REDOX ACTIVE BINUCLEAR COMPLEXES

OF RUTHENIUM AND OSMIUM

Alan J. Lindsay

Ph.D. Thesis
University of Edinburgh
1982
DECLARATION

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results presented have already been published.

Alan J. Lindsay.
To my Mother, Father and Sister
I wish to thank Dr. T.A. Stephenson and Dr. G.A. Heath for their help, encouragement and enthusiasm throughout this work. I also wish to express my gratitude to Dr. D.K. Vattis of the University of Patras, Greece, for his invaluable contribution to this study. In addition, I am grateful to Dr. D. Reed, Mr. L.H. Bell and Mr. J.A.A. Millar for recording $^{31}\text{P}$, $^{13}\text{C}$ and $^1\text{H}$ n.m.r. spectra, Dr. S.F. Watkins of Louisiana State University, U.S.A., for carrying out X-ray work and Mr. M. Grunbaum for performing microanalytical measurements. I am deeply indebted to the S.E.R.C. for their financial support and the University of Edinburgh for the use of facilities. Finally, my thanks to Miss A. Erskine for typing this thesis.
Chapter 1 gives a brief account of some of the general aspects of ruthenium and osmium chemistry.

Chapter 2 describes efforts to extend the range of triple chloro bridged binuclear ruthenium (II/II) complexes in an orderly fashion by application of two alternative synthetic strategies: assembly from appropriate monomers such as RuCl₂L₄ (L = py, 4-Mepy, MeCN and Me₂SO) and by terminal ligand displacement from existing triple chloro bridged complexes e.g. Ru₂Cl₄(PEt₂Ø)₅.

Chapter 3 discusses the formation of new non-chloro triple bridged binuclear ruthenium(II/II) complexes. This can be achieved through the action of weak acids such as H₂O or HSEt on basic ruthenium hydrido species such as [RuH(cod)(PMe₂Ø)₃]PF₆. The product of the former reaction is the hydroxo bridged complex [Ru₂(OH)₃(PMe₂Ø)₆]PF₆, which may then be converted to [Ru₂X₃(PMe₂Ø)₆]PF₆ (X = Cl⁻, Br⁻, I⁻) through treatment with the appropriate acid HX. The synthesis, characterisation and isomerisation of the neutral complex Ru₂Br₄(CO)(PØ₃)₄ is also discussed. The related chloro bridged complexes Ru₂Cl₄Y(PØ₃)₄ (Y = CO, CS) are shown to react with aqueous NaOH in CH₂Cl₂ to produce Ru₂Cl(OH)₃Y(PØ₃)₄. In the absence of excess OH⁻ ion this compound rearranges to form [RuCl(OH)₂/Y₂(PØ₃)₄]Cl and [Ru(OH)₂(PØ₃)₂]₂.

Chapter 4 attempts to account for the stereospecific formation of neutral "asymmetric" mixed-valence Ru₂(II/III) triple chloro bridged complexes of type (PR₃)₂YRuCl₃RuCl₂(PR₃) (Y = CO, CS, PR₃) from the reaction between their related
Ru$_2$(II/II) precursors, (PR$_3$)$_2$YRuCl$_3$RuCl(PR$_3$)$_2$, and concentrated HCl. In addition attempts are made to devise a method of synthesis of neutral "symmetric" mixed-valence Ru$_2$(II/III) and Os$_2$(II/III) complexes.

Chapter 5 discusses the influences, such as metal ion identity and terminal and bridging ligand characteristics, affecting the redox potentials of M$_2$(II/II), M$_2$(II/III) (M = Ru, Os) and Ru$_2$(III/III) triple bridged complexes discussed in Chapters 1-4. It will be shown that, by comparing the redox potentials of these compounds with those of their related monomers, simple, but highly effective structure/redox potential correlations can be derived.

Chapter 6 describes how variable temperature magnetic measurements in solid and solution states of triple chloro bridged Ru$_2$(III/III) compounds, and the detection and analysis of the characteristic intervalence charge transfer (IT) bands in the near-infrared absorption spectrum of the corresponding Ru$_2$(II/III) compounds reveal that the degree of metal-metal interaction in these confacial bicctahedral systems decreases as the molecular asymmetry increases.

Appendix I deals with the formation of some monomeric tertiary phosphine complexes from the hydrido compound [RuH(cod)(NH$_2$NMe$_2$)$_3$]B$_4$O$_4$.

Appendix II describes the thermodynamic relationship between the optical transition energy of an intervalence charge band and the measured and inferred E$_{1/2}$ values.
# CONTENTS

## CHAPTER 1  A General Survey of the Oxidation States Exhibited by Ruthenium

1.1  Preamble  

1.2  Introduction  

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(VIII)d⁰, Ru(VII)d¹ and Ru(VI)d²</td>
<td>3</td>
</tr>
<tr>
<td>Ru(V)d³</td>
<td>6</td>
</tr>
<tr>
<td>Ru(IV)d⁴</td>
<td>6</td>
</tr>
<tr>
<td>Ru(III)d⁵</td>
<td>11</td>
</tr>
<tr>
<td>Ru(II)d⁶</td>
<td>19</td>
</tr>
<tr>
<td>Ru(I)d⁷</td>
<td>27</td>
</tr>
<tr>
<td>Ru(0)d⁸</td>
<td>29</td>
</tr>
<tr>
<td>Ru(−I)d⁹, Ru(−II)d¹⁰</td>
<td>31</td>
</tr>
</tbody>
</table>

## CHAPTER 2  Synthesis and Characterisation of New Triple Chloro Bridged Ruthenium(II/II) Binuclear Complexes

2.1  Preamble  

2.2  Introduction  

2.3  Results and Discussion  

(a) Dimerisation of Ru(II) monomers of type RuCl₂L₄  

(i) L = Me₂SO  

(ii) L = MeCN, pyridine and 4-methylpyridine  

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
</tr>
<tr>
<td>33</td>
</tr>
<tr>
<td>47</td>
</tr>
<tr>
<td>64</td>
</tr>
</tbody>
</table>
(b) Specific nucleophilic substitution at terminal sites in existing triple chloro bridged complexes

(i) Attempted replacement of neutral diazadiene ligands

(ii) Terminal chloride substitution

2.4 Conclusions

2.5 Experimental

CHAPTER 3 Synthesis and Characterisation of New Non-Chloro Triple Bridged Ruthenium(II/II) Binuclear Complexes

3.1 Preamble

3.2 Introduction

3.3 Results and Discussion

(a) Dimerisation of Ru(II) Monomers

(i) Reactions of the weak acids \( \text{H}_2\text{O} \) and HSEt with \([\text{RuH(cod)}-(\text{NH}_2\text{NMe}_2)_3\text{X}] (X=\text{B}^-, \text{PF}_6^-)\) and excess PMe_2\( \text{O} \)

(ii) Preparation and reactions of pure \(\text{RuBr}_2(\text{P}\text{O}_3)_3\)

(b) Nucleophilic attack at bridging sites of triple chloro bridged \(\text{Ru}_2(\text{II/II})\) binuclear complexes (bridging group replacement)

(i) Attack of hydroxide ion on \(\text{Ru}_2\text{Cl}_4\text{Y}(\text{P}\text{O}_3)_4\) (Y=CO, CS)

(ii) Reactions of \([\text{Ru}_2(\text{OH})_3-(\text{PMe}_2\text{O})_6]\text{PF}_6\) with acids \(\text{HX}\)
CHAPTER 4 Preparation and Characterisation of Mixed-Valence Triple Bridged Binuclear Ru$_2$(II/III) Complexes

4.1 Preamble
4.2 Introduction
4.3 Results and Discussion
   (a) Chemical oxidation of neutral triple chloro Ru$_2$(II/II) binuclear complexes in acidic media
   (b) Direct reactions between "RuCl$_3$·3H$_2$O" or Na$_2$OsCl$_6$ and various ligands L
4.4 Conclusions
4.5 Experimental

CHAPTER 5 Electrochemical Studies on Some Triple Bridged Ruthenium and Osmium Binuclear Complexes

5.1 Preamble
5.2 Introduction
   (a) Cyclic Voltammetry (C.V.)
   (b) Stirred Linear Sweep Voltammetry
   (c) Linear Sweep a.c. Voltammetry
   (d) Electrosyntheses
5.3 Results and Discussion
(a) \([(\text{PR}_3)_3 \text{MCl}_3 \text{M(PR}_3)_3]^+\) and related \(\text{M}_2(\text{II/II})\) cations \(\text{162}\)
(b) \(\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5\) and related \(\text{Ru}_2(\text{II/II})\) neutral compounds \(\text{167}\)
(c) \(\text{Ru}_2\text{X}_4\text{Y(PR}_3)_4\) and related complexes \(\text{169}\)
(d) \(\text{M}_2\text{Cl}_5(\text{LR}_3)_4\) and related neutral mixed-valence \(\text{Ru}_2(\text{II/III})\) complexes
   (i) "Asymmetric" mixed-valence complexes \(\text{170}\)
   (ii) "Symmetric" mixed-valence complexes \(\text{172}\)
(e) \(\text{Ru}_2\text{Cl}_6(\text{AsR}_3)_3\) \(\text{173}\)
(f) Structure/redox potential correlations \(\text{176}\)

5.4 Conclusions \(\text{180}\)
5.5 Experimental \(\text{182}\)

CHAPTER 6 Spectroscopic and Magnetic Studies on Electrogendated Mixed-Valence Ruthenium Complexes

6.1 Preamble \(\text{186}\)
6.2 Introduction \(\text{187}\)
6.3 Results and Discussion
Factors influencing the degree of metal-metal interaction in triple chloro bridged binuclear ruthenium complexes at the \(\text{Ru}_2(\text{II/III})\) and \(\text{Ru}_2(\text{III/III})\) oxidation levels \(\text{192}\)
(a) Using intervalence charge-transfer bands to explore the tendency to partial charge delocalisation in the "RuCl₃Ru²⁺" core of binuclear Ru₂(II/III) complexes

(b) Using magnetic studies to explore the degree of metal-metal interaction in the "RuCl₃Ru³⁺" core of binuclear Ru₂(III/III) complexes

APPENDIX I Some Monomeric Tertiary Phosphine Complexes

Derived from the Hydrido Compound

[RuH(cod)(NH₂NMe₂)_3]BØ₄

A.1 Preamble

A.2 Introduction

A.3 Results and Discussion

(a) Reaction of [RuH(cod)(NH₂NMe₂)_3]BØ₄ with a four-fold excess of PMe₂Ø

(b) Reaction of [RuH(cod)(NH₂NMe₂)_3]BØ₄ with NaOMe and a three-fold excess of PEtØ₂

A.4 Conclusions

A.5 Experimental

APPENDIX II The Thermodynamic Relationship Between the Optical Transition Energy and the Measured and Inferred E₄ values

APPENDIX III Abbreviations

References
FIGURES

2.1  Triple chloro bridged structural reformulation of Ru$_2$Cl$_4$(Me$_2$SO)$_5$  

2.2a,b  $^1$H and $^{13}$C-$^1$H n.m.r. spectra of Ru$_2$Cl$_4$(Me$_2$SO)$_5$ in CD$_2$Cl$_2$ at 303 K  

2.3a,b,c  $^{13}$C-$^1$H n.m.r. spectra of [RuCl$_n$(Me$_2$SO)$_6$-n]-(BF$_4$)$_{2-n}$ (n = 0,1,2) in CD$_3$NO$_2$ at 303 K  

2.4  Infrared spectrum of Ru$_2$Cl$_4$(Me$_2$SO)$_5$ and Ru$_2$Cl$_4$(d$_6$-Me$_2$SO)$_5$  

3.1  $^{31}$P-$^1$H n.m.r. spectrum of RuBr$_2$(P$_3$O$_3$)$_3$ in CH$_2$Cl$_2$/d$_6$-acetone in 183 K  

3.2  $^{31}$P-$^1$H n.m.r. spectrum of Ru$_2$Br$_4$(CO(P$_3$O$_3$))$_4$ in CD$_3$C$_6$D$_5$ at 183 K  

3.3  Isomerisation of Ru$_2$X$_4$(CO)(P$_3$O$_3$)$_4$  

3.4  $^{31}$P-$^1$H n.m.r. spectrum of Ru$_2$Cl$_4$(CS)(P$_3$O$_3$)$_4$ + aqueous NaOH in CDCl$_3$ at 298 K  

3.5  $^{31}$P-$^1$H n.m.r. spectrum of Ru$_2$Cl(OH)$_3$(CS)-(P$_3$O$_3$)$_4$ in CDCl$_3$ at 298 K  

3.6  Infrared Spectrum of Ru$_2$Cl(OH)$_3$(CS)-(P$_3$O$_3$)$_4$  

3.7  $^{31}$P-$^1$H n.m.r. spectrum of Ru$_2$Cl(OH)$_3$(CO)-(P$_3$O$_3$)$_4$ in CDCl$_3$ at 298 K  

3.8a,b,c  $^{31}$P-$^1$H n.m.r. spectra of the rearrangement products of Ru$_2$Cl(OH)$_3$(CO)(P$_3$O$_3$)$_4$ in CDCl$_3$ at 298 K  

4.1  X-ray crystal structure of Ru$_2$Cl$_5$(PET$_2$O)$_4$  

4.2  Cyclic and a.c. voltammetry of the Ru$_2$Cl$_5$(dpa)$\_2$ isomeric mixture  

4.3  E.S.R. spectrum of the Ru$_2$Cl$_5$(dpa)$\_2$ isomeric mixture
5.1 Three-electrode apparatus

5.2 Cyclic voltammetry of a species undergoing reversible and irreversible charge-transfers

5.3 Stirred and unstirred stationary electrode voltammetry

5.4 A.C. voltammetric peak centred on $E_1$ of the corresponding stationary and non-stationary d.c. voltammetric techniques

5.5 Characteristic current-time response curve for controlled-potential electrolysis

5.6 Three-compartment cell for controlled-potential electrolysis

5.7 Cyclic and a.c. voltammetry of $[\text{Ru}_2\text{Cl}_3(\text{PET}_2\Phi)_6]\text{Cl}$

5.8 Stirred and unstirred voltammetry of $\text{Ru}_2\text{Cl}_4^-$

5.9 Stirred and unstirred voltammetry of $\text{Ru}_2\text{Cl}_5^-$

5.10a,b Voltammetry of $\text{Ru}_2\text{Cl}_5(\text{As}(\text{P-tol})_3)_4$

5.11 Stirred and unstirred voltammetry of $\text{Ru}_2\text{Cl}_6(\text{As}(\text{P-tol})_3)_3$

5.12 Structure/redox potential correlation diagram including both monomeric and triple bridged binuclear complexes

5.13 Structure/oxidation potential correlation diagram showing the influence of Cl$^-$ ion(s) on one Ru centre on the oxidation potential of its adjacent Ru centre

5.14 Structure/redox potential diagram showing the variation of $\Delta E$ with $\Delta \text{Cl}^-$
6.1 Energy-configurational coordinate diagram applicable for valence interchange in asymmetric complexes

6.2 Energy-configurational coordinate diagram applicable for valence interchange in symmetric complexes

6.3 Schematic representation of an OTTLE

6.4 The near-infrared spectrum of 
\[ \text{[Ru}_2\text{Cl}_6(\text{As(\text{P-tol})}_3)_3^{10/-/2-} \]

6.5 \(^{31}\text{P}-\text{H}\) n.m.r. spectra of \(\text{Ru}_2\text{Cl}_4(\text{CO})(\text{PØ}_3)_4\) before and after oxidation

6.6 Schematic representation of metal bonding orbitals in symmetric triple bridged binuclear ruthenium complexes

A.1 Mass spectral fragmentation pattern of the 
\([\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]^+\) cation

A.2 \(^{31}\text{P}-\text{H}\) n.m.r. spectrum of \([\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]\text{BØ}_4\) in CDCl\(_3\) at 298 K

A.3 \(^1\text{H}\) n.m.r. spectrum of the methyl region of 
\([\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]\text{BØ}_4\) in CDCl\(_3\) at 298 K

A.4a,b \(^{31}\text{P}-\text{H}\) n.m.r. spectra of \([\text{Ru(CH}_3\text{CO}_2)(\text{PMe}_2\text{Ø})_4]^-\text{BØ}_4\) in CDCl\(_3\) at 298 K recorded at 24.2 and 145.8 MHz

A.5 X-ray structure of \([\text{Ru(CH}_3\text{CO}_2)(\text{PMe}_2\text{Ø})_4]^+\) cation

A.6 \(^1\text{H}\) n.m.r. spectrum of the hydride region of 
\(\text{RuH}_2(\text{CO})(\text{PEtØ}_2)_3\) in CDCl\(_3\) at 298 K

A.7 \(^{31}\text{P}-\text{H}\) n.m.r. spectrum of \(\text{RuH}_2(\text{CO})(\text{PETØ}_2)_3\) in CDCl\(_3\) at 298 K

A.8 \(^{31}\text{P}-(\text{Sel.} \text{H})\) n.m.r. spectrum of \(\text{RuH}_2(\text{CO})-(\text{PETØ}_2)_3\) in CDCl\(_3\) at 298 K
SCHEMES

1.1 Reactions of OsCl$_6^{2-}$

1.2 Some general reactions of "RuCl$_3$·3H$_2$O"

1.3 Some reactions of "RuCl$_3$·3H$_2$O" with tertiary phosphines

2.1 Pyrolysis products of [Ru$_2$Cl$_3$(PR$_3$)$_6$]Cl

2.2 Transformations of RuCl$_2$(PR$_3$)$_3$, (PR$_3$ = tertiary phosphine, phosphonite, phosphinitite)

2.3 Chemical reduction of mer-RuCl$_3$(PR$_3$)$_3$

2.4 Solution rearrangements of RuCl$_2$Y(PR$_3$)$_2$(MeOH) (Y = CO, CS)

2.5 Various methods of synthesis of Ru$_2$Cl$_4$L$_2$(PØ)$_3$$_3$ (L = CO, PF$_3$, PF$_2$NMe$_2$)

2.6 The coupling reaction of RuCl$_2$(PØ)$_3$ and cis-RuCl$_2$L$_2$(PØ)$_3$$_2$ (L = PF$_3$, PF$_2$NMe$_2$)

3.1 Postulated mechanism of formation of [Ru$_2$(OH)$_3$(PMe$_2$Ø)$_6$]$^+$ cation

3.2 Proposed formation and rearrangement reactions of Ru$_2$Cl(OH)$_3$Y(PØ)$_3$$_4$ (Y = CO, CS)

3.3 Postulated mechanism of formation of [Ru$_2$X$_3$(PMe$_2$Ø)$_6$]$^+$ from [Ru$_2$(OH)$_3$(PMe$_2$Ø)$_6$]$^+$ and HX

4.1 Mechanism of formation of (PR$_3$)$_3$RuCl$_3$RuCl$_2$(PR$_3$) and (PR$_3$)$_2$YRuCl$_3$RuCl$_2$(PR$_3$) involving oxidation of binuclear Ru$_2$(II/II) complexes followed by bridge cleavage/halide attack and condensation of the resulting monomers

4.2 Mechanism of formation of (PR$_3$)$_3$RuCl$_3$RuCl$_2$(PR$_3$) and (PR$_3$)$_2$YRuCl$_3$RuCl$_2$(PR$_3$) involving specific terminal nucleophilic halide attack after activation of binuclear Ru$_2$(II/II) complexes by oxidation
Schemes (contd.)

4.3 Mechanism of formation of $(\text{PR}_3)_3\text{RuCl}_3\text{RuCl}_2(\text{PR}_3)$ and $(\text{PR}_3)_2Y\text{RuCl}_3\text{RuCl}_2(\text{PR}_3)$ involving competitive bridge cleavage/oxidation of binuclear Ru$_2$(II/II) complexes
TABLES

1.1 RuO$_4$ and some high oxidation state derivatives 4
1.2 Some nitrosyl containing complexes of Ru(II) and Os(II) 22
1.3 Some Ru(II) and Os(II) complexes containing only halides and group (V) donor ligands 23
1.4 Some Ru and Os carbonyl complexes 25
1.5 Some Ru(II) and Os(II) $^6$-arene complexes 26
2.1 Infrared Spectra of Ru$_2$Cl$_4$(Me$_2$SO)$_5$ and Ru$_2$Cl$_4$(d$^6$-Me$_2$SO)$_5$ (4000-600 cm$^{-1}$) 75
2.2 N.M.R. parameters for [RuCl$_n$(Me$_2$SO)$_{6-n}$](BF$_4$)$_2-n$ (n = 0,1,2) and Ru$_2$Cl$_4$(Me$_2$SO)$_5$ 76
5.1 Cyclic voltammetric criteria for reversible, quasi-reversible, partially-reversible and irreversible charge-transfer processes at 298 K 152
5.2 Linear sweep a.c. voltammetry criteria for a reversible charge-transfer process at 298 K 157
5.3 Electrode potentials for some triple bridged binuclear ruthenium(II/II) and osmium(II/II) complexes 183
5.4 Electrode potentials for some triple bridged ruthenium and osmium complexes in initial oxidation states (II/III) and (III/III) 185
6.1 Characteristics of the four classes of mixed-valence compounds 189
6.2 Electrochemical behaviour of some [L$_{3-x}$Cl$_x$-RuCl$_3$RuCl$_y$L$_{3-y}$] complexes 193
6.3 Intervalance charge transfer bands for some Ru$_2$(II/III) complexes 209
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>In situ characterisation of electrogenerated complexes</td>
<td>210</td>
</tr>
<tr>
<td>6.5</td>
<td>Increasing metal-metal interaction with increasing molecular symmetry</td>
<td>213</td>
</tr>
<tr>
<td>A.1</td>
<td>Some selected bond lengths and bond angles for the ( [\text{Ru(CH}_3\text{CO}_2)(\text{PMe}_2\emptyset)_4]^+ ) cation</td>
<td>225</td>
</tr>
</tbody>
</table>
CHAPTER 1

A General Survey of the Oxidation States

Exhibited by Ruthenium
1.1 Preamble

The work presented in Chapters 2-5 of this thesis deals largely with chloro bridged binuclear coordination complexes containing ruthenium (Ru), and to a lesser extent osmium (Os), in oxidation states (II) and/or (III). However, before embarking on an in-depth examination of the chemistry of these complexes, it is of interest to place the work in perspective by presenting a brief introduction to the oxidation states generally exhibited by Ru and, where applicable, a comparison with Os will be made.

1.2 Introduction

Although Ru is a member of the first triad of group VIII it has few characteristics shared with its lighter congener iron (Fe). However the similarity of both atomic and ionic radii (and hence ionisation potentials) of Ru and its heavier congener Os, and indeed second and third row transition metals of the same triad generally, ensures their properties are much more alike. For example, it is generally observed that these heavier transition metal elements are more capable of stabilising higher oxidation state compounds than those of the first transition series, e.g. $\text{RuO}_4^{(1)}$ and $\text{OsO}_4^{(2)}$ have no iron analogue.

Another common feature of second and third row transition metals is their exclusive formation of low spin complexes which is attributed to two effects, both arising from the greater size of 4d and 5d orbitals:
(a) The reduction of electron-electron repulsion and hence smaller pairing energies.

(b) The improved molecular orbital overlap with ligand orbitals which gives a larger ligand field splitting parameter $\Delta$.

Ru and Os often parallel each other closely, e.g. they both have an extensive range of formal oxidation states, ranging from -II to VIII. Both have "preferred" or common oxidation states, for which by far the greatest range of compounds is formed. For Ru these are oxidation states (II), (III) and (IV), while for Os they are (II), (III), (IV) and (VI). All Ru (II) and Os (II) (d$^6$) octahedral complexes are diamagnetic (commonly with a $t_{2g}^6$ ground state) whereas those of Ru(III) and Os(III) (d$^5$) are generally paramagnetic (commonly with a $t_{2g}^5$ ground state). Exceptions to this are found when extensive metal-metal interactions occur in some bi- or polynuclear species.

A major factor determining when high or low oxidation states of the metal are favoured is the identity of the ligands. Thus, small and electronegative ligands such as F$^-$ and O$^{2-}$ tend to stabilise high oxidation states of Ru and Os, e.g. (IV-VIII). For the O$^{2-}$ ligand in particular, these properties are at least partially associated with its high $\pi$-donor character. In general Ru and Os only exhibit oxidation states (VII) and (VIII) in oxy complexes, either with or without F$^-$ or OH$^-$ ligands, whereas unsubstituted F$^-$ complexes are formed only for oxidation state (VI) or lower.
The reverse is also true, i.e. efficient π-acceptor ligands like CN⁻, CO, PR₃ tend to stabilise low oxidation states of Ru and Os such (II), (I) or (0), whereas good σ-donors with little π-donor or π-acceptor properties (e.g. H₂O, NH₃, etc.) are often associated with the "preferred" oxidation states of Ru(III) and Os(IV).

The tendency of third row elements to form more stable higher oxidation states than their second row congeners is shown by Os (VII), (VI) and (IV) complexes being more common than their Ru analogues; conversely many more Ru(III) than Os(III) complexes are known. These differences are not nearly so marked for the lower oxidation state complexes, of which neither Ru nor Os have many examples.

Some of the compounds found in these oxidation states of Ru will now be examined (in separate sections) in more detail, and comparisons made with Os where relevant.

Ru(VIII) d°, Ru(VII) d¹ and Ru(VI) d²

These oxidation states are not favourable for Ru and Os compounds in general. However, of those that exist, the most prominent types are the tetroxides and their related oxy anions (see Table 1.1). Ruthenium and osmium tetroxides have a number of properties in common; they share the same tetrahedral symmetry and are both poisonous, volatile crystalline solids with pungent ozone-like odours. They are both extensively utilised in organic chemistry as powerful oxidising agents. They both undergo addition reactions
Table 1.1

<table>
<thead>
<tr>
<th>RuO₄ and some high oxidation state derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(VIII)</td>
</tr>
<tr>
<td>RuO₄</td>
</tr>
<tr>
<td>RuO₄·Py₂ (3)</td>
</tr>
<tr>
<td>RuO₄·NH₃ (4)</td>
</tr>
<tr>
<td>*RuO₄·PF₃ (4)</td>
</tr>
<tr>
<td>*[RuO₄]₂·PF₃ (4)</td>
</tr>
</tbody>
</table>

* Low thermal stability
with a variety of donor ligands such as py, PF$_3$ etc. to form RuO$_4$·py$_2$ (3), RuO$_4$·PF$_3$ (4) etc. which are generally black, hygroscopic solids of indeterminate structure. RuO$_4$ is more sensitive to light and temperature than OsO$_4$ and above 180°C it decomposes explosively giving RuO$_2$ and O$_2$.

On treating RuO$_4$ with HCl and Cl$_2$ gases, hygroscopic crystals of the oxy-anion [H$_3$O]$_2$[RuO$_2$Cl$_4$] (5) are produced and this anion may be isolated as either the Rb$^+$ or Cs$^+$ salt. These compounds are however readily hydrolysed to give RuO$_4$ (Equation [1]).

$$2 \text{Cs}_2[\text{RuO}_2\text{Cl}_4] + 2\text{H}_2\text{O} \rightarrow \text{RuO}_4 + \text{RuO}_2 + 4\text{Cs}_2\text{Cl} + 4\text{HCl} \quad \text{[1]}$$

Likewise, when RuO$_4$ is dissolved in dilute H$_2$SO$_4$ and reduced with NaNO$_2$, Na$_2$SO$_3$ or FeSO$_4$, green solutions containing Ru(VI) are formed. The exact formulation of the green species is not known but it is believed to contain the [RuO$_2$(SO$_4$)$_2$]$^{2-}$ anion. These green solutions are fairly unstable and decompose within a few hours to give Ru(IV) species.

A number of Ru(VI) fluoride compounds are also known e.g. RuOF$_4$ (6) and RuF$_6$, the latter being prepared by the direct fluorination of the metal (7).
Ru(V) $d^3$

Ru and Os compounds in this oxidation state are very rare, and of those that do exist virtually all are fluoride species, e.g. $[\text{RuF}_5)_4$ (1), $[\text{RuF}_6]^-$, $[\text{RuF}_6]^{2-}$ and $[\text{OsF}_6]^-$.

Compound (1) consists of discrete tetrameric units with the Ru atoms lying at the corners of a square. The fluoride ions are arranged around each Ru in a distorted octahedron such that the Ru-F-Ru bridges are non-linear.

![Ru-F-Ru bridge diagram](image)

The octahedral $[\text{RuF}_6]^-$ and $[\text{OsF}_6]^-$ ions have $t_{2g}^3$ configurations with three unpaired electrons; their magnetic moments are temperature independent, with $\mu_{\text{eff}}$ ca. 3.7 BM for $[\text{RuF}_6]^-$ (8) and ca. 3.2 BM for $[\text{OsF}_6]^-$ salts (9).

Ru(IV) $d^4$

Ru(IV) and Os(IV) complexes generally possess octahedral, or distorted octahedral, structures with a $t_{2g}^4$ low spin ground state configuration. Ru(IV) compounds have room temperature magnetic moments in the normal range expected for two unpaired electrons, i.e. 2.7-2.9 BM, which
decrease on lowering the temperature. However, Os(IV) compounds generally exhibit depressed room temperature magnetic moments of 1.2-1.7 BM which also decrease on lowering the temperature. The major reason for this apparently anomalous magnetic behaviour is the high degree of spin-orbit coupling associated with the heavier transition elements.

Ru(IV) compounds are fairly rare. The largest group of compounds in this oxidation state is the halides. Compounds such as RuF₄ and RuCl₄ have been isolated, while their bromo and iodo analogues are unknown. The yellow crystalline RuF₄ is synthesised by heating a mixture of [RuF₅]₄⁻, I₂ and IF₅ (¹⁰) while its chloro analogue only exists in the gas phase above 750°C (¹¹). Os(IV) compounds are relatively plentiful in comparison with those of Ru(IV), all the tetrahalides being known (with the exception of OsI₄). OsF₄ is a high melting point, yellow solid (¹²). OsCl₄ is a water soluble red crystalline solid (¹³), while the tetrabromide exists as black crystals (¹⁴).

Both Ru and Os form an extensive range of hexahalogeno anions [MX₆]²⁻ (M = Ru; X = F⁻, Cl⁻, Br⁻, I⁻; M = Os; X = F⁻, Cl⁻, Br⁻, I⁻). The magnetochemistries of [RuCl₆]²⁻, and [RuX₆]²⁻ generally, are normal i.e. 2.7-2.9 BM which are temperature dependent (magnetic moment decreasing with decreasing temperature) (¹⁵). In contrast [OsCl₆]²⁻, and [OsX₆]²⁻ generally, exhibit depressed magnetic moments of 1.2-1.7 BM which are subject to the same type of temperature behaviour as their Ru analogues. "Solid solution" magnetic measurements are believed to suggest that the depressed
magnetic moments are due to antiferromagnetic coupling between Os(IV) ions through intervening chloride ions (15, 16) i.e. halide mediated metal-metal antiferromagnetic interactions.

The [MX₆]²⁻ ions generally, and [OsCl₆]²⁻ in particular, react with a wide range of substrates (see Scheme 1.1 for representative examples). The Ru(IV) chloro-aquo system also shows complex behaviour, undergoing changes in colour from red to violet to yellow on addition of Cl⁻ ion to an aqueous solution of Ru(IV) perchlorate. Equilibria, kinetic and spectrophotometric studies suggest the yellow colour arises from species such as [RuCl₃(OH)₂(H₂O)]⁻ and [Ru(OH)₂Cl₄]²⁻ (and a variety of polymeric complexes), while the violet colour is possibly due to a trinuclear complex Ru₃O₂Cl₆(H₂O)₆, with a linear Ru-O-Ru-O-Ru backbone (19).

A closely related Ru(IV) complex is the diamagnetic (20) red crystalline solid K₄[Ru₂OCl₁₀]. An X-ray structural analysis showed this complex to have the unusual structure (2) (21).
Scheme 1.1  Reactions of OsCl$_6^{2-}$

[Diagram showing various reactions involving OsCl$_6^{2-}$ with different ligands and reagents, including Cl$_2$, OH$^-$, NH$_3$, PR$_3$, Br$^-$, H$_2$O, HX, HCl, and others.]
The diamagnetism of (2) and its bromo analogue (22) has been explained on the basis of a simple molecular orbital treatment of the Ru-O-Ru grouping (23). The Os analogue of (2) has also been claimed to exist (24).

Another group of related complexes are the "ruthenium reds" which may be formed in a variety of ways, the commonest being the aerial oxidation of \([\text{Ru}(\text{NH}_3)_6]\text{Cl}_3\). The structure of the red solid produced here is that of a linear trinuclear ion with oxygen bridges i.e. \([\text{(NH}_3)_5\text{Ru-O-Ru(NH}_3)_4\text{-O-Ru(NH}_3)_5]^6+\) (19). Such structures are not unique, as established by an X-ray structure of the analogous ethylenediamine derivative \([\text{(NH}_3)_5\text{Ru-O-Ru(en)}_2\text{-O-Ru(NH}_3)_5]\text{Cl}_6\) (3) (25). Since the average oxidation state of each Ru is \(3\frac{1}{2}\), the metal atoms must be in different formal oxidation states and so, the observed diamagnetism may be ascribed to the occurrence of extensive Ru-O-Ru \(\pi\)-bonding as in (2).

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{NH}_3 & \quad \text{N} & \quad \text{N} & \quad \text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{Ru} & \quad \text{O} & \quad \text{Ru} & \quad \text{O} & \quad \text{Ru} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 & \quad \text{N} & \quad \text{N} & \quad \text{H}_3\text{N} & \quad \text{NH}_3 \\
\end{align*}
\]

(3) \(\text{(N } \text{N} = \text{H}_2\text{N(CH}_2)_2\text{NH}_2\text{)})
No direct Os analogues occur for this type of complex, but several nitrido bridged complexes do exist, e.g. \([(NH_3)_4XOs-N-OsX(NH_3)_4]X_3\) (X = Cl, Br), both being diamagnetic\(^{26,27}\).

Besides these bridged N-containing Ru(IV)\(^{27}\) and Os(IV) complexes there are many monomeric complexes containing N-donor ligands e.g. \(\text{trans-RuCl}_4\text{py}_2\)\(^{28}\) and \(\text{trans-RuCl}_4\text{(bipy)}\)\(^{29}\) etc., which readily reduce to the more stable complexes of Ru(III) and Ru(II). Such complexes also exist for Os(IV), but in addition a number of tertiary arsine and phosphine complexes can also be synthesised, e.g. \(\text{trans-OsCl}_4(\text{LR}_3)_2\) (LR\(_3\) = PØ\(_3\), AsØ\(_3\) etc.)\(^{30}\).

More unusual Ru(IV) and Os(IV) complexes include the allyl complexes \(\text{Ru(CO)Cl}_2(C_{10}H_{16})\)\(^{31}\), made from \(\text{RuCl}_2(C_{10}H_{16})\), and the osmocene derivative \([\text{Os}(\eta^5-C_5H_5)_2-(OH)]\text{PF}_6\)\(^{32}\).

\(\text{Ru(III) d}^5\)

All four trihalides \(\text{RuX}_3\) (X = F\(^-\)\(^{33}\), Cl\(^-\)\(^{34}\), Br\(^-\)\(^{35}\), I\(^-\)\(^{36}\)) are known, while only three are known for \(\text{OsX}_3\) (X = Cl\(^-\)\(^{13}\), Br\(^-\)\(^{36}\), I\(^-\)\(^{37}\)). Some of these species exist in more than one form, depending on the method of preparation, e.g. \(\text{RuCl}_3\) can be made in two water insoluble forms, \(\alpha\) and \(\beta\)\(^{34}\), as well as a water soluble form\(^{38}\).
Most of the Ru(III) and Os(III) complexes prepared to date are both octahedral and paramagnetic \( (t_{2g}^5 \) ground state), with room temperature magnetic moments in the normal range, i.e. 1.8-2.1 BM. The wide range of compounds found in this oxidation state for both Ru and Os precludes any attempt at a comprehensive survey and hence only a brief discussion of the compound types will be given.

The commercial product "RuCl\(_3\).3H\(_2\)O" generally contains Ru(III) species such as RuCl\(_3\)(H\(_2\)O)\(_3\) as well as a variety of polymeric Ru(IV) oxy and hydroxochloro compounds, and occasionally the nitrosyl chloride \([\text{Ru(NO)}\text{Cl\(_3\)]\(_n\)}\) \(^{(8)}\). In order to remove Ru(IV) compounds the commercial product "RuCl\(_3\).3H\(_2\)O" must be evaporated several times with concentrated HCl to produce a mixture of Ru(III) species, shown by ion exchange experiments to be \([\text{Ru(H\(_2\)O)}\(_6\)]\(^{3+}\), \([\text{RuCl(H\(_2\)O)}\(_5\)]\(^{2+}\) and \text{cis} and \text{trans}-[\text{RuCl\(_2\)(H\(_2\)O)}\(_4\)]\(^+\) \(^{(39)}\).

Although the other trihalide compounds of Ru also have an extensive chemistry it is small compared to that of "RuCl\(_3\).3H\(_2\)O" which along with RuO\(_4\), is by far the most important starting point for preparation of Ru complexes in any oxidation state in the current literature. Various transformations of "RuCl\(_3\).3H\(_2\)O" are shown in Scheme 1.2. This point is further amplified by Scheme 1.3 which shows the diversity of reactions of RuCl\(_3\).3H\(_2\)O" with tertiary phosphines alone. Other halide complexes of Ru(III) and Os(III) occur e.g. the hexahalogeno anions \([\text{MX\(_6\)]}^3^-\) (\(M = \text{Ru}; \ X = \text{Cl}\) \(^{(28)}\), Br\(^-\) \(^{(40)}\); \(M = \text{Os}; \ X = \text{Cl}\) \(^{(41)}\), Br\(^-\) \(^{(42)}\), I\(^-\) \(^{(43)}\)) but these are of less importance.
Scheme 1.2  Some General Reactions of "RuCl₃·3H₂O"

RuCl₃(diphos)₂ → LiAlH₄ → RuCl₂(diphos)₂

RuHCl(diphos)₂ → H₂ → RuCl₂(P₃)₃

[RuCl₂(C₇H₈)]ₙ → C₇H₈

[SnCl₂]₂ → Cl₂

[RuCl₃(H₂O)]²⁻ → HCl

[OH⁻] → [RuCl₆]³⁻ → [RuCl₅(H₂O)]²⁻ → [RuCl₄⁻] + O₂

[O₂] → [Ru(ox)]⁻ → [Ru(ox)₃]⁻ → H₂O₂

[SnCl₂]₂ → SnCl₂

[Ru(NO)X₅]²⁻ → HX

[Ru(NO)(OH)(NO₂)₄]²⁻ → RuCl₃(SEt₂)₃

[Ru(en)₃]²⁺ → [Ru(NH₃)₆]²⁺ → [Ru(NH₃)₅X]X²⁻ → [Ru(NH₃)₅(H₂O)]²⁺ → [Ru(NH₃)₅Cl]²⁺ → HX

[Al + AlCl₃] → [Ru₃O₂(NH₃)₁₄]⁶⁺
Scheme 1.3  Some Reactions of "RuCl$_3$·3H$_2$O" with Tertiary Phosphines

trans-RuCl$_2$(CO)$_2$(PR$_3$)$_2$ $>$80°C in soln. $\rightarrow$ cis-RuCl$_2$(CO)$_2$(PR$_3$)$_2$

dry 160°C $\rightarrow$ Ru(CO)$_n$Cl$_m$ species

EtOH, boil + CO

strs, then + PR$_3$

Alc., boil

+ CO, 20 hrs.

Ru(CO)$_n$Cl$_m$ species

pale yellow

"RuCl$_3$·3H$_2$O" Alc. 20°C $+$ CO $+$ PR$_3$ $\rightarrow$ cis-RuCl$_2$(CO)(PR$_3$)$_3$

days

EtOH $+$ CO

3 days

EtOH, 25°C $+$ CO

Ru(CO)$_n$Cl$_m$ species

blood red

$\downarrow$

PR$_3$

1,2,6-RuCl$_3$(PR$_3$)$_3$

trans-RuCl$_2$(CO)(PR$_3$)$_3$

(solution)

EtOH, KOH $\rightarrow$ RuCl$_2$(CO)(PR$_3$)$_3$

HCl

Not isolated

Alc. = 2-methoxyethanol

$\downarrow$

[Ru$_2$Cl$_3$(PR$_3$)$_6$]Cl

EtOH $+$ KOH

CO, 50 atm.

75°C, 16 hrs.
Both Ru(III) and Os(III) form some interesting complexes with oxygen and sulphur donor chelating ligands, e.g. Ru(acac)$_3$ (44), Ru(sacsac)$_3$ (45) and their Os analogues (45,46) all of which have room temperature magnetic moments in the normal range of 1.8-2.1 BM (45,46,47).

In contrast magnetic moments of the carboxylato bridged mixed-valence Ru$_2$(II/III) complexes Ru$_2$(RCO$_2$)$_4$Cl (R = Me, Et, pr$^n$) and related compounds are anomalously high (4.0-4.6 BM/molecule) indicating a spin-free system with three unpaired electrons per binuclear unit (48). Very recently the related Os(III) compounds Os$_2$(RCO$_2$)$_4$Cl$_2$ (R = Me (49,50), pr$^n$, but$^n$ (50)) have been reported.

In recent years a series of diamagnetic binuclear Ru$_2$(III/III) dithiocarbamato complexes [Ru$_2$(S$_2$CNR$_2$)$_5$]BF$_4$ (4) (R = Me, Et, benzyl) have been synthesised and characterised (51). An X-ray structural analysis shows the molecule (4) to contain a metal-metal bond and three bridging dithiocarbamato groups which show two different bonding types (51). Very recent work by the same groups has produced similar complexes for Os (52,53) probably with the same structure as (4) although other isomeric forms are possible. A very small yield of the diamagnetic trithiocarbamato complex [Os$_2$(S$_2$CNEt$_2$)$_3$(S$_3$CNEt$_2$)$_2$]BO$_4$ (5) (53) is also produced in this reaction.
There are a large number of group VB donor ligand complexes of Ru(III) and Os(III). For example, Ru(III) and Os(III) form a variety of ammine species e.g. $[\text{M(NH}_3\text{)}_6]^{3+}$ (M = Ru$^{54}$, Os$^{55}$) and $[\text{M(NH}_3\text{)}_5\text{X}]_2^-$ (M = Ru; X = Cl$, Br^-$, $\text{I}^-$ $^{56}$: M = Os; X = Cl$, Br^-$ $^{57}$). Other examples include $[\text{Ru(NH}_3\text{)}_4\text{X}_2]^+$ (X = Cl$^-$ $^{58}$, Br$^-$ $^{59}$), $\text{RuX}_3\text{(NH}_3\text{)}_3^-$ (X = Cl$, Br^-$ $^{60}$) and the previously mentioned $[\text{(NH}_3\text{)}_5\text{Ru-O-Ru(NH}_3\text{)}_4\text{-O-Ru(NH}_3\text{)}_5]^6^+$ ("ruthenium red") cation$^{19}$. A range of heterocyclic aromatic N-donor ligand complexes are also known e.g. mer-ML$_3$L$_3$ (M = Ru; L = py, 3-Mepy, 4-Mepy etc.$^{61}$: M = Os; L = py, 4-Mepy etc.$^{61}$) and cations of the type $[\text{M(phen)}_3]^3^+$ (M = Ru, Os)$^{62,63}$.
An extensive series of mer-MCl\(_3\)(LR\(_3\))\(_3\) compounds (M = Ru; LR\(_3\) = PMe\(_2\)Ø, AsEt\(_2\)Ø etc. \((64)\); M = Os; LR\(_3\) = PEt\(_2\)Ø, Ppr\(_\frac{n}{3}\) etc.) \((64)\) have been synthesised by refluxing either "RuCl\(_3\)-3H\(_2\)O" or the [OsCl\(_6\)]\(^{2-}\) ion with an excess of LR\(_3\) in EtOH containing HCl, for a short reaction time. In contrast, reaction of "RuCl\(_3\)-3H\(_2\)O" in MeOH with a stoichiometric amount of PØ\(_3\) (or an excess in the case of AsØ\(_3\) or As(\(\beta\)-tol)\(_3\)) yields RuCl\(_3\)(LR\(_3\))\(_2\)(MeOH) \((65)\). Small variations in the reaction conditions have a striking effect on the product composition. For example the mixed-valence Ru\(_2\)(II/III) binuclear complex (As(\(\beta\)-tol)\(_3\))\(_2\)ClRuCl\(_3\)RuCl(As(\(\beta\)-tol)\(_3\))\(_2\) \((6)\) is produced by prolonged refluxing in MeOH of "RuCl\(_3\)-3H\(_2\)O" with an excess of As(\(\beta\)-tol)\(_3\) \((66)\); whereas reaction in butan-2-ol with AsR\(_3\) (R = Ø, \(\beta\)-tol, p-ClØ) gives the geometric isomer (AsR\(_3\))\(_3\)RuCl\(_3\)RuCl\(_2\)(AsR\(_3\)) \((66)\) \((7)\). Refluxing RuCl\(_3\)(AsR\(_3\))\(_2\)(MeOH) (R = Ø, \(\beta\)-tol) in benzene for short reaction times produces the di-Ru(III) complex (AsR\(_3\))\(_2\)ClRuCl\(_3\)RuCl\(_2\)(AsR\(_3\)) \((66)\) \((8)\). These triple chloro bridged complexes \((6)\), \((7)\) and \((8)\) will be discussed more fully in Chapters 4, 5 and 6.

