SYNTHESSES, REARRANGEMENT STUDIES AND REACTIONS OF SOME RUTHENIUM(II) COMPLEXES CONTAINING PHOSPHORUS DONOR LIGANDS.

Wilma J. Sime

Ph.D. Thesis
University of Edinburgh
1977
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.

Wilma J. Sime
To my father and my husband.
ACKNOWLEDGEMENT

I am deeply indebted to Dr. T.A. Stephenson for his help and encouragement throughout this work. I would also like to thank Dr. G. Heath of Stirling University for the use of facilities and help in interpreting the polarographic results, Dr. R. O. Gould and C. L. Jones for carrying out the X-ray work and my colleagues in particular P. W. Armit. I am grateful to Dr. A. S. Boyd and Mr. J. Millar for running the $^{31}$Pn.m.r. and $^1$Hn.m.r. spectra respectively, to the S.R.C. for their financial support and finally to the University of Edinburgh for the use of facilities.
Chapter 1 gives a brief description of some of the general aspects of ruthenium chemistry.

Chapter 2 deals with formation of complexes \( \text{RuCl}_2 L_n \) \((n=3, L=P(OMe)Ph_2, P(OEt)Ph_2; n=4, L=P(OMe)_3, P(OMe)_2 Ph)\) by reaction of \( \text{RuCl}_2 (PPh_3)_3 \) with excess \( L \) in non-polar solvents, and their subsequent rearrangement in polar solvents to produce eventually \( [\text{Ru}_2 \text{Cl}_2 L_6] \text{Cl} \) \((L=P(OMe)_2 Ph, P(OMe)Ph_2)\) and \( [\text{Ru}_3 \text{Cl}_5 L_9] \text{Cl} \) \((L=P(OMe)Ph_2, P(OEt)Ph_2)\). Reaction of \( \text{RuCl}_2 (PPh_3)_3 \) with \( L \) in polar solvents is also investigated, and an overall mechanism for the rearrangement of \( \text{RuCl}_2 L_{3,4} \) proposed.

Chapter 3 describes the pyrolysis of \( [\text{Ru}_2 \text{Cl}_3 (P(OMe)Ph_2)_6]X \) \((X=\text{Cl}, \text{CN}, \text{SCH}_2 S, S_2 \text{PMe}_2)\) to produce \( (P(OMe)Ph_2)_2 (P(OH)Ph_2) \text{RuCl}_3 Ru(P(OMe)Ph_2)(P(OH)Ph_2)_2 \) the structure of which was determined by X-ray analysis.

Chapter 4 describes reactions of \( \text{RuCl}_2 Y(PPh_3)_4 \) \((Y=\text{CO}, \text{CS})\) with excess \( L \) \((L=P(OMe)Ph_2, P(OEt)Ph_2, P(OMe)_2 Ph)\) to produce \( \text{RuCl}_2 YL_3 \) and \( \text{RuCl}_2 L_3 \). Formation of \( \text{RuCl}_2 (\text{CO})L_3 \) \((L=P(OMe)Ph_2, P(OEt)Ph_2)\), by reaction of \( \text{RuCl}_2 L_3 \) with \( \text{CO} \), and \( \text{RuCl}_2 (\text{CS})L_2 \) by reaction of \( [\text{RuCl}_2 (\text{CS})(PPh_3)_2]_2 \) with \( L \), is also described, in addition to reactions of \( \text{RuCl}_2 L_4 \) \((L=\text{PMe}_2 Ph, \text{PMePh}_2)\) and \( \text{RuCl}_2 (\text{PETPh}_2)_3 \) with \( \text{CS}_2 \) to produce \( [\text{Ru}(\eta \text{CS}_2)L_4] \text{Cl} \) and \( [\text{RuCl}(\eta \text{CS}_2)(\text{PETPh}_2)_3] \text{Cl} \) respectively.

