetric one with an average copper–oxygen distance of about 2.47 Å. This value is outside the normal range for copper–oxygen bond lengths.

Energy calculations have complemented these stereochemical considerations and showed that in the case of bidentate squarate a minimum of energy is obtained if the configuration around the metal ion is close to tetrahedral, a situation that would be unusual for copper(II).

These studies have helped to elucidate the coordination modes of squarate by establishing the following facts:

(i) when the oxygen atom is replaced by a larger atom, such as sulfur, the resulting ligands can be bidentate,[9,10]

(ii) when metal ions with larger ionic radii (alkaline-earth cations[5–7] and cerium(III)[2]) are used, η^4 chelation can be achieved. The average d_1 values in cerium(III) complexes are 2.69 and 2.62 Å,[2] close to the predicted one (2.47 Å) for a chelating squarate ligand.

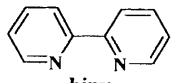
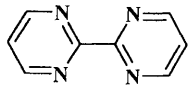
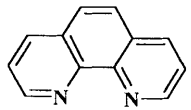
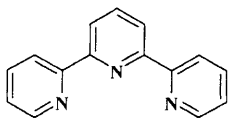
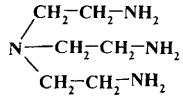
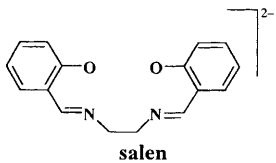
As far as squarate coordination chemistry with 3d ions is concerned, a wide variety of modes has been found: monodentate,[8,11] μ-1,2-bis(monodentate),[8,11–18] μ-1,3-bis(monodentate)[8,19–23] and tetrakis(monodentate).[24–26]

The structures of transition-metal squarate complexes consist of one-dimensional metal squarate chains interlinked by hydrogen bonding. These complexes could be possible precursors to low dimensional polymeric electrical conductors

or molecular magnets, because the linear metal squarate chains would appear to serve as a pathway for electron conduction or magnetic superexchange. This ability arises from the structural features of squarate: a set of four oxygen donors, planar stereochemistry, and π-electron delocalisation.

To control the polymerisation process and make possible the isolation of species of desired nuclearity, polydentate ligands are used as blocking groups. Most of them are polydentate ligands with delocalised π systems (Table 1). These

Table 1 *Some typical blocking ligands*

Blocking ligand	*Complex compounds*	*References*
 **bipy**	$[Cu(C_4O_4)(bipy)(H_2O)]\cdot H_2O$ $[Cu(C_4O_4)(bipy)_2(H_2O)_4]\cdot 4H_2O$ $[Cu(C_4O_4)(bipy)_4](BF_4)_2\cdot 2H_2O$	8 21 27
 **bipym**	$[Cu(C_4O_4)(bipym)(H_2O)_3]\cdot 2H_2O$ $[Cu_2(C_4O_4)(bipym)(H_2O)_6]$	28
 **phen**	$[Cu(C_4O_4)(phen)(H_2O)]\cdot H_2O$ $[Cu(C_4O_4)(phen)]\cdot H_2O$	8 27
 **terpy**	$[Cu(C_4O_4)(terpy)(H_2O)]\cdot H_2O$ $[Cu_2(C_4O_4)(terpy)_2(H_2O)_2](ClO_4)_2$	8
 **tren**	$[Ni_2(C_4O_4)(tren)_2](H_2O)](ClO_4)_2$ $[Cu_4(C_4O_4)(tren)_4](ClO_4)_6$	30 29
 **salen**	$[Fe(C_4O_4)(salen)_2(CH_3OH)_2]$	19

features allow the tailoring of the nuclearity of desired polynuclear compounds and the tuning of the magnetic properties of such squarate-bridged complexes.