A number of other double and triple halide bridged complexes of Ru(III) which contain PR\(_3\) groups have been reported. These include the double chloro bridged complexes (PR\(_3\))\(_2\)Cl\(_2\)RuCl\(_2\)RuCl\(_2\)(PR\(_3\))\(_2\) (R = Pr\(_n\), Bu\(_n\)) \((67)\) and the triple chloro bridged complexes (PR\(_3\))\(_2\)ClRuCl\(_3\)RuCl(PR\(_3\))\(_2\) (R = Bu\(_n\), pent\(_n\)) \((67)\), which has, for R = Bu\(_n\), been shown by an X-ray structural analysis to have a structure analogous to \((6)\) \((68)\).
A novel diamagnetic triple methylene bridged complex 
(PMe$_3$)$_3$Ru(CH$_2$)$_3$Ru(PMe$_3$)$_3$ has recently been synthesised\textsuperscript{(69)}. Its diamagnetism and short Ru-Ru internuclear distance of 
2.650 Å suggest it has a metal-metal single bond\textsuperscript{(69)}. Double and triple halide bridged Os(III) complexes are 
presently less well-known although both Os$_2$Cl$_5$(LO$_3$)$_4$ 
($L = P, As$) have recently been prepared\textsuperscript{(66)}.

\begin{equation}
\text{Cl} \quad \text{Cl} \quad LR_3 \\
R_3L \quad \text{M} \quad \text{Cl} \quad LR_3 \\
R_3L \quad \text{Cl} \quad \text{Cl}
\end{equation}

(6)

\begin{equation}
\text{Cl} \quad \text{Cl} \quad \text{AsR}_3 \\
R_3As \quad \text{M} \quad \text{Cl} \quad \text{M} \quad \text{AsR}_3 \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{AsR}_3
\end{equation}

(7)

\begin{equation}
\text{Cl} \quad \text{Cl} \quad \text{AsR}_3 \\
R_3As \quad \text{Ru} \quad \text{Cl} \quad \text{Ru} \quad \text{AsR}_3 \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\end{equation}

(8)

The monomeric Ru(III) complexes RuCl$_3$(LR$_3$)$_2$(MeOH) 
(LR$_3$ = PO$_3$, AsO$_3$, As(2-tol)$_3$) react with PO$_4$AsCl.HCl to give the 
anionic complexes PO$_4$As[RuCl$_4$(LR$_3$)$_2$]\textsuperscript{(70)}. Analogous products 
(LR$_3$ = PO$_3$) can also be obtained by treatment of RuCl$_2$(PO$_3$)$_3$ 
with PO$_4$AsCl.HCl, or other large cations, in polar media\textsuperscript{(70)}. This [RuCl$_4$(PO$_3$)$_2$]$^-\text{anion}$ undergoes facile chloride 
substitution by CH$_3$NO$_2$ to give RuCl$_3$(PO$_3$)$_2$(CH$_3$NO$_2$); it 
also undergoes exchange reactions with other tertiary phosphines 
and phosphites to give [RuCl$_4$(PR$_3$)$_2$]$^-\text{anions}$ (PR$_3$ = PMe$_2$O, 
P$_3$Et$_3$, P(OO)$_3$)\textsuperscript{(70)}. The compounds RuCl$_3$(LR$_3$)$_2$(MeOH) also
react with a variety of ligands \(^{(71,72)}\) to give complexes of type \(\text{RuCl}_3(LR_3)_2L\) \((L = \text{MeCN, acetone}^{(65)}, \text{THF, Me}_2\text{SO, CS}_2)\), \(\text{RuCl}_3(LR_3)L_2\) \((L = \text{Me}_2\text{S, py}; L_2 = \text{bipy, phen})\) and \(\text{RuCl}_2(LR_3)_2L_2\) \((L = \text{CO, norb})\).

Finally, very few carbon or tin donor ligand complexes of Ru(III) or Os(III) are known, examples being compounds such as \(\text{RuBr}_3(\text{CO})(\text{PO}_3)_2\) \(^{(65)}\), \(\text{PO}_3\text{As}[\text{RuCl}_4(\text{CO})\text{py}]\) \(^{(65)}\) and \(\text{PO}_3\text{PH}[\text{RuCl}_2(\text{SnCl}_3)_2]\) \(^{(73)}\).

**Ru(II) \(d^6\)**

Few simple salts of Ru(II) and Os(II) are known although \(\text{MX}_2\) \((M = \text{Ru, Os}; X = \text{Cl}^-, \text{Br}^-, \text{I}^-)\) \(^{(74,41,36,37)}\) have been claimed. However, a large number of complexes of Ru(II) and Os(II) have been characterised.

The usual preparative method involves reduction of Ru(III) or Ru(IV) halides or halogeno complexes in the presence of suitable ligands, although in some cases, the ligands themselves may act as the reductant. Virtually all complexes of Ru(II) and Os(II) are octahedral and diamagnetic, although some five coordinate species are known e.g. \(\text{RuCl}_2(\text{PO}_3)_3\) \(^{(65)}\) in which the sixth coordination site is blocked by a hydrogen of a phenyl group.

Complexes of group VI and VII donor ligands, i.e. oxygen, sulphur and halides are in general less well-known and more poorly characterised for Ru(II) and Os(II) than for Ru(III) and Os(III). When ruthenium(III)chloride solutions are
treated either with $H_2$ under pressure, Ti(III) salts or are electrolytically reduced, blue solutions are generated, and by addition of $BF_4^-$ or p-toluene-sulphonate anions, the $[Ru(H_2O)_6]^{2+}$ cation can be isolated(75). This famous "blue solution"(76), and the "blood-red solution", which is obtained on passing carbon monoxide through on ethanolic solution of "RuCl$_3$.3H_2O"(77) have been found to be excellent precursors for the preparation of a wide range of Ru(II) complexes (see Scheme 1.3 for the synthesis and some reactions of the "blood-red solution").

The number of oxygen and sulphur donor ligand complexes of Os(II) is very small although a substantial number are known for Ru(II). These include the mixed valence Ru$_2$(II/III) triple chloro bridged species(78) $[Ru_2Cl_3(H_2O)_6]^{2+}$, $[Ru_2Cl_4(H_2O)_5]^+$ and $Ru_2Cl_5(H_2O)_4$, and various nitrosyl carboxylato anions such as $[Ru(NO)(Me_2CO)_3]$ (79) and $[Ru(NO)(OX)_2(OH)]^{2-}$ (80). Dithiocarbamato complexes of Ru(II) such as $Ru(CO)_2(S_2CNR_2)_2$ (81) ($R = Me, Et, etc.$), $Ru(NO)(S_2CNET_2)_3$ (82) and various sulphoxide complexes e.g. $RuCl_2(Me_2SO)_4$ (83) have been well characterised. Unusual square planar bisdithione complexes(84,85) such as $Ru(S_2C_2O_2)_2$ (9) have also been reported.

![Scheme 1.3](image-url)
Ru(II) forms an extensive range of complexes with group VB donor ligands. For example, a multitude of ammine and amine cations such as $[\text{Ru(NH}_3)_6]^{2+}$ (54), $[\text{Ru(en)}_3]^{2+}$ (86) and the mixed-valence Ru$_2$(II/III) $[\text{Ru}_2\text{Cl}_3(\text{NH}_3)_6]^{2+}$ (87). In contrast, related Os(II) ammine and amine complexes are much rarer, although there is some evidence for the $[\text{Os(NH}_3)_6]^{2+}$ cation (88). Heterocyclic N-donor bases such as pyridine, substituted pyridines and bi- and tri-dentate N-donors such as 2,2'-bipyridine, 1,10-phenanthroline and 2,2',2''-terpyridine form a range of stable compounds. Examples include trans-$\text{RuCl}_2\text{Py}_4$ (61), trans-$\text{RuCl}_2(4\text{-Mepy})_4$ (61), $[\text{M(bipy)}_3]^{2+}$ (89, 90), $[\text{M(phen)}_3]^{2+}$ (62, 91) and $[\text{M(terpy)}_2]^{2+}$ (92) ($M = \text{Ru, Os}$). Another well-known class of N-donor ligands are the nitriles and isonitriles and examples of Ru(II) and Os(II) species containing these ligands include $\text{RuCl}_2(\text{MeCN})_2(P\text{Ø}_3)_2$ (93), $[\text{MH(CO)(PØ}_3)_2(\text{MeCN})_2]$ (96) ($M = \text{Ru, Os}$) and $\text{RuCl}_3(\text{NO})(\text{MeCN})_2$ (95).

An important feature of Os and particularly Ru chemistry is the tendency to form a large number of stable nitrosyl complexes. Several examples of these have already been mentioned and a further selection is listed in Table 1.2.

In the last twenty years a very large number of Ru(II) and Os(II) complexes containing PR$_3$, AsR$_3$ or SbR$_3$ donor ligands have been prepared. Table 1.3 illustrates the range of such species, several of which will be discussed in more detail in later chapters.
Some Nitrosyl Containing Complexes of Ru(II) and Os(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(NO)(S₂CNET₂)₃</td>
<td>(82)</td>
</tr>
<tr>
<td>[M(NO)(OH)(NO₂)₄]²⁺</td>
<td>(M = Ru, Os) (79, 99)</td>
</tr>
<tr>
<td>Ru(NO)X₃</td>
<td>(X = Cl⁻ (96), Br⁻, I⁻ (97))</td>
</tr>
<tr>
<td>[M(NO)X₅]²⁻</td>
<td>(M = Ru; X = Cl⁻, Br⁻, I⁻, NCS⁻ (96, 100); M = Os; X = Cl⁻, Br⁻, I⁻, CN⁻ (98, 101))</td>
</tr>
<tr>
<td>Ru(NO)Cl₃L₂</td>
<td>(L = PØ₃ (102), MeCN (95))</td>
</tr>
</tbody>
</table>
Table 1.3

Some Ru(II) and Os(II) Complexes Containing Only
Halides and Group (V) Donor Ligands

Ru\text{X}_2(\text{LR}_3)_3 \\
(X = \text{Cl}^-, \text{Br}^-; \text{LR}_3 = \text{PØ}_3, \text{PET}_{2}\text{Ø}, \\
\text{SbØ}_3 \text{ etc.})(65,103); \\
X = \text{Cl}^-; \text{LR}_3 = \text{PClÖ}_2, \text{AsØ}_3, \\
p(\text{p-tol})_3)(103,104,105)

Os\text{X}_2(\text{LR}_3)_3 \\
(X = \text{Cl}^-, \text{Br}^-; \text{LR}_3 = \text{PØ}_3^)(106,107); \\
X = \text{I}^-; \text{LR}_3 = \text{AsØ}_3(108)

\text{trans-RuX}_2(\text{LR}_3)_4 \\
(X = \text{Cl}^-, \text{Br}^-; \text{LR}_3 = \text{PØ}_3, \text{P}(\text{p-tol})_3, \\
\text{PMe}_2\text{Ø}, \text{AsMe}_2\text{Ø}, \text{PMe}_2(\text{CH}_2\text{Ø}), \text{P(OØ)}_3, \\
\text{PHO}_2 (65,103,105,108,110-115), \\
ditertiary phosphine and arsine etc.: \\
X = \text{Br}^-; \text{LR}_3 = \text{PClÖ}_2, \text{SbØ}_3(103,116)

\text{trans-OsX}_2(\text{LR}_3)_4 \\
(X = \text{Cl}^-, \text{Br}^-; \text{LR}_3 = \text{AsØ}_3, \text{SbØ}_3 \text{ etc.})(107,108)

[Ru\text{X}_2(\text{LR}_3)_6]^+ \\
(X = \text{Cl}^-; \text{LR}_3 = \text{PMe}_2\text{Ø}, \text{PET}_3, \text{PBU}_2\text{Ø}, \\
\text{P(OMe)}_2\text{Ø}, \text{AsEt}_2\text{Ø etc.})(113,118-120); \\
X = \text{Br}^-; \text{LR}_3 = \text{PMe}_2\text{Ø}, \text{PMe}_2(117); \\
X = \text{F}^-, \text{I}^-; \text{LR}_3 = \text{PMe}_2(117)

[Os\text{X}_2(\text{LR}_3)_6]^+ \\
(LR_3 = \text{PET}_2\text{Ø}, \text{PMe}_2\text{Ø etc.})(113)

Ru\text{X}_2(\text{LR}_3)_5 \\
(LR_3 = \text{PMe}_2\text{Ø}, \text{PET}_3 (66), \text{PET}_2\text{Ø}(121), \\
\text{PMe}_2(122) \text{ etc.})
In addition to these group VB halide complexes, may be added a host of carbonyl complexes. One of many examples is \( \text{RuCl}_2(\text{CO})_2(\text{P}0_3)_2 \) \(^\text{65}\) which is made by reacting the "blood-red solution" with \( \text{P}0_3 \). On treating this complex with \( \text{LiAlH}_4 \) the hydrido complex \( \text{RuH}_2(\text{CO})_2(\text{P}0_3)_2 \) \(^\text{123}\) can be synthesised.

Group IV carbon donor complexes are now fairly common, ranging from "sandwich" complexes such as \( \text{M(}^5\text{-C}_5\text{H}_5)_2 \) \( (\text{M} = \text{Ru}^\text{132}, \text{Os}) \) \(^\text{124}\) and their derivatives \(^\text{125,126}\) e.g. \( \text{Ru}(^5\text{-C}_5\text{H}_6)(\text{CO})_2\text{Br} \) and \( [\text{Ru}(^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_2\text{H}_4)]\text{Br} \), to carbonyl compounds such as \( \text{M(CO)}_4\text{X}_2 \) \( (\text{M} = \text{Os}; \text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-) \) \(^\text{127}\); \( \text{M} = \text{Ru}; \text{X} = \text{Cl}^-, \text{I}^-) \) \(^\text{31,128}\). Other examples of Ru and Os carbonyl complexes are shown in Table 1.4.

A number of Ru(II) and Os(II) diene complexes are known. Examples include \( \text{MC}_2(\text{cod})(\text{PET}_2\text{Ø})_2 \) \(^\text{113,137}\) made by direct reaction of cycloocta-1,5-diene with \( [\text{M}_2\text{C}_3(\text{PET}_2\text{Ø})_6]\text{Cl} \) \(^\text{113}\) and the insoluble \( [\text{RuCl}_2(\text{cod})]_n \) \(^\text{138}\).

Finally, in recent years a substantial number of Ru(II) and Os(II) \( ^6\)-arene complexes have been synthesised. These include the di-bridged \( [\text{RuX}_2(^6\text{-C}_6\text{H}_6)]_2 \) \( (\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-) \) \(^\text{139}\), the triple-bridged \( [\text{M}_2\text{X}_3(^6\text{-C}_6\text{H}_6)]^+ \) cations \( (\text{M} = \text{Ru}; \text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-; \text{M} = \text{Os}; \text{X} = \text{Cl}^-) \) \(^\text{140}\), and the monomeric \( [\text{Ru(bipy)}(\text{PMe}_2\text{Ø})(^6\text{-C}_6\text{H}_6)]^{2+} \) \(^\text{141}\) cation. More examples of these unusual compounds are shown in Table 1.5.
### Table 1.4

Some Ru and Os Carbonyl Complexes

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{M(CO)}_4\text{X}_2$</td>
<td>(M = Os; X = Cl$^-$, Br$^-$, I$^-$) (127); M = Ru; X = Cl$^-$, I$^-$) (31,128)</td>
</tr>
<tr>
<td>$[\text{Os(CO)}_3\text{X}_2]_2$</td>
<td>(X = Cl$^-$, Br$^-$, I$^-$) (127)</td>
</tr>
<tr>
<td>$[\text{M(CO)}_2\text{X}_2]_n$</td>
<td>(M = Os; X = Br$^-$, I$^-$) (127); M = Ru; X = Cl$^-$, Br$^-$, I$^-$) (129)</td>
</tr>
<tr>
<td>$[\text{Os(CO)}_4\text{X}]_2$</td>
<td>(X = Br$^-$, I$^-$) (127)</td>
</tr>
<tr>
<td>$[\text{Ru(CO)}_n\text{X}]_n$</td>
<td>(X = Br$^-$, I$^-$) (130,131)</td>
</tr>
<tr>
<td>$\text{MH(CO)}_3(\text{PØ}_3)_3$</td>
<td>(M = Os; X = Cl$^-$, Br$^-$) (132); M = Ru; X = Cl$^-$, Br$^-$, I$^-$) (109)</td>
</tr>
<tr>
<td>$[\text{Os(CO)}_6]^{2+}$</td>
<td>(133)</td>
</tr>
<tr>
<td>$\text{Os}_4\text{O}<em>4(\text{CO})</em>{12}$</td>
<td>(134)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{CO})(\text{py})_3$</td>
<td>(135)</td>
</tr>
<tr>
<td>$\text{RuH}_2(\text{CO})_2(\text{PØ}_3)_2$</td>
<td>(65)</td>
</tr>
<tr>
<td>$\text{RuX}_2(\text{CO})_2(\text{py})_2$</td>
<td>(X = Cl$^-$, Br$^-$, I$^-$) (136)</td>
</tr>
<tr>
<td>Complex</td>
<td>Formula</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>$[MX_2(\eta^6\text{-arene})]_2$</td>
<td>(M = Os; X = Cl$^-$, Br$^-; \eta^6\text{-arene} = C_6H_6$, p-cymene etc.) (142, 143); M = Ru; X = Cl, Br, Cl, Br, Br; $\eta^6\text{-arene} = C_6H_6$, p-cymene, mesitylene, C$_6$H$_5$OMe, C$_6$Me$_6$ etc.; M = Ru; X = I, SCN; $\eta^6\text{-arene} = C_6H_6$ etc.) (139, 142, 144-150)</td>
</tr>
<tr>
<td>$[M_2X_3(\eta^6\text{-arene})_2]^+$</td>
<td>(M = Ru, Os; X = Cl$^-$, OMe$^-; \eta^6\text{-arene} = C_6H_6$ etc. (140, 142); M = Ru, X = Br$^-$, I$^-$, OH$^-$, OMe$^-$, OEt$^-$, etc.; $\eta^6\text{-arene} = C_6H_6$, mesitylene, etc.) (140, 142, 151)</td>
</tr>
<tr>
<td>$[MC\text{l}(\eta^6\text{-arene})(\text{py})_2]^+$</td>
<td>(M = Ru, Os; $\eta^6\text{-arene} = C_6H_6$, p-cymene) (140)</td>
</tr>
<tr>
<td>$[\text{Ru}\text{X}(\text{mesitylene})(\text{py})_2]^+$</td>
<td>(X = Cl$^-$, Br$^-$, I$^-$) (140)</td>
</tr>
<tr>
<td>Ru$X_2(\eta^6\text{-arene})\text{py}$</td>
<td>(X = Cl$^-; \eta^6\text{-arene} = C_6H_6$, mesitylene; X = Br$^-; \eta^6\text{-arene} = C_6H_6$) (140).</td>
</tr>
</tbody>
</table>
Ru(I) d⁷

Until recent years only halide and carbonyl halide complexes of Ru(I) (or Os(I)) had been reported. Species of type "RuX" (X = Cl⁻, Br⁻, I⁻) made through the action of hypophosphoric acid on aqueous solutions of the appropriate ruthenium trihalide were claimed many years ago⁹, but the possibility remains that these products are in fact Ru(II) hydrides or Ru(III) halides.

[Ru(CO)Br]ₙ (130) and [Ru(CO)_xI]ₙ (131) have also been known for a long time. The latter is benzene soluble which suggests that it is not polymeric but binuclear like [Os(CO)₄I]₂ (127). This Os(I) compound is very stable and probably contains metal-metal bonds in addition to halide bridges.

Polymeric nitrosyl halides such as [Ru(NO)X₂]ₙ (X = Br⁻, I⁻) (152) can be prepared through the action of nitric oxide on [Ru(CO)₂X₂]₂ (129). The [Ru(NO)I₂]ₙ (152) complex is diamagnetic and believed to contain metal-metal bonds as well as halide bridges. It reacts with various Lewis bases to produce complexes of empirical formula Ru(NO)I₂L₂ (152) (L₂ = py, bipy, AsR₃, PR₃) which, if monomeric and octahedral would be paramagnetic (t²g egü configuration). These compounds are however only slightly paramagnetic which suggests a binuclear structure containing strong metal-metal bonds. A related complex [Ru(CO)₃(PMe₂)]₂ (10) has been synthesised by the reaction of Me₂PMe₂ with Ru₃(CO)₁₂ (153).
Several Ru(I) complexes containing carboxylato bridges e.g. \([\text{Ru(CO)}_2(\text{RCO}_2)]_n\) (\(R = \text{H}, \text{Me}, \text{Et}\)) have been prepared by the reaction of the appropriate carboxylic acid with \(\text{Ru}_3(\text{CO})_{12}\) \((154)\). These polymeric complexes will then react with carbon monoxide to give \([\text{Ru(CO)}_3(\text{RCO}_2)]_2\), which are claimed to be binuclear compounds containing both bridging carboxylato groups and metal-metal bonds\(^{(154)}\). All these compounds will react with Lewis bases (L) such as pyridine, MeCN, AsR\(_3\), PR\(_3\) to give the binuclear complexes \([\text{Ru(CO)}_2(\text{RCO}_2)L]_2\) \((11)\) \((154)\). Compound \((11)\) \((L = \text{PØ}_3)\) can also be prepared by reacting \(\text{Ru}_3(\text{CO})_9(\text{PØ}_3)_3\) with the appropriate carboxylic acid\(^{(154,155)}\). The addition of bulky tertiary phosphines to the yellow solution formed by treating "\(\text{RuCl}_3\cdot3\text{H}_2\text{O}\)" with carbon monoxide in 2-methoxyethanol for prolonged periods produces the closely related diamagnetic Ru(I) complexes \([\text{RuCl(CO)}_2L]_2\) \((12)\) \((L = \text{PBu}_2^+, \text{PBu}_2^+\text{P-to})\)\(^{(156)}\). Conversion of \((12)\) to \((11)\) is achieved by treatment with silver acetate\(^{(156,157)}\). In contrast, reaction of a less bulky ligand such as \(\text{PMe}_2\text{Ø}\) with the previously mentioned yellow solution gives the Ru(II) complex \(\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ø})_2\) \((158)\) and treatment of compound \((12)\) with chlorine gives the analogous Ru(II) complexes \((156,157)\).
A number of other Ru(I) complexes such as RuH(PF$_3$)$_4$ \(^{(159)}\) and Ru$_2$Cl$_3$(dmf) \(^{(160)}\) have been reported in recent years. Another example is the cation [Ru(NH$_3$)$_5$N$_2$]$^+$ which can be generated in situ by the reduction of the [Ru(NH$_3$)$_5$N$_2$]$^{2+}$ cation using electron pulse radiolysis. However the Ru(I) complex proved very unstable, undergoing disproportionation to give the original Ru(II) complex and a Ru(0) species which rapidly decomposed to ruthenium metal (Equation [2]).

\[
2\text{[Ru(NH}_3\text{)$_5$N}_2\text{]}^+ \rightarrow \text{[Ru(NH}_3\text{)$_5$N}_2\text{]}^{2+} + \text{Ru(NH}_3\text{)$_5$N}_2\text{]} \quad \text{[2]}
\]

Ru(0) \(_d^8\)

The majority of compounds found in formal oxidation state (0) are carbonyls or carbonyl derivatives. A good example of a Ru(0) carbonyl complex is the trigonal bipyramidal monomer Ru(CO)$_5$ \(^{(131)}\) which has both Fe and Os analogues.
The best known Ru(O) carbonyl complex, Ru$_3$(CO)$_{12}$ (131), was originally formulated as Ru$_2$(CO)$_9$, but an X-ray structural analysis of Ru$_3$(CO)$_{12}$ and its Os analogue (162) confirmed the D$_{3h}$ symmetry and the trinuclear structure (13) (163,164).

![Diagram of Ru$_3$(CO)$_{12}$]

Compounds (13) have a very extensive chemistry. For example, photolysis of Ru$_3$(CO)$_{12}$ in the presence of carbon monoxide produces Ru(CO)$_5$ (165), whereas in the presence of PR$_3$ a mixture of Ru(CO)$_4$(PR$_3$) and Ru(CO)$_3$(PR$_3$)$_2$ (PR$_3$ = PØ$_3$, PBu$_3$, PMeØ$_2$) is formed (165). The reaction of halogens with Ru$_3$(CO)$_{12}$ is quite complex leading to production of RuX$_2$(CO)$_4$ (X = Br$^-$, I$^-$), [RuX$_2$(CO)$_3$]$_2$ (X = Cl$^-$, Br$^-$, I$^-$), [RuX$_2$(CO)$_2$]$_3$ (X = Cl$^-$, Br$^-$) or polymeric [RuX$_2$(CO)$_2$]$_n$ (X = Cl$^-$, Br$^-$, I$^-$) (166). Some other examples of the versatile chemistry of Ru$_3$(CO)$_{12}$ are the synthesis of Ru(CO)$_3$(diene) (167) by reaction with dienes, the generation of Ru$_6$(CO)$_{18}$ (168) by refluxing in benzene or cyclohexane and the reaction with substituted pyrazolines and PØ$_3$ to give Ru$_3$(CO)$_9$(C$_{23}$H$_{20}$N$_2$), Ru(CO)$_3$(C$_{46}$H$_{36}$N$_4$) (169) and Ru$_3$(CO)$_9$(PØ$_3$)$_3$ (170) respectively.
The compound Ru$_3$(CO)$_9$(PØ$_3$)$_3$, as mentioned earlier, will react with carboxylic acids to give [Ru(CO)$_2$(RCO$_2$)(PØ$_3$)]$_2$ (11). It also reacts with Pb$_n$$_3$ to give Ru$_3$(CO)$_9$(Pb$_n$$_3$)$_3$ or with an excess of PØ$_3$ to give the five coordinate monomer Ru(CO)$_3$(PØ$_3$)$_2$ (170,171). The osmium analogue of the latter has also been synthesised, in this case by reduction of OsCl$_2$(CO)$_2$(PØ$_3$)$_2$ with zinc powder and carbon monoxide (172). Treatment of M(CO)$_3$(PØ$_3$)$_2$ (M = Ru, Os) with the acids HX (X = Cl$^-$, Br$^-$) gives MHX (CO)$_2$(PØ$_3$)$_2$ (172) whereas reaction with halogens and pseudohalogenes such as Cl$_2$ (172), (SCN)$_2$, (SeCN)$_2$ (173) produces Ru(CO)$_2$(PØ$_3$)$_2$X$_2$.

Finally, a number of arene and arene/olefin complexes of Ru(0) are known. They are generally synthesised by reduction of the appropriate Ru(II) carbocyclic ring complex. For example Na/NH$_3$ reduction of the [Ru($n^6$-C$_6$Me$_6$)$_2$]$^{2+}$ cation yields Ru($n^6$-C$_6$Me$_6$)$_2$ (174), whereas the corresponding reduction of [Ru($n^6$-C$_6$H$_6$)$_2$]$^{2+}$ yields Ru($n^4$-C$_6$H$_8$)($n^6$-C$_6$H$_6$) (174). Similar methods are used in the synthesis of the Os(0) analogues (175).

**Ru(-I) d$^9$, Ru(-II) d$^{10}$**

Few examples of these unfavourable oxidation states of Ru and Os are known. However several anionic species such as [Os(CO)$_4$H]$^-$ and [M(CO)$_4$]$^{2-}$ (M = Ru, Os) have been claimed (176).
CHAPTER 2

Synthesis and Characterisation of New Triple Chloro Bridged

Ruthenium(II/II) Binuclear Complexes
2.1 Preamble

Brief reference was made in Chapter 1 to examples of binuclear triple chloro bridged Ru and Os complexes. These systems are members of the general class of confacial bi-octahedral structures [14], which are of considerable interest in our laboratory because of their stability in at least three valence levels (see Chapters 4, 5 and 6).

\[
\begin{align*}
&L \\ &\text{M} \\ &L
\end{align*}
\begin{align*}
&\text{Cl} \\ &\text{L} \\ &\text{Cl} \\ &\text{L}
\end{align*}

(14) \quad [\text{M(II) or M(III) = Ru, Os}]

This chapter describes efforts to extend the range of complexes of type (14) in an orderly fashion by application of two alternative synthetic strategies: (a) assembly from appropriate monomers and (b) terminal ligand (L in (14)) replacement. However, it is appropriate before discussing these topics to give a short introduction to the methods of preparation of existing triple chloro bridged Ru$_2$(II/II) and Os$_2$(II/II) binuclear compounds.

Prior to the present study virtually all complexes of type (14) contained bulky terminal tertiary phosphine ligands, either alone, or in conjunction with small soft ligands such as CO, CS, PF$_3$, PF$_2$, NMe$_2$, N$_2$, Cl$^-$, SnCl$_3$. Notable exceptions were a series of $\pi$-$\text{arene}$ complexes, e.g. [(n$_6$-$\text{arene}$)RuCl$_3$Ru-(n$_6$-$\text{arene}$)]Cl (n$_6$-$\text{arene}$ = C$_6$H$_6$, $\pi$-cymene, mesitylene, C$_6$Me$_6$ etc.) (140) and the stannane complex (CO)$_3$RuCl$_3$Ru-(SnCl$_3$)(CO)$_2$ (177), neither of which will be further discussed.
2.2 Introduction

Compounds of the type \([\text{M}_2\text{Cl}_3(\text{PR}_3)_6]\text{X} \quad (\text{M} = \text{Ru, Os}; \text{PR}_3 = \text{PET}_2\text{O}, \text{PMe}_2\text{O}, \text{PMeO}_2, \text{PETO}_2; \quad \text{X} = \text{Cl}^-, \text{ClO}_4^-, \text{SCN}^-, \text{BO}_4^-, \text{picrate})\) \(^{(113)}\) were first reported by Chatt et al in 1961. They may be prepared by heating "\(\text{RuCl}_3\cdot3\text{H}_2\text{O}\)" or \(\text{Na}_2[\text{OsCl}_6]\) under \(\text{N}_2\) in a polar solvent such as MeOH or EtOH, in the presence of an excess of the appropriate \(\text{PR}_3\). The first isolated salt is that containing the \(\text{Cl}^-\) anion which may then be converted to a variety of other salts by metathesis. In recent years a greater range of tertiary arsine, phosphine, phosphonite and phosphinite analogues have been prepared, e.g. \([\text{Ru}_2\text{Cl}_3(\text{LR}_3)_6]\text{X} \quad (\text{LR}_3 = \text{AsEt}_2\text{O}, \text{AsEtO}_2, \text{PPr}_n\text{O} \quad \text{etc.}; \quad \text{X} = \text{Cl}^-; \quad \text{LR}_3 = \text{PET}_3, \text{POMe}_2\text{O}, \text{P(OMe}_2-1\text{-naphthyl)}_3 \quad \text{etc.}; \quad \text{X} = \text{BO}_4^-)\) \(^{(118-120, 178,179)}\). The initially proposed confacial biocathedral geometry \(^{(14)}\) of these compounds was confirmed in 1969 when Raspin et al published the X-ray structure of \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{O})_6][\text{RuCl}_3(\text{PET}_2\text{O})_3]\) \(^{(121)}\).

This complex and its triple chloro bridged neutral analogue \(\text{Ru}_2\text{Cl}_4(\text{PET}_2\text{O})_5\) \(^{(16)}\) were formed by pyrolysis of \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{O})_6]\text{Cl}\) in methylacetate or \(n\)-propyl propionate \(^{(121)}\) (See Scheme 2.1). Since then, two more complexes in the series \(\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5 \quad (\text{PR}_3 = \text{PMeO}_2, \text{PETO}_2)\) \(^{(180)}\) have been synthesised by this method. More recently two other methods of preparation have been developed for these neutral compounds. One involves the dimerisation of monomers of type \(\text{RuCl}_2(\text{PR}_3)_3\); for \(\text{PR}_3 = \text{PET}_2\text{O}\) and \(\text{PClO}_2\), the monomers are believed to be formed in situ by reaction of \(\text{RuCl}_2(\text{PO}_3)_3\) and the appropriate
Scheme 2.1

Pyrolysis Products of $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$

\[ \text{(15)} \quad (L = \text{PET}_2\phi) \]

\[ \text{(16)} \quad (L = \text{PET}_2\phi, \text{PET}_2\phi, \text{PMe}_2\phi) (121, 180) \]
PR$_3$ in a non-polar solvent such as n-hexane$^{(122)}$. When PR$_3$ = PEtØ$_2$ however, the monomer RuCl$_2$(PETØ$_2$)$_3$ may first be isolated. Dissolving this complex in cold degassed CH$_2$Cl$_2$ and precipitating with petroleum-ether (B.P. 60-80°C)$^{(122)}$ yields the binuclear product Ru$_2$Cl$_4$(PETØ$_2$)$_5$. The complicated rearrangement processes of RuCl$_2$(PR$_3$)$_{3,4}$ in solution which give rise to species such as Ru$_2$Cl$_4$(PR$_3$)$_5$ and [Ru$_2$Cl$_3$(PR$_3$)$_6$]$^+$ are shown in Scheme 2.2.

The other method of producing Ru$_2$Cl$_4$(PR$_3$)$_5$ complexes involves the chemical reduction, using Zn amalgam in degassed CH$_2$Cl$_2$, of mer-RuCl$_3$(PR$_3$)$_3$. Use of this method increases the range of PR$_3$ to the more basic phosphines such as PMe$_2$Ø and PEt$_3$ $^{(66)}$. The mechanism proposed for this conversion is shown in Scheme 2.3. Using the pyrolysis and Ru(II) monomer dimerisation processes, Ru$_2$Cl$_4$(PR$_3$)$_5$ can only be produced for the less nucleophilic phosphines such as PClØ$_2$, PEtØ$_2$, PMeØ$_2$, PEt$_2$Ø $^{(121,122,180)}$. This is essentially due to the relatively weak Ru-P bond strengths found for these phosphines. On using more nucleophilic phosphines, phosphonites or phosphinates, e.g. PEt$_3$, PMe$_2$Ø, P(OMe)$_2$Ø, P(OMe)Ø$_2$ $^{(113,118,119)}$, no facile Ru-P cleavage occurs and the products formed are generally of type [Ru$_2$Cl$_3$(PR$_3$)$_6$]X. However, exceptions are found; for example the attempted dimerisation of RuCl$_2$(P(OEt)Ø$_2$)$_3$ gives the trinuclear cation [Ru$_3$Cl$_5$(P(OEt)Ø$_2$)$_9$]$^+$ $^{(119)}$ $^{(17)}$. This behaviour is ascribed to a combination of steric factors (inhibiting the formation of [Ru$_2$Cl$_3$(PR$_3$)$_6$]X) and the high nucleophilicity of P(OEt)Ø$_2$, preventing facile Ru-P bond
Scheme 2.2

Transformations of RuCl$_2$(PR$_3$)$_{3,4}$, (PR$_3$ = Tertiary Phosphine, Phosphonite, Phosphinite)

$$\text{RuCl}_2(\text{PR}_3)_2 \xrightarrow{+\text{PR}_3} \text{RuCl}_2(\text{PR}_3)_3 \xrightarrow{-\text{PR}_3} \text{RuCl}_2(\text{PR}_3)_4$$

(b) \[ \text{RuCl}_2(\text{PR}_3)_3 \xrightarrow{+\text{Cl}^-} \text{[RuCl(\text{PR}_3)_3]^+} \]

(c) \[ \text{RuCl}_2(\text{PR}_3)_3 \xrightarrow{+\text{PR}_3} \text{RuCl}_2(\text{PR}_3)_3 \xrightarrow{-\text{PR}_3} \text{[RuCl(\text{PR}_3)_3]^+} \]

(a): PR$_3$ = PMe$_2$Ø, P(OMe)$_2$Ø, P(OMe)$_2$Ø, P(OEt)$_2$Ø (119)

(b): PR$_3$ = PET$_2$Ø, PETØ$_2$, PClØ$_2$ (122)

(c): PR$_3$ = P(OEt)$_2$Ø (119)

(N.B. - in solution vacant sixth coordination positions are probably occupied by solvent molecules)
Scheme 2.3

Chemical Reduction of mer-RuCl$_3$(PR$_3$)$_3$

\[
2 \text{mer-RuCl}_3(\text{PR}_3)_3 + \text{Zn amalgam} \xrightarrow{(+e)} 2 \text{mer-[RuCl}_3(\text{PR}_3)_3]^-
\]

\[
2 \text{trans-RuCl}_2(\text{PR}_3)_4 \xrightarrow{\text{PR}_3} 2 \text{"RuCl}_2(\text{PR}_3)_3"
\]

(polar solvent)

\[
[Ru_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}
\]

\[
\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5 + \text{PR}_3
\]

(Pr$_3$ = PMe$_2$0, PET$_2$0, PET$_3$) (66)
cleavage. Another exception is found when \([\text{Ru}_2\text{Cl}_3(\text{P} (\text{OMe})_2)_6]\text{Cl}\) is pyrolysed and the unusual compound \((181)\) (18), in which all the strong Ru-P bonds are maintained whilst some O-R bonds have been cleaved, is produced.

![Diagram](image)

The chemical reduction of tervalent \(\text{mer-RuCl}_3(\text{PR}_3)_3\) (\(\text{PR}_3 = \text{basic phosphines such as PMe}_2\Phi, \text{PEt}_3\)), presumably to \(\text{mer-[RuCl}_3(\text{PR}_3)_3]^-\), leads to rapid expulsion of \(\text{Cl}^-\) ion and the formation of \(\text{RuCl}_2(\text{PR}_3)_3\) which may, depending on the solvent, condense to \(\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5\) or \([\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}\) as shown in Scheme 2.2.

In recent years a number of complexes of type \(\text{Ru}_2\text{Cl}_4Y(\text{PR}_3)_4\) (\(\text{PR}_3 = P\Phi_3, P(\text{p-tol})_3\); \(Y = \text{CO, CS}\)) (181-183) (19) have been prepared. Some related mixed-phosphine and mixed-metal analogues such as \((P\Phi_3)_2\text{ClRuCl}_3\text{RuY}(P(\text{p-tol})_3)_2\) (183) \((Y = \text{CO, CS})\) and \((P\Phi_3)_2\text{ClRuCl}_3\text{Os(CO)}(P\Phi_3)_2\) (142) are also known. All these compounds are synthesised by the direct coupling of the appropriate monomeric species of general type \(\text{RuCl}_2(\text{PR}_3)_3\) (\(\text{PR}_3 = P\Phi_3, P(\text{p-tol})_3\)) and \(\text{MC}_2Y(\text{PR}_3)_2(\text{MeOH})\) (\(M = \text{Ru, Os}; \text{PR}_3 = P\Phi_3, P(\text{p-tol})_3\); \(Y = \text{CO, CS}\)) in degassed refluxing acetone or EtOH. Scheme 2.4 shows the proposed mode of formation of these neutral binuclear complexes. Complex (19) (\(\text{PR}_3 = P\Phi_3\); \(Y = \text{CS}\)) has also been produced.
Scheme 2.4

Solution Rearrangements of \( \text{RuCl}_2Y(\text{PR}_3)_2(\text{MeOH}) \)

(N.B. \( \text{PR}_3 = \text{P}0_3, \text{P}(\text{p-tol})_3; Y = \text{CO}, \text{CS}; \)

\( X = \text{Cl}^-, \text{B}0^- \))
in low yield from the direct reaction of RuCl₂(PØ₃)₃ with CS₂ (184), the structure being confirmed by X-ray analysis (185).

\[
\begin{align*}
R_3P & \quad \text{Cl} & \quad Y \\
R_3P & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PR₃} \\
\text{Cl} & \quad \text{Cl} & \quad \text{PR₃}
\end{align*}
\]

(19)

Complexes of type RuCl₂Y(PR₃)₂(MeOH) (PR₃ = PØ₃, P(p-tol)₃, PEtØ₂; Y = CO, CS) are found to readily undergo a self-condensation process in non-polar solvents leading to a mixture of the three geometric isomers (PR₃)₂YRuCl₃RuYCl(PR₃) (20a, b, c) (182,183) (see Scheme 2.4), whereas in polar media, (in the presence of an excess of PR₃), the cationic complexes [Ru₂Cl₃Y₂(PR₃)₄]X (PR₃ = PØ₃, P(p-tol)₃; Y = CO, CS; X = Cl⁻, BØ₄) (182,183) (21) can be generated. Compounds (21) are also formed by reacting the isomeric mixture (20) with an excess of PR₃ in a polar solvent.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad PR₃ \\
R_3P & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PR₃} \\
\text{Y} & \quad \text{Cl} & \quad \text{PR₃}
\end{align*}
\]

(20a)

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad PR₃ \\
R_3P & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PR₃} \\
\text{Y} & \quad \text{Cl} & \quad \text{PR₃}
\end{align*}
\]

(20b)

\[
\begin{align*}
\text{Y} & \quad \text{Cl} & \quad PR₃ \\
R_3P & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PR₃} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Y}
\end{align*}
\]

(20c)

\[
\begin{align*}
[Y & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PR₃} & \quad \text{PR₃} ] & \quad X \\
R_3P & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PR₃} & \quad \text{PR₃}
\end{align*}
\]

(21)
An analogous rearrangement reaction has also been proposed to account for the formation of the single isomers of $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{P} \text{Ø}_3)_3$ (186) and $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_5$ (177) from the monomers $\text{RuCl}(\text{SnCl}_3)(\text{CO})(\text{P} \text{Ø}_3)_2$ (acetone), acetone and $\text{RuCl}(\text{SnCl}_3)(\text{CO})_4$ respectively. The formation of a single isomer here is attributed to steric constraints.

Two further methods are known for the synthesis of the isomeric mixture (20) ($\text{PR}_3 = \text{P} \text{Ø}_3$; $Y = \text{CO}$), namely reaction of $\Phi(\text{CH}_2)\text{P} \text{Ø}_3[\text{RuCl}_3(\text{CO})(\text{norb})]$ with an excess of $\text{P} \text{Ø}_3$ in CH$_2$Cl$_2$ (182) and reaction of $\text{RuH}_2(\text{CO})(\text{P} \text{Ø}_3)_3$ with gaseous HCl in benzene (187).

The last method has also been utilised for the preparation of fluorophosphine triple chloro bridged complexes. Thus, treatment of $\text{RuH}_2(\text{PF}_3)(\text{P} \text{Ø}_3)_3$ with HCl gives an isomeric mixture analogous to (20a, b, c) but with $Y = \text{PF}_3$ (187). Nixon et al have extended both the range and the methods of synthesis of these complexes (see Scheme 2.5). These methods include the displacement of acetone and $\text{P} \text{Ø}_3$ by $\text{PF}_3$ from the di-$\mu$-chloro complex $[\text{RuCl}_2(\text{P} \text{Ø}_3)_2(\text{acetone})]_2$ (187), treatment of $\text{RuCl}_2(\text{P} \text{Ø}_3)_3$ with $\text{PF}_3$ or $\text{PF}_2\text{NMe}_2$ (in 1:1 molar ratio) (187) and the thermal decomposition of $\text{RuCl}_2L(\text{P} \text{Ø}_3)_2(\text{dmf})$.
Scheme 2.5

Various Methods of Synthesis of $\text{Ru}_2\text{Cl}_4\text{L}_2(\text{P}O_3)_3$

$L = \text{CO}, \text{PF}_3, \text{PF}_2\text{NMe}_2$

$\text{RuH}_2\text{L}(\text{P}O_3)_3$

HCl gas

$L = \text{CO}, \text{PF}_3$ (187)

$\text{RuCl}_2\text{L}(\text{P}O_3)_2(\text{dmf})$

$L = \text{PF}_3, \text{PF}_2\text{NMe}_2$ (187)

$\Delta$

excess

$\text{PF}_3, \text{PF}_2\text{NMe}_2$ (190)

$\text{cis-RuCl}_2\text{L}_2(\text{P}O_3)_2$

$[\text{RuCl}_2(\text{P}O_3)_2(\text{acetone})]_2$

$L = \text{PF}_3$

1:1 molar ratio

$L = \text{PF}_3, \text{PF}_2\text{NMe}_2$ (187)

$\text{RuCl}_2(\text{P}O_3)_3$
(L = PF$_3$, PF$_2$NMe$_2$) (187), all of which yield (PØ$_3$)$_2$LRuCl$_3$-
RuClL(PØ$_3$) (24) in its three isomeric forms. This isomeric
mixture (24) (L = PF$_3$, PF$_2$NMe$_2$) reacts with more PF$_3$ or
PF$_2$NMe$_2$ to yield cis-RuCl$_2$(PØ$_3$)$_2$L$_2$ (187). The latter
complex (L = PF$_2$NMe$_2$) can then react with an equimolar amount
of RuCl$_2$(PØ$_3$)$_3$ in acetone to give an isomeric mixture of
(PF$_2$NMe$_2$)$_2$(PØ$_3$)RuCl$_3$RuCl(PØ$_3$)$_2$ (25a, b) (187).

![Diagram of complexes](image)

However, the analogous reaction between RuCl$_2$(PØ$_3$)$_3$
and cis-RuCl$_2$(PØ$_3$)$_2$(PF$_3$)$_2$ (1:1 molar ratio) leads to the
formation of the isomeric mixture (24) (187), indicating
that a tertiary phosphine ligand transfer reaction has
occurred (see Scheme 2.6). This is believed to reflect the
relative ease of PØ$_3$ dissociation from cis-RuCl$_2$(PØ$_3$)$_2$(PF$_2$NMe$_2$)$_2$
compared to its PF$_3$ analogue.

Two other triple chloro bridged fluorophosphine complexes
of Ru(II) are known, namely (PØ$_3$)$_2$(PF$_3$)RuCl$_3$RuCl(PØ$_3$)$_2$ (26),
obtained by reaction of a 2:1 molar mixture of RuCl$_2$(PØ$_3$)$_3$ and
PF$_3$ (187) and, two of the three possible isomers of
Ru$_2$Cl$_4$(PØ$_3$)$_3$(CO)(PF$_3$), produced from the reaction of
Ru$_2$Cl$_4$(CO)(PØ$_3$)$_4$ (19) with PF$_3$ in equimolar amounts (187).

![Diagram of complex](image)
Scheme 2.6

The Coupling Reaction of RuCl$_2$(PO$_3$)$_3$ and
Cis-RuCl$_2$L$_2$(PO$_3$)$_2$ (L = PF$_3$, PF$_3$NMe$_3$)

\[
\begin{align*}
1:1 \text{ Cis-RuCl}_2(\text{PF}_3)_2(\text{PO}_3)_2 & \quad \text{acetone} \\
1:1 \text{ Cis-RuCl}_2(\text{PF}_3\text{NMe}_2)_2(\text{PO}_3)_2 & \quad \text{acetone}
\end{align*}
\]
The same workers have recently reported the synthesis of a series of heterobimetallic compounds of type

\[(\text{PO}_3)(\text{PR}_3)\text{ClRuCl}_3\text{RhCl}(\text{PO}_3)_2\]  (188)  (27)  (PR\_3 = \text{PMe}_2\text{O}, \text{PET}_2\text{O}, \text{PBU}_3\text{O}, \text{PBO}_3\text{)} through the reaction of equimolar ratios of RuCl\_2(PO_3)_3 and \text{mer-RhCl}_3(PR\_3)_3. It is evident that, as in the reaction between RuCl\_2(PO_3)_3 and \text{cis-RuCl}_2(PO_3)_2(PF_3)_2, a tertiary phosphine transfer has occurred.