Chapter 5 deals with reactions of \( \text{RuCl}_2 L_n \) \((n=4, L=\text{PMePh}_2, \text{PMe}_2 Ph, P(OMe)_2 Ph; n=3, L=P(OMe)Ph_2, P(OEt)Ph_2, \text{PETPh}_2)\) with a variety of dithiocarbamido ligands \((S-S)\). Several intermediates in the formation of \( \text{Ru}(S-S)L_2 \) were isolated \( \text{viz.} \) \( \text{RuCl}(S-S)L_2, [\text{Ru}(S-S)L_4]^+, [\text{Ru}(S-S)L_3]^+ \), \( \text{Ru}(S-S)_2 L_2 \), and a general mechanism for the formation of \( \text{Ru}(S-S)_2 L_2 \) is...
Chapter 6 describes the formation of the triple bridged complex $\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4$ by the coupling together of two monomers, $[\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\text{solvent}]$ and $\text{RuCl}_2(\text{PPh}_3)_3$. The preparation of complexes $L_2\text{YRuCl}_3\text{RuCl}_2L'$ ($L=L'=\text{P}(p\text{-tol})_3$, $Y=\text{CO}$, CS; $L=\text{PPh}_3$, $L'=\text{P}(p\text{-tol})_3$, $Y=\text{CO}$) is also discussed and the reaction of SnCl$_2$ with the 'red solution' (prepared by carbonylation of $\text{RuCl}_3\cdot3\text{H}_2\text{O}$ in ethanol) is reinvestigated and found to produce $[\text{RuCl}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2\text{acetone}]\text{acetone}$, the structure of which was determined by X-ray analysis.

Chapter 7 discusses the results of some polarographic studies on $\text{Ru}_2\text{Cl}_4\text{Y}(\text{PPh}_3)_4$ ($Y=\text{CO}$, CS) and $[\text{Ru}_2\text{Cl}_3L_6]X$ ($L=\text{PMe}_2\text{Ph}$, $X=\text{SCN}$; $L=\text{P}(\text{OMe})\text{Ph}_2$, $X=\text{BF}_4^-$).

Appendix 1 describes the Xn.m.r. spectra of a system of the type $X_n\text{AA}'X_n'$.

Appendix 2 deals with the analysis of AB and $\text{A}_2\text{B}$ spin systems in n.m.r. spectroscopy.
### CONTENTS

#### CHAPTER 1  
**A brief survey of the chemistry of ruthenium.**

1.1 Oxidation states of ruthenium
- (a) Ru(VIII), Ru(VII), Ru(VI), Ru(V)  
- (b) Ru(IV)  
- (c) Ru(III), Ru(II)  
- (d) Ru(I)  
- (e) Ru(0)

1.2 Nitrosyl complexes of ruthenium  
1.3 Ruthenium complexes as homogeneous catalysts

#### CHAPTER 2  
**Syntheses and rearrangement studies of**  
\( \text{RuCl}_2\text{L}_{3,0r4}(\text{L}=	ext{P(OR)}_3, \text{P(OR)}_2\text{Ph}, \text{P(OR)}\text{Ph}_2) \).

2.1 Introduction  
2.2 Results and discussion
- (a) Preparation of \( \text{RuCl}_2\text{L}_{3,0r4} \) by exchange reactions in non-polar solvents.  
- (b) Rearrangement of monomeric species in polar solvents.  
- (c) Reaction of \( \text{RuCl}_2(\text{PPh}_3)_3 \) with \( \text{L} \) in polar solvents.  
- (d) Mechanism of rearrangement of \( \text{RuCl}_2\text{L}_{3,0r4} \) species.

2.3 Experimental  
Tables
CHAPTER 3. Pyrolysis of complexes of the type
\[ [\text{Ru}_2\text{Cl}_3\text{L}_6]X \quad (L=\text{P(OMe)Ph}_2, \text{P(OMe)}_2\text{Ph}; \quad X=\text{BPh}_4 \]
\[ \text{Cl}^-, \text{SCN}^-, \text{CN}^-, \text{S}_2\text{PMe}_2^- \] and \[ [\text{Ru}_3\text{Cl}_5\text{L}_9]X \quad (L=\text{P(OEt)Ph}_2) \]
3.1 Introduction 73
3.2 Results and discussion 73
3.3 Experimental 81

CHAPTER 4. Exchange reactions of Ru$_2$Cl$_4$Y(PPh$_3$)$_4$
with L (L=P(OR)Ph$_2$, P(OR)$_2$Ph; Y=CO, CS).
and reactions of RuCl$_2$L$_3$ or 4 with
carbon monoxide and carbon disulphide.
4.1 Introduction 83
4.2 Results and discussion
(a) Carbonyl complexes 83
(b) Thiocarbonyl complexes 90
(c) Rearrangement of RuCl$_2$YL$_3$
complexes in polar solvents 94
(d) Reactions of RuCl$_2$L$_3$ (L=PMePh$_2$
P(OR)Ph$_2$) and RuCl$_2$L$_4$
(L=PMe$_2$Ph, PMePh$_2$, P(OMe)$_2$Ph)
with CS$_2$.
99
4.3 Experimental 118
Tables 122

CHAPTER 5. Reaction of RuCl$_2$L$_3$ or 4 (L=PPh$_2$, P$_2$Ph,
P(OR)Ph$_2$, P(OR)$_2$Ph) with some dithio-
acid ligands.
CONTENTS (cont.)