Starting from these considerations, we have chosen as blocking ligand [6-(4-chlorophenyl)pyridazin-3-yl]hydrazine, L, and synthesised the building blocks $[Fe(ClO_4)L(H_2O)_3](ClO_4)_2$ **1** and $[Fe(ClO_4)L_2(H_2O)](ClO_4)_2$ **2**. Then we assembled the polynuclear systems by reaction of the building blocks **1** or **2** with dipotassium squarate, resulting in the preparation of $[Fe(C_4O_4)(ClO_4)_2L_2(H_2O)_4](ClO_4)_2$ **3**, $[Fe_2(C_4O_4)(ClO_4)_2L_4](ClO_4)_2$ **4**, $[FeCr(C_4O_4)(ClO_4)_2L_2\text{-}(H_2O)_4](ClO_4)_2$ **5** and $[FeCr(C_4O_4)(ClO_4)_2L_4](ClO_4)_2$ **6**.

2 Experimental

2.1 Materials

[6-(4-Chlorophenyl)pyridazin-3-yl]hydrazine was obtained following the literature procedure.[31] Iron(III) perchlorate hydrate, chromium(III) perchlorate hexahydrate and squaric acid were purchased from commercial sources and used without any further purification. A dipotassium squarate solution was prepared by adding the required quantity of solid potassium hydroxide to an aqueous solution of squaric acid. The metal content was determined by atomic absorption spectrometry. The molar conductivities were measured in 10^{-3}M CH_3CN solutions.

2.2 Compound Preparations

$[Fe(ClO_4)L(H_2O)_3](ClO_4)_2$ **1** was obtained in quantitative yield from refluxing methanol solutions of [6-(4-chlorophenyl)pyridazin-3-yl]hydrazine, L, (1 mmol, 0.221 g) and iron perchlorate (1 mmol, 0.354 g). The resulting black powder was collected by vacuum filtration, washed with water, methanol and diethyl ether and stored over P_2O_5. (**1**, $C_{10}H_{15}Cl_4FeN_4O_{15}$ Calcd. C 19.1, H 2.4, N 8.9, Fe 8.9; found: C 19.0, H 2.45, N 9.0, Fe 8.75%)

$[Fe(ClO_4)L_2(H_2O)](ClO_4)_2$ **2** was obtained in quantitative yield using a procedure identical to that used for **1** except that 2 mmol, 0.442 g L were used. (**2**, $C_{20}H_{20}Cl_5FeN_8O_{13}$ Calcd. C 29.5, H 2.46, N 13.8, Fe 6.88; found: C 29.7, H 2.5, N 13.4, Fe 6.65%)

$[Fe_2(C_4O_4)(ClO_4)_2L_2(H_2O)_4](ClO_4)_2$ **3** and $[Fe_2(C_4O_4)(ClO_4)_2L_4](ClO_4)_2$ **4** were obtained in quantitative yield from refluxing an aqueous solution of dipotassium squarate (1 mmol, 0.190 g) with methanolic solutions of **1** (2 mmol, 1.258 g) or **2** (2 mmol, 1.627 g). The solid was collected by vacuum filtration, washed with water, methanol and diethyl ether and stored over P_2O_5. (**3**, $C_{24}H_{26}Cl_6Fe_2N_8O_{24}$ Calcd. C 25.4, H 2.29, N 9.87, Fe 9.87; found: C 25.7, H 2.35, N 10.1, Fe 9.76%; **4**, $C_{44}H_{36}Cl_8Fe_2N_{16}O_{20}$ Calcd.: C 35.1, H 2.39, N 14.89, Fe 7.45; found: C 35.3, H 2.45, N 15.1, Fe 7.33%)

The heterodinuclear complexes $[FeCr(C_4O_4)(ClO_4)_2L_2(H_2O)_4](ClO_4)_2$ **5** and $[FeCr(ClO_4)_2(C_4O_4)L_4](ClO_4)_2$ **6** were obtained in a similar manner, starting from chromium analogues of **1** and **2**.

2.3 Physical Measurements

IR spectra were recorded with a Nicolet 2DXFT-IR spectrophotometer as KBr pellets in the 4000–500 cm^{-1} region. The UV–visible and reflectance were run on a VSU-2G spectrometer using MgO as the reference for the reflectance spectra. Molar conductances were measured at room temperature on a Radelkis KFT conductivity meter. Metal ions were determined on a Pye-Unicam atomic absorption spectrophotometer. Elemental analyses were done by combustion with a Carlo Erba instrument CHNS Elemental Analyser Model 1106. Magnetic measurements were carried out at room temperature with a Faraday-type magnetometer.