![Chemical Structure](image)

(27)

A number of triple chloro bridged Ru\_2(II/II) binuclear complexes containing nitrogen donor ligands have been synthesised \text{e.g.} \((\text{PO}_3)_2\text{ClRuCl}_3\text{Ru}(\text{N}_2)(\text{PO}_3)_2\), which is formed on treating RuCl\_2(PO_3)_4 in tetrahydrofuran with N\_2 under pressure\((189)\). This compound reacts further with N\_2B\_10H\_8SMe\_2 to form \((\text{PO}_3)_2\text{ClRuCl}_3\text{Ru}(\text{PO}_3)_2(\text{N}_2\text{B}\_10\text{H}_8\text{SMe}_2)\) \((189)\). Very recently, Poilblanc et al have produced a new series of complexes of type \([\text{Ru}_2\text{Cl}_3(\text{PO}_3)_2(\text{diazadiene})_2]\_X\) (diazadiene = \text{Pr}+\text{NCHCHPr}+ \text{etc.}; \ X = \text{BOP}^- \text{etc.}) \((190)\) \((28)\) by reacting RuCl\_2(PO\_3)_3 and diazadiene in a 1:2 molar ratio in toluene. The neutral analogue Ru\_2Cl\_4(PO\_3)_3(\text{ONCMeCMeN}O) \((29)\) has also been prepared under similar conditions, but using a 2:1 molar ratio of RuCl\_2(PO\_3)_3 to diazadiene \((190)\).
Several triple chloro bridged complexes of this type are now known for carbon donor ligands. These include (cod)XRuX₃Ru(NCR)(cod) (X = Cl⁻, Br⁻; R = Me, ⌀), produced by heating RuX₂(cod)(NCR)₂ in MeOH under N₂ (117), and the heterocyclic oligiocarbene complexes [Ru₂X₃(C₃N₂R₂)₆]X (X = Cl⁻, I⁻; R = Me, Et) (191) and Ru₂Cl₄(PØ₃)₂(C₃N₂Me₂)₃ (192). The cationic carbene compound is prepared by heating trans-RuCl₂(C₃N₂R₂)₄ (prepared by reaction of RuCl₂(PØ₃)₃ with an excess of the electron-rich olefin [= CN(R)(CH₂)₂NR]₂ in CH₂Cl₂ under N₂) (191), while the neutral carbene complex is synthesised by heating a 1.5-fold molar excess of [=CN(Me)(CH₂)₂NMe]₂ with RuCl₂(PØ₃)₃ in toluene under N₂ (192).

In summary, it would seem that dimerisation of Ru(II) monomeric complexes offers a readily available synthetic route to Ru₂(II/II) triple chloro bridged binuclear complexes containing tertiary phosphines. Since no comparable pathway exists for non-group VB donor ligands the next section...
is devoted to extending this synthetic strategy to such ligands. In addition, attempts to advance alternative preparative routes to triple chloro bridged Ru$_2$(II/II) binuclear compounds will also be discussed.

2.3 Results and Discussion

(a) Dimerisation of Ru(II) monomer of Type RuCl$_2$L$_4$

(i) \( L = \text{Me}_2\text{SO} \)

A neutral tan-brown complex of molecular formula Ru$_2$Cl$_4$(Me$_2$SO)$_5$ has recently been reported by Tayim et al (193) to be the sole product on heating RuCl$_2$(Me$_2$SO)$_4$ (194) (30) in toluene for several hours. On the basis of elemental analysis and infrared spectral data they proposed a binuclear structure with two bridging chlorides (\(\nu_{\text{Ru-Cl}}\) 230 and 260 cm$^{-1}$), a bridging Me$_2$SO (\(\nu_{\text{S=O}}\) 965 cm$^{-1}$), two terminal chlorides (\(\nu_{\text{Ru-Cl}}\) 340 cm$^{-1}$) and a combination of both terminal O-bonded (\(\nu_{\text{S=O}}\) 910 and 928 cm$^{-1}$) and S-bonded Me$_2$SO groups (\(\nu_{\text{S=O}}\) 1110 and 1090 cm$^{-1}$) (193). There are many possible structures consistent with these data and two of the more plausible candidates are shown in (31a, b).

![Diagram](30)

![Diagram](31a)
Our interest in this binuclear complex stems from the possibility that it might, by analogy with \(\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5\) and \(\text{Ru}_2\text{Cl}_4(\text{PÖ}_3)_3\) (diazadiene), be triply chloro bridged, and hence provide a possible extension of structure/redox activity correlations in such binuclear Ru and Os systems\(^{195,196}\) (see Chapter 5 for a full discussion).

On the basis of new synthetic and structural studies, and a reappraisal of the original data, the product \(\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5\) can be confidently reformulated as the all-terminally-S-bonded \(\text{Me}_2\text{SO}\) complex (31c) with triple chloro bridges and a single terminal chloride (see Figure 2.1).

The primary evidence suggesting this structure, and certainly invalidating the originally proposed structures, are high resolution \(^1\text{H}\) and \(^{13}\text{C}-\)\(^1\text{H}\) n.m.r. spectra, measured at 360 and 120 MHz respectively in \(\text{CD}_2\text{Cl}_2\) at 303 K. Thus both \(^1\text{H}\) and \(^{13}\text{C}-\)\(^1\text{H}\) n.m.r. spectra of \(\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5\) (Figure 2.2(a,b) and Table 2.1) clearly display five equally intense closely spaced methyl resonances. The \(^1\text{H}\) n.m.r. spectrum shows \(\delta(\text{CH}_3)\) at 3.498, 3.468, 3.439, 3.379, and
Figure 2.1

Triple Chloro Bridged Structural Reformulation of

Ru<sub>2</sub>Cl<sub>4</sub>(Me<sub>2</sub>SO)<sub>5</sub>

A, B, C, D and E represent symmetry-related pairs of methyls
Figure 2.2 $^1$H and $^{13}$C-$^1$H n.m.r. Spectra of Ru$_2$Cl$_4$(Me$_2$SO)$_5$ in CD$_2$Cl$_2$ at 303 K

(a) $^1$H n.m.r

(b) $^{13}$C, proton-decoupled
3.338 ppm, the highest frequency resonance being a singlet while the other four are quartets with $^{4}J_{HH}$ ca. 0.7 Hz (resolved using line-narrowing techniques). The chemical shifts of these resonances are very much in the S-bonded Me$_2$SO region, resonating approximately 1 ppm up-frequency from free Me$_2$SO (197). Free Me$_2$SO resonates at 92.55 ppm in CD$_2$Cl$_2$ (198) and this is attributed to the large degree of methyl proton deshielding imposed by complexation through sulphur. In contrast, complexation through oxygen only slightly deshields the methyl protons, resulting in $\delta$(CH$_3$) increasing by, at most, 0.5 ppm.

An excellent demonstration of the differences between S- and O-bonded methyl resonance positions of Me$_2$SO in $^1$H n.m.r. spectroscopy, as well as the crystallographically proved ambidentate nature of sulphoxide ligands, is provided by the precursor RuCl$_2$(O-Me$_2$SO)(S-Me$_2$SO)$_3$ (83,194,198) (30) and its close analogues [RuCl(O-Me$_2$SO)$_2$(S-Me$_2$SO)$_3$]BF$_4$ (83) and [Ru(O-Me$_2$SO)$_3$(S-Me$_2$SO)$_3$]$_2$(BF$_4$)$_2$ (199).

A high resolution (360 MHz) $^1$H n.m.r. spectrum of (30) in CD$_2$Cl$_2$ shows three S-bonded Me$_2$SO ligand $\delta$(CH$_3$) resonances between 3.416 and 3.237 ppm (3.398 and 3.226 ppm in CD$_3$NO$_2$) and two further $\delta$(CH$_3$) resonances are seen below 3 ppm, one at 2.690 ppm due to O-bonded Me$_2$SO and the other at 2.55 ppm due to free Me$_2$SO (observed at 2.756 and 2.50 ppm respectively in CD$_3$NO$_2$) (83). Integration of resonance areas suggest that approximately 25% of the O-bonded Me$_2$SO ligand dissociates to give free Me$_2$SO in these solvents. This dissociation can be suppressed by addition of an excess of Me$_2$SO.
The other two complexes, i.e. \([\text{RuCl}(\text{O-Me}_2\text{SO})_2(\text{S-Me}_2\text{SO})_3]\text{BF}_4\) and \([\text{Ru}(\text{O-Me}_2\text{SO})_3(\text{S-Me}_2\text{SO})_3]\text{BF}_4\) in \(\text{CD}_3\text{NO}_2\) show S-bonded resonances between 3.355 and 3.177 ppm, and O-bonded resonances between 3.071 and 2.877 ppm. Thus in both solvents, relative to free Me\(_2\)SO, the spread of chemical shifts for S-bonded Me\(_2\)SO is +0.90 to +0.68 ppm, while that for O-bonded Me\(_2\)SO is +0.57 to +0.14 ppm (see Table 2.1 for more detail).

Hence, there appears to be little doubt that the five \(\delta(\text{CH}_3)\) resonances observed for \(\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5\) between 3.498 and 3.338 ppm (from +0.95 to +0.79 ppm relative to free Me\(_2\)SO) are firmly in the "normal" S-bonded Me\(_2\)SO ligand region. The relatively high \(\delta(\text{CH}_3)\) of the S-bonded Me\(_2\)SO ligands of \(\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5\), with respect to its related monomers, probably reflects the greater number of chlorides associated with each Ru; c.f. the trend in \(\delta(\text{CH}_3)\) of S-bonded Me\(_2\)SO ligands in \([\text{RuCl}_n(\text{Me}_2\text{SO})_{6-n}]\text{BF}_4\)\(_{n-2}\) \((n = 0, 1, 2)\) listed in Table 2.1.

The \(^1\text{H}\) n.m.r. pattern of a singlet and four quartets is fully consistent with the symmetry of the triple chloro bridged complex shown in Figure 2.1. The highest frequency resonance, i.e. the singlet, is obviously associated with the equivalent methyl groups (E) of the unique S-bonded Me\(_2\)SO ligand lying on the plane of molecular symmetry. The remaining four S-bonded Me\(_2\)SO ligands do not lie on a mirror plane and therefore methyl groups attached to the same sulphur atom are non-equivalent, and in consequence four quartets are observed.
Each of the eight non-equivalent methyl groups on any of these four S-bonded Me₂SO ligands is related through symmetry to an identical methyl group on a different S-bonded Me₂SO ligand. This leads, since the two Ru environments of the molecule are different, to two pairs of symmetry-related Me₂SO ligands.

Homonuclear decoupling experiments (Figure 2.2(a)) indicate that it is alternate rather than adjacent quartets which are coupled. This suggests that the influence exerted by the electronic environment at the ligand binding site on the chemical shift $\delta(\text{CH}_3)$ is less dominant than the orientation of any individual methyl group. A combination of this factor and the very small chemical shift range of the five resonances (ca. 0.16 ppm) makes unique assignments impossible without further investigation. However, tentative assignments have been derived in the following manner: the two methyl groups (E) are uniquely determined as a singlet at highest frequency and since the two methyl groups (D) are in a similar orientation and electronic environment to (E) they may give rise to the highest frequency quartet. Assuming this to be the case then the two methyl groups (C) relate to the second-lowest frequency quartet. The two methyl groups (A) have a similar orientation to (D) and thus may correspond to the middle of the five resonances, leaving the two methyl groups (B) responsible for the lowest frequency quartet. These assignments are shown in Figure 2.2(a).
The $^{13}$C-$^1$H n.m.r. spectrum shows five methyl resonances of equal intensity at $\delta$ 48.995, 47.893, 47.800, 47.684 and 45.883 ppm. However, owing to the fact that $^{13}$C n.m.r. data have seldom been previously reported for Me$_2$SO ligands the significance of these chemical shifts was initially obscure. A very valuable insight into the S- and O-bonded methyl region of Me$_2$SO ligands in $^{13}$C n.m.r. spectroscopy is provided by obtaining high resolution (120 MHz) $^{13}$C-$^1$H n.m.r. spectra of the previously mentioned ambidentate Me$_2$SO complexes [RuCl$_n$(Me$_2$SO)$_6$-$n$](BF$_4$)$_n$-$2$ (n = 0, 1, 2) (see Figure 2.3(a, b, c) and Table 2.1).

A $^{13}$C-$^1$H n.m.r. spectrum of RuCl$_2$(O-Me$_2$SO)(S-Me$_2$SO)$_3$ in CD$_2$Cl$_2$ at 298 K shows three S-bonded Me$_2$SO ligand $\delta_C$(CH$_3$) resonances between 47.707 and 44.366 ppm (45.991 and 42.546 ppm in CD$_3$NO$_2$) and a further two resonances at 41.25 and 38.958 ppm (39.25 and 37.069 ppm in CD$_3$NO$_2$). The higher frequency resonance is attributed, in both solvents, to free Me$_2$SO (confirmed by adding an excess of Me$_2$SO to the solution in the n.m.r. tube) while the lower frequency resonance is attributed to the single O-bonded Me$_2$SO ligand.

The $^{13}$C-$^1$H n.m.r. spectra of [RuCl(O-Me$_2$SO)$_2$-(S-Me$_2$SO)$_3$]BF$_4$ and [Ru(O-Me$_2$SO)$_3$(S-Me$_2$SO)$_3$](BF$_4$)$_2$ in CD$_2$NO$_2$ show S-bonded $\delta_C$(CH$_3$) resonances between 45.523 and 42.540 ppm, and O-bonded $\delta_C$(CH$_3$) resonances between 36.704 and 36.261 ppm (N.B. O-bonded Me$_2$SO ligand resonances are all to low frequency of free Me$_2$SO, see Figure 2.3 (a,b,c)).
Figure 2.3(a,b,c)

$^{13}$C-$^1$H n.m.r. Spectra of $\text{[RuCl}_n\text{(Me}_2\text{SO)}_6-n\text{]}^-$

$(\text{BF}_4)_2-n \ (n=0,1,2)$ in $\text{CD}_3\text{NO}_2$ at 303 K

(a) $\text{RuCl}_2\text{(O-Me}_2\text{SO)}_2\text{(S-Me}_2\text{SO)}_3$

(b) $\text{[RuCl(O-Me}_2\text{SO)}_2\text{(S-Me}_2\text{SO)}_3\text{]}\text{BF}_4$

(c) $\text{[Ru(O-Me}_2\text{SO)}_3\text{(S-Me}_2\text{SO)}_3\text{]}(\text{BF}_4)_2$

Free $\text{Me}_2\text{SO}$
Thus, in both solvents, relative to free Me$_2$SO, the spread for S-bonded Me$_2$SO is +6.76 to +3.12 ppm, while that for O-bonded Me$_2$SO is -2.99 to -2.18 ppm (see Table 2.1 for greater detail).

Hence, the five $^{13}$C-{$^{1}$H} n.m.r. $\delta_{C(CH_3)}$ resonances between 48.995 and 45.883 ppm (from +7.75 to +4.63 ppm relative to free Me$_2$SO) obtained for Ru$_2$Cl$_4$(Me$_2$SO)$_5$ are, as in the $^1$H n.m.r. spectra, firmly in the "normal" S-bonded region. The relatively high $\delta(CH_3)$ of the S-bonded Me$_2$SO ligands of Ru$_2$Cl$_4$(Me$_2$SO)$_5$, with respect to its related monomers, probably reflects, as in $^1$H n.m.r. spectroscopy, the greater number of chlorides associated with each Ru; c.f. the trend in $\delta_{C(CH_3)}$ of S-bonded Me$_2$SO ligands in [RuCl$_n$(Me$_2$SO)$_6-n$](BF$_4$)$_{n-2}$ (n = 0, 1, 2) in Table 2.1. Due to the close spacing of the methyl resonances in the $^1$H and $^{13}$C-{$^{1}$H} n.m.r. spectra no one-to-one correlation of resonance positions has been attempted.

Overall $^1$H and $^{13}$C-{$^{1}$H} n.m.r. spectra are entirely consistent with the proposed triple chloro bridged complex (31c) (Figure 2.1). However other possibilities also exist, e.g. (31a) or (31b) with four terminally S-bonded Me$_2$SO ligands. However, (31a), which contains a single Ru-O-Ru sulphoxide bridge, for which some precedent exists,$^{(142,151,200,201)}$, can be discounted since the $\delta(CH_3)$ chemical shift data (both $^1$H and $^{13}$C-{$^{1}$H} n.m.r.) establishes that the unique Me$_2$SO ligand is in the S-bonded region. It is much more difficult to discount (3lb), which contains
an unprecedented single Ru-S-O-Ru sulfoxide bridge, since simple addition of the chemical shifts from free Me₂SO due to S- and O-bonding would suggest median bridging ligand $\delta(CH_3)$ of ca. 3.7 ppm in $^1H$ n.m.r. spectroscopy and ca. 44.7 ppm in $^{13}C-(^1H)$ n.m.r. spectroscopy. Although both these figures are well outside the range of both $^1H$ and $^{13}C-(^1H)$ n.m.r. resonances found for Ru₂Cl₄(Me₂SO)₅ (e.g. 3.498 to 3.338 ppm for $^1H$ n.m.r. and 48.995 to 45.883 ppm for $^{13}C-(^1H)$ n.m.r.) they are uncomfortably close to the "unique" resonance in both $^1H$ and $^{13}C-(^1H)$ n.m.r. (see Figure 2.2 (a,b)).

On the positive side, the spread of both $^1H$ and $^{13}C-(^1H)$ n.m.r. resonances of Ru₂Cl₄(Me₂SO)₅ is less than the corresponding spread delimited by the three "normal" S-bonded Me₂SO ligands of [RuClₓ(Me₂SO)ₓ⁻⁶](BF₄)ₓ (n = 1, 2) i.e. 0.16 ppm against 0.18 ppm for both n = 1, 2 in $^1H$ n.m.r. spectroscopy, and 2.31 ppm against 2.34 ppm for n = 2 and 2.98 ppm for n = 1 in $^{13}C-(^1H)$ n.m.r. spectroscopy. Thus there is little internal indication of one Me₂SO ligand in Ru₂Cl₄(Me₂SO)₅ being bonded any differently from the rest.

Nuclear magnetic resonance spectroscopy is not the only useful technique used in structural elucidations of Me₂SO complexes. Infrared spectroscopic data are well recognised as a valuable guide to the bonding of dialkyl sulfoxide ligands, with $v_{S=O}$ found characteristically in the range 1050-1200 cm⁻¹ for S-coordination and 890-1050 cm⁻¹ for O-coordination (197). However, it is important to note that many pitfalls await the unwary in assigning these bands,
since $v_{S=O}$ is not a pure vibration but is coupled with methyl rocking modes which occur in the same region, i.e. 900-1030 cm$^{-1}$ (197). In order to eliminate such complications, an isotopic substitution is necessary since this moves the methyl rocking modes down frequency out of the $v_{S=O}$ region, leaving relatively pure assignable $v_{S=O}$ vibrations.

By comparing the infrared data of Ru$_2$Cl$_4$(Me$_2$SO)$_5$ and its deuterated analogue Ru$_2$Cl$_4$(d$^6$-Me$_2$SO)$_5$ (made by dimerising the deuterated monomer RuCl$_2$(d$^6$-Me$_2$SO)$_4$) (Figure 2.4 and Table 2.2) it can clearly be seen that bands assigned by Tayim et al (193) to be (a) bridging Me$_2$SO at 965 cm$^{-1}$ and (b) O-bonded Me$_2$SO at 910 and 928 cm$^{-1}$ are in fact methyl rocking modes which shift on deuteration to 780 and 765 cm$^{-1}$ respectively, leaving no infrared bands in the range 830-1007 cm$^{-1}$. In marked contrast the S-bonded Me$_2$SO ligands show very little positional variation on deuteration i.e. $v_{S=O}$ bands shift from 1135, 1115 and 1095 cm$^{-1}$ to 1137, 1110 and 1100 cm$^{-1}$ respectively.

Thus infrared data appear to be fully consistent with the previously detailed n.m.r spectroscopic studies in that they both strongly suggest coordination exclusively through sulphur. Proving this definitively, and thus disproving the Ru-O-Ru and Ru-S-O-Ru bridging sulphonate possibilities, is very difficult using only infrared data since the positions expected for $v_{S=O}$ are not well defined in these unusual circumstances.
Figure 2.4 Infrared Spectra of 
$\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5$ and $\text{Ru}_2\text{Cl}_4(\text{d}^6-\text{Me}_2\text{SO})_5$

$[\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5]$
Only two examples of compounds with M-O-M sulphoxide bridges have been crystallographically proved, namely the binuclear Hg(II) complex \( \text{HgCl}_2 \cdot (\text{Me}_2\text{SO})\text{HgCl}_2 \) (200) and the infinitely linked Ag(I) compound \([\text{Ag(Me}_2\text{SO})_2] \text{ClO}_4\) (201). The \( \nu_{S=O} \) stretching vibrations were tentatively assigned to 995 and 1020 cm\(^{-1}\) for the Hg(II) and Ag(I) complexes respectively. However, in neither case was a deuterated analogue prepared and thus a degree of uncertainty remains in these assignments.

Since no example of a M-S-O-M complex yet exists no comparative appraisal of \( \nu_{S=O} \) in this situation is possible. Whether the constraining influence of bonding through both oxygen and sulphur would invalidate predictions of \( \nu_{S=O} \) being less than 1055 cm\(^{-1}\) (based on simple addition of the bathochromic shift associated with O-bonding and the hypsochromic shift associated with S-bonding) is uncertain. Thus it is just conceivable that one or more bands in the infrared region 1020⁻1028 cm\(^{-1}\) of \( \text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5 \) arise from a Ru-S-O-Ru bridging sulphoxide unit. There is little doubt that these bands move to 815⁻830 cm\(^{-1}\) on deuteration, thus identifying them as methyl rocking modes. Unfortunately symmetric and asymmetric methyl deformations at 1322, 1295 cm\(^{-1}\) and 1425, 1410 cm\(^{-1}\) shift to 1020, 1007 cm\(^{-1}\) and 1035, 1030 cm\(^{-1}\) respectively on deuteration and thus obscure the 1020⁻1028 cm\(^{-1}\) region. (N.B. Exactly analogous shifts were observed by Wilkinson et al during infrared studies of deuterated and non-deuterated samples of \( \text{RuCl}_2(O\text{-Me}_2\text{SO})_2(S\text{-Me}_2\text{SO})_3 \) (30)) (194).
Thus, the suggested Ru-S-O-Ru bridging sulphoxide is effectively disproved, except in the improbable circumstance of its having $\nu_{S=O}$ fall within the normal S-bonded region or under the 1020 cm$^{-1}$ band, or being infrared "silent", i.e. very weakly absorbing.

Varying the reaction conditions required for synthesising Ru$_2$Cl$_4$(Me$_2$SO)$_5$ affords useful information on its mechanism of formation. The original paper by Tayim et al stated that Ru$_2$Cl$_4$(Me$_2$SO)$_5$ was the sole product formed on heating compound (30) under reflux in toluene. However, the reaction is not as simple as this suggests, since heating under reflux in dry toluene under N$_2$ leads to the retention of starting material whereas heating to reflux under air in dry toluene yields the required binuclear product, as does heating to reflux in wet toluene (dry toluene with two drops of water added per 0.1 mmol Ru) under dry N$_2$.

This information combined with the previously mentioned $^1$H and $^{13}$C-$^1$H n.m.r. spectroscopic data concerning the ease of dissociation of O-bonded Me$_2$SO from (30) (ca. 25\% dissociation in "non-coordinating" solvents like CDC$_3$ and CD$_2$Cl$_2$, and 100\% dissociation is coordinating solvents like D$_2$O), suggests a coherent mechanism for the formation of the triple chloro bridged complex Ru$_2$Cl$_4$(Me$_2$SO)$_5$ (31c).
In wet solvents (30) readily dissociates the hard O-bonded Me₂SO ligand from its soft Ru(II) centre to give RuCl₂(S-Me₂SO)₃(H₂O). Thus on heating under reflux in toluene or EtOH the aquo ligand would be easily displaced, leading to the formation of the five coordinate intermediate "RuCl₂(S-Me₂SO)₃" which may then dimerise with loss of Me₂SO to give the triple chloro bridged complex (3lc) (N.B. it is interesting that this structure is favoured over the hypothetical double chloro bridged product Ru₂Cl₄(Me₂SO)₆ which would not require displacement of an S-bonded Me₂SO ligand).

Similar molecular condensation reactions of "RuCl₂(PR₃)₃" (PR₃ = PMe₂Ø, PEt₂Ø, PEt₃, PEtØ₂, PClØ₂) were earlier also shown to give rise to confacial biocahedral triple chloro bridged complexes such as [Ru₂Cl₃(PR₃)₆]Cl and Ru₂Cl₄(PR₃)₅ (16) (Schemes 2.2 and 2.3); the ionic products being favoured in polar solvents such as MeOH and the neutral products in non-polar solvents such as n-hexane (66,113,118,122).

The fact that the cation [Ru₂Cl₃(Me₂SO)₆]⁺ is not formed under conditions similar to those yielding phosphine analogues such as [Ru₂Cl₃(PMe₂Ø)₆]⁺ might be attributed to the thermodynamic factor, the trans influence. Formation of [Ru₂Cl₃L₆]⁺ for L = PMe₂Ø and not for Me₂SO is then ascribed to the weaker Ru-Cl bonds in "RuCl₂(PMe₂Ø)₃" relative to "RuCl₂(S-Me₂SO)₃", dictated by the considerably higher trans influence of basic phosphines over S-bonded Me₂SO (197,202). Limited insight into the comparative Ru-Cl bond strengths of
the "five coordinate intermediates" may be drawn from metal chloride stretching frequencies in the infrared spectra of their precursors RuCl₂(O-Me₂SO)(S-Me₂SO)₃ (30) and cis-RuCl₂(PMe₂O)₄ since νₐₜₜ occurs at 348 and 292 cm⁻¹ respectively.

All attempts to produce the [Ru₂Cl₃(Me₂SO)₆]⁺ cation by heating (30) under reflux in MeOH, EtOH or CH₃NO₂ under air produced Ru₂Cl₄(Me₂SO)₅ (3lc) whereas in dry solvents under N₂ only starting material was isolated. Attempted chloride abstraction by treating a two-fold excess of (30) with AgBF₄ in CH₃NO₂ under argon yielded an unidentified unstable pale yellow solid when extracted into CH₂Cl₂ and precipitated with diethyl ether.

In conclusion, there seems little doubt that the complex Ru₂Cl₄(Me₂SO)₅ is best represented by the triple chloro bridged structure (3lc). Accordingly the class of confacial bioctahedral systems is radically extended by the wholesale incorporation of S-bonded Me₂SO ligands in place of phosphines. Comparison of the redox and spectroscopic properties is thus of great interest and will be developed more fully in Chapter 5.
2.3(a) (ii) \( L = \text{MeCN, Pyridine and 4-Methyl-Pyridine} \)

It was originally hoped, by analogy with the monomeric complex \( \text{RuCl}_2(\text{Me}_2\text{SO})_4 \) (30), that complexes of type \( \text{RuCl}_2L_4 \) (L = MeCN, py, 4-Mepy)\(^{61,203}\) would dimerise in solution to yield further triple chloro bridged binuclear compounds of type \( \text{Ru}_2\text{Cl}_4L_5 \). This does not in fact occur since heating the monomers \( \text{RuCl}_2L_4 \) (MeCN, py, 4-Mepy) under reflux in air in polar solvents such as EtOH or non-polar solvents such as toluene leads to partial decomposition to give a mixture of unidentified paramagnetic products whereas heating under reflux in the same solvents under \( \text{N}_2 \) leads to retention of starting material.

In retrospect, attempts to produce neutral triple chloro bridged binuclear complexes of type \( \text{Ru}_2\text{Cl}_4L_5 \) (L = MeCN, py, 4-Mepy) under similar conditions to their Me\(_2\)SO analogue (31c) were less likely to succeed since, unlike (30), \( \text{RuCl}_2L_4 \) (L = MeCN, py, 4-Mepy) are all \textit{trans} structures containing no especially labile ligands.

Further methods of synthesising \( \text{Ru}_2\text{Cl}_4(4\text{-Mepy})_5 \) have been attempted, for example photolysis of \textit{trans}-\( \text{RuCl}_2(4\text{-Mepy})_4 \) in \( \text{CH}_2\text{Cl}_2 \) using a medium pressure mercury U.V. lamp. On reducing the volume of the solution, a yellow solid precipitated. This complex is too insoluble for \textsuperscript{1}H n.m.r. spectroscopic studies but infrared, electrochemical and microanalytical data show it to be a \( \text{CH}_2\text{Cl}_2 \) solvate of the original compound. This solvate can also be made by simply allowing a \( \text{CH}_2\text{Cl}_2 \) solution of \textit{trans}-\( \text{RuCl}_2(4\text{-Mepy})_4 \) to stand under \( \text{N}_2 \).
Another attempt involved shaking $\text{trans-RuCl}_2(4\text{-Mepy})_4$ in MeOH with an excess of HBF$_4$, the aim being to weaken Ru-N bonds by protonation of the 4-Mepy N-donor ligands. However, the highly conducting red crystalline product formed is shown by microanalysis, infrared data ($\nu_{\text{Ru-Cl}}$ 342 cm$^{-1}$) and broad $^1$H n.m.r. signals in CDCl$_3$ to be the paramagnetic complex $\text{trans-[RuCl}_2(4\text{-Mepy})_4]BF_4$. This formulation is confirmed by electrochemical studies since stirred and unstirred cyclic voltammetric and linear a.c. voltammetric studies show this complex to have a reversible one-electron reduction at the same potential as $\text{trans-RuCl}_2(4\text{-Mepy})_4$ shows a reversible one-electron oxidation, i.e. +0.32 V versus an Ag/AgI reference electrode (against which ferrocene oxidises at $E_{1/2} =$ +0.60 V).

Thus, rather than producing a labilising of the Ru-N bonds through protonation, treatment with HBF$_4$, in the presence of air, has resulted in the facile oxidation of $\text{trans-RuCl}_2(4\text{-Mepy})_4$ to $\text{trans-[RuCl}_2(4\text{-Mepy})_4]BF_4$. Interestingly, this cationic Ru(III) complex does not give rise to an e.s.r. pattern in CH$_2$Cl$_2$ at 133 K (see Chapter 6 for further discussion).
2.3 (b) **Specific nucleophilic substitution at terminal sites in existing triple chloro bridged complexes**

(i) **Attempted replacement of neutral diazadiene ligands**

It was hoped that it might prove possible to replace the bidentate \((\text{CyNCH}_2)_2\) ligands from the cationic diazadiene complex \([\text{Ru}_2\text{Cl}_3(\text{P}_3\text{O})_2(\text{CyNCH}_2)_2]^+\)\(^{(190)}\) (28) with other N-donor ligands such as bidentate 1,10-phenanthroline or monodentate 4-methyl-pyridine. Since most triple chloro bridged \(\text{Ru}_2(\text{II/II})\) complexes are very susceptible to nucleophilic bridge cleavage it was decided to use mild reaction conditions, (i.e. stirring at room temperature with the appropriate amount of the selected nucleophile) in these studies.

Thus, shaking a degassed solution of (28) with an excess of \(\text{HBF}_4\) and two equivalents of 1,10-phenanthroline, or four equivalents of 4-methyl-pyridine, for two days yielded brown microcrystalline solids on reducing the volume of solution. In both cases \(^{31}\text{P}-^{1}\text{H}\) n.m.r. spectroscopic studies in CDCl\(_3\) at 298 K gave good evidence that no diazadiene replacement had occurred, the original cationic complex being recovered as a mixture of its \(\text{Cl}^-\) and \(\text{BF}_4^-\) salts. Curiously these have different \(^{31}\text{P}-^{1}\text{H}\) n.m.r. resonances i.e. \(\text{Cl}^-\) counterion at \(\delta_p\) 37.88 ppm and \(\text{BF}_4^-\) counterion at \(\delta_p\) 37.65 ppm, either due to discrete ion-pairing or a change in isomeric form.
In retrospect it is not surprising to find that the Ru-N bonds in diazadiene complexes are strong since these ligands have previously been shown to have excellent π-back-donating properties (190).

2.3(b)

(ii) Terminal chloride substitution

As mentioned in the introduction to this chapter, terminal chloride replacement reactions are known for triple chloro bridged Ru₂(II/II) complexes e.g. \([\text{Ru}_2\text{Cl}_3\text{Y}_2(\text{PR}_3)_4]\)X (PR₃ = PØ₃, P(2-tol)₃; Y = CO, CS; X = Cl⁻, BØ₄⁻) (21) is produced from the isomeric mixture \(\text{Ru}_2\text{Cl}_4\text{Y}_2(\text{PR}_3)_3\) (20a, b, c) in polar solvents in the presence of 1:1 molar ratios of PØ₃ and NaBØ₄ (182), by eliminating NaCl (see Scheme 2.4).

Similarly, a highly conducting green compound \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{O})_5(\text{MeCN})]\)BØ₄ (32) has now been isolated by prolonged shaking of a CH₂Cl₂ solution of \(\text{Ru}_2\text{Cl}_4(\text{PET}_2\text{O})_5\) (16) with 1:1 molar ratios of MeCN and NaBØ₄.

\[
\begin{array}{c}
\text{MeCN} & \text{Ru} & \text{Cl} & \text{Ru} & \text{PET}_2\text{Ø} \\
\text{ØET}_2\text{P} & \text{Cl} & \text{PET}_2\text{Ø} & \text{ØET}_2\text{P} \\
\end{array}
\]

BØ₄

(32)
This formulation is confirmed by microanalysis, infrared studies, ($\nu_{C=\text{N}}$ 2270 cm$^{-1}$ and the absence of terminal $\nu_{\text{Ru-Cl}}$ bands) and also by $^{31}\text{P}{-^1\text{H}}$ n.m.r. spectroscopic studies in C$_2$H$_2$. At 300 K the spectrum consists of a singlet at $\delta_P$ 41.8 ppm (at higher resolution this resonance splits into a quartet with $^4J_{PP}$ ca. 0.9 Hz) and two fairly broad resonances between $\delta_P$ 33 and $\delta_P$ 37 ppm. On cooling the solution to 232 K these resonances were resolved into a poorly defined AB$_2$ pattern ($\delta_A$ 35.7 ppm; $\delta_B$ 35.0 ppm; $\delta_{AB}$ 20.5 Hz; $^2J_{AB}$ 31 Hz) [c.f. the $^{31}\text{P}{-^1\text{H}}$ n.m.r. spectrum of Ru$_2$Cl$_4$(PEt$_2$O)$_5$ (16) in CCl$_3$ at 295 K which consists of a singlet at $\delta_P$ 44.3 ppm and an AB$_2$ pattern ($\delta_A$ 39.1 ppm; $\delta_B$ 35.1 ppm; $\delta_{AB}$ 84.2 Hz; $^2J_{AB}$ 29.0 Hz)] (122).

The fact that the AB$_2$ pattern is broad at 300 K and sharp at 223 K suggests fluxionality, via a bridge opening process. Such a process can also be invoked to explain the slow irreversible rearrangement of (32) to an unidentified product which gives rise to a $^{31}\text{P}{-^1\text{H}}$ n.m.r. spectrum consisting of an AB pattern (centred at $\delta_P$ 43.4 ppm; $\delta_{AB}$ 103.8 Hz; $^2J_{AB}$ 32.6 Hz) and a number of other low intensity singlets in the region $\delta_P$ 30-50 ppm.

Attempts to displace terminal chloride from other neutral triple chloro bridged compounds have unfortunately proved unsuccessful. $^{31}$Phosphorus-$^1$H n.m.r. spectroscopic evidence clearly shows that rearrangement, probably to monomers, takes place when Ru$_2$Cl$_4$(CS)(P$_3$O)$_4$ (19) is treated with NaB(O$_2$) and MeCN, whilst no reaction at all occurs when Ru$_2$Cl$_4$(PCl$_2$O)$_5$ (16) is used.
The mechanism of formation of (32) is not known; however, possibilities include cleavage to monomers, followed by recombination, or direct substitution of the terminal chloride in the binuclear unit. The high yield of the reaction, with no apparent side-products, is indicative of the latter process.

The non-reactivity of Ru$_2$Cl$_4$(PCl$\Phi_2$)$_5$ (16) and the decomposition of Ru$_2$Cl$_4$(CS)(P$\Phi_3$)$_4$ (19) clearly contrasts with the well behaved reaction of Ru$_2$Cl$_4$(PET$_2\Phi$)$_5$ (16) and might suggest that substantial variation in both terminal and bridging Ru-Cl bond strengths occur in this limited series.

2.4 Conclusions

Neither of the synthetic approaches designed to increase the range of triple chloro bridged Ru$_2$(II/II) complexes met with much success. Both the monomer coupling reactions and the diazadiene displacement reaction failed (the compound RuCl$_2$(Me$_2$SO)$_4$ (30) being an obvious exception), probably because of the inertness of the ligand-to-metal bonds. In the cases where chloride replacement reactions were attempted it became obvious that specific terminal chloride replacement was the exception rather than the rule.

Studies on the mode of formation of triple chloro bridged Ru$_2$(II/II) compounds containing PR$_3$ or Me$_2$SO ligands from monomers suggest that an interplay of many diverse factors are at work. These include:- steric, thermodynamic
(e.g. the *trans* influence) and kinetic factors e.g. the *trans* labilising effect. Considerations such as these are useful in predicting how easily complexes such as "RuCl$_2$L$_3$" are formed, whether they are stable, and if not, whether they will form a neutral or cationic triple chloro bridged binuclear complex. Why complexes of type "RuCl$_2$L$_3$" almost exclusively dimerise to give a triple chloro bridged compound rather than double bridged ones is not really understood.

Although synthetic innovations were somewhat limited, a number of useful discoveries were made. The most important of these concerns the development of $^{13}$C n.m.r. spectroscopy as a powerful technique for differentiating between S- and O-bonded Me$_2$SO ligands. High resolution $^{13}$C-{$^1$H} n.m.r. spectra (120 MHz) of [RuCl$_n$(Me$_2$SO)$_{6-n}$](BF$_4$)$_{n-2}$ in CD$_3$NO$_2$ (Figure 2.3 (a,b,c)) clearly show a very striking difference in the S- and O-bonded methyl regions. They show that S-bonded Me$_2$SO ligand resonances are well separated from their O-bonded counterparts, which actually move in an opposite sense with respect to free Me$_2$SO (S-bonded Me$_2$SO moving to high frequency and O-bonded to low frequency). Whether these observations are of universal application or are only applicable to Ru(II) complexes is not yet known but is at present under investigation in our laboratory.

$^{13}$C n.m.r. spectra of Me$_2$SO complexes may also offer higher resolution than $^1$H n.m.r. spectra e.g. a $^{13}$C-{$^1$H} n.m.r. spectrum (120 MHz) of [RuCl(O-Me$_2$SO)$_2$(S-Me$_2$SO)$_3$]BF$_4$ in CD$_3$NO$_2$ shows five 1:1:1:1:1 resonances as expected, while $^1$H n.m.r. spectrum (360 MHz) of the same complex in the same solvent shows only four 2:1:1:1 resonances.
2.5 Experimental

Microanalysis were performed in the Chemistry Department, University of Edinburgh and by Canadian Microanalytical Services Ltd., Vancouver B.C. Melting points (uncorrected) were determined with a Köfler hot-stage microscope and conductivity measurements with a Portland Electronics Model 310 conductivity bridge. Infrared spectra were recorded on a Perkin-Elmer 577 grating spectrometer using Nujol mulls on caesium iodide plates (4000-250 cm\(^{-1}\)) and pressed KCl discs (4000-625 cm\(^{-1}\)). \(^1\)Hydrogen and \(^{13}\)C-\(^1\)H\) n.m.r. spectra were measured on a Bruker WH360 spectrometer operating in the pulse and Fourier transform mode at 360 and 120 MHz respectively (chemical shifts are reported in ppm to high frequency of SiMe\(_4\)). \(^{31}\)Phosphorus-\(^1\)H\) n.m.r. spectra were measured on Jeol FX60Q and Varian XL100 spectrometers operating in the pulse and Fourier transform mode at 24.2 and 40.5 MHz respectively (chemical shifts are reported in ppm to high frequency of 85% H\(_3\)PO\(_4\)). Electron Spin Resonance (e.s.r.) experiments were carried out in the Department of Biochemistry, University of Edinburgh on a Varian E4 spectrometer employing 100 KHz magnetic field modulation. Standard Schlenk and vacuum line techniques were used when necessary.

Electrochemical studies employed a PAR model 170 potentiostat and programmer and 0.50 M Bu\(_4\)NBF\(_4\)/CH\(_2\)Cl\(_2\) solutions, with Pt working and auxiliary electrodes and a Ag/AgI reference electrode (against which ferrocene oxidises at \(E_\frac{1}{2} = +0.60\) V). Scan rates were from 50 to 500 mvs\(^{-1}\) (C.V.) and 10 mvs\(^{-1}\) (A.C.V.) with \(\omega = 205\) Hz.
Reagents

The following compounds were prepared using literature methods: RuCl$_2$(Me$_2$SO)$_4$ (194), RuCl$_2$(d$_6$-Me$_2$SO)$_4$ (194), trans-RuCl$_2$L$_4$ (L = MeCN, pyridine and 4-methyl-pyridine) (61,203), [Ru$_2$Cl$_3$(PO$_3$)$_2$(Cy$_2$N$_2$(CH$_2$)$_2$)$_2$]Cl (190), Ru$_2$Cl$_4$(CS)(PO$_3$)$_4$ (182) and Ru$_2$Cl$_4$(PR$_3$)$_5$ (PR$_3$ = PEt$_2$Ø, PClØ$_2$) (122).

def-Tri-μ-chloro-a-chloro-bcghi-pentakis(dimethylsulphoxide)-diruthenium(II)

(i) Yellow microcrystalline RuCl$_2$(Me$_2$SO)$_4$ (0.20 g) was suspended in dry toluene (20 ml), 2 drops of water were added and the solution heated under reflux under air or N$_2$ for 3 hours. The orange-brown precipitate was washed with acetone and diethylether and dried in vacuo at 40°C (95% yield).

(ii) As (i) above, but in boiling EtOH (20 ml) for 30 minutes (95% yield). M.P. 250°C (decomp.), [Found: C, 16.6; H, 4.2; Cl, 19.4. Calculated for C$_{10}$H$_{30}$Cl$_4$O$_5$S$_5$Ru$_2$: C, 16.5; H, 4.1; Cl, 19.4%], non-conducting in CH$_2$Cl$_2$. Infrared spectrum (600-250 cm$^{-1}$): 450(m), 430(s), 387(m), 350(m), 340(doublet)(m), 310(m), 290(w).

def-Tri-μ-chloro-a-chloro-bcghi-pentakis(d$_6$-dimethylsulphoxide)diruthenium(II)

This product was synthesised exactly as in method (i) above using RuCl$_2$(d$_6$-Me$_2$SO)$_4$ (95% yield).
M.P. 252°C (decomp.), [Found: C, 16.1; D, 7.9; Cl, 18.8. Calculated for C_{10}D_{30}Cl_{4}O_{5}S_{5}Ru_{2}: C, 15.7; D, 7.9; Cl, 18.6%], non-conducting in CH_{2}Cl_{2}.

Infrared spectrum (600-250 cm\(^{-1}\)): 410 (m), 395 (s), 360 (m), 330 (doublet) (m), 305 (m), 290 (w).

**Trans-di-chloro-tetrakis(4-methyl-pyridine)ruthenium(III)-tetrafluoroborate**

Orange microcrystalline trans-RuCl_{2}(4-Mepy)_{4} (0.20 g) was suspended in MeOH (20 ml) and an excess of HBF_{4} (4 ml, 40% aqueous solution) and shaken in air for 2 days. The resulting red crystals were washed with a minimum amount of EtOH and diethylether and dried in vacuo at 40°C. Partial filtrate evaporation gave more red crystals which were treated similarly (combined yield 88%).

M.P. 160°C (decomp.), [Found: C, 45.9; H, 4.5; N, 8.9. Calculated for C_{24}H_{28}B_{4}Cl_{2}F_{4}N_{4}Ru: C, 45.6; H, 4.4; N, 8.9%]. Infrared spectrum: \(\nu_{\text{Ru-Cl}}\) 342 cm\(^{-1}\) (s).

\[\Lambda(1 \times 10^{-3} \text{ M}) \text{ in CH}_{2}\text{Cl}_{2} = 45 \text{ OH cm}^{-2} \text{ mol}^{-1}.\]
def-Tri-µ-chloro-a-acetonitrile-bcghi-pentakis(diethylphenylphosphine)diruthenium(II) tetrapheny1boronate

Orange Ru$_2$Cl$_4$(PET$_2$Ø)$_5$ (0.20 mmol, 0.24 g) was dissolved in degassed CH$_2$Cl$_2$ (20 ml) containing suspended NaBØ$_4$ (0.20 mmol, 0.07 g). Degassed MeCN (0.20 mmol, 0.008 g) was added to the above mixture with the aid of a vacuum line. The reaction mixture was then shaken under a N$_2$ atmosphere, the green filtrate was reduced in volume under reduced pressure and on addition of EtOH a green solid precipitated. This product was washed with a minimum amount of cold EtOH and diethylether and dried in vacuo at 40°C (80% yield).