5.1 Introduction 
5.2 Results and discussion.
   (a) Diphenyl and dimethylphosphinothioate complexes
   (b) Ω-substituted dithiocarbonate complexes
   (c) N,N disubstituted dithiocarbamate complexes
   (d) Proposed mechanism for formation of Ru(S-S)$_2$L$_2$ from RuCl$_2$L$_3$ or 4

5.3 Experimental
 Tables

CHAPTER 6 Syntheses of some triple bridged complexes of ruthenium and determination of their mechanism of formation.

6.1 Introduction
6.2 Determination of mechanism of formation of (PPh$_3$)$_2$(CS)RuCl$_3$RuCl(PPh$_3$)$_2$
6.3 Preparation of L$_3$YRuCl$_3$RuClL'$_2$
   (L=L'=P(p-tol)$_3$ Y=CO,CS; L=PPh$_3$
   L'=P(p-tol)$_3$ Y=CO)
6.4 Synthesis and rearrangement of
   [RuCl(SmCl$_3$)(Co)(PPh$_3$)$_2$ acetone] acetone
6.5 Experimental
 Tables
CHAPTER 7  Some polarographic studies on ruthenium (II) triple bridged dimeric species.

7.1 Introduction  211
7.2 Results and discussion  215
7.3 Experimental  223

APPENDIX 1  Characteristics of the X_n.m.r. spectra of systems of the $\text{X}_n\text{AA}'\text{X}'_n$ type.  224

APPENDIX 2  Analysis of AB and $\text{AB}_2$ spin systems in n.m.r. spectroscopy.
(a) AB spin systems  227
(b) $\text{AB}_2$ spin systems  227

APPENDIX 3  Abbreviations  230

REFERENCES
<table>
<thead>
<tr>
<th>FIGURES</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 2.1</td>
<td>Model for Mechanism A for rearrangement of RuH₂L₄ species.</td>
</tr>
<tr>
<td>Fig. 2.2</td>
<td>Model for Mechanism B for rearrangement of RuH₂L₄ species.</td>
</tr>
<tr>
<td>Fig. 2.3</td>
<td>¹H n.m.r. spectrum of RuCl₂(P(OMe)₃)₄ in CDCl₃ at 301K.</td>
</tr>
<tr>
<td>Fig. 2.4</td>
<td>Plot of conductivity vs. time for RuCl₂(P(OR)Ph₂)₃ in CH₂Cl₂.</td>
</tr>
<tr>
<td>Fig. 2.5</td>
<td>³¹P n.m.r. spectra of RuCl₂(P(OMe)Ph₂)₃ in (CD₃)₂CO/CH₂Cl₂ at various temperatures.</td>
</tr>
<tr>
<td>Fig. 2.6</td>
<td>Expansion of ³¹P n.m.r. spectrum of the rearrangement products of RuCl₂(P(OMe)Ph₂)₃ in (CD₃)₂CO/CH₂Cl₂ at 213K.</td>
</tr>
<tr>
<td>Fig. 2.7</td>
<td>³¹P n.m.r. spectra of RuCl₂(P(OEt)Ph₂)₃ in (CD₃)₂CO/CH₂Cl₂ at various temperatures.</td>
</tr>
<tr>
<td>Fig. 2.8</td>
<td>³¹P n.m.r. spectrum of the ionic rearrangement product of RuCl₂(P(OEt)Ph₂)₃ in CDCl₃ at 213K.</td>
</tr>
<tr>
<td>Fig. 2.9</td>
<td>Far infrared spectrum of [Ru₃Cl₅(P(OEt)Ph₂)₉]EPPh₄.</td>
</tr>
</tbody>
</table>
FIGURES (cont.)

Fig. 2.10 Possible structures of $[\text{Ru}_3\text{Cl}_5(\text{P(OEt})\text{Ph}_2)_9]^+$  

Fig. 2.11 $^{31}\text{Pnm.r. spectra of } [\text{RuCl}(\text{P(OMe})\text{Ph}_2)_4]-$  

$\text{BPh}_4$ in $(\text{CD}_3)_2\text{CO}$ at various temperatures.  

Fig. 2.12 $^{31}\text{Pnm.r. spectrum of } [\text{RuCl}(\text{P(OMe})\text{Ph}_2)_4]-$  

$\text{BPh}_4$ in $(\text{CD}_3)_2\text{CO}$ at 173K.  