2.4 Results and Discussion

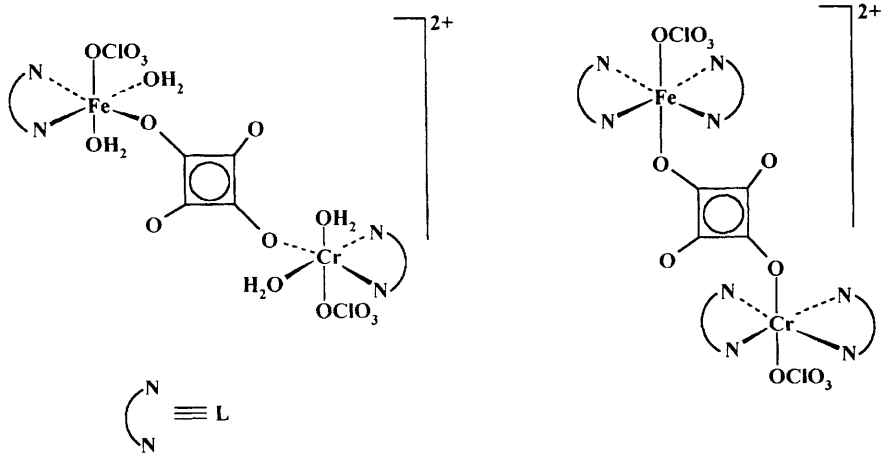
Elemental chemical analyses, molar conductivity data, IR and electronic spectra and magnetic susceptibility values lead us to propose the structures in Figure 3.

2.5 IR Spectra

The most characteristic bands, useful in a diagnostic sense, are collected in Table 2.

The ν_{N-N} band in **1** and **2** is shifted to higher values than in the free bases, pointing to the involvement of the unsubstituted hydrazine N-atom in the coordination process, as occurs when hydrazine acts as an unidentate ligand.[32]

In addition, calculation of charge density of L, using HyperChem 4.0, supports the conclusions from the IR data, showing that for such unsymmetrically sub-



1:2 type electrolyte

Figure 3 *Proposed structures for* $[FeCr(C_4O_4)(ClO_4)_2L_2(H_2O)_4](ClO_4)_2$ **5** *and* $[FeCr(ClO_4)_2(C_4O_4)L_4](ClO_4)_2$ **6**

Table 2 *Characteristic bands in IR spectra of complexes* **1–6** *(ν, cm*$^{-1}$*, KBr)*

Compound	δ_{NH}	ν_{CN}	ν_{OH}	ν_{ClO}	ν_{NN}	ν_{CO}
	1610	1460	–	–	827	–
1	1628	1416	3404	1083	833	–
				625		
2	1666	1452	3428	1093	843	–
				625		
3	1620	1430	3390	1090	855	1485
				625		1725
4	1659	1450	3410	1170	850	1495
				625		1710
5	1615	1455	3270	1135	850	1480
				649		1690
6	1615	1430	3260	1130	852	1480
				649		1690

stituted hydrazines the nitrogen atoms involved in coordination are the ones located in the 1 and 3 positions (Figure 4).

We have also observed in the IR spectra of the squarate-containing complexes **3–6** the C–O stretching bands specific to μ-1,3-bis(monodentate) coordination of squaric acid (*ca.* 1480 cm^{-1} for C–O and 1710 cm^{-1} for localised double-bonded C=O).

2.6 Electronic Spectra and Magnetic Measurements

For the mono- and di-nuclear iron(III) complexes **1–4** the transition bands appear in the range of 373–503 nm, characteristic of Fe^{3+} in a distorted octahedral geometry (Figure 5a). For heterodinuclear complexes **5** and **6** the specific Fe^{3+} transitions are partially superposed upon those of Cr^{3+}. The position and shape of these bands confirm octahedral coordination at both Fe^{3+} and Cr^{3+} metal ions (Figure 5b).