M.P. 87-89°C (decomp.), [Found: C, 60.2; H, 6.8; N, 0.9. Calculated for C$_{76}$H$_{89}$BCl$_3$NP$_5$Ru$_2$: C, 60.9; H, 6.6; N, 0.9%]. Infrared spectrum: v$_{CN}$ 2270 cm$^{-1}$(w). |

$\Lambda$(1 x $10^{-3}$) in CH$_2$Cl$_2$ = 46 Ω$^{-1}$cm$^2$mol$^{-1}$. |
Table 2.1 Infrared Spectra of Ru$_2$Cl$_4$(Me$_2$SO)$_5$ and Ru$_2$Cl$_4$(d$_6$-Me$_2$SO)$_5$ (4000-600 cm$^{-1}$)\(^{a,b,c,d}\)

<table>
<thead>
<tr>
<th>position, cm$^{-1}$</th>
<th>assignment</th>
<th>position, cm$^{-1}$</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3005 m</td>
<td>asym. C-H stretch</td>
<td>2260 m</td>
<td>asym. C-O stretch</td>
</tr>
<tr>
<td>2920 m</td>
<td>sym. C-H stretch</td>
<td>2130 m</td>
<td>sym. C-O stretch</td>
</tr>
<tr>
<td>1425 m</td>
<td>asym. CH$_3$</td>
<td>1035 m</td>
<td></td>
</tr>
<tr>
<td>1410 m</td>
<td>deformation</td>
<td>1030 m</td>
<td>asym. and sym.</td>
</tr>
<tr>
<td>1322 m</td>
<td>sym. CH$_3$</td>
<td>1020 m</td>
<td>CD$_3$ deformation</td>
</tr>
<tr>
<td>1295 m</td>
<td>deformation</td>
<td>1007 m</td>
<td></td>
</tr>
<tr>
<td>1135 vs db</td>
<td>S-O stretch</td>
<td>1137 vs db</td>
<td></td>
</tr>
<tr>
<td>1115 vs db</td>
<td></td>
<td>1110 vs db</td>
<td>S-O stretch</td>
</tr>
<tr>
<td>1095 vs</td>
<td></td>
<td>1100 vs</td>
<td></td>
</tr>
<tr>
<td>1028 s</td>
<td></td>
<td>830 m</td>
<td></td>
</tr>
<tr>
<td>1020 s</td>
<td></td>
<td>815 m</td>
<td>CD$_3$ rock</td>
</tr>
<tr>
<td>970 m</td>
<td>CH$_3$ rock</td>
<td>780 m</td>
<td></td>
</tr>
<tr>
<td>930 w</td>
<td></td>
<td>765 m</td>
<td></td>
</tr>
<tr>
<td>914 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>720 m</td>
<td>asym. and sym.</td>
<td>620 m</td>
<td>C-S stretch</td>
</tr>
<tr>
<td>625 m</td>
<td>C-S stretch</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) for 600-250 cm$^{-1}$ data, see Experimental Section

\(^{b}\) data from pressed KCl discs, fully consistent with Nujol mull spectra

\(^{c}\) assignments following Wilkinson et al\(^{(194)}\)

\(^{d}\) \(v = \text{very}, s = \text{strong}, m = \text{medium}, w = \text{weak}, \text{db} = \text{doublet}\)
Table 2.2: N.M.R. Parameters for $[\text{RuCl}_n(\text{Me}_2\text{SO})_{6-n}]\text{(BF}_4\text{)}_2-n$ and $\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5$

($\delta$ values in ppm vs. $\text{SiMe}_4$)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>S-bound $\text{Me}_2\text{SO}$</th>
<th>O-bound $\text{Me}_2\text{SO}$</th>
<th>free $\text{Me}_2\text{SO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RuCl}_2(\text{Me}_2\text{SO})_4$</td>
<td>3.416 s 3.364 q 3.237 q</td>
<td>2.690 s</td>
<td>2.55</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{Me}_2\text{SO})_4$</td>
<td>3.398 s 3.349 q 3.226 q</td>
<td>2.756 s</td>
<td>2.50</td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{Me}_2\text{SO})_5]\text{BF}_4$</td>
<td>3.355 s 3.177 s</td>
<td>2.877 q 2.856 q 2.50</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru}(\text{Me}_2\text{SO})_6]\text{(BF}_4\text{)}_2$</td>
<td>3.331 s</td>
<td>3.071 s</td>
<td>2.50</td>
</tr>
<tr>
<td>$\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5$</td>
<td>3.498 s 3.468 q 3.439 q 3.379 q 3.338 q</td>
<td>-</td>
<td>2.55</td>
</tr>
</tbody>
</table>

$^{13}\text{C}-^{1}\text{H}$ data:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{13}\text{C}$</th>
<th>S-bound $\text{Me}_2\text{SO}$</th>
<th>O-bound $\text{Me}_2\text{SO}$</th>
<th>free $\text{Me}_2\text{SO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RuCl}_2(\text{Me}_2\text{SO})_4$</td>
<td>47.907 46.279 44.366</td>
<td>38.958</td>
<td>41.25</td>
<td></td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{Me}_2\text{SO})_4$</td>
<td>45.991 44.317 42.546</td>
<td>37.069</td>
<td>39.25</td>
<td></td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{Me}_2\text{SO})_5]\text{BF}_4$</td>
<td>45.523 45.078 42.540</td>
<td>36.704 36.261 39.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru}(\text{Me}_2\text{SO})_6]\text{(BF}_4\text{)}_2$</td>
<td>44.418</td>
<td>36.548</td>
<td>39.25</td>
<td></td>
</tr>
<tr>
<td>$\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5$</td>
<td>48.995 47.893 47.800 47.684 45.883</td>
<td>-</td>
<td>41.25</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ in CD$_2$Cl$_2$

$^b$ s = singlet, q = quartet $^4J_{HH}$ ca. 0.7 Hz in all cases

$^c$ checked in the presence of 10-fold excess of $\text{Me}_2\text{SO}$

$^d$ in CD$_3$NO$_2$

$^e$ double intensity due to overlapping resonances
CHAPTER 3

Synthesis and Characterisation of New Non-Chloro

Triple Bridged Ruthenium(II/II) Binuclear Complexes
3.1 Preamble

Two major routes have been used in attempts to synthesise new non-chloro triple bridged Ru$_2$(II/II) binuclear species. These are dimerisation of suitable Ru(II) monomers and nucleophilic attack on bridging sites in existing triple chloro bridged Ru$_2$(II/II) binuclear complexes.

Since the methods of synthesis of known non-chloro triple bridged Ru$_2$(II/II) complexes are often different from those described in Chapter 2 it is useful to include a short introductory section on this topic. As for the triple chloro bridged Ru$_2$(II/II) compounds, almost all of the known non-chloro triple bridged Ru$_2$(II/II) complexes contain bulky tertiary phosphines, phosphites etc. The only notable exceptions are the heterocyclic oligocarbene complexes [Ru$_2$I$_3$(C$_3$N$_2$R$_2$)$_6$I (R = Me, Et)]$^+$ (191) and a series of $\eta^6$-arene cations such as [($\eta^6$-arene)RuX$_3$Ru($\eta^6$-arene)]$^+$, ($X = Br^-, I^-, OH^-, OMe^-, OEt^-, O\tilde{O}^-; \ \eta^6$-arene = C$_6$H$_6$, mesitylene etc.)$^{140,142,151}$, which will not be further considered in this thesis.

3.2 Introduction

Although Table 1.3 in Chapter 1 by no means includes an exhaustive survey of Ru$_2$(II/II) and Os$_2$(II/II) triple bridged binuclear complexes, it does indicate that non-chloro triple bridged complexes are much rarer than their chloro analogues. Indeed, prior to the recent preparation of [($\eta^6$-C$_6$H$_6$)OsX$_3$Os($\eta^6$-C$_6$H$_6$)]B$\tilde{O}$$_4$ ($X = OH^-, OMe^-)$ (151), no
non-chloro triple bridged Os₂(II/II) binuclear complexes were known.

In 1968 Shaw et al reported the first synthesis of non-chloro triple bridged Ru₂(II/II) complexes, e.g. [Ru₂X₃(PMe₂Ø)₆]X (X = Br⁻, I⁻) (118). However, new evidence, to be discussed in Section 3.3b (ii) shows both the bromo, (synthesised by heating "RuCl₃·3H₂O" under reflux in Pr¹-OH with an excess of LiBr and PMe₂Ø), and iodo complexes, (prepared through the action of excess NaI on [Ru₂Cl₃(PMe₂Ø)₆]Cl in refluxing Pr¹-OH), to be mixtures.

More recently Robinson et al reported similar cationic complexes i.e. [Ru₂X₃(PR₃)₆]B⁴ (X = Cl⁻, Br⁻; PR₃ = P(OEt)₂Ø, P(OEt)₃ etc.) from the reaction between [RuX₂(norb)] and PR₃ in refluxing MeOH (204,205).

A recent communication by Ashworth et al reported a novel route to complexes of type [Ru₂X₃(PR₃)₆]Y (X = OH⁻; PR₃ = PMe₂Ø, PMeØ₂, P(OMe)Ø₂: X = F⁻, I⁻, SH⁻, SMe⁻; PR₃ = PMe₂Ø: X = Cl⁻, Br⁻; PR₃ = PMe₂Ø, PMeØ₂; Y = PF⁶⁻, B⁴⁻) which involved the action of the appropriate acids HX on [RuH(cod)(PR₃)₃]Y (117). The compound [Ru₂H₃(PMe₂Ø)₆]PF₆ was also isolated by the same group from the reaction between [Ru(O₂CH)(PMe₂Ø)₄]PF₆ and MeOH (117). The formulation of all these complexes as triple bridged species was supported by a crystal structure determination on [Ru₂(OH)₃(PMe₂Ø)₆]B⁴ (117) (33). The Ru...Ru distance of 3.08 Å is considerably less than that in [Ru₂Cl₃(PMe₂Ø)₆]PF₆ (3.39 Å) (206), but this is believed
to reflect the differing ruthenium-to-bridging-ligand distances and angles rather than an increased metal-metal interaction.

![Diagram of compound (33)](image)

The postulated mechanism of formation of compound (33), shown in Scheme 3.1, envisages the hydrolysis of a basic ruthenium hydrido species to give hydroxo monomers which then condense with deprotonation of a further aquo ligand to give the required triple hydroxo bridged product. This mechanism may be generalised to include all bridges by interaction with the appropriate weak acids H₂S, HSMe etc.

More recently Wilkinson et al. have synthesised [Ru₂(OH)₃(PMe₃)₆]BF₄ from the reaction of Φ₃CBF₄ and Ru₂(CH₂)₃(PMe₃)₆ in tetrahydrofuran (207). The X-ray structure of this hydroxo bridged complex is very similar to that of (33) (e.g., the Ru...Ru distance is 3.004(1) Å).

Wilkinson et al. have also recently reported the synthesis and X-ray structural analysis of the triple hydrido bridged complex [Ru₂H₃(PMe₃)₆]BF₄ (34). This complex, which was prepared in high yield by the reaction of Ru₂H₄(PMe₃)₆ (derived from Ru₂(CH₂)₃(PMe₃)₆) and an excess of HBF₄ in tetrahydrofuran, has been found to have an anomalously short Ru...Ru distance of 2.540(1) Å (208). Whether this distance represents a formal Ru=Ru double bond, or is merely a
Scheme 3.1

Postulated Mechanism for the Formation of [Ru\(_2\)(OH)\(_3\)(PM\(_2\)Ø)\(_6\)]\(^+\) Cation

\[
2\left[(\text{PM}_2\text{Ø})_n\text{RuH}\right]^+ + 2\text{H}_2\text{O} \rightarrow 2\left[(\text{PM}_2\text{Ø})_{n-1}\text{RuH(H}_2\text{O)}\right]^+ + 2\text{PM}_2\text{Ø}
\]

(33)
consequence of the ruthenium-to-bridging-ligand distances and angles, is a matter of conjecture.

$$\begin{array}{c}
\begin{array}{c}
\text{Me}_3\text{P} \\
\text{H} \\
\text{PMe}_3
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{Me}_3\text{P} \\
\text{Ru} \\
\text{H}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{Ru} \\
\text{PMe}_3
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{Me}_3\text{P} \\
\text{H} \\
\text{PMe}_3
\end{array}
\end{array}
= \text{BF}_4
\end{array}
$$

(34)

Several neutral triple bridged complexes containing phosphorus donor ligands and varied bridges have been reported (180,182). These include (PØ₃)₂BrRuCl₂BrRu(CO)(PØ₃)₂ (35) (produced from the reaction of RuBr₂(PØ₃)₃ (65) and RuCl₂(CO)(PØ₃)₂(dmf) (209) in acetone, in 1:1 molar ratio), (PØ₃)₂ClRuBr₂ClRu(CO)(PØ₃)₂ (36) (produced from the reaction of equimolar amounts of RuCl₂(PØ₃)₃ and RuBr₂(CO)(PØ₃)₂(dmf) (209) in acetone), and (PØ₃)₂BrRuBr₃Ru(CO)(PØ₃)₂ (37) (prepared by reaction of RuBr₂(PØ₃)₃ and RuBr₂(CO)(PØ₃)₂(dmf) [1:1 molar ratios] in acetone) (182).

$$\begin{array}{c}
\begin{array}{c}
\text{OC} \\
\text{Cl} \\
\text{PØ₃}
\end{array}
\begin{array}{c}
\text{Ø₃P} \\
\text{Ru} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{Ru} \\
\text{PØ₃}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{OC} \\
\text{Cl} \\
\text{PØ₃}
\end{array}
\begin{array}{c}
\text{Ø₃P} \\
\text{Ru} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{Ru} \\
\text{PØ₃}
\end{array}
\end{array}
$$

(35)

$$\begin{array}{c}
\begin{array}{c}
\text{OC} \\
\text{Cl} \\
\text{PØ₃}
\end{array}
\begin{array}{c}
\text{Ø₃P} \\
\text{Ru} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{Ru} \\
\text{PØ₃}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{OC} \\
\text{Cl} \\
\text{PØ₃}
\end{array}
\begin{array}{c}
\text{Ø₃P} \\
\text{Ru} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{Ru} \\
\text{PØ₃}
\end{array}
\end{array}
$$

(36)

$$\begin{array}{c}
\begin{array}{c}
\text{OC} \\
\text{Br} \\
\text{Ø₃P}
\end{array}
\begin{array}{c}
\text{Ø₃P} \\
\text{Ru} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{Ru} \\
\text{PØ₃}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{OC} \\
\text{Br} \\
\text{Ø₃P}
\end{array}
\begin{array}{c}
\text{Ø₃P} \\
\text{Ru} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{Ru} \\
\text{PØ₃}
\end{array}
\end{array}
$$

(37)
However, compounds (35) and (36) have identical complex $^{31}\text{P}$-{H} n.m.r. spectra, indicating that some, or all, of the six possible geometrical isomers of Ru$_2$Cl$_2$Br$_2$(CO)(PO$_3$)$_4$ have been formed(180,182).

Compound (37) also gives rise to a complex $^{31}\text{P}$-{H} n.m.r. spectrum indicating that it too is not a pure single compound(180).

Another reported complex is (PEt$_2$O)$_2$BrRuBr$_3$Ru(PEt$_2$O)$_3$ (38), the bromo analogue of (16), which is formed on heating RuBr$_2$(PO$_3$)$_3$ under reflux with an excess of PEt$_2$O in petroleum ether (B.P. 60-80°C)(122). However, the $^{31}\text{P}$-{H} n.m.r. spectrum obtained for this compound suggests that a mixture of species containing chloro and bromo bridges may be present. Such observations are by no means unexpected since pure RuBr$_2$(PO$_3$)$_3$ (derived from the reaction of RuCl$_2$(PO$_3$)$_3$ with LiBr)(65) has always proved very difficult to isolate. $^{31}\text{P}$-{H} n.m.r. studies reveal that a mixture of RuCl$_2$(PO$_3$)$_3$, RuClBr(PO$_3$)$_3$ and RuBr$_2$(PO$_3$)$_3$ is usually isolated(210).

$$\begin{align*}
\text{OEt}_2\text{P} & \quad \text{Br} & \quad \text{Ru} & \quad \text{Br} & \quad \text{Ru} & \quad \text{PET}_2\text{O} \\
\text{Br} & \quad \text{Ru} & \quad \text{Br} & \quad \text{Ru} & \quad \text{PET}_2\text{O} \\
\text{OEt}_2\text{P} & \quad \text{Br} & \quad \text{PET}_2\text{O} & \quad \text{PET}_2\text{O}
\end{align*}$$

(38)
In recent years a number of very unusual triple bridged Ru$_2$(II/II) binuclear complexes have been reported. These include: - (PO$_3$)(diazadiene)RuCl(OH)$_2$-RuH(PO$_3$)$_2$ (39) (diazadiene = (Pr$^i$NCHCHNPr$^i$), produced from the reaction of RuHCl(PO$_3$)$_2$(diazadiene) with H$_2$O in toluene (190) and the previously mentioned complexes (cod)XRuX$_3$(NCR)(cod) (X = Cl$, Br$; $R = Me, O$(117)$ and [Ru$_2$X$_3$(C$_3$N$_2$R$_2$)$_6$]X (X = Cl$, I$; $R = Me, Et$(191).

Finally Ashworth et al have recently synthesised and obtained the X-ray structure of the novel triple bridged compounds (cod)XRu(H)X(NH$_2$NMe$_2$)RuH(cod) (X = Cl$, Br$) (40), which are formed on heating [RuH(cod)(NH$_2$NMe$_2$)$_3$]B$_2$O$_4$ under reflux in acetone:MeOH solutions with an excess of LiCl or LiBr respectively (211).
3.3 Results and Discussion

(a) Dimerisation of Ru(II) monomers

(i) Reactions of the weak acids $H_2O$ and HSEt with $[\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]X$ ($X = \text{BOF}_4^-, \text{PF}_6^-$) and excess PMe$_2$Ø

As previously stated, Ashworth et al reported the preparation of the novel Ru(II) cationic complex $[\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]X$ ($X = \text{BOF}_4^-, \text{BF}_6^-$) in 1977 and used it, via the synthesis of $[\text{RuH(cod)}(\text{PMe}_2\text{Ø})_3]\text{BOF}_4$ (211), to prepare the triple hydroxo bridged complex $[\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{Ø})_6]\text{BOF}_4$ (33) (117). Since the reaction conditions for the formation of (33) were ill-defined in the preliminary communication, various permutations of solvent types and proportions were tried by us before the best conditions were found, and in so doing a number of interesting hydridio and di-hydridio Ru(II) monomeric complexes were isolated and characterised (see Appendix I).

The optimum conditions for reaction were found to involve heating $[\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]X$ ($X = \text{BOF}_4^-, \text{PF}_6^-$) under reflux in a degassed acetone:MeOH solvent mixture (2:1 V/V) under $N_2$ with a three fold excess of PMe$_2$Ø until the solution became dark red. Addition of an excess of degassed $H_2O$ then gave a yellow solution which on heating under reflux overnight deposited pale yellow crystals of the triple hydroxo bridged complex (33).
Both the $\text{BØ}_4^-$ and $\text{PF}_6^-$ salts are sharp-melting compounds which are highly conducting in acetone. Formulation of the products as (33) are confirmed by elemental analysis and the presence of a single sharp $\nu_{\text{O-H}}$ band of medium intensity at 3600 cm$^{-1}$ in the infrared spectrum. In addition, a $^{31}\text{P}-^1\text{H}$ n.m.r. spectrum in CDCl$_3$ at 298 K shows a singlet at $\delta_p$ 25.3 ppm, whilst the $^1\text{H}$ n.m.r. spectrum in CDCl$_3$ at ambient temperature contains a slightly broadened resonance at $\delta$-2.1 ppm assigned to the bridging hydroxide groups. The intensity ratio of this resonance to those of the methyl and phenyl resonances supports this assignment.

An electrochemical study of this complex in CH$_2$Cl$_2$ showed that the trace amount of HCl present in the solvent was sufficient to cleave the triple hydroxo bridges and form the well-known triple chloro bridged complex $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ø})_6]\text{Cl}$ (see Chapter 5). Other reactions of (33) ($X = \text{PF}_6^-$) with acids HX will be discussed in Section 3.3b (ii).

A sharp-melting and highly conducting yellow-green compound was isolated as the sole product on reacting an excess of HSET with the previously mentioned red solution. A $^{31}\text{P}-^1\text{H}$ n.m.r. spectrum in CDCl$_3$ at 298 K shows a singlet at $\delta_p$ 4.0 ppm, which in conjunction with microanalytical data suggests the formation of $[\text{Ru}_2(\text{SEt})_3(\text{PMe}_2\text{Ø})_6]\text{BØ}_4$ (41).
A $^1$H n.m.r. spectrum in CDCl$_3$ at ambient temperature shows the methyl resonances of the PMe$_2$Ø groups at ca. $\delta$1.7 ppm, but the methylene and methyl resonances of the SEt bridging units appear as a poorly resolved multiplet at ca. $\delta$1.2 ppm. The observation of overlapping -CH$_2$- and -CH$_3$ resonances from SEt bridges is not common, but not unprecedented e.g. it occurs in the binuclear Co$_2$(III/III) complex [Co(S$_2$CSR)(SEt)]$_2$ where the phenomenon is attributed to paramagnetic anisotropy (212).

3.3(a) (ii) Preparation and reactions of pure RuBr$_2$(PØ$_3$)$_3$

The prominent position of the five coordinate Ru(II) complex RuCl$_2$(PØ$_3$)$_3$ (65) as an important precursor for the synthesis of many triple chloro bridged Ru$_2$(II/II) binuclear compounds has been discussed in Chapter 2. In contrast, the bromo analogue RuBr$_2$(PØ$_3$)$_3$ has never been prepared in a pure form (65, 210), and consequently the synthesis of pure triple bromo bridged Ru$_2$(II/II) binuclear complexes has been very difficult.

It has now been found that treatment of $(\phi_3(\phi$CH$_2$)P)$_3$-[Ru$_2$Br$_9$] with an excess of PØ$_3$ in MeOH under N$_2$ leads to spontaneous reduction of the Ru(III) bromo complex and isolation in quantitative yield of RuBr$_2$(PØ$_3$)$_3$ as a
sharp-melting, red-brown, microcrystalline product. Infrared spectroscopic data (identical with RuCl$_2$(PO$_3$)$_3$ except in the region below 350 cm$^{-1}$) and microanalyses establish the complex as RuBr$_2$(PO$_3$)$_3$. This formulation is confirmed by a $^{31}$P-$^1$H n.m.r. spectrum in CH$_2$Cl$_2$/d$_6$-acetone at 183 K which shows a triplet at $\delta$$_P$ 80.1 ppm and doublet at $\delta$$_P$ 27.5 ppm ($^2$J$_{P\mathbf{H}}$ 29.3 Hz), an AB pattern centred at $\delta$$_P$ 58.2 ppm ($^2$J$_{AB}$ 41.5 Hz; $\gamma_{AB}$ 162.4 Hz) and a singlet due to free PO$_3$ at $\delta$$_P$ -8.1 ppm (see Figure 3.1). These patterns, positions and coupling constants closely parallel those ascribed by Caulton et al as representing RuBr$_2$(PO$_3$)$_3$ in a tertiary mixture containing RuBr$_2$(PO$_3$)$_3$, RuClBr(PO$_3$)$_3$ and RuCl$_2$(PO$_3$)$_3$ (210).

The high degree of consistency shown by the chemical shifts and coupling constants on changing from RuCl$_2$(PO$_3$)$_3$ to RuBr$_2$(PO$_3$)$_3$ strongly indicates that they both have the same square pyramidal structure. The formation of the binuclear complex [RuBr$_2$(PO$_3$)$_2$]$_2$ (42), which gives rise to the AB pattern in the $^{31}$P-$^1$H n.m.r. spectrum at $\delta$$_P$ 58.2 ppm may be accounted for in an exactly analogous manner to that of [RuCl$_2$(PO$_3$)$_2$]$_2$ (42) (122,210) from RuCl$_2$(PO$_3$)$_3$ i.e. dissociation of PO$_3$ to give "RuX$_2$(PO$_3$)$_2" (X = Cl\textsuperscript{-}, Br\textsuperscript{-}) which may then undergo self-dimerisation (Equation [3]). Both RuX$_2$(PO$_3$)$_3$

(X = Cl\textsuperscript{-}, Br\textsuperscript{-}) exhibit fluxional behaviour in solution since on raising the temperature the $^{31}$P-$^1$H n.m.r.
doublet and triplet patterns first broaden, then coalesce at ca. 250 K and finally give rise to sharp singlets at $\delta$$_P$ 41.1 ppm (X = Cl\textsuperscript{-})(122) and $\delta$$_P$ 43.8 ppm (X = Br\textsuperscript{-})(210).
Figure 3.1  $^{31}\text{P}-\text{^1H\ n.m.r.\ Spectrum\ of\ RuBr}_2(\text{P}_3)_3\ in\ \text{CH}_2\text{Cl}_2/d^6\text{-acetone\ at\ 183}\ K$
Having prepared RuBr₂(P₃O)₃ in pure form it was hoped to use it to prepare samples of RuBr₂(CO)(P₃O)₂(dmf), RuBr₂(CO)(P₃O)₂(MeOH), and ultimately the triple bromo bridged complex Ru₂Br₄(CO)(P₃O)₄ (37) (from the reaction of equimolar amounts of RuBr₂(P₃O)₃ and RuBr₂(CO)(P₃O)₂(MeOH)).

Thus, briefly stirring a warm solution of RuBr₂(P₃O)₃ in dimethyl formamide while passing CO gas gave rise to an orange microcrystalline precipitate of RuBr₂(CO)(P₃O)₂(dmf) in high yield. Microanalytical and infrared spectroscopic data (νC=O 1926 cm⁻¹, νC=O (dmf) 1650 cm⁻¹) are consistent with this formulation. The ³¹P-{¹H} n.m.r. spectra in CDCl₃ and CH₂Br₂/d₆-acetone at 298 K, which consists of a singlet at δP 35.5 ppm (c.f. δP 33.9 ppm for the chloro analogue) (182, 209), suggest that no halide exchange occurs under these conditions, and that the structure is of type (43).
Heating RuBr$_2$(CO)(PØ$_3$)$_2$(dmf) under reflux in MeOH gives a sharp-melting, non-conducting creamy-yellow precipitate, shown by elemental analysis and infrared spectroscopic data ($\nu_{C=O}$ 1920 cm$^{-1}$, $\nu_{O-H}$(MeOH) 3500 cm$^{-1}$ (broad)) to be RuBr$_2$(CO)(PØ$_3$)$_2$(MeOH). A $^{31}$P-$^1$H n.m.r. spectrum in CDCl$_3$ at ambient temperature shows a singlet at $\delta$ $^P$ 35.6 ppm suggesting that this complex also has the structure (43).

A 1:1 molar ratio of RuBr$_2$(PØ$_3$)$_3$ and RuBr$_2$(CO)(PØ$_3$)$_2$(MeOH) in refluxing acetone gives rise to a red-brown microcrystalline solid in high yield. Microanalytical and infrared spectroscopic data ($\nu_{C=O}$ 1960 cm$^{-1}$) are in excellent agreement with the desired formulation Ru$_2$Br$_4$(CO)(PØ$_3$)$_4$ (37).

A $^{31}$P-$^1$H n.m.r. spectrum of this complex in degassed C$_6$D$_5$CD$_3$ at 183 K shows two AB quartets (Figure 3.2), one centred at $\delta$ $^P$ 50.4 ppm ($^2J_{AB}$ 35.4 Hz; $^6AB$ 74.0 Hz) and the other at $\delta$ $^P$ 37.7 ppm ($^2J_{AB}$ 20.8 Hz; $^6AB$ 113.4 Hz). The well-known triple chloro bridged complex Ru$_2$Cl$_4$(CO)(PØ$_3$)$_4$ (19) has a very similar $^{31}$P-$^1$H n.m.r. spectrum, in the same solvent at the same temperature, consisting of an AB pattern at $\delta$ $^P$ 48.4 ppm ($^2J_{AB}$ 38.5 Hz; $^6AB$ 80.3 Hz) and another at $\delta$ $^P$ 39.1 ppm ($^2J_{AB}$ 25.0 Hz; $^6AB$ 63.8 Hz) (182). Thus there seems little doubt that Ru$_2$Br$_4$(CO)(PØ$_3$)$_4$ has structure (37), which like the chloro complex (19), is believed to have the terminal halide end of the molecule associated with the high frequency resonance in the $^{31}$P-$^1$H n.m.r. spectrum, while the CO end is associated with the low frequency resonance (182).
Figure 3.2 \[ ^{31}P-{ }^{1}H \text{ n.m.r. Spectrum of } \text{Ru}_2\text{Br}_4(\text{CO})(\text{P}0_3)_{4} \]
in \( \text{CD}_3\text{C}_6\text{D}_5 \) at 183 K

\[ \delta_p \quad 50.4 \text{ ppm} \quad \delta_p \quad 37.7 \text{ ppm} \]
However, the $^{31}\text{P-}{^1\text{H}}$ n.m.r. spectrum of (37) in C$_6$D$_5$CD$_3$ changes significantly on increasing the temperature above 273 K. Thus by 293 K, the two AB resonances have lost their couplings and broadened appreciably. At 313 K the resonances are very broad with no readily identifiable band centres and at 333 K the two broad resonances begin to coalesce to singlets so that at 363 K, two sharp singlets are observed at $\delta_p$ 48.3 and $\delta_p$ 38.8 ppm. On cooling the solution back to 273 K the original two AB patterns return and hence the rearrangement occurring in solution is reversible.

Since the above reversible rearrangement process is independent of the concentration of (37) in solution it would seem likely that the process is intramolecular in nature. This is confirmed by the rapid bridge cleavage of (37) in C$_6$D$_5$CD$_3$ at 298 K in the presence of a stoichiometric amount of PØ$_3$ i.e. intermolecular exchange of free and bound phosphine does not occur.

A plausible explanation of the temperature dependence of the $^{31}\text{P-}{^1\text{H}}$ n.m.r. data is the facile isomerisation of (37) to (44) (see Figure 3.3) via an intermediate of type (45). Certainly the two broad $^{31}\text{P-}{^1\text{H}}$ n.m.r. resonances can be readily accounted for by invoking a fast bridge/terminal halide exchange process via such an intermediate, since the environment of its PØ$_3$ groups would be averaged. Similarly, the formation of the new isomer, (44), with a plane of symmetry, in which the phosphines at either end of the
molecule are equivalent, readily explains the observation of the two sharp singlets in the $^{31}\text{P}-{^1}\text{H}$ n.m.r. spectra at high temperatures.

**Figure 3.3**

Isomerisation of \( \text{Ru}_2\text{X}_4(\text{CO})(\text{P}0_3)_4 \)

\[
\text{OC} \quad \begin{array}{c}
\text{X} \\
\text{Ru} \\
\text{P}0_3
\end{array} \quad \text{X} \\
\begin{array}{c}
\text{Ru} \\
\text{P}0_3
\end{array} \quad \text{OC} \\
\text{X} \\
\text{Ru} \\
\text{P}0_3
\]

(37)

\[
\text{OC} \quad \begin{array}{c}
\text{X} \\
\text{Ru} \\
\text{P}0_3
\end{array} \quad \text{X} \\
\begin{array}{c}
\text{Ru} \\
\text{P}0_3
\end{array} \quad \begin{array}{c}
\text{X} \\
\text{Ru} \\
\text{P}0_3
\end{array} \quad \text{OC}
\]

(44)

\[
\text{OC} \quad \text{Ru} \quad \begin{array}{c}
\text{P}0_3
\end{array} \quad \text{Ru} \quad \text{X} \\
\text{X} \\
\text{OC} \\
\text{S}
\]

(45)

\( (X = \text{Cl}^-, \text{Br}^-) \)

\( (S = \text{solvent}) \)
Models of isomers (37) and (44) clearly indicate that there is a greater steric interaction in the eclipsed isomer (44), thus helping to explain the predominance of (37) at low temperature. Further evidence for the greater steric interaction of eclipsed PØ₃ groups in such triple halide bridged complexes is given by the following series of compounds:– (PR₃)₂ΥRuCl₃RuCl(PR₃)₂ (19) and
[(PR₃)₂ΥRuCl₃RuΥ(PR₃)₂]BΟ₄ (21) (Υ = CO, CS; PR₃ = PØ₃, P(E-tol)₃)(182–184). These are all produced from monomer coupling reactions where two possible isomers could exist and yet only the staggered isomer is found. In contrast, the less sterically demanding complexes (PØ₃)₂ΥRuCl₃RuΥCl(PØ₃) (20) (Υ = CO, CS; PR₃ = PØ₃, P(E-tol)₃)(182,183) (again synthesised from monomer coupling reactions) exist in all three of their possible isomeric forms.

In order to investigate the possibility that triple chloro bridged complexes may also undergo a similar terminal/bridging halide exchange, a sealed tube 3¹P-{¹H} n.m.r. study was conducted on Ru₂Cl₄(CO)(PØ₃)₄ (19) in C₆D₅CD₃ in the temperature range 183–373 K. The data at 183 K in C₆D₅CD₃ has already been detailed earlier in this section. Two AB patterns are observed, one centred at δ_p 48.4 ppm and the other at δ_p 39.1 ppm and this situation prevails up to 333 K. However, by 353 K both resonances are broadened and phosphorus-phosphorus coupling is lost. By 373 K the two AB patterns coalesce to give broad resonances centred at δ_p 48.7 ppm and δ_p 39.4 ppm. On cooling the two AB resonances return, with positions and coupling constants unaltered.
Although the chloro complex (19) in C₆D₅CD₃ could not be heated above 373 K in search of two sharp singlets (as observed for its bromo analogue (37)) it seems clear that the same terminal/bridging halide exchange is occurring.

The lower thermal barrier to isomerisation exhibited by the bromo complex (37) with respect to its chloro analogue (19) probably reflects the longer, weaker bonds which bromide, having both a smaller charge/radius ratio and greater polarisability than chloride, generally forms with Ru(II) centres.

Finally, preliminary studies regarding the reactions of RuBr₂(PØ₃)₃ with small, basic, tertiary phosphines such as PMe₂Ø suggest that exactly analogous products to those formed by RuCl₂(PØ₃)₃ are obtained. Hence, reacting RuBr₂(PØ₃)₃ with a three fold excess of PMe₂Ø in refluxing MeOH under N₂ produces a bright yellow microcrystalline precipitate [Ru₂Br₃(PMe₂Ø)_6]Br in near quantitative yield.

Infrared spectroscopic data (identical with [Ru₂Cl₃(PMe₂Ø)_6]Cl in the region 4000-250 cm⁻¹) and microanalytical data support this formulation, which is further established by a singlet at δp 18.2 ppm in the ³¹P-{¹H} n.m.r. spectrum in CDCl₃ at 298 K and by electrochemical studies in CH₂Cl₂ (see Chapter 5).
Thus, using phosphines which are less basic than PMe$_2\theta$ e.g. PMe$_2\theta$, PEt$_2\theta$, PCl$_2\theta$ and non-polar solvents it should be possible to synthesise the bromo analogues of the triple chloro bridged neutral complexes Ru$_2$Cl$_4$(PR$_3$)$_5$ (PR$_3$ = PMe$_2\theta$, PEt$_2\theta$, PEt$_2\theta$, PCl$_2\theta$) (122) (16) by this route.

3.3(b) **Nucleophilic attack at bridging sites of triple bridged Ru$_2$(II/II) binuclear complexes**

(bridging group replacement)

(i) **Attack of hydroxide ion on Ru$_2$Cl$_4$Y(PØ$_3$)$_4$$^\dagger$$^\dagger$

\(Y = \text{CO, CS} \) (19)

In Chapter 2 it was shown that specific nucleophilic attack at terminal sites in triple chloro bridged Ru$_2$(II/II) complexes, e.g. in the synthesis of [Ru$_2$Cl$_3$(PEt$_3\theta$)$_5$(MeCN)]BØ$_4$ (32) by displacement of terminal chloride from Ru$_2$Cl$_4$(PEt$_2\theta$)$_5$ (16), was the exception rather than the rule. In general bridge cleavage occurs to give unidentified mixtures of products.

However, during $^{31}$P-$^1$H n.m.r. studies on Ru$_2$Cl$_4$(CS)(PØ$_3$)$_4$ (19) plus an excess of dilute aqueous NaOH in CDCl$_3$ at 298 K, a number of interesting observations were made. Thus within 30 minutes the two AB patterns associated with (19) centred at $\delta_P$ 48.3 ppm ($^2$J$_{AB}$ 37.4 Hz; $\delta_{AB}$ 94.0 Hz) and $\delta_P$ 36.1 ppm ($^2$J$_{AB}$ 24.6 Hz; $\delta_{AB}$ 54.9 Hz) were largely replaced by a singlet at $\delta_P$ 53.7 ppm and an AB pattern centred at $\delta_P$ 39.8 ppm ($^2$J$_{AB}$ 24.4 Hz; $\delta_{AB}$ 211.0 Hz)
(produced at the expense of a transient singlet at $\delta_P$ 40.7 ppm) of comparable intensity. Eventually all the original resonances associated with (19) disappeared, while the newly formed singlet and AB pattern began to lose intensity and two new AB patterns centred at $\delta_P$ 56.7 ppm ($^2J_{AB}$ 34.2 Hz; $\delta_{AB}$ 38.9 Hz) and $\delta_P$ 39.7 ppm ($^2J_{AB}$ 23.2 Hz; $\delta_{AB}$ 120.1 Hz) (Figure 3.4) appeared. After 12 hours, only the species associated with the two new AB patterns was indicated by a $^{31}P-^1H$ n.m.r. spectrum (Figure 3.5).

A scaled-up version of the n.m.r. tube experiment involving prolonged shaking of (19) in CH$_2$Cl$_2$ and dilute aqueous NaOH yielded a sharp-melting, non-conducting, bright orange, microcrystalline precipitate in low yield. Elemental analysis and infrared spectroscopic data ($v_{O-H}$ 3550, 3580 cm$^{-1}$, $v_C=S$ 1270 cm$^{-1}$ and no observed terminal $v_{Ru-Cl}$ band) (Figure 3.6) suggest a compound of formula Ru$_2$Cl(OH)$_3$ (CS)(PO$_3$)$_4$. This sparingly soluble compound shows no discernable hydroxide resonances in its $^1H$ n.m.r. spectrum in CDC$_3$ at 298 K. A $^{31}P-^1H$ n.m.r. spectrum in CDC$_3$ at ambient temperature shows the two familiar AB patterns centred at $\delta_P$ 56.7 ppm and $\delta_P$ 39.7 ppm (Figure 3.5). Selectively decoupling the phenyl protons makes no difference to the $^{31}P$ n.m.r. spectrum indicating that no terminal or bridging hydrides are present.
Figure 3.4 $^{31}\text{P}-{^1\text{H}}$ n.m.r. Spectrum of $\text{Ru}_2\text{Cl}_4(\text{CS})(\text{P\O}_3)_4$

+ Aqueous NaOH in CDCl$_3$ at 298 K

$\delta_p$ 53.7 ppm

$\delta_p$ 56.7 ppm

$\delta_p$ 39.7 ppm

$\delta_p$ 39.8 ppm
Figure 3.5 \[ \Delta P - (^1H) \text{n.m.r. Spectrum of Ru}_2\text{Cl(OH)}_3(CS)(P\dbar)_4 \text{ in CDCl}_3 \text{ at 298 K} \]
Figure 3.6  Infrared Spectrum of Ru$_2$Cl(OH)$_3$(CS)(PØ$_3$)$_4$
Before discussing possible structures for this compound and its mode of formation, it is worthwhile describing the preparation of its carbonyl analogue \( \text{Ru}_2\text{Cl}(\text{OH})_3(\text{CO})(\text{PO}_3)_4 \). This non-conducting, bright orange microcrystalline complex is synthesised in a similar manner to \( \text{Ru}_2\text{Cl}(\text{OH})_3(\text{CS})(\text{PO}_3)_4 \) i.e. by prolonged shaking of \( \text{Ru}_2\text{Cl}_4(\text{CO})(\text{PO}_3)_4 \) (19) in \( \text{CH}_2\text{Cl}_2 \) and dilute aqueous \( \text{NaOH} \). Monitoring this reaction by \( ^{31}\text{P}-(^1\text{H}) \) n.m.r. spectroscopy in \( \text{CDCl}_3 \) at 298 K shows the rapid loss of the two AB patterns associated with (19) and the simultaneous rapid growth of a singlet at \( \delta_p \) 53.7 ppm and an AB pattern at \( \delta_p \) 44.7 ppm (\( ^2J_{\text{AB}} \) 23.4 Hz; \( \delta_{\text{AB}} \) 209.7 Hz) (produced at the expense of a transient singlet at \( \delta_p \) 45.7 ppm) of comparable intensity.

As in the formation of its Cs analogue, the singlet and AB pattern are then slowly replaced by two new AB patterns, centred at \( \delta_p \) 56.7 ppm (\( ^2J_{\text{AB}} \) 35.1 Hz; \( \delta_{\text{AB}} \) 18.1 Hz) and \( \delta_p \) 45.1 ppm (\( ^2J_{\text{AB}} \) 23.1 Hz; \( \delta_{\text{AB}} \) 119.2 Hz) (Figure 3.7). The microanalytical and infrared spectroscopic data (\( \nu_{\text{O-H}} \) 3580, 3600 cm\(^{-1} \), \( \nu_{\text{C}=\text{O}} \) 1933 cm\(^{-1} \) and no observed terminal \( \nu_{\text{Ru-Cl}} \) band) are all in good agreement with the formulation \( \text{Ru}_2\text{Cl}(\text{OH})_3(\text{CO})(\text{PO}_3)_4 \).

The \( ^{31}\text{P}-(^1\text{H}) \) n.m.r. and infrared spectra are very useful in determining the detailed structure of these unusual mixed bridged complexes (\( \text{PO}_3 \))\(_2\text{YRuCl}(\text{OH})_2\text{Ru}(\text{OH})_2(\text{PO}_3 \))\(_2\) (\( \text{Y} = \text{CO}, \text{CS} \)) which are represented below as (46). Fortunately useful precedents such as (\( \text{PO}_3 \))(diazadiene)\( \text{RuCl}(\text{OH})_2\text{RuH}(\text{PO}_3 \))\(_2\) (39) are known.
Figure 3.7 $^{31}\text{P}-{^1\text{H}}$ n.m.r. Spectrum of $\text{Ru}_2\text{Cl}(\text{OH})_3(\text{CO})(\text{P}\text{OP}_3)_4$

in CDCl$_3$ at 298 K

$\delta_p$ 56.7 ppm

$\delta_p$ 45.1 ppm
Structure (46) is in agreement with the non-observance of a terminal $\nu_{\text{Ru-Cl}}$ band in the far-infrared region. In addition, comparing $(\text{PO}_3)_2\text{YRuCl}_3\text{RuCl}(\text{PO}_3)_2$ (19) with $(\text{PO}_3)_2\text{YRuCl(OH)}_2\text{Ru(OH)}(\text{PO}_3)_2$ (46) ($Y = \text{CO, CS}$) we note that the $31P$ n.m.r. chemical shift associated with $\text{PO}_3^-$ groups is increased by ca. 4.2 ppm as against ca. 8.5 ppm for $\text{PO}_3^{\prime \prime}$ groups. This is in accord with replacement of terminal chloride ion by the more deshielding hydroxide ion (in addition to the bridge replacements which affects both centres).

The formation of only one isomer of (46) reflects the previously noted steric favourability of staggered rather than eclipsed $\text{PO}_3$ ligands. The $\delta_{AB}$ values of the two AB patterns associated with the terminal OH$^-$ and terminal $Y$ ($Y = \text{CO, CS}$) ends of (46) are very different i.e. on average ca. 30 Hz for the high frequency $\text{PO}_3^{\prime \prime}$ pair and ca. 120 Hz for the low frequency $\text{PO}_3^\prime$ pair. This may be simply explained in terms of the $\text{PO}_3^\prime$ ligands being more magnetically inequivalent (one trans to a bridging Cl$^-$ ion while the other is trans to a bridging OH$^-$ ion) than the $\text{PO}_3^{\prime \prime}$ pair which are both trans to bridging hydroxide ions.
The small decrease in the value of $v_{\text{C=O}}$ from 1951 cm$^{-1}$ (19) ($Y = \text{CO}$) to 1933 cm$^{-1}$ (46) ($Y = \text{CO}$) and the parallel decrease of $v_{\text{C=S}}$ from 1284 cm$^{-1}$ to 1270 cm$^{-1}$ probably reflects the better $\sigma$-donor characteristics of the $\text{OH}^-$ ion compared to that of $\text{Cl}^-$ ion (a weak $\pi$-donor). This will tend to increase the effective electron density on the metal, leading to an expansion of filled metal $\pi$ orbitals, and thereby allowing a greater $\pi$-overlap between the metal and CO.

Two very recent pieces of $^{31}\text{P-}^{1\text{H}}$ n.m.r. data shed considerable light on the nature and structures of the intermediates in the synthesis of (46) from (19) ($Y = \text{CO, CS}$) i.e. the singlet at $\delta_p$ 53.7 ppm, the transient singlets at $\delta_p$ 40.7 ppm ($Y = \text{CS}$) and $\delta_p$ 45.7 ppm ($Y = \text{CO}$) and their rearrangement products with AB patterns centred at $\delta_p$ 39.8 ppm ($Y = \text{CS}$) and $\delta_p$ 44.7 ppm ($Y = \text{CO}$). First, a $^{31}\text{P-}^{1\text{H}}$ n.m.r. study of the reaction between $\text{RuCl}_2(\text{PO}_3)_3$ and dilute aqueous NaOH in CDCl$_3$ shows the rapid formation of free $\text{PO}_3$ together with a species exhibiting a singlet at $\delta_p$ 53.7 ppm. This clearly suggests that the singlet at $\delta_p$ 53.7 ppm and the AB patterns centred at $\delta_p$ 39.8 ppm ($Y = \text{CS}$) and $\delta_p$ 44.7 ppm ($Y = \text{CO}$) observed in the course of preparing (46) are derived from two separate species rather than one binuclear molecule with inequivalent phosphines.
Second, a $^{31}\text{P}\text{-}^{1}\text{H}$ n.m.r. sealed tube experiment in CDC$_3$ at 298 K shows that the formation of the binuclear complexes (46) ($Y = \text{CO, CS}$) is reversible, at least to the "singlet plus AB pattern" stage. Thus allowing (46) ($Y = \text{CO}$) to stand in a sealed n.m.r. tube in CDC$_3$ at ambient temperature for several hours produces a decrease in intensity of the two AB patterns (Figure 3.7) due to growth of a singlet at $\delta_p$ 53.7 ppm and a transient singlet at $\delta_p$ 45.7 ppm ($\delta_p$ 40.7 ppm when $Y = \text{CS}$). After several days the original AB patterns are wholly replaced by the singlet at $\delta_p$ 53.7 ppm and an AB pattern centred at $\delta_p$ 44.7 ppm (Figure 3.8(a)) ($\delta_p$ 39.8 ppm when $Y = \text{CS}$) i.e. the first observed intermediates of (46) on reacting (19) ($Y = \text{CO, CS}$) with aqueous NaOH. Furthermore, measurement of the AB pattern centred at $\delta_p$ 44.7 ppm on a very narrow spectral width clearly shows that the two low frequency lines are split into doublets (with $^{4}J_{\text{PP}} \approx 1.5$ Hz) whilst the two high frequency lines are unaltered (Figure 3.8(b)). Reducing the temperature from 298 K to 213 K has little effect on the AB pattern other than shift its position by a few tenths of a ppm.

Comparing $^{31}\text{P}$ n.m.r. chemical shifts, $\delta_{\text{AB}}$ and coupling constants of the AB centred at $\delta_p$ 44.7 ppm with those associated with the AB pattern of the $Y$ end of (46) ($Y = \text{CO}$), it becomes obvious that a binuclear complex of the type $[\{\text{P}_3\}_2\text{YRuCl(OH)}_2\text{RuY(P}_3\}_2]\text{Cl}$ (47) ($Y = \text{CO, CS}$) is formed.
Figure 3.8 $^{31}$P-$^1$H n.m.r. Spectrum of the Rearrangement Products of Ru$_2$Cl(OH)$_3$(CO)(P)$_2$Cl$_4$ in CDCl$_3$ at 298 K

$\delta_P$ 53.7 ppm

$\delta_P$ 44.7 ppm

Expansion of the Above AB Pattern

$^{31}$P-$^1$H n.m.r. Spectrum of the Above Singlet at 213 K in CDCl$_3$
It is therefore reasonable to propose that the initial Y containing fragment (Y = CO, CS) from (46) dissolved in CDCl$_3$ are the transient species "RuCl(OH)Y(PØ$_3$)$_2$" (giving rise to $^{31}$P-{$^1$H} n.m.r. singlet resonances in CDCl$_3$ at $\delta_p$ 45.7 ppm (Y = CO) and $\delta_p$ 40.7 ppm (Y = CS)) which may then rapidly self-condense to give (47) (c.f. the $^{31}$P-{$^1$H} n.m.r. singlet species RuCl$_2$Y(PØ$_3$)$_2$(MeOH) (Y = CO, CS) which self-dimerise to give the $^{31}$P-{$^1$H} n.m.r. AB pattern species [((PØ$_3$)$_2$YRuCl$_3$RuY(PØ$_3$)$_2$]Cl (21))$^{182}$.