Fig. 2.13 $^{31}\text{Pnm.r. spectra of } \text{cis-FeH}_2(\text{P(OMe})_2\text{Ph})_4$  
in 50% CH$_2$Cl$_2$-50% CHF$_2$Cl at various temperatures.  

Fig. 2.14 $^{31}\text{Pnm.r. spectra of }$  

$[\text{Ru}_2\text{Cl}_2(\text{P(OEt})\text{Ph}_2)_8](\text{BPh}_4)_2$ in $(\text{CD}_3)_2\text{CO}$  
at various temperatures.  

Fig. 2.15 $^{31}\text{Pnm.r. spectrum of }$  

$[\text{Ru}_2\text{Cl}_2(\text{P(OEt})\text{Ph}_2)_8](\text{BPh}_4)_2$ in $(\text{CD}_3)_2\text{CO}$  
at 173K.  

Fig. 3.1 Structure of  

$(\text{P(OMe})\text{Ph}_2)_2(\text{P(OH})\text{Ph}_2)\text{RuCl}_3\text{Ru}(\text{P(O})\text{Ph}_2)_2$  

$(\text{P(OH})\text{Ph}_2)_2$.  

Fig. 3.2 Proposed molecular structure of  

$(\text{P(OMe})\text{Ph}_2)_2(\text{P(OH})\text{Ph}_2)\text{RuCl}_3\text{Ru}(\text{P(O})\text{Ph}_2)_2$  

$(\text{P(OH})\text{Ph}_2)_2$.  

Fig. 4.1 Structure of $\text{RuCl}_2(\text{CO})(\text{P(OMe})_2\text{Ph})_3$.  

PAGE

42  

47  

49  

52  

56  

57  

75  

74  

86
Fig. 4.2  $^{31}$P n.m.r. spectrum of RuCl$_2$(CS)(P(OMe)$_2$Ph)$_3$ in C$_6$D$_6$ at 298K.  

Fig. 4.3  $^{31}$P n.m.r. spectrum of [RuCl(CO)(P(OEt)Ph$_2$)$_3$]$_2$(BPh$_4$)$_2$ in CDCl$_3$ at 213K.  

Fig. 4.4  Possible isomers of [Ru$_2$Cl$_2$Y$_2$P$_6$]$^{2+}$  

Fig. 4.5  $^{31}$P n.m.r. spectrum of [Ru($\eta$CS$_2$)(PMe$_2$Ph)$_4$]Cl$_2$ at 298K in CDCl$_3$.  

Fig. 4.6  Calculated ABC$_2$ spectrum for parameters  

\[ J_A = 19.43, \ J_B = 15.71, \ J_C = 12.48 \text{p.p.m.} \]  

\[ J_{AB} = 3.83, \ J_{AC} = -14.75, \ J_{BC} = 31.66 \text{Hz.} \]  

Fig. 4.7  $^{31}$P n.m.r. spectrum of [Ru($\eta$CS$_2$)(PMe$_2$Ph)$_4$]Cl$_2$ at 298K in CDCl$_3$.  

Fig. 4.8  Calculated ABC$_2$ spectrum for parameters  

\[ J_A = 12.96, \ J_B = 10.66, \ J_C = 6.84 \text{p.p.m.} \]  

\[ J_{AB} = 9.67, \ J_{AC} = 28.36, \ J_{BC} = 4.78 \text{Hz.} \]  

Fig. 4.9  $^{31}$P n.m.r. spectrum of the rearrangement product of [Ru($\eta$CS$_2$)(PMe$_2$Ph)$_4$]$^{2+}$ in CDCl$_3$ at 298K.  

Fig. 4.10  $^{31}$P n.m.r. spectrum of [RuCl($\eta$CS$_2$)(PETPh$_2$)$_3$]Cl in CDCl$_3$ at 298K.
Fig. 4.11 $^{31}$Pn.m.r. spectrum of
$[\text{RuCl}(\text{CS}_2)(\text{PETPh}_2)_3](\text{BPh}_4)_2$ in CDCl$_3$ at 298K.

Fig. 4.12 $^{31}$Pn.m.r. spectrum of $\text{Ru}_2\text{Cl}_4(\text{CS}_2)(\text{PETPh}_2)_3$
in CDCl$_3$ at 298K.

Fig. 5.1 Diagramatic representation of
cis-$\text{Ru}(\text{S}_2\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2$.