The observed transitions were assigned on the basis of the magnetic moments

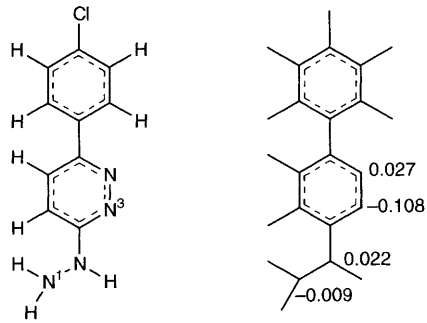
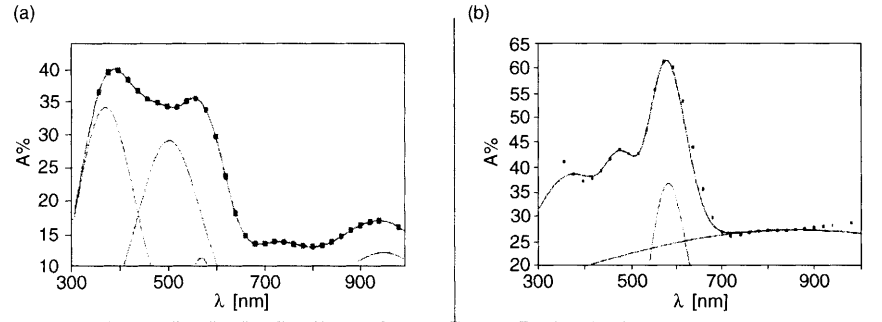


Figure 4 *Optimised structure and charge density for [6-(4-chlorophenyl)-pyridazin-3-yl]hydrazine, L*



$^2T_{2g} \rightarrow {}^4T_{1g}(Fe^{3+})$	$^4T_{2g}(Fe^{3+})$	$^4A_{2g} \rightarrow {}^4T_{2g}$ (Cr^{3+})	$^4A_{2g} \rightarrow {}^4T_{1g}$ (Cr^{3+})	$^2T_{2g} \rightarrow {}^4T_{2g}$ (Fe^{3+})
503 nm	373 nm	585 nm	469 nm	368 nm

Figure 5 *Electronic spectra of* (a) $[Fe_2(C_4O_4)(ClO_4)_2L_2(H_2O)_4](ClO_4)_2$, **3**; (b) $[FeCr(C_4O_4)(ClO_4)_2L_2(H_2O)_4](ClO_4)_2$, **5**

Table 3 *Magnetic moments for the complexes* **1–6**

Compound	μ_{eff}, *BM*
1	1.42
2	2.78
3	4.65
4	4.73
5	5.33
6	4.06

(Table 3) which indicate that the iron compounds are low-spin complexes.

This supports again the proposed structures where iron is coordinated to perchlorate, a strong ligand forcing spin pairing.

The magnetic moments of the compounds which contain both chromium(III) and iron(III) compounds are slightly lower than expected for low-spin and high-spin complexes of these metals (Table 3) which suggests a weak interaction between the two paramagnetic ions (Fe^{3+} and Cr^{3+}).

3 Conclusions

We have reported the synthesis and the characterisation of a new series of the polynuclear complex compounds of iron(III) and chromium(III) where the bridging ligand is squarate dianion, coordinated in a μ-1,3-bis(monodentate) manner.

Further studies (EPR and Mössbauer spectroscopies) will complete the structural characterisation of these complexes and perhaps confirm the ability of squarate to serve as a pathway for magnetic superexchange interaction between paramagnetic ions.

4 References

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Index of People and Places

People

Places

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Coordination chemistry, as we know it today, has been shaped by major figures from the past, one of whom was Joseph Chatt. Beginning with a description of Chatt's career presented by co-workers, contemporaries and students, this fascinating book then goes on to show how many of today's leading practitioners in the field, working in such diverse areas as phosphines, hydrogen complexes, transition metal complexes and nitrogen fixation, have been influenced by Chatt. The reader is then brought right up-to-date with the inclusion of some of the latest research on these topics, all of which serves to underline Chatt's continuing legacy.

Intended as a permanent record of Chatt's life, work and influence, this book will be of interest to lecturers, graduate students, researchers and science historians.

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