The observation of a $^4$J$_{pp}$ coupling of ca. 1.5 Hz on the low frequency half (i.e. that associated with the chemically equivalent PØ$_3$ groups (A) and (A') which are trans to bridging Cl$^-$ ion) of the $\delta_p$ 44.7 ppm AB pattern of (47) (Y = CO) is consistent with a "trans" four bond coupling between the magnetically inequivalent phosphorus nuclei of PØ$_3$ groups (A) and (A'). Due to the angle effect, imposed by (47) adopting the more sterically favoured structure with staggered PØ$_3$ groups, no four bond "cis" coupling is seen on either the high or low frequency halves of the AB pattern.

Since compound (46) in CDCl$_3$ is thought to cleave initially to give the fragment "RuCl(OH)Y(PØ$_3$)$_2$" (Y = CO, CS), then it is reasonable to suggest that the accompanying singlet species at $\delta_p$ 53.7 ppm is derived from "Ru(OH)$_2$(PØ$_3$)$_2$".
On warming the solution back to ambient temperature the singlet at $\delta_p 53.7$ ppm is restored. This reversible process may parallel the situation found for the postulated isomerisation of $\text{Ru}_2X_4(CO)(\text{P}O_3)_4$ ($X = \text{Cl}^-, \text{Br}^-$) i.e. exchange of terminal and bridging hydroxide ligands leading to a rearrangement in structure.

Hydroxo species such as (48a,b,c) are not wholly unprecedented since their chloro analogues have been suggested as minor constituents on dissociation of $\text{P}O_3$ from $\text{RuCl}_2(\text{P}O_3)_3$ in CDC13 (122).

Overall it would appear that Scheme 3.2 represents a reasonable approximation to the formation and rearrangement of $\text{Ru}_2\text{Cl}(\text{OH})_3\text{Y}(\text{P}O_3)_4$ (46) ($\text{Y} = \text{CO}, \text{CS}$). Thus in the presence of $\text{OH}^-$ ions, $\text{Ru}_2\text{Cl}_4\text{Y}(\text{P}O_3)_4$ (19) ($\text{Y} = \text{CO}, \text{CS}$) bridge cleaves to initially give the transient, coordinatively-unsaturated monomers "$\text{Ru}(\text{OH})_2(\text{P}O_3)_2$" (not observed) and "$\text{RuCl}(\text{OH})\text{Y}(\text{P}O_3)_2$" ($\text{Y} = \text{CO}, \text{CS}$) (observed as $^{31}\text{P}-^{1}\text{H}$ n.m.r. singlet resonances). The unsaturated species then readily self-dimerise to give $[\text{Ru}(\text{OH})_2(\text{P}O_3)_2]_2$ (48) and $[\text{Ru}_2\text{Cl}(\text{OH})_2\text{Y}_2(\text{P}O_3)_4]_{\text{Cl}}$ (47) ($\text{Y} = \text{CO}, \text{CS}$) respectively. In the presence of excess $\text{OH}^-$ ion these binuclear species undergo bridge cleavage
Scheme 3.2 Proposed Formation and Rearrangement Reactions of Ru$_2$Cl(OH)$_3$Y(PO$_3$)$_4$ (Y = CO, CS)

Scheme with chemical structures and reactions:

\[
\text{RuCl}_2(\text{PO}_3)_3 \quad \text{CDCl}_3 \quad \text{OH}^- \\
\text{Ru(OH)}_2(\text{PO}_3)_2^+ + \text{RuCl(OH)Y(PO}_3)_2^+ \quad \text{OH}^- \\
\text{Ru}^2\text{Cl(OH)}_3\text{Y(PO}_3)_4 (\text{Y} = \text{CO, CS})
\]

\[53.7 \text{ (S)}^a\]
\[54.2 \text{ (AB)}^b\]

\[45.7 \text{ (S)}^a \quad 40.7 \text{ (S)}^a \quad 44.7 \text{ (AB)}^a \quad 39.8 \text{ (AB)}^a\]

\[56.7 \text{ (AB)}^a \quad 56.7 \text{ (AB)}^a \quad 39.7 \text{ (AB)}^a\]

\[\delta_p \text{ in ppm at } 298 \text{ K in CDCl}_3; \quad (\text{S}) = \text{singlet}, (\text{AB}) = \text{AB resonance centre}\]
\[\text{as (a) but at } 213 \text{ K}.\]
to reform the coordinatively unsaturated monomers which
cross-couple to give (46). In the absence of hydroxide ion,
(46) rapidly rearranges to the transient unsaturated monomers
and thence to (47) and (48). Although the mode of
formation and rearrangement of (46) in Scheme 3.2 helps
to explain most of the experimental observations, it
undoubtedly requires further refinement in a number of
respects e.g. accounting for the formation of coordinatively
unsaturated monomers in the presence of a large excess of
OH$^-$. ion.

Attempts to extend the range of this reaction by using
other nucleophiles failed. For example, reaction of (19)
($Y = CS$) with NaSH, NaOMe or NaBr in CDCl$_3$ lead only to
mixtures which show a number of singlet resonances in their
$^{31}$P-$^1$H n.m.r. spectra. Attempts to extend the reaction
with OH$^-$ to other complexes also failed e.g. $^{31}$P-$^1$H n.m.r.
studies show that no change occurs on prolonged treatment
of [Ru$_2$Cl$_3$(PMe$_2$Ø)$_6$]Cl with concentrated aqueous NaOH
in CDCl$_3$.

3.3(b) (ii) Reactions of [Ru$_2$(OH)$_3$(PMe$_2$Ø)$_6$] (33) with
acids HX

The $^{31}$P-$^1$H n.m.r. spectra in CDCl$_3$ at 298 K of
products claimed by Shaw et al to be the triple bromo and
iodo bridged complexes [Ru$_2$X$_3$(PMe$_2$Ø)$_6$]X ($X = Br^-$, I$^-$)\(^{(118)}\)
show the materials to be mixtures. For example the material
synthesised by heating [Ru$_2$Cl$_3$(PMe$_2$Ø)$_6$]Cl under reflux
in Pr\textsuperscript{2+}OH with an excess of NaI exhibits a singlet at \( \delta_p \) 20.4 ppm due to unreacted \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ø})_6]^{+}\) and a singlet at \( \delta_p \) 10.8 ppm assigned to \([\text{Ru}_2\text{I}_3(\text{PMe}_2\text{Ø})_6]^{+}\). Similarly, the product obtained by mixing "RuCl\textsubscript{3}.3H\textsubscript{2}O" with an excess of LiBr and PMe\textsubscript{2}Ø in refluxing Pr\textsuperscript{2+}OH exhibits four singlets at \( \delta_p \) 20.4, 19.7, 19.1 and 18.2 ppm in intensity ratio 1:2:4:3. The highest frequency singlet arises from \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ø})_6]^{+}\) and that at lowest frequency from \([\text{Ru}_2\text{Br}_3(\text{PMe}_2\text{Ø})_6]^{+}\) while the others are assigned to the \([\text{Ru}_2\text{Cl}_x\text{Br}_{3-x}(\text{PMe}_2\text{Ø})_6]^{+}\) \((x = 1, 2)\) complexes.

However, the availability of the hydroxo bridged complex (33) suggests a means of obtaining chloro, bromo or iodo bridged complexes without scrambling. Thus after treating (33) with hydrochloric acid, (an experiment prompted by the previously mentioned electrochemical observation, [see Section 3.3(a) (i)]) , the \(^{31}\text{P}\}-{^1}\text{H} \text{n.m.r. spectrum in CDC\textsubscript{13} at 298 K exhibits only a singlet at } \delta_p \text{ 20.4 ppm, indicating complete conversion to } [\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ø})_6]^+}. Analogous n.m.r. tube experiments using HBr and HI also show the clean conversion of \([\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{Ø})_6]PF_6 \text{ (33) to } [\text{Ru}_2\text{Br}_3(\text{PMe}_2\text{Ø})_6]^+ \text{ and } [\text{Ru}_2\text{I}_3(\text{PMe}_2\text{Ø})_6]^+ \text{ respectively.}

The n.m.r. tube reactions can be easily scaled-up. Thus shaking a concentrated CH\textsubscript{3}NO\textsubscript{2} solution of (33) with concentrated aqueous HX \((X = \text{Cl}^-, \text{Br}^-, \text{I}^-)\) yields the corresponding \([\text{Ru}_2X_3(\text{PMe}_2\text{Ø})_6]X\text{ in high yield.}
Microanalytical and infrared spectroscopic data together with $^{31}P-{\text{H}}$ n.m.r. data recorded in CDCl$_3$ solutions at 298 K confirm the above formulations for the recrystallised products. Electrochemical studies on these cations (to be discussed in Chapter 5) support these conclusions.

The mechanism of formation for the above reaction is not established, but a pathway involving monomer formation, as shown in Scheme 3.3, is a reasonable possibility. However, it should be noted that a stepwise or concerted bridging ligand exchange process, though apparently unlikely, cannot be dismissed at this point.

**Scheme 3.3**

Postulated mechanism of formation of $[\text{Ru}_2X_3(\text{PMe}_2\text{O})_6]^+$ from $[\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{O})_6]^+$ and HX

![Scheme 3.3](image)

The mechanism shown in Scheme 3.3 is consistent with the known tendency of "RuCl$_2$(PR$_3$)$_3" to dimerise in polar solvents to give $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$ (see Scheme 2.2).
3.4 Conclusions

In general the systematic formation of pure \([\text{Ru}_2X_3(\text{PR}_3)_6]X\) complexes \((X = \text{halides, pseudohalides etc.})\) should be possible by treatment of the appropriate \([\text{Ru}_2(\text{OH})_3(\text{PR}_3)_6]\text{PF}_6\) (made via literature methods) with the acids HX. Further extensions to synthesis of complexes of other terminal ligands e.g. \([\text{Ru}_2X_3L_6]X\) \((X = \text{halides, pseudohalides; } L = 4\text{-Mepy, MeCN etc.})\) may be possible using \([\text{RuH(cod)L}_3]\text{BOP}\) \((211)\) in an analogous manner to \([\text{RuH(cod)}_3]\text{PF}_6\) \((\text{PR}_3 = \text{PMe}_2\text{Ø}, \text{PMeØ}_3, \text{P(OMe)Ø}_2 \text{etc.})\) \((211)\) (see Section 3.3(a)(i)).

Direct reactions between neutral triple chloro bridged \(\text{Ru}_2(\text{II/II})\) binuclear complexes and nucleophiles are in general not very profitable. Only in the case where \(\text{Ru}_2\text{Cl}_4\text{Y(PØ}_3\text{)}_4\) \((19)\) \((\text{Y} = \text{CO, CS})\) was reacted with NaOH was fruitful recombination of monomers observed, and even then the process appears to be reversible in the absence of excess OH\(^{-}\) ion. Isolation of the "\(\text{Ru(OH)}_2(\text{PØ}_3)_2\)" fragment should be possible and may prove to be a useful starting point for the synthesis of other ruthenium hydroxo complexes.

The discovery of a convenient synthetic route to pure \(\text{RuBr}_2(\text{PØ}_3)_3\) means that a versatile precursor of further ruthenium bromo complexes is now available. The complex \(\text{Ru}_2\text{Br}_4(\text{CO})(\text{PØ}_3)_4\) \((37)\), synthesised from \(\text{RuBr}_2(\text{PØ}_3)_3\) and \(\text{RuBr}_2(\text{CO})(\text{PØ}_3)_2(\text{MeOH})\), has been shown to undergo reversible intramolecular rearrangements in solution. Nuclear magnetic resonance data \(^*\) consistent with bridge and terminal bromide exchange leading to a higher energy conformation in which
the P\(_3\) groups are eclipsed rather than staggered. Examination of the analogous chloro complex Ru\(_2\)Cl\(_4\)(CO)(P\(_3\))\(_4\) (19) reveals that the same phenomenon occurs at higher temperatures and this is believed to reflect the stronger, shorter metal-halide bonding in the -RuCl\(_3\)Ru+ core.

3.5 Experimental

Physical measurements were performed as described in Chapter 2.

Reagents

The following were prepared using literature methods:

\(\text{[RuH(cod)(NH}_2\text{NMe}_2)_3X} (X = \text{Bø}_4^-, \text{PF}_6^-)\) \(\text{[211]}\), Ru\(_2\)Cl\(_4\)Y(P\(_3\))\(_4\) \((Y = \text{CO, CS})\) \(\text{[182,184]}\) and \([\text{Ru}_2\text{Cl}_3\text{(PMe}_2\text{O})_6]\)\(_{\text{Cl}}\) \(\text{[122]}\).

**Tri-\(\nu\)-hydroxohexakis(dimethylphenylphosphine)diruthenium(II)-tetraphenylboronate**

\(\text{[RuH(cod)(NH}_2\text{NMe}_2)_3\text{Bø}_4\} (0.25 \text{~g})\) and a three fold excess of PMe\(_2\)Ø \((0.14 ~\text{ml})\) were maintained under \(\text{N}_2\) in refluxing degassed acetone \((20 ~\text{ml})\) and MeOH \((10 ~\text{ml})\) for 20 minutes to give a deep red solution. Degassed H\(_2\)O \((5 ~\text{ml})\) was then added to the solution which became bright yellow. The solution was left to reflux overnight under \(\text{N}_2\) and the pale yellow microcrystalline precipitate which formed was washed with MeOH and diethylether and dried in vacuo at 40\(^\circ\)C \((80\% \text{ yield})\).
M.P. 218-220°C, [Found: C, 60.5; H, 6.2. Calculated for C\textsubscript{72}H\textsubscript{89}BO\textsubscript{3}P\textsubscript{6}Ru\textsubscript{2}: C, 60.7; H, 6.3%].

Infrared spectrum: \( \nu_{\text{O-H}} = 3600 \text{ cm}^{-1} \) (m). \([\Lambda(1 \times 10^{-3} \text{ M}) \text{ in acetone} = 74 \text{ \(\Omega\)}^{-1} \text{cm}^{2} \text{mol}^{-1}].\)

**Tri-\(\mu\)-hydroxohexakis(dimethylphenylphosphine)diruthenium(II) hexafluorophosphate**

This was prepared as above, but starting with \([\text{RuH(cod)(NH\textsubscript{2}NMe\textsubscript{2})\textsubscript{3}]PF\textsubscript{6}. \) The pale yellow microcrystalline precipitate formed was washed with EtOH and diethylether and dried in vacuo at 40°C (76% yield).

M.P. 196-197°C, [Found: C, 47.0; H, 5.6. Calculated for C\textsubscript{48}H\textsubscript{69}F\textsubscript{6}O\textsubscript{3}P\textsubscript{7}Ru\textsubscript{2}: C, 47.0; H, 5.6%].

Infrared spectrum: \( \nu_{\text{O-H}} = 3600 \text{ cm}^{-1} \) (m) \([\Lambda(1 \times 10^{-3} \text{ M}) \text{ in acetone} = 121 \text{ \(\Omega\)}^{-1} \text{cm}^{2} \text{mol}^{-1}].\)

**Tri-\(\mu\)-ethylthiolhexakis(dimethylphenylphosphine)diruthenium(II) tetraphenylboronate**

This was prepared in the same way as the hydroxo complex but adding an excess of HSET (2 ml) in place of H\textsubscript{2}O after the red solution was formed. Heating this solution under reflux for a further 3 hours gave a yellow-green precipitate. This was washed with EtOH and dried in vacuo at 40°C (91% yield). M.P. 104-106°C (decomp.), [Found: C, 60.0; H, 6.7. Calculated for C\textsubscript{78}H\textsubscript{91}BP\textsubscript{6}Ru\textsubscript{2}S\textsubscript{3}: C, 61.1; H, 6.6%] \([\Lambda(1 \times 10^{-3} \text{ M}) \text{ in acetone} = 72 \text{ \(\Omega\)}^{-1} \text{cm}^{2} \text{mol}^{-1}].\)
(Triphenylbenzylphosphonium)[Tri-μ-bromohexakis(bromo)-diruthenate(III)]

"RuCl₃·3H₂O" (0.50 g) was dissolved in concentrated hydrobromic acid (48%) (50 ml) and EtOH (50 ml) and heated under reflux, under a N₂ atmosphere, for 2 hours. The deep purple solution produced was reduced in volume and treated with an aqueous saturated solution of Ø₃(ØCH₂)PCl (5 ml). This resulted in the immediate precipitation of a purple solid which was washed with H₂O and diethylether and dried in vacuo at 40°C (24% yield). M.P. 135-137°C (decomp) [Found: C, 44.3; H, 3.4; Br, 36.3; P, 4.4. Calculated for C₇₅H₆₆Br₉P₃Ru: C, 45.4; H, 3.3; Br, 36.3; P, 4.6%]. [λ(1 x 10⁻³ M) in CH₃NO₂ = 232 cm⁻² mol⁻¹].

Dibromotris(triphenylphosphine) ruthenium(II)

A solution of (Ø₃(ØCH₂)P)₃[Ru₂Br₉] (2.0 g) in degassed MeOH (150 ml) under N₂ was heated under reflux for 20 minutes, then filtered through celite. An excess of PØ₃ (6.0 g) was added to the resulting clear purple solution under N₂ and heating continued for a further 30 minutes. The red-brown microcrystalline precipitate which formed was collected by filtration, washed with EtOH and diethylether and dried in vacuo at 40°C (88% yield). M.P. 129-131°C, [Found: C, 61.7; H, 4.3. Calculated for C₅₄H₄₅Br₂P₃Ru: C, 61.9; H, 4.3%]. This compounds is non-conducting in CH₂Cl₂ and has an infrared spectrum (4000-300 cm⁻¹) which is identical with that of RuCl₂(PØ₃)₃.
Dibromo(NN-dimethylformamide) carbonyl bis(triphenylphosphine)-ruthenium(II)

RuBr$_2$(PØ$_3$)$_3$ (0.40 g) was suspended in warm (60°C), degassed, NN-dimethylformamide (20 ml) while carbon monoxide (ca. 1 atm.) was bubbled through the stirred solution for 30 seconds. The bright orange solution which formed was reduced in volume to ca. 3 ml at which point orange microcrystals precipitated. Further precipitation occurred on addition of excess EtOH. The orange microcrystalline solid was filtered, washed with EtOH and diethylether and dried in vacuo at 40°C (77% yield). M.P. 160-162°C, [Found: C, 54.0; H, 4.1; N, 1.4. Calculated for C$_{40}$H$_{37}$Br$_2$NO$_2$P$_2$Ru: C, 54.2; H, 4.2; N, 1.6%]. This compound is non-conducting in CH$_2$Cl$_2$. Infrared spectrum: $\nu_{\text{C=O}}$ 1926 cm$^{-1}$(s), $\nu_{\text{C=O (dmf)}}$ 1650 cm$^{-1}$(m).

Dibromo(methanol) carbonylbis(triphenylphosphine)ruthenium(II)

RuBr$_2$(CO)(PØ$_3$)$_2$(dmf) (0.30 g) was maintained under reflux in degassed MeOH (20 ml) for 3 hours under N$_2$. The orange suspension quickly lost colour to give a creamy yellow precipitate. This was filtered, washed with EtOH and diethylether and dried in vacuo at 40°C (93% yield). M.P. 142-144°C, [Found: C, 53.8; H, 3.9. Calculated for C$_{38}$H$_{34}$Br$_2$O$_2$P$_2$Ru: C, 54.0; H, 4.0%]. This complex is non-conducting in CH$_2$Cl$_2$. Infrared spectrum: $\nu_{\text{O-H (MeOH)}}$ 3500 cm$^{-1}$(m), $\nu_{\text{C=O}}$ 1920 cm$^{-1}$(s).
Tri-μ-bromo-a-carbonyl-g-bromo-tetrakis(triphenylphosphine)-
diruthenium(II)

The compound RuBr$_2$(PO$_3$)$_3$ (0.25 g) was heated under reflux in degassed acetone (60 ml) under a N$_2$ atmosphere with a 1:1 molar ratio of RuBr$_2$(CO)(PO$_3$)$_2$(MeOH) (0.20 g) for 9 hours. The red-brown microcrystalline precipitate which formed was filtered, washed with EtOH and diethylether and dried in vacuo at 40°C (74% yield). M.P. 142°C, [Found: C, 55.0; H, 4.1. Calculated for C$_{73}$H$_{60}$Br$_4$O$_4$P$_4$Ru$_2$: C, 55.1; H, 4.0%]. This compound is non-conducting in CH$_2$Br$_2$.

Infrared spectrum: $\nu_{C=O}$ 1960 cm$^{-1}$(s).

μ-d-chloro-di-μ-ef-hydroxo-a-carbonyl-g-hydroxo-tetrakis-
(triphenylphosphine)diruthenium(II)

The complex Ru$_2$Cl$_4$(CO)(PO$_3$)$_4$ (0.30 g) was shaken for 20 hours in degassed CH$_2$Cl$_2$ (20 ml) and aqueous 2M NaOH (10 ml). The dark brown solution formed in the non-aqueous phase was extracted into degassed C$_6$H$_6$ (30 ml). After volume reduction and addition of petroleum ether (B.P. 40-60°C) (5 ml) an orange solid precipitated, which was filtered and dried in air. The clear filtrate slowly deposited a small quantity of bright orange microcrystals which were filtered, washed with diethylether and dried in vacuo at 40°C. More microcrystalline material was obtained by redissolving the crude orange product in C$_6$H$_6$ and repeating the work-up procedure (total yield 15%).
M.P. 169-170°C, [Found: C, 63.5; H, 4.8; Cl, 2.7].
Calculated for C_{73}H_{63}ClO_{4}P_{4}Ru_{2}: C, 64.2; H, 4.6; Cl, 2.6%].
This sparingly soluble compound is non-conducting in CH_{2}Cl_{2}.
Infrared spectrum: \nu_{O-H} 3580, 3600 cm\(^{-1}\)(m), \nu_{C=O} 1933 cm\(^{-1}\)(s).

\(\mu\)-d-chloro-di-\(\mu\)-ef-hydroxo-a-thiocarbonyl-g-hydroxo-tetrakis-(triphenylphosphine)diruthenium(II)

This complex was synthesised from Ru_{2}Cl_{4}(CS)(P\(\Phi\)_{3})_{4} using the same procedure as the previous preparation (total yield 23%). M.P. 160-161°C (decomp), [Found: C, 64.5; H, 4.9.
Calculated for C_{73}H_{63}ClO_{3}Ru_{2}: C, 63.5; H, 4.6%].
This sparingly soluble complex is non-conducting in CH_{2}Cl_{2}.
Infrared spectrum: \nu_{O-H} 3550, 3580 cm\(^{-1}\)(m), \nu_{C=S} 1270 cm\(^{-1}\)(s).

Tri-\(\mu\)-bromohexakis(dimethylphenylphosphine)diruthenium(II)-bromide monohydrate

(a) The complex [Ru_{2}(OH)_{3}(PMe_{2}\(\Phi\))_{6}]PF_{6} (0.20 g) was dissolved in degassed CH_{3}NO_{2} (2 ml) and shaken with aqueous concentrated hydrobromic acid (48%) (2 ml) for 5 minutes. The yellow crystals formed were filtered, washed with EtOH and diethylether and dried in vacuo at 40°C (87% yield).

(b) The pure complex RuBr_{2}(P\(\Phi\)_{3})_{3} (0.30 g) was heated under reflux under N_{2} in degassed MeOH (30 ml) with a three fold excess of PMe_{2}\(\Phi\) (0.12 ml) for 3 hours. The yellow solution formed was reduced in volume to yield a bright yellow microcrystalline solid which was filtered, washed with EtOH and diethylether and dried in vacuo at 40°C (95% yield).
M.P. 122-123°C, [Found: C, 42.2; H, 4.9. Calculated for C\(_{48}\)H\(_{68}\)Br\(_4\)OP\(_6\)Ru\(_2\): C, 42.1; H, 5.0\%].

Infrared spectrum: (4000-250 cm\(^{-1}\)) is identical with that of [Ru\(_2\)Cl\(_3\)(PMe\(_2\)Ø)\(_6\)]Cl. [\(\Lambda(1 \times 10^{-3} \text{ M})\) in acetone = 113 \(\Omega^{-1} \text{cm}^2 \text{mol}^{-1}\)].

Tri-\(\mu\)-iodohexakis(dimethylphenylphosphine)diruthenium(II)-triiodide dihydrate

This preparation follows procedure (a) immediately above but using aqueous concentrated hydroiodic acid (55\%) (2 ml) in place of HBr. The dark orange-brown microcrystalline product was collected, washed with EtOH and diethylether and dried in vacuo at 40°C (89\% yield).

M.P. 162-164°C, [Found: C, 31.2; H, 3.7. Calculated for C\(_{48}\)H\(_{70}\)I\(_6\)O\(_2\)P\(_6\)Ru\(_2\): C, 31.5; H, 3.8\%].

Infrared spectrum (4000-250 cm\(^{-1}\)) is identical with that of [Ru\(_2\)Cl\(_3\)(PMe\(_2\)Ø)\(_6\)]Cl. [\(\Lambda(1 \times 10^{-3} \text{ M})\) in acetone = 98 \(\Omega^{-1} \text{cm}^2 \text{mol}^{-1}\)].

Tri-\(\mu\)-iodohexakis(dimethylphenylphosphine)diruthenium(II)-hexafluorophosphate dihydrate

The complex [Ru\(_2\)I\(_3\)(PMe\(_2\)Ø)\(_6\)]I\(_3\).2H\(_2\)O (0.10 g) was shaken vigorously in MeOH for 6 days with an excess of NH\(_4\)PF\(_6\) (0.03 g). The orange microcrystalline solid produced was filtered, washed with MeOH and diethylether and dried in vacuo at 40°C (83\% yield). M.P. 123-125°C, [Found: C, 36.0; H, 4.1. Calculated for C\(_{48}\)H\(_{70}\)F\(_6\)I\(_3\)O\(_2\)P\(_7\)Ru\(_2\): C, 36.2; H, 4.3\%]. [\(\Lambda(5 \times 10^{-4} \text{ M})\) in acetone = 55 \(\Omega^{-1} \text{cm}^2 \text{mol}^{-1}\)].
CHAPTER 4

Preparation and Characterisation of Mixed-Valence

Triple Bridged Binuclear Ru$_2$(II/III) Complexes
4.1 Preamble

Since Ru(II)L₆ (18 e⁻) and Ru(III) L₆ (17 e⁻) complexes are the most commonly encountered in ruthenium chemistry, it may seem that neutral mixed-valence Ru₂(II/III) triple bridged binuclear complexes such as L₂ClRuCl₃RuClL₂ provide the best opportunity for realising the complete oxidation state sequence (Equation [4]) within the same molecule (by chemical or electrochemical means).

Such a redox sequence ranges from 36 valence electrons for Ru₂(II/II) to 34 valence electrons for Ru₂(III/III), thus permitting the formation of a metal-metal bond. Since systematic spectroscopic and structural changes are known to accompany similar redox series in double and single bridged iron and manganese compounds (213, 214), it was decided to investigate the possibility of similar behaviour in the above binuclear systems (see Chapter 6).

However, in order to be able to correlate the degree of metal-metal interaction with any particular terminal or bridging property (or properties) e.g. bridging angle,
polarisabilities, basicities, donor/acceptor properties etc. a systematic change in terminal and bridging ligands is necessary.

In order to accomplish this, it is necessary to synthesise as diverse a series of mixed-valence triple bridged binuclear complexes as possible. However, realisation of this objective requires a profound understanding of the processes which control the formation of such compounds. Accordingly, considerable efforts have been made in obtaining a seemingly diverse array of experimental observations and rationalising them in terms of coherent mechanisms of formation, e.g. in the formation of mixed-valence Ru$_2$(II/III) triple chloro bridged complexes from their related Ru$_2$(II/II) triple chloro bridged precursors via aerial oxidation in either acetone or CH$_3$NO$_2$ in the presence of concentrated aqueous HCl.

In addition to these mechanistic studies attempts have also been made to synthesise new mixed-valence triple bridged binuclear complexes via direct reactions between "RuCl$_3$:3H$_2$O" or Na$_2$OsCl$_6$ and various bidentate ligands L (L = 2,2'-bipy, 1,10-phen, dpae, dppe etc.).

However, before discussing these topics it is instructive to give a brief introduction to the synthesis, structure and characterisation of previously known mixed-valence triple bridged Ru$_2$(II/III) and Os$_2$(II/III) binuclear complexes.
4.2 Introduction

Virtually all known isolable, mixed-valence, triple bridged Ru$_2$(II/III) and Os$_2$(II/III) complexes have two common features. They are invariably chloro bridged and they are nearly always uncharged. An obvious exception is [(NH$_3$)$_3$RuCl$_3$Ru(NH$_3$)$_3$]Cl$_2$ (78) (see later).

The first reported mixed-valence triple bridged Ru$_2$(II/III) binuclear compounds were of type $(PR_3)_2$ClRuCl$_3$RuCl$(PR_3)_2$ $(PR_3 = PBu_3^\text{N},$ P pent$_{\text{N}}^\text{3}$). These were synthesised by Nicholson in 1967 by the prolonged interaction of excess PR$_3$ on "RuCl$_3$.3H$_2$O" in EtOH (67). These dark red, paramagnetic complexes (1.5 BM per molecule) were believed, from carbonyl bridge cleavage reactions, to possess the "symmetric" structure (6). Nicholson et al later confirmed this "symmetric" structure by an X-ray structural analysis of the PBu$_3^\text{N}$ compound (68).

Since then a number of other mixed-valence triple chloro bridged Ru$_2$(II/III) and Os$_2$(II/III) binuclear complexes containing group VB donor ligands have been synthesised and characterised. These include the "symmetric" complexes $(LR_3)_2$ClMCl$_3$MCl$(LR_3)_2$ $(M = Os; LR_3 = P\overline{O}_3; M = Ru; LR_3 = As\overline{O}_3, As(\text{p-tol})_3$ (66), $\text{(15)}(6)$ and the "asymmetric" complexes $(LR_3)_3$MCl$_3$MCl$_2$(LR$_3$) $(M = Os; LR_3 = As\overline{O}_3, As(\text{p-tol})_3; M = Ru; LR_3 = As(\text{p-tol})_3, As(\text{p-ClO})_3$ (66)) (7).

All these compounds, irrespective of their geometry, were prepared by similar methods, i.e., heating "RuCl$_3$.3H$_2$O" or Na$_2$OsCl$_6$ under N$_2$ with an excess of the appropriate ligand in MeOH, EtOH or butan-2-ol.
Despite the fact that none of the above paramagnetic complexes (temperature invariant $\mu_{\text{eff}}$ 1.7-2.1 BM per molecule) have been the subject of an X-ray study the distribution of the terminal ligands about each metal atom M is well established. This has been achieved by combining the results from two complimentary techniques, namely electrochemical and e.s.r. spectroscopic studies. Electrochemical measurements establish the distribution of halides between the ruthenium centres (i.e. "symmetric" or "asymmetric") (See Chapter 5) whilst e.s.r. indicates the overall molecular symmetry; in combination, these two lines of evidence have led to numerous consistent structural assignments (66).

A number of other mixed-valence, triple chloro bridged Ru$_2$(II/III) binuclear complexes have been synthesised by the action of concentrated aqueous HCl on neutral triple chloro bridged Ru$_2$(II/II) binuclear complexes in acetone or CH$_3$NO$_2$ (see Section 4.3(a) for postulated mechanisms of formation). In this way (PR$_3$)$_2$YRuCl$_3$RuCl(PR$_3$)$_2$, for example, yields (PR$_3$)$_2$YRuCl$_3$RuCl$_2$(PR$_3$) ($Y = \text{CO, CS}$; PR$_3 = \text{PØ, P(p-tol)}_3$) (49)(142) or ($Y = \text{PR}_3 = \text{PET}_2\text{Ø}$) (50)(142).

As before a combination of electrochemical measurements (see Chapter 5) and e.s.r. spectroscopic studies proved sufficient to uniquely define the "asymmetric" structures (49) and (50) of these paramagnetic complexes (temperature invariant $\mu_{\text{eff}}$ 1.8-2.0 BM per molecule). Very recently
the "asymmetric" structure (50) was confirmed by a single crystal X-ray structure determination (195) (Figure 4.1).

\[
\begin{align*}
R_3P & \quad Cl & \quad Cl \\
\text{Y} & \quad Ru & \quad Cl & \quad Ru & \quad PR_3 \\
R_3P & \quad Cl & \quad Cl & \quad Cl & \quad Cl
\end{align*}
\]

Finally, a number of electroactive, mixed-valence, triple chloro bridged Ru\(_2\) (II/III) binuclear complexes without phosphine or arsine ligands have been prepared. These include the previously mentioned complex \([\text{(NH}_3\text{)}_3\text{RuCl}_3\text{Ru-}(\text{NH}_3\text{)}_3\text{]}\text{Cl}_2\) (78), made via the action of NH\(_2\text{NH}_2\cdot\text{H}_2\text{O}\) and concentrated aqueous HCl on "RuCl\(_3\cdot3\text{H}_2\text{O}\)" in H\(_2\text{O}\), and the aquo species \([\text{Ru}_2\text{Cl}_3(\text{H}_2\text{O})_6]^{2+}\), \([\text{Ru}_2\text{Cl}_4(\text{H}_2\text{O})_5]^+\) and \(\text{Ru}_2\text{Cl}_5(\text{H}_2\text{O})_4\), which were synthesised by the electroreduction of H\(_2\)[RuCl\(_5\)(H\(_2\text{O}\))] in H\(_2\)SO\(_4\) (87).

Before going on to describe possible mechanisms of formation of the "asymmetric" mixed-valence compounds (49) and (50), it is worth pointing out that the bland term "mixed-valence" generally embraces the limiting cases "isolated-valence" and "average-valence" (and every degree between these two extreme cases). A qualitative appraisal of the degree of "mixed-valency" (and the related concept of metal-metal interaction) of some of the complexes mentioned in this chapter will be described in Chapter 6 using the position (energy) and characteristics of inter-valence charge transfer (IT) bands as a probe at the 35-valence electron level (II/III valence state) and antiferromagnetic coupling -2J values at the 34-valence electron level (III/III valence state).
Figure 4.1  X-Ray Crystal Structure of Ru$_2$Cl$_5$(PET$_2$O)$_4$
4.3 Results and Discussion

(a) Chemical oxidation of neutral triple bridged
\( \text{Ru}_2(\text{II/II}) \) binuclear complexes in acidic media

In this section possible mechanisms of formation of neutral "asymmetric" mixed-valence \( \text{Ru}_2(\text{II/III}) \) triple chloro bridged binuclear complexes e.g. \((\text{PR}_3)_2 \text{YRuCl}_3\text{RuCl}_2(\text{PR}_3)\) \((Y = \text{CO, CS}; \text{PR}_3 = \text{P}_3, \text{P}(\text{p-tol})_3)\) (49) and \((\text{PET}_2\text{O})_3 \text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{O})\) (50) will be discussed. The two conditions any mechanism must satisfy are to explain why the reaction occurs for triple chloro bridged \( \text{Ru}_2(\text{II/II}) \) binuclear complexes such as \( \text{Ru}_2\text{Cl}_4(\text{PET}_2\text{O})_5 \), but not for analogous complexes such as \( \text{Ru}_2\text{Cl}_4(\text{PCl}_2)_5 \) and \( \text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5 \), and why the reaction yields a single "asymmetric" isomer.

It is instructive to begin by considering the complexes for which the reaction does, or does not, occur, as well as surveying the extent and nature of the side-products, which also need to be accounted for by any proposed mechanism.

Arthur has shown that \((\text{PO}_3)_2 \text{YRuCl}_3\text{RuCl}(\text{PO}_3)_2\) \((Y = \text{CO, CS})\) (19) may be oxidised in high yield (85-90\%) to \((\text{PO}_3)_2 \text{YRuCl}_3\text{RuCl}_2(\text{PO}_3)_2\) (49) by prolonged shaking in acetone/concentrated aqueous HCl or \(\text{CH}_3\text{NO}_2/\text{concentrated aqueous HCl mixtures}(142)\). However, the more soluble \((\text{PET}_2\text{O})_3 \text{CO} \text{RuCl}_3\text{RuCl}(\text{PET}_2\text{O})_3\) (19), under the same conditions, gave \((\text{PET}_2\text{O})_3 \text{CO} \text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{O})_3\) (49) (70\% yield) and the three isomers of \((\text{PET}_2\text{O})_3 \text{CO} \text{RuCl}_3\text{RuCl}(\text{PET}_2\text{O})_3\) (20 a,b,c) (30\% yield\{142\).
In contrast, shaking a suspension of \( \text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{P}0_3)_3 \) (20a, b, c) in \( \text{CH}_3\text{NO}_2/\text{concentrated aqueous HCl} \) for several days gives no paramagnetic mixed-valence product (e.s.r. spectroscopic evidence). \(^{31}\text{Phosphorus}-\{^1\text{H}\} \) n.m.r. spectroscopy and electrochemical studies, which show an irreversible oxidation wave at +1.50 V (see Chapter 5), strongly suggest that the major identifiable product is \([\text{Ru}_2\text{Cl}_3(\text{CS})_2(\text{P}0_3)_4]\)Cl (21), together with unreacted starting material.

Similar treatment of neutral triple chloro bridged \( \text{Ru}_2(\text{II}/\text{II}) \) binuclear complexes of type \( \text{L}_3\text{RuCl}_3\text{RuCl}_2\text{L} \) leads to a variety of products depending on \( \text{L} \). For example when \( \text{L} = \text{PET}_2\varnothing, \text{PMe}_2\varnothing, \text{PMe}_2\varnothing \) and \( \text{PET}_2\varnothing \), mixed-valence products of type \( \text{L}_3\text{RuCl}_3\text{RuCl}_2\text{L} \) are formed in \( \text{ca.} \) 50% yield (neither \( \text{L}_3\text{RuCl}_3\text{RuCl}_2\text{L} (\text{L} = \text{PMe}_2\varnothing, \text{PMe}_2\varnothing) \)) have been isolated pure, however, persuasive electrochemical evidence exists for both (see Chapter 5); in addition compelling e.s.r. spectroscopic evidence has been obtained for \((\text{PMe}_2\varnothing)_3\text{RuCl}_3\text{RuCl}_2(\text{PMe}_2\varnothing)\), i.e. \( g \parallel 2.47, g \perp 1.66 \) \( (c.f. \ g \parallel 2.46, g \perp 1.63 \) for \((\text{PET}_2\varnothing)_3\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\varnothing)) \); (see Experimental Section 4.5 for characterisation of \((\text{PET}_2\varnothing)_3\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\varnothing))\). \(^{31}\text{Phosphorus}-\{^1\text{H}\} \) n.m.r. spectroscopic and electrochemical studies (see Chapter 5) reveal that the ionic complexes \([\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\)Cl are also formed in \( \text{ca.} \) 50% yield.

In contrast, similar treatment of \( \text{L}_3\text{RuCl}_3\text{RuCl}_2\text{L} \) \( (\text{L} = \text{PCl}_2\varnothing) \) results in non-reaction \((^{31}\text{P}-\{^1\text{H}\} \) n.m.r. evidence), whilst when \( \text{L} = \text{Me}_2\text{SO} \) a small amount of unidentified solid is isolated (shown to be a mixture by electrochemical studies).
At least two mechanisms of formation for the above mixed-valence \( \text{Ru}_2(\text{II/III}) \) compounds can be discerned, these are: oxidation followed by bridge cleavage/halide attack and condensation of the resulting monomers (see Scheme 4.1a,b) or specific terminal nucleophilic attack by halide after activation by oxidation (see Scheme 4.2a,b). A further possible pathway involving cleavage of the triple chloro bridged \( \text{Ru}_2(\text{II/II}) \) binuclear complexes, prior to oxidation, would seem unlikely since species of type \( [\text{RuCl}_4(\text{PR}_3)_2]^{2-} \) or \( [\text{RuCl}_3(\text{PR}_3)_2(\text{CH}_3\text{NO}_2)]^- \) (i.e. plausible bridge cleavage products of \( (\text{PR}_3)_3\text{RuCl}_3\text{RuCl}(\text{PR}_3)_2 \) in \( \text{CH}_3\text{NO}_2/\text{concentrated aqueous HCl} \) are not known and electrochemical studies on the well characterised complexes \( \text{NMe}_4[\text{RuCl}_4(\text{L}_3)_2] \) (\( \text{L} = \text{P, As} \)) and \( \text{RuCl}_3(\text{PØ}_3)_2(\text{CH}_3\text{NO}_2) \) indicate only irreversible reductions to \( \text{Ru(II)} \) di- and mono-anions respectively.

In each of the suggested mechanisms the first stage (i) is the same i.e. oxidation of the \( \text{Ru}_2(\text{II/II}) \) neutral complexes to cationic mixed-valence \( \text{Ru}_2(\text{II/III}) \) species. The fact that only complexes with oxidation potentials for the half reaction \( \text{Ru}_2\text{Cl}_4\text{YL}_4 \longrightarrow [\text{Ru}_2\text{Cl}_4\text{YL}_4]^+ + e^- \) of less than +0.80 V (e.g. \( \text{Y} = \text{CO, CS}; \text{L} = \text{PØ}_3, \text{P(P-tol)}_3 \); \( \text{Y} = \text{L} = \text{PMe}_2\text{Ø}, \text{PMe}_2\text{Ø}, \text{PET}_2\text{Ø}, \text{PET}_2\text{Ø} \)) (see Chapter 5) undergo the reaction, while those with oxidation potentials of +1.20 V, or greater, (e.g. \( \text{Y} = \text{L} = \text{PClØ}_2, \text{Me}_2\text{SO} \)) and \( \text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PØ}_3)_3 \) (see Chapter 5) do not, is consistent with the fact that aerial oxidation under acidic conditions exerts an effective potential of ca. +1.0 V.
Scheme 4.1

Mechanism of Formation of (PR₃)₃RuCl₃RuCl₂(PR₃) and (PR₃)₂YRuCl₃RuCl₂(PR₃) involving oxidation of binuclear Ru₂(II/II) complexes followed by bridge cleavage/halide attack and condensation of the resulting monomers

(a) R₃P-Ru-Cl-Ru-PR₃

(i) concentrated HCl

(ii) Cl⁻

(16)

(b) R₃P-Ru-Cl-Ru-PR₃

(i) concentrated HCl

(ii) Cl⁻

(19)

(PR₃ = PMe₀, PMe₀₂, PET₂₀, PET₂₀)
Scheme 4.2

Mechanism of Formation of \((\text{PR}_3)_3 \text{RuCl}_3 \text{RuCl}_2 (\text{PR}_3)\) and 
\((\text{PR}_3)_2 \text{YRuCl}_3 \text{RuCl}_2 (\text{PR}_3)\) Involving Specific Terminal 
Nucleophilic Halide Attack after Activation of Binuclear 
\(\text{Ru}_2(\text{II/II})\) Complexes by Oxidation

(a) \[
\begin{align*}
R_3\text{P} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{Cl} & \quad R_3\text{P} & \quad \text{Cl} & \quad R_3\text{P} \\
R_3\text{P} & \quad \text{Cl} & \quad R_3\text{P} & \quad \text{PR}_3
\end{align*}
\]

\((\text{PR}_3)_3 \text{RuCl}_3 \text{RuCl}_2 (\text{PR}_3)\)

(b) \[
\begin{align*}
R_3\text{P} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{Cl} & \quad R_3\text{P} & \quad \text{Cl} & \quad R_3\text{P} & \quad \text{PR}_3 \\
R_3\text{P} & \quad \text{Cl} & \quad R_3\text{P} & \quad \text{PR}_3 & \quad \text{Y}
\end{align*}
\]

\((\text{PR}_3)_2 \text{YRuCl}_3 \text{RuCl}_2 (\text{PR}_3)\)

(i) \[
\begin{align*}
\text{concentrated HCl} & \quad \text{CH}_3\text{NO}_2 & \quad E^\circ < 1.2\text{V}
\end{align*}
\]

(iii) 
\[
\begin{align*}
\text{PR}_3 & \quad \text{Cl} & \quad \text{PR}_3
\end{align*}
\]

\((\text{PR}_3)_3 \text{RuCl}_3 \text{RuCl}_2 (\text{PR}_3)\)

(i) \[
\begin{align*}
\text{concentrated HCl} & \quad \text{CH}_3\text{NO}_2 & \quad E^\circ < 1.2\text{V}
\end{align*}
\]

(ii) 
\[
\begin{align*}
\text{Cl}^- & \quad (-\text{PR}_3)
\end{align*}
\]

\((\text{PR}_3)_2 \text{YRuCl}_3 \text{RuCl}_2 (\text{PR}_3)\)

\((\text{PR}_3 = \text{PMe}_2\text{O}, \text{PMeO}_2, \text{PET}_2\text{O}, \text{PETO}_2)\)
Stage (ii) of Scheme 4.1(a,b) infers that attack of Cl\textsuperscript{-} ion causes bridge cleavage of the mixed-valence cations, formed in stage (i), to give coordinatively unsaturated or weakly solvated Ru(II) and Ru(III) monomers. These monomers may then undergo either self-dimerisation or intermolecular cross-coupling to form the required neutral mixed-valence complexes (49) and (50). Side-products such as [Ru\textsubscript{2}Cl\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]Cl in Scheme 4.1(a) and Ru\textsubscript{2}Cl\textsubscript{4}Y\textsubscript{2}(PR\textsubscript{3})\textsubscript{3} (20a,b,c) and [Ru\textsubscript{2}Cl\textsubscript{3}Y\textsubscript{2}(PR\textsubscript{3})\textsubscript{4}]Cl (21) in Scheme 4.1(b) may be attributed to the well-known self-dimerisation of "RuCl\textsubscript{2}(PR\textsubscript{3})\textsubscript{3}(solv)" and "RuCl\textsubscript{2}Y(PR\textsubscript{3})\textsubscript{2}(solv)" respectively (see Schemes 2.2 and 2.4). The driving-force for the assembly of such binuclear products is the formation of six strong Ru-X bonds.

However, this mechanism is unconvincing in two important respects. First, the isolable and well characterised complexes RuCl\textsubscript{2}(CO)(PØ\textsubscript{3})\textsubscript{2}(MeOH) and RuCl\textsubscript{3}(PØ\textsubscript{3})\textsubscript{2}(CH\textsubscript{3}NO\textsubscript{2}) do not undergo reaction to give (PØ\textsubscript{3})\textsubscript{2}(CO)RuCl\textsubscript{3}RuCl\textsubscript{2}(PØ\textsubscript{3}) (49) when shaken in 1:1 molar ratios in acetone (either alone or with an excess of concentrated HCl). \textsuperscript{31}Phosphorus-{\textsuperscript{1}H} n.m.r. and infrared spectroscopic studies indicate that a complex mixture of unidentified products and starting materials is formed. This observation would appear to be at odds with stage (iii) of Scheme 4.1(b). Furthermore, the neutral mixed-valence products (49) would surely be produced in several isomeric forms if recombination of coordinatively unsaturated monomers is a key step (c.f. the closely related process in which three geometrical isomers of Ru\textsubscript{2}Cl\textsubscript{4}Y\textsubscript{2}(PR\textsubscript{3})\textsubscript{3}
(Y = CO, CS; PR₃ = PØ₃, P(p-tol)₃) (20a,b,c) are produced). This is simply because, as stated in 3.3a(ii), the steric requirements of three PØ₃ or P(p-tol)₃ groups per binuclear unit are much less than that of four, where a single isomer containing staggered phosphines, as in Ru₂Cl₄Y(PR₃)₄ (19), is formed.

In contrast, stage (ii) of Schemes 4.2(a,b) provides a better rationale of the stereospecificity of the reaction since no bridge cleavage and rearrangement is proposed. In these schemes Cl⁻ ion attack, and consequent PR₃ displacement, occurs at the "harder" terminal Cl⁻ end of the mixed-valence cation which was specifically activated toward nucleophilic attack on oxidation to Ru(III) in stage (i). However, the formation of Ru₂Cl₄Y₂(PR₃)₃ (20a,b,c) and [Ru₂Cl₃Y₂(PR₃)₄]Cl (21) is not easily explained by invoking Scheme 4.2(b) since neither of these two types of complex are known products of the reaction between Ru₂Cl₄Y(PR₃)₄ (19) and PR₃ in polar solvents.

Thus, on the basis of the above facts a modified form of Schemes 4.2(a,b) is required. It needs to be modified to account for the formation of (20a,b,c) and (21), and for the non-observance of any Ru(III) complex other than the neutral mixed-valence species (49) and (50).

Scheme 4.3(a,b) appears to reconcile all the above arguments since it postulates a competitive bridge cleavage/oxidation mechanism which explains the formation of stereospecific neutral mixed-valence compounds as well as the required Ru₂(II/II) binuclear, high oxidation potential (see Chapter 5), side-products. Hence, the relative
Scheme 4.3
Mechanism of Formation of \( (PR_3)_3RuCl_3RuCl_2(PR_3) \) and \( (PR_3)_2YRuCl_3RuCl_2(PR_3) \) Involving Competitive Bridge Cleavage/Oxidation of Binuclear \( Ru_2(II/II) \) Complexes

(a) R₃P—Ru—I—I—Ru—PR₃

(i) concentrated HCl

(ii) \( \text{CH}_3\text{NO}_2 \)

\( E^\text{f} < 1.2V \)

(ii) Cl⁻ (−PR₃)

(vi) BuCl₂ (.?R₃) +PR₃

(50)

(II) Cl⁻ (−PR₃)

(PR₃ = PMe₂O, PMe₂O₂, PEt₂O, PEt₂O₂)

(b) R₃P—Ru—I—I—Ru—PR₃

(i) concentrated HCl

(ii) \( \text{CH}_3\text{NO}_2 \)

\( E^\text{f} < 1.2V \)

(ii) Cl⁻ (−PR₃)

(vi) BuCl₂ (.?R₃) +PR₃

(49)

(II) Cl⁻ (−PR₃)

(PR₃ = PO₃, P(p-tol)₃, Y = CO, CS)
amounts of different products observed reflects the ease of oxidation of \( \text{Ru}_2(\text{II}/\text{II}) \) compounds to mixed-valence \( \text{Ru}_2(\text{II}/\text{III}) \) compounds versus the ease of bridge cleavage to \( \text{Ru(II)} \) monomers.

\(^{31}\text{Phosphorus-(}^{1}\text{H)} \) n.m.r. spectroscopic evidence gives some experimental backing for stage (iii) of Schemes 4.3(a,b) since it shows that small amounts of \([\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl},\) and \(\text{Ru}_2\text{Cl}_4Y_2(\text{PR}_3)_3\) (20a,b,c) and \([\text{Ru}_2\text{Cl}_3Y_2(\text{PØ}_3)_4]\text{Cl}\) (21) are produced on shaking \(\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5\) (16) and \(\text{Ru}_2\text{Cl}_4Y(\text{PR}_3)_4\) (19) respectively in \(\text{CH}_3\text{NO}_2\) with \(\text{Pr}_{4}\text{NCl}\).

It should also be noted that the role which the acid plays (i.e. in aiding the aerial oxidation process and acting as a source of \(\text{Cl}^-\) ion) may be more efficiently undertaken by gaseous \(\text{Cl}_2\) or by controlled potential electrosynthesis (see Chapter 5), in a chlorinated solvent. Thus, oxidation of \(\text{Ru}_2\text{Cl}_4Y(\text{PR}_3)_4\) (19) in \(\text{THF}\) at 233 K using gaseous \(\text{Cl}_2\) gives a green solution (containing \([\text{Ru}_2\text{Cl}_4Y(\text{PR}_3)_4]^+\) which within minutes (or seconds at ambient temperature) rearranges to give an orange solution which has been shown to be predominantly \((\text{PR}_3)_2Y\text{RuCl}_3\text{RuCl}_2(\text{PR}_3)\) (49) by electrochemical studies (see Chapter 5). Similarly, bulk electrochemical oxidation of \(\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5\) (16) or \(\text{Ru}_2\text{Cl}_4Y(\text{PR}_3)_4\) (19) in 0.5 M \(\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2\) at 213 K produces green solutions containing the appropriate mixed-valence cations. These species are stable at this temperature for several hours, (see Chapter 6 for their \textit{in situ} characterisation), however, on warming to ambient temperature electrochemical studies (see Chapter 5) indicate these solutions contain largely the neutral mixed-valence complexes \((\text{PR}_3)_3\text{RuCl}_3\text{RuCl}_2(\text{PR}_3)\) (50) and \((\text{PØ}_3)_2Y\text{RuCl}_3\text{RuCl}_2(\text{PR}_3)\) (49).
These studies are fully consistent with Schemes 4.3(a,b) since they infer that oxidation of these Ru\(_2\)(II/II) binuclear complexes to mixed-valence Ru\(_2\)(II/III) cations is a necessary prerequisite for formation of neutral mixed-valence products. Whether the source of Cl\(^-\) ion, responsible for nucleophilic attack on the specifically activated Ru\(_2\)(II/III) cations, is HCl in the CH\(_2\)Cl\(_2\) solvent or the solvent itself is unknown.

Finally, recent attempts to synthesise (P\(\Phi\)\(_3\))\(_2\)ClOsCl\(_3\)OsCl\(_2\)(P\(\Phi\)\(_3\)) by an analogous procedure i.e. the prolonged shaking of a suspension of the neutral "symmetric" mixed-valence complex (P\(\Phi\)\(_3\))\(_2\)ClOsCl\(_3\)OsCl(P\(\Phi\)\(_3\))\(_2\) (6) (E\(_{1/2}\) = +0.50 V) in aerated CH\(_3\)NO\(_2\)/concentrated aqueous HCl failed. However, oxidation of the mixed-valence complex did occur, albeit with bridge cleavage, to give a near quantitative yield of trans-OsCl\(_4\)(P\(\Phi\)\(_3\))\(_2\). Microanalytical, spectroscopic and electrochemical data are consistent with that previously reported for this complex\(^{216}\).

4.3(b) Direct reactions between "RuCl\(_3\)\(\cdot\)3H\(_2\)O" or Na\(_2\)OsCl\(_6\) and various ligands L

Attempts have been made to increase both the scope and stereospecificity of the previously mentioned direct reactions (i.e. those involving reactions between metal halides and groups VB donor ligands such as PR\(_3\) and AsR\(_3\)) by using bidentate nitrogen, sulphur, phosphorus and arsenic containing donor ligands. In particular it was hoped that by using bidentate ligands it might prove possible to achieve
the direct synthesis of "symmetric" mixed-valence triple chloro bridged Ru$_2$(II/III) or Os$_2$(II/III) binuclear complexes, i.e. those with equal numbers of chloride ligands attached to each metal centre.

Thus, it was discovered that heating a degassed butan-2-ol solution, containing 1:1 molar ratios of "RuCl$_3$·3H$_2$O" and bis(1,2-diphenylarsino)ethane (dpae), under reflux under N$_2$ for 5 hours, yielded a dark green, non-conducting, compound whose microanalytical and infrared spectroscopic data (terminal $v_{\text{Ru-Cl}}$ 320 cm$^{-1}$ and bridging $v_{\text{Ru-Cl}}$ 250 cm$^{-1}$) were consistent with (dpae)ClRuCl$_3$RuCl(dpae). Electrochemical studies, including cyclic and linear sweep a.c. voltammetries (see Chapter 5) show adjacent reversible one-electron oxidations of unequal height at +0.10 and +0.26 V with corresponding reversible one-electron reductions at -0.40 and -0.64 V (see Figure 4.2). The separations between the related couples of 0.50 V (major component) and 0.90 V (minor component) respectively, and an e.s.r. spectrum consisting of both a rhombic pattern ($g_{\perp}$ 2.29, $g_2$ 2.08, $g_3$ 1.93) and a superimposed more prominent axial pattern ($g_{\perp}$ 2.59, $g_{||}$ 1.74) (Figure 4.3) strongly suggests that both the possible "symmetric" isomers (51a,b) have been formed.

\begin{align*}
\text{(51a)} & \quad \begin{array}{c}
\text{Cl} \\
L \quad \text{Ru} \\
\text{Cl} \\
\text{Cl} \\
\text{L}
\end{array} \\
\text{Cl} \\
\text{Cl} \\
\text{L} \\
\text{L} \\
\text{L} \\
\text{(51b)} & \quad \begin{array}{c}
\text{Cl} \\
L \quad \text{Ru} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{L}
\end{array}
\end{align*}

(L = $\varnothing_2\text{As(CH}_2\text{)}_2\text{As}$)
Figure 4.2  Cyclic and A.C. Voltammetry of the Ru$_2$Cl$_5$(dpae)$_2$ Isomeric Mixture
Figure 4.3  E.S.R. Spectrum of the Ru$_2$Cl$_5$(dpae)$_2$
Isomeric Mixture in CH$_2$Cl$_2$ at 133 K

200 Gauss
Reaction for longer time periods (up to 20 hours) made no significant difference to the amount of the major isomer (51b) produced. However, species (51a) apparently rearranges to give further unidentified products. No attempt has yet been made to separate the two components of the binary isomeric mixture either by recrystallisation or by chromatography.

Preliminary studies on the reaction between "RuCl₃·3H₂O" and bidentate phosphorus donors such as tetramethyl-diphosphine-1,2-disulphide and bis(1,2-diphenylphosphino)-ethane (dppe) in degassed butan-2-ol under reflux have produced a highly insoluble dark brown decomposition product for the former and two highly insoluble unidentified products for the latter, one grey and the other green.

Finally, heating Na₂OsCl₆ under reflux in degassed butan-2-ol under N₂ for 6 hours with 1:1 molar ratios of either 2,2'-bipyridine or 1,10-phenanthroline gave rise to impure, brown, water soluble, highly conducting complexes which are believed to contain Na[OsCl₄(N-N)] (N-N = bipy or phen). This was confirmed by isolation and characterisation of the pure complexes as their Ø₃(ØCH₂)P⁺ salts. Electrochemical studies on these complexes confirm that [OsCl₄(N-N)]⁻ anions have been formed since the potentials measured for these species are the same as those obtained for genuine samples of the anions made by literature methods (217). Thus, (Ø₃(ØCH₂)P)[OsCl₄(N-N)] (N-N = bipy, phen) undergo reversible one-electron oxidations at 0.00 and -0.02 V
respectively and reversible one-electron reductions at -1.31 and -1.29 V respectively. The oxidations should be regarded as metal based i.e. yielding the well-known species OsCl₄(N-N), while the reductions are probably essentially ligand based i.e. giving N-N⁻.

4.4 Conclusions

Attempts to increase the range of both "symmetric" and "asymmetric" mixed-valence Ru₂(II/III) and Os₂(II/III) complexes have been generally unsuccessful. The possible method of preparation of the "symmetric" compounds, involving direct reaction of the appropriate metal halide with a variety of bidentate ligands in butan-2-ol, proved disappointing since only when "RuCl₃·3H₂O" was reacted with (dpae) was a mixed-valence product formed.

Extension of the synthetic route applicable to "asymmetric" compounds, which involves aerial oxidation (under acidic conditions) of binuclear Ru₂(II/II) complexes, also proved difficult. In this case the major difficulties concern:- (a) the lack of a suitable range of substrates with amenable oxidation potentials and (b) the difficulty of separating the required products, cleanly, from the side-products. However, these problems may be overcome by using gaseous Cl₂ as the oxidising agent or employing electrochemical oxidation in the presence of Cl⁻ ion.

The postulated competitive bridge cleavage/oxidation mechanism for the formation of the "asymmetric" complexes is consistent with the available data. In contrast, no
mechanistic information is currently available on the formation of the "symmetric" complexes (indeed Nicholson's original preparation of (PBi$_3$)$_2$ClRuCl$_3$RuCl(PBi$_3$)$_2$ has never been successfully repeated by the group at Edinburgh despite many attempts) and hence extension of this preparative route has proved very difficult.

4.5 Experimental

Experimental details were as for those described in Chapter 2. Solution magnetic measurements were obtained in 2% TMS/CH$_2$Cl$_2$ solutions by Evans' method (218) using a Varian HA100 N.M.R. Spectrometer.

Reagents

The following complexes were prepared using literature methods:

\[ \text{Ru}_2\text{Cl}_4(\text{CS})_2(P\text{O}_3)_3 \] (182), \[ \text{Ru}_2\text{Cl}_4(PR_3)_5 \] \( PR_3 = \text{PMe}_2\text{O} \) (66), \[ \text{PMe}_2\text{O}, \text{PET}_2\text{O}, \text{PET}_2\text{O}_2, \text{PCl}_2 \] (122), \[ \text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5 \] (see Experimental Section 2.5), \[ \text{RuCl}_3(P\text{O}_3)_2(\text{CH}_3\text{NO}_2) \] (70) and \[ \text{RuCl}_2(\text{CO})(P\text{O}_3)_2(\text{MeOH}) \] (182).

def-Tri-$\mu$-chloro-$g,i$-dichlorotetrakis(ethyldiphenylphosphine)-diruthenium (II/III) nitromethane (3/2)

The compound \[ \text{Ru}_2\text{Cl}_4(\text{PET}_2\text{O})_5 \] (0.30 g) was shaken in CH$_3$NO$_2$ (20 ml) and concentrated aqueous hydrochloric acid (15 ml) for 3 days. The colour of the CH$_3$NO$_2$ layer of the solution changed from red to bright green. The green organic soluble layer was evaporated to dryness and the
green residue shaken for 2 hours in butan-2-ol (100 ml) which gave a pale green solution. Reducing the volume of the solution to ca. 5 ml and adding petroleum ether (B.P. 40-60°C) (3 ml) resulted in the precipitation of a pale green solid which was washed with petroleum ether (B.P. 40-60°C) and dried in vacuo at 40°C (26% yield).

M.P. 105-106°C, [Found: C, 52.3; H, 4.7; N, 1.9. Calculated for \( \text{C}_{57.5} \text{H}_{64.5} \text{N}_{1.5} \text{Cl}_{5} \text{P}_4 \text{Ru}_2 \): C, 52.0; H, 4.9; N, 1.6%], non-conducting in CH\(_2\)Cl\(_2\).

**Infrared Spectrum:** \( \nu_{\text{Ru-Cl}} \) 325 (m), 250 (w) cm\(^{-1}\). Solution magnetic moment \( \mu_{\text{eff}} \) (Evans' method) 1.94 BM at 298 K. Axial e.s.r. pattern \( g_\perp \) 2.49, \( g_\parallel \) 1.73 at 133 K in CH\(_2\)Cl\(_2\).

**Trans-Tetrachlorobis(triphenylphosphine)osmium(IV)**

The complex \( \text{Os}_2 \text{Cl}_5 (\text{P}\_3 \text{O})_4 \) (0.15 g) was shaken in CH\(_3\)NO\(_2\) (25 ml) and concentrated aqueous hydrochloric acid (20 ml) for 18 hours. The CH\(_3\)NO\(_2\) layer was separated, reduced in volume and allowed to stand for 20 minutes in the cold. The dark brown crystals produced were filtered off, washed with diethylether and dried in vacuo at 40°C (83% yield).

M.P. 235-237°C, [Found: C, 49.9; H, 3.5. Calculated for \( \text{C}_{36} \text{H}_{30} \text{Cl}_4 \text{P}_2 \text{Os} \): C, 50.5; H, 3.5%], non-conducting in CH\(_2\)Cl\(_2\). **Infrared spectrum:** \( \nu_{\text{Os-Cl}} \) 330 (s), 323 (s) cm\(^{-1}\).
Isomeric mixture of def-Tri-\(\mu\)-chloro-\(\alpha,\iota\)-dichlorobis-(bis(1,2-diphenylarseno)ethane) diruthenium(II/III) and def-Tri-\(\mu\)-chloro-\(\alpha,\gamma\)-dichlorobis(bis(1,2-diphenylarseno)ethane) diruthenium(II/III)

The commercial material "RuCl\(_3\).3H\(_2\)O" (0.20 g) was heated under reflux under N\(_2\) in degassed butan-2-ol (20 ml) with a 1:1 molar ratio of bis(1,2-diphenylarseno)ethane (0.37 g) for 5 hours. The dark green product formed was filtered hot, washed with EtOH and diethylether and dried in vacuo at 40\(^\circ\)C (78% yield). M.P. 225-227\(^\circ\)C (decomp), [Found: C, 46.2; H, 3.8. Calculated for C\(_{52}\)H\(_{128}\)As\(_4\)Cl\(_5\)Ru\(_2\): C, 46.2; H, 3.6%], non-conducting in CH\(_2\)Cl\(_2\).

Infrared Spectrum: \(\nu_{\text{Ru-Cl}}\) 320(m), 250(w) cm\(^{-1}\).

Axial e.s.r. pattern \(g_\perp 2.59, g_\parallel 1.74\) and a rhombic e.s.r. pattern \(g_1 2.29, g_2 2.08, g_3 1.93\) at 133 K in CH\(_2\)Cl\(_2\).

(Triphenylbenzylphosphonium) [Tetrachloro(2,2'-bipyridine)osmate(III)]

Na\(_2\)OsCl\(_6\) (0.2 g) was heated under reflux under a N\(_2\) atmosphere with a 1:1 molar ratio of 2,2'-bipyridine (0.07 g) in butan-2-ol (20 ml) for 4 hours. The crude brown product formed was filtered and dried in air. This product was then shaken in degassed H\(_2\)O (50 ml) for 2 hours. The deep red-brown solution formed was filtered through celite before treatment with a saturated solution of \(\text{OsCl}_3(\text{CH}_2\text{O})\) in MeOH. The purple solid which formed was filtered, washed with EtOH and diethylether and dried in vacuo at 40\(^\circ\)C (62% yield).
M.P. 215°C (decomp), [Found: C, 50.2; H, 3.4; N, 3.1. Calculated for C$_{35}$H$_{30}$N$_2$Cl$_4$PO$_5$: C, 49.9; H, 3.6; N, 3.3%]. Infrared spectrum: $\nu$$_{Os-Cl}$ 300 cm$^{-1}$ (s) 
$\Lambda$(1 x 10$^{-3}$ M) in CH$_2$Cl$_2$ = 23 cm$^{-1}$ mol$^{-1}$.

(Triphenylbenzylphosphonium)[Tetrachloro(1,10-phenanthroline)osmate(III)]

Exactly analogous to the above preparation, but using 1,10-phenanthroline instead of 2,2'-bipyridine (71% yield). M.P. 150°C (decomp), [Found: C, 51.2; H, 3.6; N, 3.2. Calculated for C$_{37}$H$_{30}$N$_2$Cl$_4$PO$_5$: C, 51.3; H, 3.5; N, 3.2%]. Infrared spectrum: $\nu$$_{Os-Cl}$ 300 cm$^{-1}$ (s) 
$\Lambda$(1 x 10$^{-3}$ M) in CH$_2$Cl$_2$ = 22 cm$^{-1}$ mol$^{-1}$.
CHAPTER 5

Electrochemical Studies on Some Triple Bridged

Ruthenium and Osmium Binuclear Complexes
5.1 Preamble

One of the most interesting, and increasingly popular ways of investigating the electronic structure of coordination compounds is to examine the redox processes they undergo. Accordingly, references have been made to the redox activity exhibited by Ru and Os triple bridged binuclear complexes throughout Chapters 2, 3 and 4. However, it is now intended to discuss in greater depth our extensive electrochemical studies of many Ru and Os triple bridged compounds in formal oxidation states (II/II), (II/III) and (III/III). This will be presented as a discussion of influences, such as metal ion identity and terminal and bridging ligand characteristics, on the redox potentials within individual classes of compounds e.g. \([M_2X_3(PR_3)_6]X, Ru_2Cl_4(PR_3)_5, Ru_2X_4Y(PR_3)_4\) etc. It will then be shown that, by comparing these redox potentials with those of related monomers, a simple, but highly effective, structure/redox potential correlation diagram can be derived.

However, before these studies are discussed further, it is appropriate to give a brief description of the electrochemical techniques involved.
5.2 Introduction

Although analytical chemists have routinely employed electrochemical techniques for over fifty years, it is only really in the last ten years that organometallic and coordination chemistries have found familiarity with such techniques. This is very largely due to the establishment in modern instrumentation of the three-electrode configuration (Figure 5.1) and the subsequent development of positive-feedback circuitry, to overcome cell impedance, which has heralded the advent of a new range of non-aqueous solvents as feasible electrochemical media.

Although approximately a dozen distinct electrochemical techniques are in general use today only those techniques which are widely used in the present study will be discussed. Thus polarographic techniques, i.e. those utilising the dropping mercury electrode (d.m.e.), will not be discussed since our phosphine complexes, i.e. the majority of compounds under investigation, give very poor behaviour at such electrodes due to apparently specific Hg electrode/complex interactions.

(a) Cyclic voltammetry (c.v.)

Linear sweep cyclic voltammetry (c.v.), which was introduced by Matheson et al.\(^{(219)}\) in 1938 and given a theoretical basis by Randles\(^{(220)}\) and Sevick\(^{(221)}\) ten years later, is conceptually different from polarographic techniques in that a stationary electrode is used instead of a d.m.e. so that the solution is "quiet", i.e. un unstirred, and hence
Figure 5.1  Three-Electrode Apparatus

C, counter electrode
W, working electrode
R, reference electrode
diffusion of reactants and products between the bulk solution and the solution/electrode interface is the only means of mass transport.

In cyclic voltammetry (c.v.), the potential of the stationary working electrode is varied at a finite rate, the "scan rate", \( v \), as a linear function of time (typically 50 - 500 mVs\(^{-1}\)). Upon reaching a pre-set value, the "switching potential", the voltage scan is reversed to its base potential at the same rate used in the forward scan. Figure 5.2 shows typical current-potential response curves for both reversible and irreversible charge-transfer processes. The cyclic voltammetric scan rate is thus of critical importance since it effectively controls the time-scale of the experiment.

Four measureable parameters can be obtained for a reversible process; the net current \( (i^F_p) \), the potential at the maximum of the forward curve \( (E^F_p) \) and the corresponding parameters for the reverse curve \( (i^R_p \text{ and } E^R_p) \). The parameters can then be used to determine whether the charge-transfer process is reversible, quasi-reversible or irreversible in nature. If the charge-transfer process is "reversible" then the process occurs at a considerably faster rate than the diffusion rate. In contrast, a reaction in which the charge-transfer process is controlled by both diffusion and charge-transfer kinetics is termed "quasi-reversible", and a reaction in which the charge-transfer process is much slower than the diffusion rate is called "irreversible" (see Table 5.1 for the criteria
Figure 5.2  Cyclic Voltammetry of a Species Undergoing Reversible and Irreversible Charge-Transfer
Table 5.1  Cyclic voltammetric criteria for reversible, quasi-reversible, partially-reversible and irreversible charge transfer processes at 298 K

<table>
<thead>
<tr>
<th>Type</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reversible</td>
<td>( E_p ) is independent of ( \nu )</td>
</tr>
<tr>
<td></td>
<td>( E^F_p - E^R_p = 59/n \text{ mv} ) and is independent of ( \nu )</td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{2}[E^F_p + E^R_p] = E^* ), independent of concentration</td>
</tr>
<tr>
<td></td>
<td>( i_p/\nu^{\frac{1}{2}} ) (current function) is independent of ( \nu )</td>
</tr>
<tr>
<td></td>
<td>( i^R_p/i^F_p ) = 1 and independent of ( \nu )</td>
</tr>
<tr>
<td>Quasi-reversible</td>
<td>( E_p ) shifts with ( \nu )</td>
</tr>
<tr>
<td></td>
<td>( E^F_p - E^R_p ) increases as ( \nu ) increases</td>
</tr>
<tr>
<td></td>
<td>( i_p/\nu^{\frac{1}{2}} ) is independent of ( \nu )</td>
</tr>
<tr>
<td></td>
<td>( i^R_p/i^F_p ) generally = 1</td>
</tr>
<tr>
<td>Partially-reversible</td>
<td>( E_p ) increases by 30/n \text{ mv} for a ten fold increase</td>
</tr>
<tr>
<td>(i.e. Irreversible chemical reaction following charge transfer, E.C. mechanism)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( i_p/\nu^{\frac{1}{2}} ) is independent of ( \nu ).</td>
</tr>
<tr>
<td></td>
<td>( i^R_p/i^F_p ) increases toward 1 as ( \nu ) increases</td>
</tr>
<tr>
<td>Irreversible</td>
<td>( E_p ) shifts with ( \nu )</td>
</tr>
<tr>
<td></td>
<td>( i_p/\nu^{\frac{1}{2}} ) is independent of ( \nu ).</td>
</tr>
<tr>
<td></td>
<td>There is no current on the reverse scan</td>
</tr>
</tbody>
</table>

\( \nu = \text{sweep rate in mvs}^{-1} \)

\( n = \text{number of electrons involved in the redox process} \)
governing these and other types of charge-transfer processes).

5.2 (b) Stirred linear sweep voltammetry

When one stirs a test solution, containing a species which undergoes both a reversible oxidation and a reversible reduction (both processes involving the same number of electrons), whilst scanning ($\nu$ is ca. 10 mvs$^{-1}$) to increasingly cathodic or anodic potentials the voltammogram shown in Figure 5.3 results. These observations are of great importance since they allow oxidations (current under $i=0$ line) and reductions (current above $i=0$ line) of electroactive species to be distinguished. In addition, it is also possible to tell the number of electrons involved in the electrode process simply by comparison with limiting currents of known charge-transfer reactions.

Despite the distinct similarity of the above waves (Figure 5.3) to that of a damped polarogram, analysis of such a voltammogram requires a totally different set of assumptions regarding the nature of the mass transport of the electroactive species to the cathode or anode $^{(222)}$ i.e. the mathematical models appropriate in the wave profiles are different. In stirred voltammetry the mass transport is carried out by forced convection and diffusion, thus the mathematical treatment is necessarily more complicated than that used for polarography or for cyclic voltammetry in "quiet" solutions, although in the limit of efficient stirring, the polarographic ideal, where there is continuous replacement of electrolysed solution adjacent to the electrode, is approached.
Figure 5.3  Stirred and Unstirred Stationary Electrode Voltammetry

unstirred

stirred

Reduction

i = 0

+1.7 V

Oxidation
5.2(c) Linear sweep a.c. voltammetry

This very modern and elegant electrochemical technique is complementary to cyclic voltammetry and involves the superposition of a small alternating potential upon a linearly scanning d.c. potential. The net alternating current component is recorded as a function of the linear d.c. potential and, for a reversible redox step, the output current signal thus recorded is a symmetric peak, centred upon \( E_\text{½} \) of the corresponding d.c. polarogram, Figure 5.4. The superimposed voltage is generally sinusoidal in form (though any cyclic, small amplitude waveform, such as sawtooth or triangular may be used) normally with an amplitude of 10 mV and, with modern instrumentation a range of frequencies, \( \omega \), from ca. 10 - 1000 Hz may be used.

In a simple model, if the cell is considered as a capacitor-resistor network to which the sinusoidal voltage superimposed on a linear ramp is applied, the shape of the a.c. wave follows straightforwardly from considering it as the "first derivative" of the d.c. wave (see Figure 5.4). However, although this argument correctly predicts the shape of the wave, more sophisticated treatments are required to interpret the very valuable additional kinetic information contained in the cell response to variation in a.c. frequency, \( \omega \). Thus it would be wrong to regard an a.c. voltammogram as merely a first derivative presentation. An a.c. voltammogram contains the additional variable, \( \omega \), which effectively controls the time-scale of the experiment and provides a particularly sensitive test of departure from reversibility (see Table 5.2 for the reversibility criteria for linear sweep a.c. voltammetry).
Figure 5.4  A.C. Voltammetric Peak Centred on $E_1$ of the Corresponding Stationary and Non-Stationary d.c. Voltammetric Techniques.
Table 5.2  Linear sweep a.c. voltammetry criteria for a reversible charge-transfer process at 298 K

\[ E_p = E_{1/2} (d.c.), \text{ independent of concentration and } \omega \]

The wave is highly symmetric with a width at half high of 90 mV.

\[ i_p/\omega^{1/2} \] gives a linear plot which passes through the origin
A considerable advantage of a.c. voltammetry is that the technique discriminates against the background "residual" or "capacitative" current. This is possible because of the differing phase relationships which the "faradic" and "capacitative" current components have with the applied voltage. By phase-sensitive detection the relevant faradic current can be measured exclusively, thus increasing the sensitivity to $10^{-6}$ or $10^{-7}$ M solutions. Another virtue of a.c. voltammetry is that two adjacent waves can be accurately resolved even if the difference in formal potentials is 0.08 volts, which is very small compared with the 0.15 volts necessary for cyclic voltammetry. Even closer a.c. waves (40 mV) can be qualitatively distinguished; the degree of resolution increasing with decreasing alternating voltage amplitude.

It is worth noting that while a.c. polarography at a d.m.e. and a.c. voltammetry at a stationary electrode precisely parallel each other experimentally and theoretically for "reversible" systems this is no longer true for "quasi-reversible" systems which show displacements akin to those seen in linear sweep stationary electrode voltammetry (except where the electrode kinetics are sufficiently facile to maintain a reversible d.c. response, while none-the-less showing significant charge-transfer resistance to the a.c. perturbation)(223).
5.2(d) Electrosyntheses

For the synthetic chemist the ultimate goal of electrochemical studies is the electrogeneration of compounds which might be difficult, or impossible, to prepare by other means. Preparative-scale electrolyses fall into two classes: (a) controlled current (galvanostatic); and (b) controlled-potential (potentiostatic) (only type (b) will be discussed here since this technique was used in the electrogeneration of some unstable triple bridged binuclear complexes in Chapter 6).

Controlled-potential electrolysis consists straightforwardly of an experiment in which an electrochemical reaction is allowed to proceed at an electrode, the potential of which is held constant. This fixed potential is selected on the plateau of a polarographic or voltammetric wave (i.e. beyond $E_1$). As the starting material is consumed the current decays exponentially so that the approach to completion is indefinitely drawn out (Figure 5.5).

The currents passing through the solution may be relatively large (tens of milliamps in our apparatus) and so it is necessary to work with a three-electrode cell (Figure 5.6). This large current flows between the working electrode and the counter electrode, while that passing between the working and reference electrodes is negligible.

The response for this technique produces a graph of current against time, Figure 5.5. The area under the curve gives the total quantity of electrical charge which has passed during the electrolysis. In order to maintain a smooth fall in current during the electrolysis stirring should be steady and the electrodes not subject to fouling.
Figure 5.5  Characteristic Current-Time Response for Controlled-Potential Electrolysis
Figure 5.6  Three-Compartment Cell for Controlled-Potential Electrolysis

1 Reference Electrode
2 \( \text{N}_2 \) Inlet
3 Working Electrode
4 \( \text{N}_2 \) Outlet
5 Counter Electrode
Although we have emphasised in situ characterisation of electrode products, which are often unstable (as described in Chapter 6), a number of workers have reported successful isolation of pure products from electrolytic reductions\(^{66,224}\) and oxidations\(^{224}\).

5.3 Results and Discussion

The data summarised in Tables 5.3 and 5.4, i.e. the electrode potentials of the redox processes exhibited by some \(M_2(II/II), M_2(II/III)\) \((M = Ru, Os)\) and \(Ru_2(III/III)\) triple bridged complexes, will now be discussed in separate sub-sections before being unified by a number of structure/electrode potential correlations.

\(a\) \([(PR_3)_3MX_3M(PR_3)_3]^+\) and related \(M_2(II/II)\) cations

In a brief communication\(^{225}\) in 1978 a number of triple chloro bridged complexes of type \([Ru_2Cl_3(PR_3)_6]B\bar{O}_4\) (e.g. \(PR_3 = PMe_2\bar{O}, P(OMe)\bar{O}_2\)) were described as undergoing an irreversible oxidation at \(ca. +1.0\) V and a reversible one-electron oxidation at \(ca. +1.3\) V in 0.5 M \(Bu_4NClO_4/CH_2Cl_2\) electrolyte solutions against a Ag/AgI reference electrode.

However, new studies in 0.5 M \(Bu_4NBF_4/CH_2Cl_2\) or MeCN electrolyte solutions (changing the electrolyte or the solvent has no apparent effect on the redox behaviour) indicate that the irreversible oxidation at \(ca. +1.0\) V is attributable to \(B\bar{O}_4^-\). These new studies also show that the previously mentioned reversible one-electron oxidation at \(ca. +1.3\) V is the easier of two successive reversible one-electron
oxidations which are separated by ca. 0.5 V (Figure 5.7).
Furthermore, Table 5.3 shows the separation of the two redox couples exhibited by \([\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]^+\) cations (\(\text{PR}_3 = \text{PMe}_2\emptyset, \text{PMe}\emptyset_2, \text{PET}_2\emptyset, \text{PET}\emptyset_2\)) is also ca. 0.5 V (despite the small, but significant, effect of variable PR₃ basicities and back-bonding capabilities on the \(E_{1/2}\) values of both redox couples).

The availability of \([\text{Ru}_2\text{X}_3(\text{PMe}_2\emptyset)]^+\) cations (\(X = \text{Br}^-, \text{I}^-, \text{OH}^-\) and \(\text{SEt}^-\)) (see Chapter 3) allows us to investigate the effect of changing the identity of the bridging ligands on the redox properties of the otherwise identical cations. Table 5.3 shows that exchanging bridging Cl⁻ ion for Br⁻ or I⁻ ions has very little effect on the redox properties of these compounds. The small decrease in \(E_{1/2}\) (for both the first and second redox couples, which are still separated by ca. 0.5 V) of ca. 10 mV for the bromo bridged complex and ca. 70 mV for the iodo bridged complex (with respect to the chloro bridged complex) is probably primarily due to the decreasing charge/radius ratio of \(\text{I}^- < \text{Br}^- < \text{Cl}^-\). Both the chloro and bromo bridged complexes undergo two successive fully reversible one-electron oxidations. In contrast, the iodo complex undergoes only one fully reversible one-electron oxidation, the second oxidation being only "partially-reversible". These observations may be simply explained in terms of I⁻ ion

\[^{+}\text{i.e. in C.V. } i_p^{R/i_p^{F}}\text{ increases toward unity with increasing scan rate, consistent with slow reaction of electrode product following reversible charge-transfer.}\]
Figure 5.7  Cyclic and A.C. Voltammetry of $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ø})_6]\text{Cl}$
being much "softer", or polarisable, than either Cl\(^-\) or Br\(^-\) ion and hence less likely to stabilise high oxidation state products.

Table 5.3 shows that exchanging bridging OH\(^-\) or SEt\(^-\) ions for bridging halide ion in \([\text{Ru}_2X_3(\text{PMe}_2\text{Ø})_6]\)^+ causes a substantial effect on the redox potentials of these compounds. The \([\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{Ø})_6]\)^+ cation undergoes a reversible one-electron oxidation at +0.86 V (ca. 0.5 V more facile than its Cl\(^-\), Br\(^-\) or I\(^-\) analogues) and an irreversible oxidation at +1.37 V (again the separation between the two processes is ca. 0.5 V). The dramatic decrease in the two oxidation potentials when X = OH\(^-\) ion, compared with X = Cl\(^-\), Br\(^-\), I\(^-\) ion, is attributed to the far superior electron donating characteristics of the "hard" OH\(^-\) ligand (which has a tendency to form high oxidation state products) over the "softer" weak \(\pi\)-acceptor Cl\(^-\), Br\(^-\) and I\(^-\) ligands. The irreversibility of the second oxidation may reflect the extreme kinetic lability of the Ru\(_2\)(III/III)^3+ product, (which will be strongly activated toward nucleophilic attack in the highly coordinating MeCN solvent) rather than the intrinsic thermodynamic instability of the Ru\(_2\)(III/III)^3+ trication itself. (N.B. the poorly coordinating solvent CH\(_2\)Cl\(_2\) contains sufficient HCl to protonate the OH\(^-\) bridges and yield the triple chloro bridged complex almost instantly).

The SEt\(^-\) bridged cation \([\text{Ru}_2(\text{SEt})_3(\text{PMe}_2\text{Ø})_6]\)^+ differs from the halide and OH\(^-\) bridged complexes by having a single significantly easier, partially-reversible oxidation
at +0.67 V at 233 K. Since the oxidation is partially reversible, i.e. the electron-transfer process is fast but is accompanied by a slow following reaction, the significance of $E_i$ is not clear and will require further work.

Comparison of the electrochemical properties of the cations $[\text{M}_2\text{Cl}_3(\text{PETO}_2)_6]^+$ (M = Ru, Os) shows that for these symmetric, isostructural complexes, the separation of successive reversible couples is roughly the same (i.e. ca. 0.5 V). However, the Os cation undergoes these redox processes at potentials ca. 0.2 V easier than its Ru analogue. This is readily understandable since it reflects the previously noted (Chapter 1) ability of osmium to stabilise higher oxidation state complexes with respect to ruthenium. This is principally due to the smaller successive ionisation potentials of osmium with respect to ruthenium.

Electrochemical studies on the diazadiene containing cation $[\text{Ru}_2\text{Cl}_3(\text{CY}_2\text{N}_2(\text{CH}_2)_2(\text{PETO}_3)_2)]^+$ (28) show it to undergo a single reversible one-electron oxidation at +1.10 V and a reversible one electron reduction at -1.18 V. The former reflects a metal-based oxidation to give the mixed-valence dication, whilst the latter is believed to be essentially ligand-based. The formation of coordinated diazadiene$^-$ is certainly not unexpected since 2,2'-bipy and 1,10-phen (essentially "closed" diazadienes) both exhibit such behaviour.
Table 5.3 shows the electrochemical behaviour of

$\text{Ru}_2\text{Cl}_4(\text{PR}_3)_5$ (PR$_3$ = PMe$_2$Ø, PMeØ$_2$, PET$_2$Ø, PETØ$_2$, PClØ$_2$) (16)
and $\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5$ (31c). At ambient temperatures these neutral complexes undergo a single reversible one-electron oxidation at modest potentials and a "partially reversible" one-electron oxidation ca. 1.0 V beyond the first. At low temperatures e.g. 233 K $\text{Ru}_2\text{Cl}_4(\text{PET}_2\text{Ø})_5$ shows two successive one-electron oxidations at +0.47 V and +1.50 V (Figure 5.8). The first oxidation occurs at the "harder" Ru(II) centre i.e. that containing the terminal Cl$^-$ ion, whilst the second oxidation occurs at the "softer" Ru(II) centre i.e. that containing three terminal PR$_3$ groups.

Thus, the first oxidation potential of $\text{Ru}_2\text{Cl}_4(\text{PET}_2\text{Ø})_5$ is 0.73 V less positive than that of its related cation $[\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ø})_6]^+$, and it appears that replacing a PR$_3$ ligand by a Cl$^-$ ion on the redox active centre results in a ca. 0.7 V decrease in its oxidation potential. This proves to be a general observation (see later). The donor/acceptor properties of the neutral ligands may also have considerable effect if they are drastically varied e.g. the first oxidation potential of the PEt$_2$Ø (high basicity) complex is ca. 0.7 V easier than that of the analogous PClØ$_2$ (low basicity) complex.
Figure 5.8 Stirred and Unstirred Voltammetry of $\text{Ru}_2\text{Cl}_4(\text{PET}_2\varnothing)_5$ at 233 K
5.3(c) **Ru$_2$X$_4$Y(PR$_3$)$_4$ and related complexes**

In 1978 a brief communication by Heath, Stephenson and co-workers\(^{225}\) reported the electrochemical characteristics of (PØ$_3$)$_2$YRuCl$_3$RuCl(PØ$_3$)$_2$ (Y = CO, CS) (19). The authors showed that replacement of CO by CS had a negligible effect on the oxidation potential (0.01 V easier) which was interpreted to mean that the adjacent Ru centre, remote from CO/CS, was involved in the redox couple (see Chapter 6 for $^3$P-$^1$H n.m.r. spectroscopic confirmation). Further electrochemical evidence for an essentially localised oxidation on the "harder" terminal chloride end of (19) is given by comparing the oxidation potentials of (PØ$_3$)$_2$YRuCl$_3$RuClY(PØ$_3$) (Y = CO, CS) (20a,b,c) with (19) (Y = CO, CS) (see Table 5.3). Thus, (20a,b,c) (Y = CO) oxidises at a potential ca. 0.7 V less accessible than (19) (Y = CO) and (20a,b,c) (Y = CS) oxidises at a potential ca. 0.5 V less accessible than (19) (Y = CS) (the CS complex oxidises ca. 0.2 V more easily than its CO analogue due to the ability of CS to donate more electron density to the metal centre). The almost negligible effect on the oxidation potential of replacing the Ru(II) carbonyl containing centre of (19) by an Os(II) centre is also consistent with the oxidation occurring at the "harder" terminal chloride bearing end of the molecule.

Table 5.3 shows that replacing PØ$_3$ by the more basic P(P-tol)$_3$ has the small, but significant, effect of reducing the oxidation potential of (19) (Y = CO, CS) by 0.10 V.
Comparison of the oxidation potential of (19) (Y = CO) and its bromo analogue (37) confirms the impression created by electrochemical studies on \([\text{Ru}_2X_3(\text{PMe}_2\emptyset)_6]^+\) (X = Cl\(^-\), Br\(^-\)) i.e. replacement of chloride ligands by bromide ligands has a negligible effect on the ease of oxidation. Comparison of the electrochemical properties of (19) (Y = CO, CS) with \((\text{P}\emptyset_3)_2\text{YRuCl(OH)}_2\text{Ru(OH)}(\text{P}\emptyset_3)_2\) (Y = CO, CS) (46) again reinforces the impression created by electrochemical studies of \([\text{Ru}_2X_3(\text{PMe}_2\emptyset)_6]^+\) (X = Cl\(^-\), OH\(^-\)) i.e. replacement, or partial replacement, of chloride ligands by hydroxide ligands greatly facilitates oxidation (see Table 5.3).

Finally, an electrochemical study of \([((\text{P}\emptyset_3)_2(\text{CS})\text{RuCl}_3\text{Ru(CS)}(\text{P}\emptyset_3)_2)]^+\) shows an irreversible oxidation at ca. +1.5 V, thus showing the inability of "soft" terminal ligands such as P\emptyset_3 and CS to stabilise Ru(III) centres at moderate potentials.

5.3(d) \(\text{M}_2\text{Cl}_5(\text{LR}_3)_4\) and related neutral mixed-valence \(\text{Ru}_2(\text{II}/\text{III})\) complexes

(i) "Asymmetric" mixed-valence complexes

These complexes (see Table 5.4) generally undergo a reversible one-electron oxidation and a reversible one-electron reduction which are characteristically separated by ca. 1.5 V [the major exceptions being \((\text{PR}_3)_2\text{YRuCl}_3\text{RuCl}_2(\text{PR}_3)\) \((\text{PR}_3 = \text{P}\emptyset_3; \ \ Y = \text{CO, CS}; \ \text{PR}_3 = \text{P}(\emptyset\text{-tol})_3; \ \ Y = \text{CO}) (49) which, as shown in the previous section, undergo oxidations at the soft, Y end of the molecule only with extreme reluctance]. Figure 5.9 shows the electrochemical
Figure 5.9  Stirred and Unstirred Voltammetry of $\text{Ru}_2\text{Cl}_5(\text{PET}_2\text{O})_4$
behaviour associated with the "asymmetric" neutral triple chloro bridged complex \((\text{PEt}_2\bar{\text{O}})_3\text{RuC}_3\text{RuCl}_2(\text{PEt}_2\bar{\text{O}})\) (50). Such an electrochemical "signature" is characteristic of all the "asymmetric" mixed-valence complexes of type (50) in Table 5.4 since they all undergo facile reductions at the "hard" terminal chloride end of the binuclear unit and difficult oxidations at the adjacent "soft" metal centre.

Although the separation between the two redox couples is characteristically and consistently ca. 1.5 V, the actual potentials naturally depend on both the donor/acceptor properties of the neutral ligands and the identity of the metal centre in the individual complex. Thus the complex \((\text{PR}_3)_3\text{RuCl}_3\text{RuCl}_2(\text{PR}_3)\) (50) with \(\text{PR}_3 = \text{PMe}_2\bar{\text{O}}\) (high basicity) oxidises ca. 0.06 V more easily than its \(\text{PMeO}_2\) (low basicity) analogue, and equally, the latter complex reduces ca. 0.05 V more easily than the former. The redox properties of the mixed-valence compounds \((\text{As(p-tol})_3)_3\text{MCl}_3\text{MCl}_2(\text{As(p-tol})_3)\) \(\text{M} = \text{Ru, Os}\) (7) clearly demonstrate the ability of Os to stabilise higher oxidation states more easily than Ru. Thus both the II/II / II/III and II/III / III/III couples are shifted to less positive potentials by ca. 0.5 V for the Os complex.

(ii) "Symmetric" mixed-valence complexes

Due to our inability to synthesise the complexes described by Nicholson, i.e. \((\text{PR}_3)_2\text{ClRuCl}_3\text{RuCl}(\text{PR}_3)_2\) \(\text{PR}_3 = \text{PBu}_3^n, \text{P pent}_3^n\) (67) (6), only three complexes are available for study, these are: \((\text{LR}_3)_2\text{ClMCl}_3\text{MCl}(\text{LR}_3)_2\)
Table 5.4 shows that all three complexes undergo both reversible one-electron oxidations and reductions at modest potentials (compared to the "asymmetric" complexes of the same stoichiometry, described above) [See Figure 5.10(a)]. The Os complex undergoes oxidation and reduction at less anodic potentials than its Ru analogues, as has been described previously. Curiously however, the separation between the redox couples of the Os complex of ca. 0.5 V is ca. 0.2 V less than that observed for the two Ru complexes. This observation is regarded as significant and will be considered again later.

Although apparently fully reversible at room temperature the more soluble Ru complex with $LR_3 = As(p$-tol)$_3$ exhibits evidence of a slow charge-transfer for the reduction at 213 K, the oxidation being unaffected (Figure 5.10(b)). It is possible that the sluggish step may be associated with a structural rearrangement such as the loss of a metal-metal interaction.

Only two of the above complexes are known, these are for $AsR_3 = As\Phi_3$ and $As(p$-tol)$_3$. Both these complexes exhibit two successive reversible one-electron reductions which are separated by ca. 1.0 V (Figure 5.11). Note that the degree of asymmetry, in terms of terminal chloride ligands, is intermediate between that of the "symmetric" and "asymmetric" $M_2X_5L_4$ compounds and equivalent to that of the $M_2X_4L_5$ compounds (see below).
Figure 5.10 Voltammetry of $\text{Ru}_2\text{Cl}_5(\text{As}(\text{p-tol})_3)_4$
Figure 5.11 Stirred and Unstirred Voltammetry of $\text{Ru}_2\text{Cl}_6(\text{As(p-tol)}_3)_3$
5.3(f) Structure/Redox Potential Correlations

By correlating the electrode potentials of the $M_2$(II/II), $M_2$(II/III) ($M = \text{Ru, Os}$) and Ru$_2$(III/III) complexes (Tables 5.3 and 5.4) with relevant structural parameters such as the number of chlorides per metal centre or the asymmetry in chloride distribution a great deal of valuable information can be obtained.

Thus Figure 5.12, which correlates the $E_{1/2}$ of the Ru$_2$(II/II)/Ru$_2$(II/III) redox couple (Ru II/III redox couple for monomeric complexes) with the number of chloride ions per Ru centre for a number of monomeric and triple chloro bridged binuclear complexes (which contain only the metal, chloride and PMe$_2$Ø ligands), shows quite simply that bridging chlorides may be considered as $\frac{1}{2}$ Cl$^-$ ions as far as their influence on $E_{1/2}$ is concerned. The diagram suggests that the effect of replacing one neutral PMe$_2$Ø ligand by a terminal chloride, on the redox centre, in a monomeric or binuclear complex, is to make the redox couple ca. 0.7 V more negative (N.B. these correlations apply equally well to other neutral ligand systems such as PEt$_2$Ø or As(2-tol)$_3$ and not merely to PMe$_2$Ø).

Figure 5.13, is designed to show that the systematic effect of terminal chloride ions on the remote centre is to make the redox couple of the active metal centre ca. 0.25 V more negative per Cl$^-$ ion (i.e. substantially less than a directly attached Cl$^-$ ion, as expected).
Figure 5.12  Structure/Redox Potential Correlation Diagram
Including both Monomeric and Triple Bridged Binuclear complexes

represents Ru(I)/Ru(II) redox couple
represents Ru(II)/Ru(II/III) redox couple
indicates the Ru centre undergoing oxidation
P = PMe₂Ø

N.B. The remote (uninvolved) metal centre (for the binuclear complexes) is unchanged (-Ru(PMe₂Ø)₃ moiety in the above plot).
Parallel plots exist for other remote moieties
Figure 5.13 Structure/Oxidation Potential Correlation Diagram showing the Influence of Cl$^-\,$ Ion(s) of One Ru Centre on the Oxidation Potential of its adjacent Ru Centre

![Diagram showing the correlation between $\Delta Cl^-$ and oxidation potential. The diagram contains points representing different complexes with $P = PEt_2\phi$ and $P = PMe_2\phi$. The $\Delta Cl^-$ axis represents asymmetry in Cl$^-\,$ ion distribution.]

$\Delta Cl^-$ (Asymmetry in Cl$^-\,$ ion distribution)

- * represents $P = PEt_2\phi$
- . represents $P = PMe_2\phi$
- indicates the Ru centre undergoing oxidation

Figure 5.14 Structure/Redox Potential Diagram Showing the variation of $\Delta E$ with $\Delta Cl^-$

![Diagram showing the variation of $\Delta E$ with $\Delta Cl^-$ for different complexes. The diagram includes points for different complexes with $P = PEt_2\phi$ and $As = As(p$-tol)$_3$.]

$\Delta E(\Delta E_{Ru(III)/Ru(II)}/\Delta E_{Ru(III)/Ru(II)}/\Delta E_{Ru(II)/Ru(II)})$ vs $\Delta Cl^-$ (Asymmetry in Cl$^-\,$ ion distribution)

- $P = PEt_2\phi$
- $As = As(p$-tol)$_3$
Figure 5.14 which correlates the separation in successive couples for certain binuclear Ru complexes, with the asymmetry in chloride ion distribution, shows a linear relationship for \((\text{PET}_2\text{O})_3\text{RuCl}_3\text{RuCl}(\text{PET}_2\text{O})_3-x\) \((x = 0, 1, 2)\). A parallel line connects \((\text{As}(\text{p-tol})_3)_3\text{ClRuCl}_3\text{RuCl}_2(\text{As}(\text{p-tol})_3)_x\) \((x = 0, 1)\) but the separation of couples for \((\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As}(\text{p-tol})_3)_2\) (6) is ca. 0.2 V higher than anticipated (N.B. this extra ca. 0.2 V was also noted earlier when compared with the separation in the two redox couples of the "symmetric" Os complex \((\text{PO}_3)_2\text{ClOsCl}_3\text{OsCl}_-(\text{PO}_3)_2\) (6)).

By applying the criterion derived from Figure 5.13 i.e. the effect of "distant" terminal chloride is to make the redox couple of the adjacent metal centre ca. 0.25 V more negative per Cl\(^-\) ion, to \((\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}_2(\text{As}(\text{p-tol})_3)_3\) (8), the predicted Ru\(_2\)(II/III)/Ru\(_2\)(III/III) redox couple for \((\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As}(\text{p-tol})_3)_2\) (6) is +0.83 V (which is precisely confirmed experimentally). Thus, it would appear that the greater separation of couples for this complex is derived from its resistance to reduction at the expected potential of ca. +0.27 V.

Both the resistance to reduction, and the slow rate of charge-transfer of the reduction of \((\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3-\text{RuCl}(\text{As}(\text{p-tol})_3)_2\) (6) may indicate the presence of a metal-metal interaction in this compound. The former might indicate the excess energy required to overcome the interaction, while the latter, as described earlier, might be due to a
small structural perturbation caused through loss of such an interaction (see Chapter 6 for the discussion of magnetic and spectroscopic evidence supporting the concept of a metal-metal interaction in this compound).

Finally, the correlations derived from Figures 5.12 and 5.13 can also be used to calculate thermodynamic data which is useful in predicting the position (energy) of intervalence charge transfer (IT) bands for "asymmetric" mixed-valence complexes (see Chapter 6 and Appendix II).

5.4 Conclusions

The electrochemical data in Table 5.3 clearly shows that complexes of type \([M_2X_3(PR_3)_6]X\) generally undergo two successive reversible one-electron oxidations which are separated by ca. 0.5 V. The potentials of the oxidations are markedly sensitive to both the identity of the metal centres \(M\) (\(M = \text{Ru}, \text{Os}\)) and the donor/acceptor characteristics of the \(PR_3\) ligands. Changing the bridging units, \(X\), from halides such as \(\text{Cl}^-\), \(\text{Br}^-\) or \(\text{I}^-\) to a better \(\sigma\)-donor such as \(\text{OH}^-\) greatly decreases the first oxidation potential of these complex cations. Although the hydroxide containing species is more thermodynamically stable than its halide analogues, it is likely that it is more kinetically labile, especially after activation to nucleophilic attack by oxidation.
The electrochemical properties of Ru$_2$Cl$_4$L$_5$ (L = PR$_3$, Me$_2$SO) (16, 31c) and Ru$_2$X$_4$Y(PR$_3$)$_4$ (19, 37) are very similar when L = PClO$_2$ or Me$_2$SO i.e. both types of complex show only a single one-electron oxidation (at the terminal Cl$^-$ ligand end of the molecule), the adjacent Ru(II) centre, which contains "soft" ligands such as PØ$_3$, P(º-tol)$_3$, CO, CS for (19) and PClO$_2$, Me$_2$SO for (16) or (31c), being incapable of supporting a Ru(III) centre. However, when PR$_3$ is a basic phosphine such as PEt$_2$Ø, two successive reversible one-electron oxidations separated by ca. 1.0 V are observed.

Both "symmetric" and "asymmetric" mixed-valence complexes exhibit a reversible one-electron oxidation and reduction. The "asymmetric" complexes generally have a ca. 1.5 V separation between redox couples, while the "symmetric" Ru complexes have an anomalously high separation of ca. 0.7 V (ca. 0.2 V higher than that predicted from structure/electrode potential correlations and ca. 0.2 V higher than that observed for the "symmetric" mixed-valence Os complex $(PØ_3)_2C10sCl_3OsCl(PØ_3)_2$ (6)). Both the Ru$_2$(III/III) complexes of type $(AsR_3)_2C1RuCl_3RuCl_2(AsR_3)$ (8) undergo two successive reversible one-electron reductions which are separated by ca. 1.0 V.

Finally, structure/electrode potential correlations show that replacement of a neutral PR$_3$ or AsR$_3$ ligand by Cl$^-$ ion in monomeric or triple chloro bridged binuclear Ru complexes decreases the redox couple of the metal centre it is bound to by ca. 0.7 V per Cl$^-$ ion. In addition,
the effect of a terminal Cl\textsuperscript{−} ion on one metal centre of a triple chloro bridged complex is to decrease the redox couple of the adjacent metal centre by ca. 0.25 V.

5.5 Experimental

Experimental details were as for those described in Chapter 2, except that in addition to the usual electrolyte consisting of 0.5 M Bu\textsubscript{4}NBF\textsubscript{4}/CH\textsubscript{2}Cl\textsubscript{2}, 0.5 M solutions of Bu\textsubscript{4}NBF\textsubscript{4}/MeCN or LiClO\textsubscript{4}/THF were also used, where indicated (see Tables 5.3 and 5.4).

Complexes subject to electrochemical investigation

The following compounds were prepared using literature methods: RuCl\textsubscript{3}(PMe\textsubscript{2}Ø)\textsubscript{3} (64), RuCl\textsubscript{2}(PMe\textsubscript{2}Ø)\textsubscript{4} (122), [Ru\textsubscript{2}Cl\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]Cl (PR\textsubscript{3} = PMe\textsubscript{2}Ø, PMeØ\textsubscript{2}, PET\textsubscript{2}Ø, PETØ\textsubscript{2}) (113), [Os\textsubscript{2}Cl\textsubscript{3}(PETØ\textsubscript{2})\textsubscript{6}]Cl (113), [Ru\textsubscript{2}Cl\textsubscript{3}(Cy\textsubscript{2}N\textsubscript{2}(CH\textsubscript{2})\textsubscript{2}(PØ\textsubscript{3})\textsubscript{2}]Cl (190), Ru\textsubscript{2}Cl\textsubscript{4}(PR\textsubscript{3})\textsubscript{5} (PR\textsubscript{3} = PMe\textsubscript{2}Ø (66), PMeØ\textsubscript{2} (122), PET\textsubscript{2}Ø (122), PETØ\textsubscript{2} (122), PC1Ø\textsubscript{2} (122), Ru\textsubscript{2}Cl\textsubscript{4}Y(PR\textsubscript{3})\textsubscript{4} (Y = CO, CS; PR\textsubscript{3} = PØ\textsubscript{3}, P(p-tol)\textsubscript{3}) (181-183), RuOsCl\textsubscript{4}(CO)(PØ\textsubscript{3})\textsubscript{4} (142), Ru\textsubscript{2}Cl\textsubscript{4}Y\textsubscript{2}(PØ\textsubscript{3})\textsubscript{3} (Y = CO, CS) (182), [Ru\textsubscript{2}Cl\textsubscript{3}(CS)\textsubscript{2}(PØ\textsubscript{3})\textsubscript{4}]Cl (182), (LR\textsubscript{3})\textsubscript{2}ClMCl\textsubscript{3-MCl(LR\textsubscript{3})\textsubscript{2}} (M = Os; LR\textsubscript{3} = PØ\textsubscript{3}; M = Ru; LR\textsubscript{3} = AsØ\textsubscript{3}, As(p-tol)\textsubscript{3}) (66), [Ru\textsubscript{2}Cl\textsubscript{3}(PØ\textsubscript{3})\textsubscript{5}(MeCN)]BØ\textsubscript{4}, Ru\textsubscript{2}Cl\textsubscript{4}(Me\textsubscript{2}SO)\textsubscript{5} were prepared as described in Chapter 2. [Ru\textsubscript{2}Br\textsubscript{3}(PMe\textsubscript{2}Ø)\textsubscript{6}]Br, [Ru\textsubscript{2}I\textsubscript{3}(PMe\textsubscript{2}Ø)\textsubscript{6}]PF\textsubscript{6}, [Ru\textsubscript{2}(OH)\textsubscript{3}(PMe\textsubscript{2}Ø)\textsubscript{6}]PF\textsubscript{6}, [Ru\textsubscript{2}(SEt)\textsubscript{3}(PMe\textsubscript{2}Ø)\textsubscript{6}]BØ\textsubscript{4}, Ru\textsubscript{2}Br\textsubscript{4}(CO)(PØ\textsubscript{3})\textsubscript{4}, Ru\textsubscript{2}Cl(OH)\textsubscript{3}Y(PØ\textsubscript{3})\textsubscript{4} (Y = CO, CS) were prepared as in Chapter 3.
<table>
<thead>
<tr>
<th>Compound</th>
<th>(II/II)/(II/III)</th>
<th>(II/II)/(III/III)</th>
<th>Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(PMe$_2$Ø)$_3$RuCl$_3$Ru(PMe$_2$Ø)$_3$]Cl</td>
<td>+1.33</td>
<td>+1.87</td>
<td>0.54 a,b</td>
</tr>
<tr>
<td>[(PMe$_2$Ø)$_3$RuBr$_3$Ru(PMe$_2$Ø)$_3$]Br</td>
<td>+1.32</td>
<td>+1.84</td>
<td>0.52 a,b</td>
</tr>
<tr>
<td>[(PMe$_2$Ø)$_3$RuI$_3$Ru(PMe$_2$Ø)$_3$]PF$_6$</td>
<td>+1.26 (+1.77)</td>
<td>(+1.77)</td>
<td>0.51 a</td>
</tr>
<tr>
<td>[(PMe$_2$Ø)$_3$Ru(OH)$_3$Ru(PMe$_2$Ø)$_3$]PF$_6$ (33)</td>
<td>+0.86 [+1.37]</td>
<td>[+1.37]</td>
<td>0.51 b</td>
</tr>
<tr>
<td>[(PMe$_2$Ø)$_3$Ru(SEt)$_3$Ru(PMe$_2$Ø)$_3$]BO$_4$ (41)</td>
<td>(+0.67)*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[(PMeØ)$_3$RuCl$_3$Ru(PMeØ)$_3$]Cl</td>
<td>+1.42 (+1.93)</td>
<td>(+1.93)</td>
<td>0.51 a</td>
</tr>
<tr>
<td>[(PET$_2$Ø)$_3$RuCl$_3$Ru(PET$_2$Ø)$_3$]Cl</td>
<td>+1.20</td>
<td>+1.75</td>
<td>0.55 a,b</td>
</tr>
<tr>
<td>[(PETØ)$_3$RuCl$_3$Ru(PETØ)$_3$]Cl</td>
<td>+1.27 (+1.83)</td>
<td>(+1.83)</td>
<td>0.56 a</td>
</tr>
<tr>
<td>[(PETØ)$_3$OsCl$_3$Os(PETØ)$_3$]Cl</td>
<td>+1.07</td>
<td>+1.61</td>
<td>0.54 a</td>
</tr>
<tr>
<td>[(PET$_2$Ø)$_3$RuCl$_3$Ru(PET$_2$Ø)$_3$]MeCN)BO$_4$ (32)</td>
<td>+1.18 (+1.74)</td>
<td>(+1.74)</td>
<td>0.56 a</td>
</tr>
<tr>
<td>[(PØ)$_3$(Cy$_2$N$_2$(CH$_2$)$_2$)RuCl$_3$Ru(Cy$_2$N$_2$(CH$_2$)$_2$)(PØ)$_3$]Cl (28)</td>
<td>+1.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(PMe$_2$Ø)$_3$RuCl$_3$RuCl(PMe$_2$Ø)$_2$ (16)</td>
<td>+0.55 (+1.55)</td>
<td>+1.55</td>
<td>1.00 a</td>
</tr>
<tr>
<td>(PMeØ)$_3$RuCl$_3$RuCl(PMeØ)$_2$ (16)</td>
<td>+0.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(PET$_2$Ø)$_3$RuCl$_3$RuCl(PET$_2$Ø)$_2$ (16)</td>
<td>+0.47</td>
<td>+1.50*</td>
<td>1.03 a</td>
</tr>
<tr>
<td>(PETØ)$_3$RuCl$_3$RuCl(PETØ)$_2$ (16)</td>
<td>+0.58 (+1.53)</td>
<td>(+1.53)</td>
<td>0.95 a</td>
</tr>
<tr>
<td>(PC$_2$Ø)$_3$RuCl$_3$RuCl(PC$_2$Ø)$_2$ (16)</td>
<td>+1.20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Me$_2$SO)$_3$RuCl$_3$RuCl(Me$_2$SO)$_2$ (31c)</td>
<td>+1.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Formula</td>
<td>$E'_{\text{red}}$ (V)</td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>-----------------------</td>
<td>---</td>
<td>----</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CO)}\text{RuCl}_3\text{RuCl}(\text{P}^\circ_3)_2)</td>
<td>+0.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CO)}\text{RuBr}_3\text{RuBr}(\text{P}^\circ_3)_2)</td>
<td>+0.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CS)}\text{RuCl}_3\text{RuCl}(\text{P}^\circ_3)_2)</td>
<td>+0.74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}(\text{p-tol})_3)^2\text{(CO)}\text{RuCl}_3\text{RuCl}(\text{P}(\text{p-tol})_3)_2)</td>
<td>+0.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}(\text{p-tol})_3)^2\text{(CS)}\text{RuCl}_3\text{RuCl}(\text{P}(\text{p-tol})_3)_2)</td>
<td>+0.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CO)}\text{RuCl(OH)}_2\text{Ru(OH)}(\text{P}^\circ_3)_2)</td>
<td>+0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CS)}\text{RuCl(OH)}_2\text{Ru(OH)}(\text{P}^\circ_3)_2)</td>
<td>+0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CO)}\text{OsCl}_3\text{RuCl}(\text{P}^\circ_3)_2)</td>
<td>+0.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CO)}\text{RuCl}_3\text{RuCl}(\text{CO})(\text{P}^\circ_3)_2)</td>
<td>+1.42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>((\text{P}^\circ_3)^2\text{(CS)}\text{RuCl}_3\text{RuCl}(\text{CS})(\text{P}^\circ_3)_2)</td>
<td>+1.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{[(P}^\circ_3)^2\text{(CS)}\text{RuCl}_3\text{RuCl}(\text{P}^\circ_3)_2}]\text{Cl})</td>
<td>[+1.50]</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\( a, b, c \) versus Ag/AgI reference at which ferrocene is oxidised at +0.60 volts in 0.5M \( \text{Bu}^\text{4} \)\text{NBF}_4/\text{CH}_2\text{Cl}_2 or MeCN or 0.5M \text{LiClO}_4/\text{THF} with platinum as working electrode

( ) partially reversible

* Measured at \(-40^\circ\text{C}\)

[ ] irreversible
Table 5.4  Electrode Potentials for some Triple Bridged Ruthenium and Osmium Complexes 

in Initial Oxidation States (II/III) and (III/III) $E^\circ$ (volts) at 20°C in $\text{CH}_2\text{Cl}_2/0.5\text{M Bu}_n^+\text{NBF}_4^-$

<table>
<thead>
<tr>
<th>Compound</th>
<th>(II/III)/(II/II)</th>
<th>(II/III)/(III/III)</th>
<th>Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{As}_3\text{O}_3)_2\text{ClRuCl}_3\text{RuCl(As}_3\text{O}_3)_2$</td>
<td>+0.14</td>
<td>+0.90</td>
<td>0.76</td>
</tr>
<tr>
<td>$(\text{P}_3\text{O}_3)_2\text{ClOsCl}_3\text{OsCl(P}_3\text{O}_3)_2$</td>
<td>-0.06</td>
<td>+0.50</td>
<td>0.56</td>
</tr>
<tr>
<td>$(\text{As(p-tol)}_3)_2\text{ClRuCl}_3\text{RuCl(As(p-tol)}_3\text{)_2}$</td>
<td>+0.10</td>
<td>+0.83</td>
<td>0.73</td>
</tr>
<tr>
<td>$(\text{As(p-tol)}_3)_3\text{RuCl}_2\text{RuCl(As(p-tol)}_3\text{)_3}$</td>
<td>-0.22</td>
<td>+1.25</td>
<td>1.47</td>
</tr>
<tr>
<td>$(\text{As(p-tol)}_3)_3\text{OsCl}_3\text{OsCl(As(p-tol)}_3\text{)_3}$</td>
<td>-0.71</td>
<td>+0.82</td>
<td>1.53</td>
</tr>
<tr>
<td>$(\text{As}_3\text{O}_3)_3\text{OsCl}_3\text{OsCl}_2(\text{As}_3\text{O}_3)_2$</td>
<td>-0.78</td>
<td>+0.60</td>
<td>1.38</td>
</tr>
<tr>
<td>$(\text{As(p-CI}_3\text{O)}_3)_3\text{RuCl}_3\text{RuCl}_2(\text{As(p-CI}_3\text{O)}_3)_3$</td>
<td>-0.42</td>
<td>+1.26</td>
<td>1.68</td>
</tr>
<tr>
<td>$(\text{PMe}_2\text{O}_2)_3\text{RuCl}_3\text{RuCl}_2(\text{PMe}_2\text{O}_2)_3$</td>
<td>-0.20</td>
<td>+1.36</td>
<td>1.56</td>
</tr>
<tr>
<td>$(\text{PMeO}_2)_3\text{RuCl}_3\text{RuCl}_2(\text{PMeO}_2)_3$</td>
<td>-0.15</td>
<td>+1.42</td>
<td>1.57</td>
</tr>
<tr>
<td>$(\text{PET}_2\text{O}_2)_3\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{O}_2)_3$</td>
<td>-0.28</td>
<td>+1.27</td>
<td>1.55</td>
</tr>
<tr>
<td>$(\text{P}_3\text{O}_3)_2(\text{CO})\text{RuCl}_3\text{RuCl}_2(\text{P}_3\text{O}_3)_2$</td>
<td>+0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{P}_3\text{O}_3)_2(\text{CS})\text{RuCl}_3\text{RuCl}_2(\text{P}_3\text{O}_3)_2$</td>
<td>+0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{PET}_2\text{O}_2)_3(\text{CO})\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{O}_2)_3$</td>
<td>-0.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{As(p-tol)}_3)_2\text{ClRuCl}_3\text{RuCl}_2(\text{As(p-tol)}_3)_2$</td>
<td>-0.44</td>
<td>+0.58</td>
<td>1.02</td>
</tr>
<tr>
<td>$(\text{As}_3\text{O}_3)_2\text{ClRuCl}_3\text{RuCl}_2(\text{As}_3\text{O}_3)_2$</td>
<td>-0.44</td>
<td>+0.62</td>
<td>1.06</td>
</tr>
</tbody>
</table>

*versus Ag/AgI reference electrode at which ferrocene is oxidised at +0.60 volt in 0.5 M Bu$^+_n$NBF$_4^-$/CH$_2$Cl$_2$ with platinum as working electrode.*
CHAPTER 6

Spectroscopic and Magnetic Studies on Electrogenerated

Mixed-Valence Ruthenium Complexes
6.1 Preamble

In Chapters 1-4 a large number of triple chloro bridged binuclear ruthenium complexes (ranging from Ru$_2$(II/II) to Ru$_2$(III/III)) of general structure [L$_{3-x}$Cl$_x$RuCl$_3$RuCl$_y$L$_{3-y}$] (where the charge is unspecified and L = soft neutral ligands such as PR$_3$, AsR$_3$ etc.) have been described. Extensive cyclic d.c. and linear sweep a.c. voltammetric studies in Chapter 5 have established that many of these compounds display at least one and generally two stepwise, reversible one-electron transfers without change in their gross molecular structure (195,225).

We now report that electrochemical synthesis has enabled several strict sequences (fixed L, x and y) of such complexes, i.e. [L$_{3-x}$Cl$_x$RuCl$_3$RuCl$_y$L$_{3-y}$]$_{2/z+1/z+2}$, to be generated in bulk. This chapter describes new complementary physico chemical measurements which are designed to explore the degree of interaction between the adjacent electron deficient metal centres in the Ru$_2$(II/III) and Ru$_2$(III/III) states.

The variable temperature magnetic measurements in solid and solution states of the Ru$_2$(III/III) compounds, and the detection and analysis of the characteristic intervalence charge transfer (IT) bands in the near-infrared absorption spectrum of the corresponding Ru$_2$(II/III) compounds reveal that the degree of metal-metal interaction in these confacial biocathedral systems decreases as the molecular asymmetry (y-x) increases.
Before discussing the experimental evidence supporting these conclusions it is important to give a brief introduction to the origin and significance of IT bands in the optical spectra of mixed-valence species, since the interpretation of these bands plays a central role in ascertaining the degree of metal-metal interaction in the above systems.

6.2 Introduction

In 1967 Hush\(^{(226)}\) defined optical intervalence transfer as an optical transition which involves transfer of an electron from one nearly localised site to an adjacent one, the donor and acceptor being metal ions which possess more than one accessible oxidation state. Through the quantum-mechanically based Theory of Radiative and Radiationless Intervalance Transfer, Hush was able to account for characteristic features of IT bands such as their positional dependence on solvent and their broad, low-intensity Gaussian profile. The theory also yields the very useful Equation \([5]^{(226)}\) which allows the degree of electron delocalisation, \(\alpha^2\), to be calculated (N.B. the Hush approach and thereby \(\alpha^2\) apply only to the so-called "weak-interaction", i.e. almost complete localisation of the optical electron on the donor centre in its ground state).

\[
\alpha^2 = \frac{(4.24 \times 10^{-4}) \epsilon_{\text{max}} \Delta \nu \nu_{\text{max}}}{v_{\text{max}} R_2 \delta} \quad [5]
\]

\(R = R^2\)
Where $\varepsilon_{\text{max}}$ is the maximum extinction coefficient; $\nu_{\text{max}}$ is the position of the band centre; $\Delta\nu_{1/2}$ is the full width of the band at half height; $R$ is the internuclear distance between the metal centres.

Robin and Day (227) used the degree of electron delocalisation as one of a number of criteria to more fully characterise mixed-valence compounds (Table 6.1) i.e. to distinguish between "isolated-valence", "trapped-valence" and "average-valence" compounds.

"Isolated-valence" complexes invariably arise from heavily asymmetric species e.g. the metal ions may be in ligand fields of very different symmetry and/or strength. In strictly "isolated-valence" complexes no IT bands are seen and $a^2$ is thus zero (Robin and Day class I) (227).

Complexes in which the metal ions are in ligand fields of nearly identical symmetry and/or strengths are generally termed "trapped-valence" complexes (Robin and Day class II) (227). Such complexes possess distinguishable valences, but with slight delocalisation ($a^2 > 0$), and give rise to one or more IT bands in the visible or near-infrared regions.

Figure 6.1 shows the reaction coordinates for valence interchange of an asymmetric complex $M_{x+y}^{X+Y} \rightarrow M_{x}^{Y} M_{y}^{X}$. This diagram shows the optical transition energy, $E_{\text{op}}$, is equal to the Franck-Condon energy, $E_{\text{FC}}$, plus $E_0$ (the internal energy difference between the thermally equilibrated species $M_{x+y}^{X+Y}$ and its oxidation-state isomer $M_{x}^{Y} M_{y}^{X}$).

i.e. $E_{\text{op}} = E_{\text{FC}} + E_0$ [6] (226).
<table>
<thead>
<tr>
<th>Class I</th>
<th>Class II</th>
<th>Class III-A</th>
<th>Class III-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Metal ions in ligand fields of very different symmetry and/or strength, i.e. tetrahedral vs octahedral</td>
<td>1. Metal ions in ligand fields of nearly identical symmetry, relative distortion $\xi$ 50 pm</td>
<td>1. Metal ions indistinguishable but grouped into polynuclear clusters</td>
<td>1. All metal ions indistinguishable</td>
</tr>
<tr>
<td>2. $\alpha=0$; valences very firmly trapped</td>
<td>2. $\alpha&gt;0$; valences distinguishable, but with slight delocalisation</td>
<td>2. $\alpha$ maximal locally</td>
<td>2. $\alpha$ maximal; complete delocalisation over the cationic sublattice</td>
</tr>
<tr>
<td>3. Insulator; resistivity of $10^{10}$ $\Omega$ cm or greater</td>
<td>3. Semiconductor; resistivity in the range $10^{-10}$ $\Omega$ cm.</td>
<td>3. Probably insulating</td>
<td>3. Metallic conductivity; resistivity in the range $10^{-2}$-$10^{-6}$ $\Omega$ cm</td>
</tr>
<tr>
<td>4. No mixed-valence transitions in the visible region</td>
<td>4. One or more mixed-valence transitions in the visible region</td>
<td>4. One or more mixed-valence transitions in the visible region</td>
<td>4. Absorption edge in the infrared, opaque with metallic reflectivity in the visible region.</td>
</tr>
<tr>
<td>5. Clearly shows spectra of constituent ions, IR, UV, Mössbauer</td>
<td>5. Shows spectra of constituent ions at very nearly normal frequencies</td>
<td>5. Spectra of constituent ions not discernable</td>
<td>5. Spectra of constituent ions not discernable</td>
</tr>
<tr>
<td>6. Magnetically dilute, paramagnetic or diamagnetic to very low temperatures</td>
<td>6. Magnetically dilute, with both ferromagnetic and antiferromagnetic interactions at low temperatures</td>
<td>6. Magnetically dilute</td>
<td>6. Either ferromagnetic with a high Curie temperature or diamagnetic, depending on the presence of absence of local moments</td>
</tr>
</tbody>
</table>
Figure 6.1 Energy-Configurational Coordinate Diagram
Applicable for Valence Interchange in Asymmetric Complexes

Figure 6.2 Energy-Configurational Coordinate Diagram
Applicable for Valence Interchange in Symmetric Complexes
The high-energy oxidation-state isomer $M^Y_{A}M^X_{B}$, in which the oxidation-state configuration is reversed from the configuration of the ground-state species, is thus the product of light-induced electron transfer (IT absorption) which has undergone vibrational and rotational relaxation.

Day et al.\textsuperscript{228} have shown that wholly symmetric "mixed-valence" complexes such as $M^X_{A}M^Y_{A}$ (in which $E_0 = 0$ and therefore $E_{op} = E_{FC}$) may belong to either the "trapped-valence" category of complexes (class II) or the "average-valence" category of complexes (class III) depending on the magnitude of the resonance interaction, $H_{res}$, between the metal sites. If $H_{res}$ is small (implying a "weak-interaction") compared with $E_{Ad}$ (the adiabatic or thermal transition energy i.e. the crossing point of the energy surface associated with the valence exchange $M^X_{A}M^Y_{A} \leftrightarrow M^Y_{A}M^X_{A}$ in the absence of resonance interaction between the two sites) then we have valence trapping and class II behaviour (see Figure 6.2). However, if $H_{res}$ is large (implying a "strong-interaction") compared with $E_{Ad}$ we have complete electron delocalisation and hence class III behaviour (see Figure 6.2). The same workers have shown\textsuperscript{228} (using first-order perturbation theory) that class II ("trapped-valence") complexes should obey the criterion $a^2 < 0.07$; obviously completely delocalised class III ("average-valence") complexes have $a^2 = 0.5$ by definition.
Having given a brief introduction to the origin and significance of intervalence charge transfer bands it is now appropriate to discuss the information they provide on the factors influencing the degree of metal-metal interaction of triple chloro bridged binuclear ruthenium complexes at the Ru\(_2\)(II/III) (35-valence electron) level.

6.3 Results and Discussion

Factors influencing the degree of metal-metal interaction in triple chloro bridged binuclear ruthenium complexes at the Ru\(_2\)(II/III) and Ru\(_2\)(III/III) oxidation levels.

In order to better explore the structural and electronic changes which might accompany the stepwise electron transfer processes in triple chloro bridged complexes of type \([L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]^{2/Z+1/Z+2}\), some of the charged species shown in Table 6.2 have been electrogenerated (using controlled potential electrosynthesis [See Chapter 5]) on a preparative scale at low temperature, and characterised in situ by a variety of spectroscopic techniques\(^+\) (Tables 6.3 and 6.4).

\(^+\) With very few exceptions these electrogenerated species readily decompose if the temperature rises above 260 K and therefore no attempts were made to isolate them from solution.
Table 6.2  Electrochemical Behaviour of some $[L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]$ Complexes$^{a,b}$

<table>
<thead>
<tr>
<th>Asymmetry $\Delta Cl = y-x$</th>
<th>36e</th>
<th>35e</th>
<th>34e</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{Ru}(P\text{Et}_2\text{O})_3]^+$</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{Ru}(P\text{Et}_2\text{O})_3]^{2+}$</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{Ru}(P\text{Et}_2\text{O})_3]^{3+}$</td>
</tr>
<tr>
<td>1</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{RuCl}(P\text{Et}_2\text{O})]^{-}$</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{RuCl}(P\text{Et}_2\text{O})_2]^{2+}$</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{RuCl}(P\text{Et}_2\text{O})]^{+}$</td>
</tr>
<tr>
<td>2</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{RuCl}_2(P\text{Et}_2\text{O})]^{-}$</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{RuCl}_2(P\text{Et}_2\text{O})_2]^{2+}$</td>
<td>$[(P\text{Et}_2\text{O})_3\text{RuCl}_3\text{RuCl}_2(P\text{Et}_2\text{O})]^{+}$</td>
</tr>
</tbody>
</table>

$^a$ Stable complex underlined

$^b$ $E_1/2$ (volts) measured at 20°C in 0.50 M $\text{Bu}_4\text{BF}_4/\text{CH}_2\text{Cl}_2$ vs Ag/AgI reference electrode at which ferrocene is oxidised at +0.60 V.
Most of the complexes to be discussed have been generated at 223 K in 0.5 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ solutions at a platinum gauze working electrode. The solutions were then transferred, with rigorous exclusion of air, to pre-cooled n.m.r. or e.s.r. tubes and the integrity of the solutions, at the end of the spectroscopic measurement, was confirmed by voltammetric monitoring. In contrast, the optical measurements were recorded in situ using a chilled Optically Transparent Thin Layer Electrode (OTTLE) cell such as that shown in Figure 6.3 (For further details see Experimental Section 6.5).

6.3 (a) Using intervalence charge transfer bands to explore the tendency to partial charge delocalisation in the "RuCl$_3$Ru$^{2+}$" core of Binuclear Ru$_2$(II/III) complexes

All the mixed-valence Ru$_2$(II/III) 35-electron systems studied by us to date exhibit characteristic near-infrared or visible absorption bands (see Introduction 6.2), absent in their Ru$_2$(II/II) and Ru$_2$(III/III) congeners, and directly attributable to intervalence excitation (Figure 6.4 and Table 6.3). Further confirmation of the correct assignment of these near-infrared or visible bands as intervalence charge transfer bands is provided by the orderly shift in $\nu_{\text{max}}$ from symmetric to asymmetric complexes. This may be explored by successful calculation of the approximate position of $\nu_{\text{max}}$ for asymmetric complexes (226,229) (see Appendix II and Table 6.3). Owing to the insolvibility of our compounds in a range of solvents having significantly
Figure 6.3  Schematic Representation of OTTLE

- Reference and auxiliary electrode ports
- Teflon cell block
- Pt minigrid
- Optical path
- Thin-layer cell
- 0.33 mm
- Quartz
- Electrolyte
Figure 6.4  The Near Infrared Spectrum of \([\text{Ru}_2\text{Cl}_6\text{(As(p-tol)_3)}_3]\)

I  \([\text{Ru}_2\text{Cl}_6\text{(As(p-tol)_3)}_3]^2^-\)

II  \([\text{Ru}_2\text{Cl}_6\text{(As(p-tol)_3)}_3]^-%\)

III  \(\text{Ru}_2\text{Cl}_6\text{(As(p-tol)_3)}_3\)

\[\text{\(\lambda/\text{nm}\)}\]

800  1200  1600  2000  2400
different refractive indices, $n$, and static dielectric constants, $D$, $[v_{\text{max}} = (1/n^2 - 1/D)]^{(226)}$, we have been unable to investigate the dependence of $v_{\text{max}}$ with solvent. However, as noted by Meyer et al.\textsuperscript{(230)}, if the molecular radii of the redox sites are large enough (ca. 4.5 Å) compared to the internuclear distance (ca. 3.3 Å) then the electron transfer process is likely to be almost exclusively via an inner-sphere mechanism, with correspondingly small solvent dependence.

Several significant observations are immediately possible from an examination of Table 6.3. First, both the triad of PEt$_2\Omega$ complexes and the triad of As(p-tol)$_3$ complexes having $\Delta Cl^- = 0, 1, 2^+$ show a significant trend to higher transition energies and lower intensities as the molecular asymmetry increases. This shift in $v_{\text{max}}$, which reflects the increasing difference in orbital energies for the two ruthenium centres, is roughly comparable to the influence of asymmetric ligation on the observed separation of electrode potentials for the two Ru II/III couples (See Appendix II).

Furthermore, for these two triads, analysis of the implied degree of delocalisation, $a^2$, calculated from the Hush Equation [5] clearly indicates that this interaction is markedly increased by closer matching of the adjacent metal sites, to the extent that the symmetric ($\Delta Cl^- = 0$) complexes are "relatively delocalised", though not "average-valence"

\textsuperscript{+} The degree of asymmetry, $\Delta Cl^-$, is defined as $(y-x)$ and for the compounds discussed, $\Delta Cl^-$ takes values of 0, 1 and 2.
complexes, and outside the scope of Hush's weakly-interacting model. Thus these symmetric complexes do not fall neatly into either class II ("weak-interaction") or class III ("strong-interaction") mixed-valence categories but lie in the "grey area" of "moderate-interaction".

Table 6.3 also reveals the considerable influence exerted by π-acid, CO and CS ligands, both in reducing the tendency to delocalisation and, when asymmetrically located, in shifting the IT transition to higher energies. The reduction in $\alpha^2$ for such complexes is not surprising since CO and CS are both strongly electron withdrawing ligands and will tend to lower the "$t_{2g}$" electron density on their associated metal centre and hence reduce the tendency for metal-metal interaction (one may envisage distortion of the relevant d-orbitals towards the terminal CO/CS and away from the confacially bridging Cl$_3$ plane). The shift to higher transition energies when CO or CS is asymmetrically located, e.g. in $[(P\bar{O}_3)_2(CS)RuCl_3RuCl(P\bar{O}_3)_2]^+$ with respect to $[(P\bar{O}_3)_2(CS)RuCl_3RuCl(CS)(P\bar{O}_3)]^+$, is largely accounted for by the increased $E_0$ of ca. 3500 cm$^{-1}$ (calculated using the method described in Appendix II) for the latter over the former, appropriate to the relative stabilisation of Ru(II) sites by CO or CS.
Overall, the general observation of assignable intervalence bands for all the mixed-valence triple bridged complexes so far examined confirms our preliminary conclusion based on electrode potential data (Chapter 5), that the asymmetrically substituted complexes at least, can be realistically viewed as "trapped-valence" systems i.e. exhibiting class II mixed-valence behaviour. In the particular case of the asymmetrically located CO and CS complexes \([(PR_3)_2YRuCl_3RuCl(PR_3)_2]^+ \) (\(PR_3 = P\theta_3\); \(Y = CO\), CS: \(PR_3 = P(\text{p-tol})_3\); \(Y = CO\)) the degree of electron delocalisation is so small that the two centres can almost be considered to have isolated valencies.

An excellent demonstration of the isolated valencies in the above electrogenerated CO- and CS-containing cations is provided by their \(^{31}P-{^1}H\) n.m.r. spectra. In each case a paramagnetically broadened, contact-shifted resonance is observed together with a sharp AB pattern whose resonance centre, \(\delta_{AB}\) and \(^{2}J_{AB}\) are virtually unchanged from the \(^{31}P-{^1}H\) n.m.r. resonance which is characteristic of the -RuY(PR_3)_2 site in the Ru_2(II/II) precursor (see Figure 6.5 and Table 6.4).
Figure 6.5 \[ ^{31}P-(^{1}H) \text{n.m.r. spectra of Ru}_2\text{Cl}_4(\text{CO})(\text{P}O_3)_4 \]

Before and After Oxidation

Ru\(_2\text{Cl}_4(\text{CO})(\text{P}O_3)_4 \)

[Ru\(_2\text{Cl}_4(\text{CO})(\text{P}O_3)_4 \)]^+
6.3 (b) Using magnetic studies to explore the degree of metal-metal interaction in the "RuCl$_3$Ru$^{3+}$" core of binuclear Ru$_2$(III/III) complexes

Table 6.4 shows that the magnetic behaviour of mixed-valence binuclear Ru$_2$(II/III) complexes are not responsive to the degree of metal-metal interaction; the solution magnetic moments (measured by Evans' method)\(^{(218)}\) are in general close to the spin-only value, irrespective of the molecular geometry or the temperature. In contrast, the solution magnetic moments of their structurally related Ru$_2$(III/III) species are heavily dependent on both temperature and the extent of molecular asymmetry. Thus, the Ru$_2$(III/III) complexes (with 34-valence electrons) all show a depression of $\mu_{\text{eff}}$ with decreasing temperature, and the degree of antiferromagnetic interaction is markedly sensitive to the mismatch ($\Delta$Cl$^-$ value) between the adjacent metal centres (Table 6.4). In general, increasing the molecular symmetry of these triple chloro bridged binuclear Ru$_2$(III/III) complexes causes an accompanying increase in the metal-metal interaction between the adjacent centres which is expressed in the decrease in $\mu_{\text{eff}}$ (or increase in the exchange coupling constant\(^{+}\) $-2J$\(^{(231)}\)) with decreasing temperature.

\(^{+}\) The exchange coupling constant, $-2J$, represents the energy required to excite an electron from its singlet electronic ground-state to its triplet electronic first excited-state.
Interestingly, none of the electrogenerated Ru$_2$(III/III) or Ru$_2$(II/III) cations gave any e.s.r. signals, even at 133 K. This is in marked contrast to their isoelectronic neutral precursors of type L$_2$ClRuCl$_3$RuClL$_2$, L$_3$RuCl$_3$RuCl$_2$L or L$_2$YRuCl$_3$RuCl$_2$L which display strong two g-value or three g-value axial or rhombic g-tensors, depending on the particular molecular geometry involved. In addition, both the neutral 34-electron complex (As(p-tol)$_3$)$_2$ClRuCl$_3$RuCl$_2$- (As(p-tol)$_3$)$_2$ (8) and its isostructural 35-electron anion give strong two g-value e.s.r. spectra with $g_{ll} = 2.48$, $g_{ll} = 1.73$ and $g_{ll} = 2.41$, $g_{ll} = 1.54$, respectively, in accord with their common axial symmetry. Meyer et al. (232) have attributed the absence of e.s.r. signals in their Ru$_2$(III/III) binuclear cations of type [(N-N)$_2$(NO$_2$)$_2$RuORu-(NO$_2$)(N-N)$_2$]$^{12+}$ (N-N = bipy, phen) to the presence of strong spin-orbit coupling interactions. In our complexes, at least, it seems reasonable that the increased solvent interactions on going from anionic or neutral to cationic species will also be an important factor in shortening the electron spin-lattice relaxation time, $T_{1e}$, and this aspect may have been overlooked in other systems.

6.4 Conclusions

The general observation of assignable intervalence bands for all the mixed-valence triple chloro bridged complexes so far examined confirms our preliminary conclusion based on electrode potential data (Chapter 5), that the asymmetrically substituted complexes at least, can be realistically
viewed as "trapped-valence", class II systems. The influence of asymmetrically located π-acid, CO and CS ligands is to further intensify the degree of electron localisation such that the two metal sites can almost be considered as isolated from one another. Such an approach toward class I behaviour is also indicated by $^{31}$P-$^1$H n.m.r. spectra of the phosphine ligands which show a paramagnetically broadened contact-shifted resonance for the Ru(III) centre, while the AB pattern associated with the CO or CS containing Ru(II) centre is essentially unchanged from its pre-oxidation chemical shift and coupling constant.

For redox-related isostructural complexes, the combination of magnetic measurements at the Ru$_2$(III/III) 34-electron level, and measurements of the degree of electron delocalisation, $\alpha^2$, at the 35-electron level indicate a coherent trend of increasing metal-metal interaction with increasing molecular symmetry (Table 6.5). Thus, as the complexes become less symmetric ($\Delta Cl^- = 1, 2$) the metal centres are subject to a weak degree of interaction; at the 35-electron level this observed as a greater degree of charge localisation, i.e. valence-trapping or class II behaviour, while at the 34-electron level the weak-interaction is manifested as a small depression of $\mu_{eff}$ from its non-interacting maximal value of ca. 1.8 BM/Ru.
However, in the symmetric complexes, where $\Delta Cl^- = 0$, the metal centres are subject to a moderate degree of interaction; at the 35-electron level this is observed as a high degree of electron delocalisation, i.e. intermediate between class II and class III behaviour, while at the 34-electron level the moderate-interaction is perceived as a substantial depression of $U_{eff}$.

Many of the electronic features of the symmetric compounds can be accounted for by the molecular orbital diagram devised by Orgel$^{(233)}$ and applied by Watkins et al$^{(234)}$ (Figure 6.6). For example, the additional degree of stabilisation in the symmetric complex $\text{As(p-tol)}_3\text{ClRuC}_3\text{RuCl(As(p-tol)}_3\text{Cl}_2$ (6) (shown by slight, but significant, anomalies in the position of its intervalence band and the separation of its successive redox couples, as well as the uniquely sluggish charge transfer properties of its electro-reduction [see Chapter 5]) may be rationalised on the basis of structural relaxation accompanying the loss of a metal-metal bond (bond order 0.5) on reducing from the Ru$_2$(II/III) 35-electron level to the Ru$_2$(II/II) 36-electron level.

The magnetic behaviour of the Ru$_2$(III/III) system can also be explained in terms of the M.O. diagram in Figure 6.6. Thus if the energy difference between the triplet first excited electronic state $A_1^2E^4E^*3A_1^*$ and the singlet ground-state $A_1^2E^4E^*4$ is of similar magnitude to the electron pairing energy in the singlet level, then,
Figure 6.6  Schematic Representation of Metal Bonding Orbitals in Symmetric Triple Bridged Binuclear Ruthenium Complexes

\[ A_1 \quad A_1^* \quad E^* \quad E \quad A_1 \]

\[ d_{xy}, d_{yz}, d_{xz} \quad d_{xy}, d_{yz}, d_{xz} \]

Ru(1)       Ru(1) - Ru(2)       Ru(2)
as found experimentally, the $\mu_{\text{eff}}$ value would be expected to be substantially depressed at low temperatures from the maximal values found for non-interacting centres.

To achieve a deeper understanding of the mechanism mediating metal-metal interactions (e.g. through direct metal-metal bonds or via the intervening bridges) further electrochemical, spectroscopic and theoretical studies will be required, together with the synthesis of further judiciously chosen variants, with modified bridging or terminal ligands (as discussed in Chapter 2 and 3). However, the present results make it clear that this family of triple halide bridged binuclear complexes is exceptionally well-suited to developments in the understanding of intervalence charge transfer and related phenomena.

6.5 Experimental

The chilled Optically Transparent Thin Layer Electrode (OTTLE) cell used in the present study was designed and built in the Department of Chemistry, University of Edinburgh, in accordance with the original principles of Murray et al. The OTTLE cell consists of a fine Pt gauze working electrode (transparency ca. 40%), a Pt wire counter electrode (both the working and counter electrodes being protected by frits) and either an Ag/AgI reference electrode or a Pt quasi-reference electrode, all mounted in a gas-tight poly(tetrafluoroethylene) cell block (Figure 6.3). Temperature control, monitored by
thermocouple/digital thermometer, was maintained by passage of chilled dry N₂ gas (the cell's quartz optical windows being protected from fogging by further quartz optical windows, the intervening space being flushed with dry N₂ gas).

Solutions of the test species (ca. 1 mmol⁻¹) in dry CH₂Cl₂, THF containing 0.5 M Bu₄NBF₄ or LiClO₄ respectively were purged with dry argon and electrolysed at the platinum minigrid working electrode of the above OTTLE cell which was mounted in the beam of a spectrophotometer (Unicam SP8-400 and Beckman 5270). The progress of electrolysis was monitored both spectroscopically to the limiting curve and by the decay of the current to a constant residual value.

Standard practice was to return the test species to its original state by reverse electrolysis in order to ensure that the process was a chemically reversible event and to ensure that incidental loss of compound (degradation) was kept to less than 10%.

All the bulk electrogenerations were carried out using a three electrode HI-Tek DT201 potentiostat using standard procedures (223). The cell used was a 20 cm³ cell with three compartments (Figure 5.6). One contained the reference electrode (Ag/AgI) separated from the cell solution by a salt bridge containing a frit. The Pt wire counter electrode was placed in a one cm tube with a frit. The cylindrical Pt gauze working electrode (ca. 9.5 cm² total area) was positioned vertically in the test solution.
The electrogenerated species (generally produced at 223 K) were transferred by syringe, with rigorous exclusion of air, to pre-cooled n.m.r. or e.s.r. tubes and the integrity of the solutions, at the end of the spectroscopic measurements, was confirmed by voltammetric monitoring.

$^{31}$Phosphorus-$\text{H}$ n.m.r. and e.s.r. spectroscopic measurements were obtained at 24.2 MHz and 100 KHz respectively, as described in Chapters 2 and 3. Solution magnetic moments were measured using Evans' method (218) (see Chapter 4). Solid state magnetic measurements were made on a Faraday balance in the Department of Chemistry, University of Dundee.

**Complexes subject to magnetic and spectroscopic investigation**

The following compounds were prepared using literature methods: $(LR_3)_3RuCl_3RuCl_2(LR_3)$ $(LR_3 = \text{As}(\text{p-tol})_3$ (66), $\text{PET}_2\text{Ø}$ (142), $(\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}$(As(\text{p-tol})_3)_2 (66), $(\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}_2$(As(\text{p-tol})_3) (66), $[\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ø})_6]\text{Cl}$ (113), $\text{Ru}_2\text{Cl}_4(\text{PET}_2\text{Ø})_5$ (122), $\text{Ru}_2\text{Cl}_4\text{Y}(\text{PR}_3)_4$ $(\text{PR}_3 = \text{Pø}_3$; $\text{Y} = \text{CO, CS}$; $\text{PR}_3 = \text{P(2-tol)}_3$; $\text{Y} = \text{CO}$) (181-183), $\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{Pø}_3)_3$ (182).
Table 6.3  Intervalence Charge Transfer Bands for Some Ru$_2$(II/III) Complexes

<table>
<thead>
<tr>
<th>Cl$^{-}=$y-x</th>
<th>Complex</th>
<th>$\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>$\varepsilon_{\text{max}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$10^3 \sigma^2$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>[(PET$_2$)$_3$RuCl$_3$Ru(PET$_2$)$_3$]$^{2+}$</td>
<td>4,350</td>
<td>3750</td>
<td>delocalised</td>
</tr>
<tr>
<td>1</td>
<td>[(PET$_2$)$_3$RuCl$_3$Ru(PET$_2$)$_2$]$^{+}$</td>
<td>9,700 (10,600)</td>
<td>700</td>
<td>9.5</td>
</tr>
<tr>
<td>2</td>
<td>[(PET$_2$)$_3$RuCl$_3$RuCl(PET$_2$)$_2$]</td>
<td>13,500 (12,800)</td>
<td>550</td>
<td>5.1</td>
</tr>
<tr>
<td>0</td>
<td>[(As(p-tol)$_3$)$_2$ClRuCl$_3$RuCl(As(p-tol)$_3$)$_2$]</td>
<td>5,900</td>
<td>1700</td>
<td>delocalised</td>
</tr>
<tr>
<td>1</td>
<td>[(As(p-tol)$_3$)$_2$ClRuCl$_3$RuCl(As(p-tol)$_3$)$_2$]</td>
<td>7,800 (10,100)</td>
<td>830</td>
<td>8.9</td>
</tr>
<tr>
<td>2</td>
<td>[(As(p-tol)$_3$)$_3$RuCl$_3$RuCl(As(p-tol)$_3$)$_2$]</td>
<td>12,200 (13,700)</td>
<td>400</td>
<td>3.2</td>
</tr>
</tbody>
</table>

|                      | [(PET$_3$)$_2$(CO)RuCl$_3$RuCl(PET$_3$)$_2$]$^{+}$ $^c$ | 14,800 | 100 | 0.7 |
|                      | [(PET$_3$)$_2$(CS)RuCl$_3$RuCl(PET$_3$)$_2$]$^{+}$ $^c$ | 14,800 | 100 | 0.7 |
|                      | [(P(p-tol)$_3$)$_2$(CO)RuCl$_3$RuCl(P(p-tol)$_3$)$_2$]$^{+}$ | 14,800 | 100 | 0.7 |
|                      | [(PET$_3$)$_2$(CS)RuCl$_3$RuCl(CS)(PET$_3$)$_2$]$^{+}$ | 10,850 | 200 | 1.6 |

$^a$ Measured in 0.50 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ at 233 K unless otherwise stated.

$^b$ Degree of delocalisation $2 = (4.24 \times 10^{-4}) \frac{\Delta \nu_{\text{max}}}{\nu_{\text{max}} R^2}$ where $\varepsilon_{\text{max}}$ = maximum extinction coefficient; $\nu_{\text{max}}$ = position of band centre; $\Delta \nu_{\text{max}}$ = full width of band at half height; $R$ = internuclear distance between ruthenium ion centres (a value of 3.3 Å is assumed here) (226).

$^c$ Measured in 0.50 M LiClO$_4$/THF at 223 K. ( ) Indicates a value calculated via method outlined in Appendix II.

$^*$ Only this compound is strictly comparable with the (ΔCl$^{-} = 1$) compounds above the line, since the rest have asymmetric CO or CS as well.
Table 6.4 In Situ Characterisation of Electrogenerated Complexes

<table>
<thead>
<tr>
<th>(No. of Electrons) Complex</th>
<th>Generating Potential (V)</th>
<th>Colour</th>
<th>Solution $\mu_{eff}$ at T/K$^a$</th>
<th>$^{31}$P-$^1$H n.m.r. at 223 K in CH$_2$Cl$_2$/d$_6$-acetone (e.s.r. pattern at 133 K in CH$_2$Cl$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(PET$_2$Ø)$_3$RuCl$_3$Ru(PET$_2$Ø)$_3$]$^{2+}$</td>
<td>+1.4</td>
<td>Green</td>
<td>1.78 228</td>
<td>Nothing observed (Nothing observed)</td>
</tr>
<tr>
<td>[(PET$_2$Ø)$_3$RuCl$_3$RuCl(PET$_2$Ø)$_2$]$^+$</td>
<td>+1.0</td>
<td>Green</td>
<td>2.02 231</td>
<td>Broad resonance at ca. $\delta_p$ -16 ppm (Nothing observed)</td>
</tr>
<tr>
<td>[(PØ$_3$)$_2$(CO)RuCl$_3$RuCl(PØ$_3$)$_2$]$^+$</td>
<td>+1.0</td>
<td>Green</td>
<td>1.64 235</td>
<td>Broad resonance at ca. $\delta_p$ 121 ppm + AB resonance centred at $\delta_p$ 40.8 ppm ($^{2}J_{AB}$ 24.4 Hz; $\delta_{AB}$ 61.9 Hz) (Nothing Observed)</td>
</tr>
<tr>
<td>[(PØ$_3$)$_2$(CS)RuCl$_3$RuCl(PØ$_3$)$_2$]$^+$</td>
<td>+1.0</td>
<td>Green</td>
<td>1.60 235</td>
<td>Broad resonance at ca. $\delta_p$ 123 ppm + AB resonance centred at $\delta_p$ 37.3 ppm ($^{2}J_{AB}$ 26.9 Hz; $\delta_{AB}$ 66.5 Hz) (Nothing Observed)</td>
</tr>
<tr>
<td>[(P(5-tol)$_3$)$_2$(CO)RuCl$_3$RuCl-</td>
<td>+1.0</td>
<td>Green</td>
<td>2.10 231</td>
<td>Broad resonance at ca. $\delta_p$ 131 ppm + AB resonance centred at $\delta_p$ 40.9 ppm ($^{2}J_{AB}$ 26.9 Hz; $\delta_{AB}$ 105.8 Hz) (Nothing Observed)</td>
</tr>
<tr>
<td>[(PEt$_2$Ø)$_3$RuCl$_3$RuCl$_2$(PET$_2$Ø)]$^-$</td>
<td>-0.7</td>
<td>Red</td>
<td>Diamagnetic</td>
<td>Singlet at $\delta_p$ 56.2 ppm + AB resonance centred at $\delta_p$ 33.8 ppm (-)</td>
</tr>
<tr>
<td>Reaction</td>
<td>Charge</td>
<td>Color</td>
<td>$\text{g}_{\perp}$</td>
<td>$\text{g}_{\parallel}$</td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
<td>-------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>(34) $[(\text{PEt}_2\phi)_3\text{RuCl}_3\text{RuCl}_2(\text{PEt}_2\phi)]^+$</td>
<td>+1.5</td>
<td>Green</td>
<td>1.78/Ru</td>
<td>233</td>
</tr>
<tr>
<td>(36) $[(\text{As}(p\text{-tol})_3)_3\text{RuCl}_3\text{RuCl}_2(\text{As}(p\text{-tol})_3)]^-$</td>
<td>-0.7</td>
<td>Red</td>
<td>Diamagnetic</td>
<td>(-)</td>
</tr>
<tr>
<td>(34) $[(\text{As}(p\text{-tol})_3)_3\text{RuCl}_3\text{RuCl}_2(\text{As}(p\text{-tol})_3)]^+$</td>
<td>+1.5</td>
<td>Green</td>
<td>2.01/Ru</td>
<td>235</td>
</tr>
<tr>
<td>(36) $[(\text{As}(p\text{-tol})_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As}(p\text{-tol})_3)_2]^-</td>
<td>-0.3</td>
<td>Yellow</td>
<td>Diamagnetic</td>
<td>(-)</td>
</tr>
<tr>
<td>(34) $[(\text{As}(p\text{-tol})_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As}(p\text{-tol})_3)_2]^+$</td>
<td>+1.3</td>
<td>Green</td>
<td>0.91/Ru</td>
<td>233</td>
</tr>
<tr>
<td>(35) $[(\text{As}(p\text{-tol})_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As}(p\text{-tol})_3)_2]^- b$</td>
<td>+0.2</td>
<td>Green</td>
<td>1.73</td>
<td>227</td>
</tr>
<tr>
<td>(36) $[(\text{As}(p\text{-tol})_3)_2\text{ClRuCl}_3\text{RuCl}_2(\text{As}(p\text{-tol})_3)_2]^- b$</td>
<td>-1.0</td>
<td>Yellow</td>
<td>Diamagnetic</td>
<td>(-)</td>
</tr>
</tbody>
</table>
a Solution magnetic moments (Evans' method) are quoted per molecule for the Ru₂(II/III) complexes (which are temperature invariant) and per Ru for the temperature dependent Ru₂(III/III) complexes (Temperature range 193 - 253 K).

b Stable at 273 K

c Exchange coupling constant obtained by solving the Bleaney-Bowers equation

\[ X_A = \frac{N_g B^2}{3 kT} \left[ 1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} \] where \( X_A \) is the molar susceptibility calculated per metal ion.
Table 6.5  Increasing Metal-Metal Interaction with Increasing Molecular Symmetry

<table>
<thead>
<tr>
<th>Cl^{-}</th>
<th>ΔE(v)</th>
<th>Complexes</th>
<th>Exchange Energy^{a} (-2J \text{ cm}^{-1}) for 34e Species</th>
<th>10^{3}\alpha^{2} \text{ for } 35e^{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.55</td>
<td>([(\text{PET}_2\text{Ø})_3\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{Ø})]^0/^{+})</td>
<td>185</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>1.50</td>
<td>([(\text{As}(\text{p-tol})_3)_3\text{RuCl}_3\text{RuCl}_2(\text{As}(\text{p-tol})_3)]^0/^{+})</td>
<td>150</td>
<td>3.2</td>
</tr>
<tr>
<td>1</td>
<td>1.04</td>
<td>([(\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}_2(\text{As}(\text{p-tol})_3)]^{-/^{0}})</td>
<td>276*</td>
<td>8.9</td>
</tr>
<tr>
<td>0</td>
<td>0.73</td>
<td>([(\text{As}(\text{p-tol})_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As}(\text{p-tol})_3)_2]^0/^{+})</td>
<td>420</td>
<td>Highly Delocalised</td>
</tr>
</tbody>
</table>

ΔCl^{-} = y-x;  ΔE = The separation between the two successive redox couples

^{a} The exchange coupling constant, \(-2J\), is calculated from the Bleaney-Bowers equation (231) over the temperature range 193-252 K

^{b} The degree of electron delocalisation, \(\alpha^{2}\), is calculated from the Hush Equation (226)

*-2J value based on solid state magnetic measurements (Faraday method), whereas all other -2J values are based on solution state magnetic measurements (Evans' method) (218).
APPENDIX I

Some Monomeric Tertiary Phosphine Complexes

Derived from the Hydride Compound

\[ \text{[RuH(cod)(NH}_2\text{NMe}_2)_3]B\bar{O}_4 \]
A.1 Preamble

During attempts to synthesise the triple hydroxo bridged complex \([\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{O})_6]\text{BØ}_4\) \((117)\) \((33)\), from the reaction between \([\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]\text{BØ}_4\) and \(\text{PR}_3\) in mixed MeOH:acetone solvents, a number of interesting, monomeric tertiary phosphine complexes were formed. Before discussing the preparation and characterisation of these complexes (most of which have been synthesised by other routes in other laboratories) it is useful to give a brief description of the versatile chemistry exhibited by \([\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]X\) \((X = \text{BØ}_4^-, \text{PF}_6^-)\) itself.

A.2 Introduction

The complexes \([\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]X\) \((X = \text{BØ}_4^-, \text{PF}_6^-)\) \((236)\), which were first reported in 1977 via the reaction of \([\text{RuCl}_2(\text{cod})]_n\) with N,N-dimethylhydrazine in mixed MeOH:H\text{H}_2\text{O} solvents, have proved to be useful precursors for the synthesis of novel monomeric and binuclear systems. These include previously mentioned complexes such as

\([\text{Ru}_2X_3(\text{PMe}_2\text{O})_6]\text{PF}_6\) \((X = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-, \text{SH}^-, \text{SMe}^-)\) \((117)\)

and \([\text{RuH(cod)L}_3]X\) \((X = \text{PF}_6^-; \text{L} = \text{PMe}_2\text{O}, \text{PMeO}_2, \text{PMe}_3, \text{P(OMe)O}_2)\) \((237)\); \(X^- = \text{BØ}_4^-; \text{L} = \text{MeCN}(211), \text{py etc.})\) \((236)\).

In addition, many other compounds have recently been prepared e.g. \(\text{RuHX(cod)L}_2\) \((X = \text{Cl}^-, \text{Br}^-; \text{L} = \text{PMeO}_2, \text{AsO}_3, \text{SbO}_3, \text{py})\) \((211)\), \([\text{RuH(PMe}_2\text{O})_5]\text{PF}_6\) \((238)\) and zwitterionic complexes such as the arene-bonded \(\text{BØ}_4^-\) complex \(\text{Ru(BO}_4^-)\text{(cod)}\) \((236)\).
A.3 Results and Discussion

(a) Reaction of [RuH(cod)(NH₂NMe₂)₃]BØ₄ with a four-fold excess of PMe₂Ø

(i) The reaction between [RuH(cod)(NH₂NMe₂)₃]BØ₄ and PMe₂Ø depends critically on the molar ratio of Ru:PMe₂Ø. Thus reacting the above complex with a three-fold excess of PMe₂Ø leads to the formation of [Ru₂(OH)₃(PMe₂Ø)₆]BØ₄ (33), as described in Chapter 3. However, when a four-fold excess of PMe₂Ø is employed the sharp-melting, highly-conducting, white microcrystalline complex [RuH(CO)(PMe₂Ø)₄]BØ₄ (52) is isolated in high yield (N.B. this complex was first reported in a brief communication by Ashworth et al (239) from the reaction between [RuH₃(PMe₂Ø)₄]PF₆ (synthesised from the action of PMe₂Ø on [RuH(cod)(NH₂NMe₂)₃]PF₆ in MeOH) and measured quantities of CO in alcohols).
Microanalytical, infrared and mass spectroscopic data are consistent with structure (52). Thus the infrared spectrum of compound (52) shows a very strong broad band at 1950 cm\(^{-1}\) which may be attributed to both \(v_{C=O}\) and \(v_{Ru-H}\) stretching vibrations, while mass spectroscopy gives the fragmentation pattern shown in Figure (A.1). The mass spectrum of the ruthenium containing species giving rise to patterns at 544, 516, 406, 378 and 240 a.m.u. exactly concur with computer synthesised spectra of "\([RuH(CO)(PMe_2\text{Ø})_3]^+\)", "\([RuH(PMe_2\text{Ø})_3]^+\)", "\([RuH(CO)(PMe_2\text{Ø})_2]^+\)", "\([RuH(PMe_2\text{Ø})_2]^+\)" and "\([RuH(PMe_2\text{Ø})]^+\)" fragments respectively.

The \(^{31}P-{^1}H\) n.m.r. spectrum of compound (52) in CDC\(_3\) at 298 K is very complicated, consisting of complex multiplets at ca. \(\delta_p -2.5\) ppm and ca \(\delta_p -14.7\) ppm (Figure (A.2)). However, no accurate computer simulation of the expected ABC\(_2\) spin system has proved possible to date.

The \(^1H\) n.m.r. spectrum of compound (52) at 100 MHz in CDC\(_3\) at 298 K over the "normal region" (0-10 ppm) shows phenyl resonances from PMe\(_2\text{Ø}\) between \(\delta 7.2-7.5\) ppm and \(\delta 6.8-7.2\) ppm for those of BØ\(_4\). A complex pattern of four methyl resonances (1:1:1:1 integral) are observed as two doublets at \(\delta 1.60\) ppm \((^2J_{PH} 6\) Hz\)) and \(\delta 0.91\) ppm \((^2J_{PH} 7\) Hz\)) respectively and two "virtually coupled triplets" at \(\delta 1.40\) ppm \((^4J_{PH} 3\) Hz\)) and \(\delta 1.14\) ppm \((^4J_{PH} 3\) Hz\)) respectively (Figure (A.3)).
Figure (A.1) Mass Spectral Fragmentation Pattern of the $[\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]^+$ Cation

$[\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]^+$ $\xrightarrow{-\text{PMe}_2\text{Ø}}$ not observed $[\text{RuH(CO)}(\text{PMe}_2\text{Ø})_3]^+$ $\xrightarrow{-138}$ $[\text{RuH(CO)}(\text{PMe}_2\text{Ø})_2]^+$

$[682]$

$[544]$

$[506]$

$[406]$

$[378]$

$[240]$
Figure A.2 $^{31}P-{^1H}$ n.m.r. Spectrum of $[\text{RuH(CO)(PMe}_2\text{Ø)}_4]\text{BØ}_4$

in CDCl$_3$ at 298 K

ca. $\delta_P$ -2.5 ppm

ca. $\delta_P$ -14.7 ppm
Figure A.3  $^1$H n.m.r. Spectrum of the Methyl Region of
$[\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]B\text{Ø}_4$ in CDCl$_3$ at 298 K

$\delta_{1.60}$ ppm  $\delta_{1.40}$ ppm  $\delta_{1.14}$ ppm  $\delta_{0.91}$ ppm
The two "virtually coupled triplets" arise from the four bond coupling between $P_{AI}$ and the chemically and magnetically inequivalent $Me^I$ and $Me^{II}$ protons, superimposed on the larger $2J_{PH}$ coupling i.e. $\frac{2J_{PA}P_{AI}}{2} >> |2J_{PH} - 4J_{PH}|$. The two doublets arise from the two sets of chemically and magnetically distinct protons on $Me^{III}$ and $Me^{IV}$ coupling with $P_B$ and $P_C$ respectively. From shielding/deshielding arguments it is proposed that the $Me^{III}$ protons (trans to CO) are manifested as the high frequency doublet, the low frequency doublet being ascribed to the $Me^{IV}$ protons (trans to hydride).

Further validation of structure (52) is derived from the high resolution (360 MHz) $^1H$ n.m.r. spectral data collected in CDCl$_3$ at 298 K. This shows the hydride region to consist of an overlapping doublet ($2J_{PH}$ 75.1 Hz) of quartets ($2J_{PH}$ 23.8 Hz) at $\delta$-8.88 ppm. This spectrum is readily explained by a large trans $2J_{PH}$ coupling between the hydride and $P_C$ giving rise to a widely spaced doublet, while the quartet pattern arises from the coincidental equivalence of cis $2J_{PH}$ coupling constants between the hydride and $P_A, P_{AI}$ (equivalent with respect to the hydride) and $P_B$. 
A.3(a) (ii) Although the complex \([\text{RuH(CO)}(\text{PMe}_2\text{Ø})_4]\text{BØ}_4\) (52) was the generally isolated product from the reaction between \([\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]\text{BØ}_4\) and a four-fold excess of \(\text{PMe}_2\text{Ø}\), on one occasion a pale yellow crystalline precipitate was deposited in high yield. This sharp-melting, highly conducting compound was shown to be a \(\text{BØ}_4^-\) salt (infrared spectroscopic data, i.e. strong bands in the region 650-750 cm\(^{-1}\), and \(^1\text{H}\) n.m.r. data at 60 MHz in CDCl\(_3\) at 298 K, i.e. phenyl protons in the region \(\delta 7.2-8.2\) ppm) of a cationic complex.

\(^3\text{P}\) phosphorus\(-\(^1\text{H}\)\) n.m.r. spectroscopy at 145.8 MHz in CDCl\(_3\) at 298 K shows two triplets at \(\delta_p 22.43\) ppm and \(\delta_p 4.81\) ppm respectively (\(^2J_{pp} 28.83\) Hz) (Figure (A.4(a))) (N.B. at 24.2 MHz this \(A^2X^2\) spin system becomes an \(AA^1XX^1\) spin system consisting of a twelve line pattern (Figure (A.4(b))). \(^1\text{H}\) hydrogen n.m.r. spectroscopy at 60 MHz in CDCl\(_3\) at 298 K shows phenyl resonances from \(\text{PMe}_2\text{Ø}\) superimposed on those of \(\text{BØ}_4^-\), while the phosphine methyl resonances are broad and structureless in the region \(\delta 1.5-2.5\) ppm. Integration of the resonance areas shows the phenyl:methyl ratio to be ca. 5:3.
Figure A.4  $^{31}$P--$^1$H n.m.r. Spectra of [Ru(CH$_3$CO$_2$)(PMe$_2$Ø)$_4$]BØ$_4$ in CDCl$_3$ at 298 K recorded at 24.2 and 145.8 MHz

$\delta_p$ 22.43 ppm

$\delta_p$ 4.81 ppm
Thus, despite knowing that two pairs of PMe₂Ø groups were cis to each other in the complex and that the remaining two coordination sites consisted of an anionic ligand(s), (the complex being a Ru(II) mono cation) nothing more could be accomplished without an X-ray structural analysis. Suitable crystals were grown by cooling a saturated solution of the complex in CDC₁₃. The X-ray structure of the complex [Ru(CH₃CO₂)(PMe₂Ø)₄]BØ₄ (53) is shown in Figure (A.5). It should be noted that the structural parameters of this cation (Table (A.1)) are very similar to those of its PF₆⁻ analogue [Ru(CH₃CO₂)(PMe₂Ø)₄]PF₆, (prepared by the reaction of [RuH(PMe₂Ø)₅]PF₆ with CO in MeOH or EtOH) the structure of which has been reported by Ashworth et al (240).

On closer scrutiny, the infrared spectrum of compound (53), as a KBr disc, shows bands at 1581 cm⁻¹ (medium intensity) and 1460 cm⁻¹ (strong intensity) attributable to υO-C-O stretches and a strong band at 1095 cm⁻¹ attributable to a υC-O-C stretch.

The mechanism of formation of compound (53) from the reaction mixture remains unresolved, although it must be assumed that one or other of the solvents was contaminated, perhaps with acetic acid. Certainly heating the previously mentioned red solution under reflux in the presence of excess glacial acetic acid results in the formation of compound (53) in high yield.
Figure A.5

X-Ray Structure of $[\text{Ru}(\text{CH}_3\text{CO}_2)(\text{PMe}_2\text{Ø})_4]^+$ Cation
Table (A.1)  Some Selected Bond Lengths and Bond Angles
for the [Ru(CH$_3$CO$_2$)(PMe$_2$Ø)$_4$]+ Cation

### Selected Bond Distances

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance (Å)</th>
<th>Atoms</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-P1</td>
<td>2.300(1)</td>
<td>P1-C3</td>
<td>1.811(5)</td>
</tr>
<tr>
<td>Ru-P2</td>
<td>2.261(1)</td>
<td>P1-C3</td>
<td>1.821(6)</td>
</tr>
<tr>
<td>Ru-P3</td>
<td>2.424(1)</td>
<td>P2-C9</td>
<td>1.827(6)</td>
</tr>
<tr>
<td>Ru-P4</td>
<td>2.389(1)</td>
<td>P2-C9</td>
<td>1.827(6)</td>
</tr>
<tr>
<td>Ru-O1</td>
<td>2.176(3)</td>
<td>P3-C17</td>
<td>1.838(5)</td>
</tr>
<tr>
<td>Ru-O2</td>
<td>2.33(3)</td>
<td>P3-C17</td>
<td>1.830(6)</td>
</tr>
<tr>
<td>C33-O1</td>
<td>1.252(6)</td>
<td>P3-C19</td>
<td>1.809(5)</td>
</tr>
<tr>
<td>C33-O2</td>
<td>1.272(6)</td>
<td>P4-C25</td>
<td>1.820(6)</td>
</tr>
<tr>
<td>C33-C34</td>
<td>1.520(8)</td>
<td>P4-C26</td>
<td>1.809(6)</td>
</tr>
<tr>
<td>P1-C1</td>
<td>1.831(6)</td>
<td>P4-C27</td>
<td>1.837(6)</td>
</tr>
<tr>
<td>P1-C2</td>
<td>1.830(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Selected Bond Angles

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angle (°)</th>
<th>Atoms</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1-Ru-P2</td>
<td>93.09(5)</td>
<td>P2-Ru-01</td>
<td>86.06(9)</td>
</tr>
<tr>
<td>P1-Ru-P3</td>
<td>91.91(5)</td>
<td>P3-Ru-02</td>
<td>83.62(9)</td>
</tr>
<tr>
<td>P1-Ru-P4</td>
<td>93.22(5)</td>
<td>P4-Ru-01</td>
<td>86.40(9)</td>
</tr>
<tr>
<td>P1-Ru-O1</td>
<td>170.98(10)</td>
<td>P4-Ru-02</td>
<td>79.76(9)</td>
</tr>
<tr>
<td>P1-Ru-O2</td>
<td>111.77(10)</td>
<td>O1-Ru-02</td>
<td>59.28(12)</td>
</tr>
<tr>
<td>P2-Ru-P3</td>
<td>98.94(5)</td>
<td>Ru-01-C33</td>
<td>92.1(3)</td>
</tr>
<tr>
<td>P2-Ru-P4</td>
<td>96.59(5)</td>
<td>Ru-02-C33</td>
<td>89.0(3)</td>
</tr>
<tr>
<td>P2-Ru-O1</td>
<td>95.90(10)</td>
<td>O1-C33-02</td>
<td>119.6(5)</td>
</tr>
<tr>
<td>P2-Ru-O2</td>
<td>154.96(10)</td>
<td>O1-C33-C34</td>
<td>120.9(5)</td>
</tr>
<tr>
<td>P3-Ru-P4</td>
<td>163.34(5)</td>
<td>O2-C33-C34</td>
<td>119.5(5)</td>
</tr>
</tbody>
</table>
Prompted by the success in producing the triple hydroxo bridged complex \([\text{Ru}_{2}(\text{OH})_3(\text{PMe}_2)_6]\text{B}0_4\) (33) (see Chapter 3) it was decided to attempt to synthesise triple alkoxo bridged complexes via similar types of reaction. However, heating the deep red solution (produced by heating \([\text{RuH} (\text{cod}) (\text{NH}_2\text{NMe}_2)_3]\text{B}0_4\) under reflux in degassed acetone:MeOH (2:1) with a three fold excess of \(\text{PETO}_2\)) under reflux with an excess of freshly prepared \(\text{NaOMe}\) under \(\text{N}_2\) for several hours led to the precipitation of the mildly air sensitive Ru(II) dihydrido monomer \(\text{RuH}_2(\text{CO})(\text{PETO}_2)_3\) (54) (c.f. \(\text{RuH}_2(\text{CO})(\text{P}_3)_3\) made by bubbling CO gas through benzene solutions of \(\text{RuH}_4(\text{P}_3)_3\) or \(\text{RuH}_2(\text{P}_3)_4\)) (241).

Elemental analysis was in good agreement with that expected for the non-conducting, sharp-melting compound (54). Infrared spectroscopy shows two weak \(\nu_{\text{Ru-H}}\) stretches at 1915 cm\(^{-1}\) and 1900 cm\(^{-1}\) and a strong, broad \(\nu_{\text{C=O}}\) stretch at 1925 cm\(^{-1}\). A combination of \(^{31}\text{P}-(^1\text{H})\) and \(^1\text{H}\) n.m.r. spectroscopic measurements in CDCl\(_3\) at 298 K clearly shows one hydride to be trans to a \(\text{PETO}_2\) group, while the other is trans to a carbonyl group. A \(^1\text{H}\) n.m.r. study at
360 MHz shows the hydride trans to PEt\(\theta_2\) as a doublet \(^{2}J_{PH} 73.2\) Hz) of triplets \(^{2}J_{PH} 26.9\) Hz) of doublets \(^{2}J_{HH} 6.1\) Hz) at \(\delta-8.88\) ppm, while the hydride trans to CO is seen as a triplet \(^{2}J_{PH} 24.4\) Hz) of doublets \(^{2}J_{PH} 21.4\) Hz) of doublets \(^{2}J_{HH} 6.1\) Hz) at \(\delta-7.45\) ppm (Figure (A.6)).

A \(^{31}P-\{^1H\}\) n.m.r. spectrum at 24.2 MHz shows two resonances, a doublet at \(\delta_p 51.7\) ppm and a triplet at \(\delta_p 38.2\) ppm \(^{2}J_{PP} 17.3\) Hz) (Figure (A.7)). A \(^{31}P-\{\text{sel.}^1H\}\) n.m.r. experiment (decoupling ethyl and phenyl protons) transforms the doublet into an overlapping doublet of triplets, while the triplet becomes an overlapping doublet of doublets of triplets (Figure (A.8)).

A.4 Conclusions

The reactions discussed in this appendix serve to further illustrate the rich chemistry of the novel hydride complex \([\text{RuH(cod)}(\text{NH}_2\text{NMe}_2)_3]\text{B} \theta_4\), whose diverse reaction products were briefly outlined in Introductory Section A.2. For example, the hydrido and dihydrido carbonyl complexes (52) and (54) respectively, which are undoubtedly formed via the well-known phenomenon of reductive decarbonylation of solvent, may be isolated in high yield as the sole product from their respective complex reaction mixtures. Whether the acetate complex (53) is produced by a solvent decomposition, or more likely via solvent contamination, is not known.
Figure A.6  $^1$H n.m.r. Spectrum of the Hydride Region of $\text{RuH}_2(\text{CO})(\text{PET}_2)_3$ in $\text{CDCl}_3$ at $\delta=7.45$ ppm $\text{at } 298 \text{ K.}$
Figure A.7 \[^{31}P-(^1\text{H})\text{n.m.r. Spectrum of } \text{RuH}_2(\text{CO})(\text{PEt}2)3\]

in CDCl₃ at 298 K

\(\delta_P 51.7\text{ ppm}\)

\(\delta_P 38.2\text{ ppm}\)
Figure A.8  $^{31}P-(^1H)$ n.m.r. Spectrum of $\text{RuH}_2(\text{CO})(\text{PET}_2)_3$ in CDCl$_3$ at 298 K
A.5  Experimental

All physical measurements were obtained as in Chapter 2.
In addition, all $^{31}$P-{$^1$H} n.m.r. spectra measured at
145.8 MHz were obtained on a Bruker WH360 spectrometer
operating in the pulse and Fourier transform modes, while
all {$^1$H} n.m.r. spectra measured at 100 MHz were obtained on
a Varian HA100 spectrometer operating in the continuous
wave mode.

Reagents

[RuH(cod)(NH$_2$NMe$_2$)$_3$]BØ$_4$ was prepared using the
literature method$^{(236)}$.

[n$^2$-Acetatotetrakis(dimethylphenylphosphine)ruthenium(II)]-
tetraphenylboronate

The complex [RuH(cod)(NH$_2$NMe$_2$)$_3$]BØ$_4$ (0.25 g) was heated
under reflux under N$_2$ in degassed EtOH:acetone (10 ml of
each) with a four-fold excess of PMe$_2$Ø (0.20 ml) for twenty
minutes. The deep red solution formed was then treated with an
excess of glacial acetic acid (2 ml). The bright yellow
solution thus formed was heated under reflux under N$_2$ for a
further 6 hours and on cooling the solution, pale yellow
microcrystals precipitated. These were filtered, washed
with EtOH and diethyl ether and dried in vacuo at 40°C
(86% yield). M.P. 137-139°C (decomp), [Found:  C, 66.2;
H, 6.4. Calculated for C$_{58}$H$_{67}$BO$_2$P$_4$Ru:  C, 66.0;  H, 6.4%].

Ir"ared spectrum:  \nu_{O-C-O}  1581 (m), 1460 (s) cm$^{-1}$ and
\nu_{C-O-C}  1095 (s) cm$^{-1}$. \[\AA (1 \times 10^{-3} \text{ M}) \text{ in acetone} =
76 \ \text{\Omega cm}^2\text{mol}^{-1}\].
Carbonyldihydridotris(ethylidiphenylphosphine)ruthenium(II)

The compound [RuH(cod)(NH₂NMe₂)₃]BØ₄ (0.50 g) was heated under reflux under an N₂ atmosphere in dry degassed MeOH:acetone (20 ml and 10 ml respectively) with a three-fold excess of PEt₀₂ (0.42 ml) for twenty minutes. The dark red solution formed was treated with an excess of freshly prepared NaOMe in MeOH (15 ml) and heated under reflux under N₂ for a further 6 hours. On cooling an off-white solid precipitated. This solid was recrystallised from MeOH:CHCl₃ as off-white microcrystals, filtered, washed with MeOH and H₂O and dried in vacuo at 40°C (60% yield).

M.P. 143°C (decomp), [Found: C, 65.6; H, 6.1. Calculated for C₄₃H₄₇OP₃Ru: C, 66.8; H, 6.1%], non-conducting in CH₂Cl₂. Infrared spectrum: νCO 1925 (s) cm⁻¹, νRu-H 1915 (w), 1900 (w) cm⁻¹.

[Carbonylhydridotetrakis(dimethylphenylphosphine)ruthenium(II)]-tetraphenylboronate

The compound [RuH(cod)(NH₂NMe₂)₃]BØ₄ (0.25 g) was heated under reflux under a N₂ atmosphere in degassed MeOH:acetone (10 ml of each) with a four-fold excess of PMe₂Ø (0.20 ml) for twenty minutes. The deep red solution formed was treated with an excess of degassed H₂O (3 ml) and heated under reflux under N₂ for a further 12 hours. The off-white microcrystalline product was filtered, washed with MeOH and diethylether and dried in vacuo at 40°C (85% yield).
M.P. 152-154°C, [Found: C, 68.1; H, 6.6. Calculated for C$_{57}$H$_{65}$BOP$_4$Ru: C, 68.3; H, 6.5%].

**Infrared Spectrum**  
$\nu_{C=O}$ and $\nu_{Ru-H}$ 1950 (br. s) cm$^{-1}$.  
[$\Lambda(1 \times 10^{-3} \text{ M})$ in acetone = 81 $\Omega$ cm$^2$ mol$^{-1}$].
APPENDIX II

The Thermodynamic Relationship between the Optical Transition Energy and the Measured and Inferred $E_x$ Values
From Table 6.3 and Figure 6.2 it can be seen that for the symmetric dication \[\left((\text{PET}_2\text{Ø})_3\text{RuCl}_3\text{Ru(PEt}_2\text{Ø})_3\right)^{2+}\] the Franck-Condon energy, \(E_{\text{FC}}\), is equivalent to the optical transition energy, \(E_{\text{op}}\), which is ca. 4350 cm\(^{-1}\). Assuming the difference in \(E_{\text{FC}}\) between \[\left((\text{PET}_2\text{Ø})_3\text{RuCl}_3\text{Ru(PEt}_2\text{Ø})_3\right)^{2+}\] and the asymmetric complex \((\text{PET}_2\text{Ø})_3\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{Ø})\) (50) is small with respect to the internal energy, \(E_{\text{O}}\), of (50) (see Figure 6.1) then \(E_{\text{op}}\) for the asymmetric complex can be calculated from Equation [6] i.e. \(E_{\text{op}} = E_{\text{FC}}(\Delta\text{Cl}^-=0) + E_{\text{O}}(E_{\text{FC}}(\Delta\text{Cl}^-=0) \sim E_{\text{FC}}(\Delta\text{Cl}^-=1,2))\); \(E_{\text{O}}\) can be calculated from the simple thermodynamic cycle below.

\[\begin{array}{c}
\text{Ru}^{\text{II}}_{\text{A}}\text{Cl}_3\text{Ru}^{\text{III}}_{\text{B}} \quad \Delta G \quad \text{Ru}^{\text{III}}_{\text{A}}\text{Cl}_3\text{Ru}^{\text{II}}_{\text{B}} \\
E_{\frac{1}{2}}(1) \quad \text{Ru}^{\text{II}}_{\text{A}}\text{Cl}_3\text{Ru}^{\text{II}}_{\text{B}} \quad \text{Ru}^{\text{III}}_{\text{A}}\text{Cl}_3\text{Ru}^{\text{II}}_{\text{B}} \quad E_{\frac{1}{2}}(2)
\end{array}\]

Assuming \(\Delta G = E_{\text{O}}\) (a reasonable assumption if \(\Delta S\) for the valence interchange is ca. 0) then \(E_{\text{O}} = [E_{\frac{1}{2}}(2) - E_{\frac{1}{2}}(1)]\text{eV} = 8066 [E_{\frac{1}{2}}(2) - E_{\frac{1}{2}}(1)] \text{cm}^{-1}\). \(E_{\frac{1}{2}}(1)\) can be measured directly by experiment e.g. \(E_{\frac{1}{2}}(1)\) for (50) is \(-0.28\) V. \(E_{\frac{1}{2}}(2)\) cannot be determined experimentally but it can be calculated using the structure/electrode potential correlations established in Chapter 5, thus \(E_{\frac{1}{2}}(2)\) for (50) can be estimated to be ca. 0.77 V. These values for \(E_{\frac{1}{2}}(1)\) and \(E_{\frac{1}{2}}(2)\) yield an estimated \(E_{\text{O}}\) of ca. 1.05 eV or 8470 cm\(^{-1}\).
Substituting 8470 cm\(^{-1}\) for \(E_0\) and 4350 cm\(^{-1}\) for \(E_{FC}\) yields a predicted value of ca. 12820 cm\(^{-1}\) for the optical transition energy, \(E_{op}\), for \((\text{PET}_2\text{Ø})_3\text{RuCl}_3\text{RuCl}_2(\text{PET}_2\text{Ø})\) (50) (c.f. the experimentally determined value of 13500 cm\(^{-1}\)) (see Table 6.3 for further examples of predicted and experimentally determined values of the optical transition energy).

The predicted values of \(E_{op}\) are generally in good agreement with the experimentally determined values, thus validating the electrochemical correlations and the inherent assumptions of the treatment.

Finally, it is worth noting that although the difference in the successive redox potentials of the symmetric complexes \([(\text{PET}_2\text{Ø})_3\text{RuCl}_3\text{Ru}(\text{PET}_2\text{Ø})_3]\text{Cl}\) and \((\text{As}(\text{E-tol})_3)_2\text{ClRu-Cl}_3\text{RuCl}(\text{As}(\text{E-tol})_3)_2 \) (6) (ca. 4440 (0.55 eV) and 5890 (0.73 eV) cm\(^{-1}\) respectively) is very close (within 2%) to the \(E_{op}\) values for these complexes i.e. 4350 and 5900 cm\(^{-1}\), there is no direct correlation between the two parameters i.e. the coincidence of \(E_{op}\) and the separation of the two redox potentials (\(\Delta E_{\frac{1}{2}}\)) for each compound is fortuitous. Thus, \(\Delta E_{\frac{1}{2}}\) is a measure of the position of the highly favoured conproportionation equilibrium of thermally relaxed species in their ground-states:

\[
\begin{align*}
\text{Ru}_2(\text{III/III}) + \text{Ru}_2(\text{II/II}) & \rightarrow 2 \text{Ru}_2(\text{II/III}) \\
34 \text{ e}^- & \quad 36 \text{ e}^- \quad 2 \times 35 \text{ e}^- 
\end{align*}
\]

whereas \(E_{op}\) measures the vertical excitation energy, \(E_{FC}\), from \(\text{Ru}_2(\text{II/III})\) to its thermally excited oxidation-state isomer \(\text{Ru}_2(\text{III/II})^*\).
**APPENDIX III**

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>acac</td>
<td>acetylacetonate</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>BM</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>Bu&lt;sup&gt;n&lt;/sup&gt;</td>
<td>normal butyl</td>
</tr>
<tr>
<td>cod</td>
<td>cycloocta-1,5-diene</td>
</tr>
<tr>
<td>dmf</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>dpae</td>
<td>(1,2-diphenylarseno)ethane</td>
</tr>
<tr>
<td>dppe</td>
<td>(1,2-diphenylphosphino)ethane</td>
</tr>
<tr>
<td>en</td>
<td>ethylenediamine</td>
</tr>
<tr>
<td>e.s.r.</td>
<td>electron spin resonance</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>3-Mepy</td>
<td>3-methyl-pyridine</td>
</tr>
<tr>
<td>4-Mepy</td>
<td>4-methyl-pyridine</td>
</tr>
<tr>
<td>M.P.</td>
<td>melting point</td>
</tr>
<tr>
<td>n.m.r.</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>norb</td>
<td>norbornadiene</td>
</tr>
<tr>
<td>ox</td>
<td>oxalate</td>
</tr>
<tr>
<td>ø</td>
<td>phenyl</td>
</tr>
<tr>
<td>pent&lt;sup&gt;n&lt;/sup&gt;</td>
<td>normal pentyl</td>
</tr>
<tr>
<td>phen</td>
<td>1,10-phenanthroline</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>Pr&lt;sup&gt;i&lt;/sup&gt;</td>
<td>iso propyl</td>
</tr>
<tr>
<td>Pr&lt;sup&gt;n&lt;/sup&gt;</td>
<td>normal propyl</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>sacsac</td>
<td>di-thioacetylacetonate</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>terpy</td>
<td>2,2',2''-terpyridine</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>T.M.S.</td>
<td>tetramethysilane</td>
</tr>
<tr>
<td>p-tol</td>
<td>4-methylphenyl</td>
</tr>
<tr>
<td>U.V.</td>
<td>ultra violet</td>
</tr>
</tbody>
</table>
REFERENCES

32. E.O. Fischer and H. Grubert, Ber., 1959, 92, 2302.
47. B.N. Figgis, J. Lewis, F.E. Mabbs and G.A. Webb, 
   1966, 28, 2285.
50. T.A. Stephenson, D.A. Tocher and M.D. Walkinshaw, 
   1976, 15, 564.
52. K.W. Given, S.H. Wheeler, B.S. Jick, L.J. Maheu and 
   13, 135.
   3533.
   237; 1938, 235, 356.
   304, 308.


96. A. Joly, Compt. Rend., 1890, 111, 964.
97. A. Joly, and H. Remy, Encyclopedie Chimique, Paris, 1900, 17, 156.
101. C.A. Martius, Ann., 1861, 117, 357.


129. W. Manchot and E. König, Ber., 1924, 57, 2130.
130. W. Manchot and E. Enk, Ber., 1930, 63, 1635.
202. D.A. Doddrell, P.L. Goggin and R.J. Goodfellow, 

7, 349.

13(2), 456.

9(1), 39.


1771.

208. R.A. Jones, G. Wilkinson, I.J. Calquohoun, W. McFarlane 
2480.

209. B.R. James, L.D. Markham, B.C. Hui and G.L. Rempel, 

97, 4221 and references therein.

211. T.V. Ashworth, R.H. Reimann and E. Singleton, 
therein.


213. J.C.T.R. Burkett-St. Laurent, M.R. Caira, R.B. English, 


Post Graduate Courses Attended

"Synchrotron Radiation and its Applications"
by Dr. I. Munro, Dr. C.D. Garner, Dr. P. Norman,
Dr. J. Helliwell and Dr. I. Hillier

"Zeolites"
By Dr. B.M. Lowe

"Homogeneous Catalysis"
By Dr. T.A. Stephenson

"Mass Spectrometry"
By Dr. J.H. Beynon

"Cage and Cluster Compounds"
By Dr. A.J. Welch

"Fourier Transform Infrared Spectroscopy"
By Dr. A. Morrison, Dr. J. Duncan and Dr. S. Cradock

"Interpreting the Results of Crystallography"
By Dr. R.O. Gould, Dr. M.D. Walkinshaw and Dr. A.J. Welch

University of Strathclyde Inorganic Club Conferences 1980, 1981, 1982

Departmental and Research Seminars and Colloquia.