Fig. 5.2 X-ray structure of $[\text{Ru}(\text{S}_2\text{PPh}_2)(\text{PMe}_2\text{Ph})_3]^{3+}$

Fig. 5.3 $^{31}$Pn.m.r. spectrum of
$[\text{Ru}(\text{S}_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3]\text{BPh}_4$ in CDCl$_3$ at 298K.

Fig. 5.4 $^1$Hn.m.r. spectrum of
$[\text{Ru}(\text{S}_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3]\text{BPh}_4$ in CDCl$_3$ at 301K.

Fig. 5.5 $^{31}$Pn.m.r. spectrum of
$\text{RuCl}(\text{S}_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$ in CDCl$_3$ at 213K.

Fig. 5.6 $^1$Hn.m.r. spectrum of
$\text{RuCl}(\text{S}_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$ at 233K in CDCl$_3$.

Fig. 5.7 Possible geometries for
$\text{RuCl}(\text{S}_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$.

Fig. 5.8 $^{31}$Pn.m.r. spectrum of $\text{Ru}(\text{S}_2\text{COMe})_2(\text{PMe}_2\text{Ph})_3$
at 298K in CDCl$_3$.

Fig. 5.9 $^1$Hn.m.r. spectrum of $\text{Ru}(\text{S}_2\text{COMe})_2(\text{PMe}_2\text{Ph})_3$
in CDCl$_3$ at 301K.
Fig. 5.10  Methylene region of $^1$H n.m.r. spectrum of 
$\text{Ru(S}_2\text{CNET}_2)_2\text{(PMePh}_2)_2$ in CCl$_3$ at 301K. 155

Fig. 6.1  Schematic representation of metal bonding 
orbitals in tri-$\mu$-chloro-diruthenium 
complexes. 177

Fig. 6.2  The geometric isomers of (PPh$_3$)LClRuCl$_3$-
RuL(PPh$_3$)$_2$. 181

Fig. 6.3  $^{31}$P n.m.r. spectrum of Ru$_2$Cl$_4$(CS)$_2$(PPh$_3$)$_3$
in CCl$_3$ at 213K. 187

Fig. 6.4  $^{31}$P n.m.r. spectrum of Ru$_2$Cl$_4$(CS)(P(p-tol)$_3$)$_4$
in CCl$_3$ at 298K. 195

Fig. 6.5  $^{31}$P n.m.r. spectrum of Ru$_2$Cl$_4$(CO)$_2$(P(p-tol)$_3$)$_3$
in CCl$_3$ at 298K. 196

Fig. 6.6  $^{31}$P n.m.r. spectrum of reaction product 
from coupling of RuCl$_2$(PPh$_3$)$_3$ with 
RuCl$_2$(CO)(P(p-tol)$_3$)$_2$ dmf in CCl$_3$ at 298K. 197

Fig. 6.7  X-ray structure of 
RuCl(SnCl$_3$)(CO)(PPh$_3$)$_2$ acetone 200

Fig. 7.1  Example of a cyclic voltammetric curve. 213

Fig. 7.2  Example of an a.c. polarogram. 215

Fig. 7.3  A.C. polarograms of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$. 217
Fig. 7.4  Cyclic voltammogram of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$ (cathodic scan). 218

Fig. 7.5  Cyclic voltammogram of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$ (anodic scan). 219

Fig. 7.6  Cyclic voltammogram of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$ (anodic scan to potentials $>$ 0.6V). 221

Fig. 7.7  Cyclic voltammogram of [Ru$_2$Cl$_3$(P(OMe)Ph$_2$)$_6$]BP$_4$ (anodic scan). 222

Fig. A.1  Variation of the $X$ spectrum of an $X_3A'$A$'$X$_3$ system with changes in $L/|J_A|$. 225

Fig. A.2  Schematic representation of an AB spectrum. 227

Fig. A.3  Schematic representation of an AB$_2$ spectrum. 228
### TABLES

| Table 2.1 | Analytical data for some ruthenium complexes containing tertiary phosphite, phosphinite and phosphonite ligands. | 68 |
| Table 2.2 | Far infra-red spectra ($400-200 \text{ cm}^{-1}$) of some ruthenium complexes. | 69 |
| Table 2.3 | $^1\text{H}	ext{n.m.r.}$ data for some ruthenium complexes. | 70 |
| Table 2.4 | $^{31}\text{P}	ext{n.m.r.}$ data for some ruthenium complexes. | 71 |
| Table 2.5 | $^{13}\text{C}	ext{n.m.r.}$ data for some ruthenium complexes. | 72 |
| Table 3.1 | Selected bond lengths of $(\text{P(OMe)P}_2)_2(\text{P(OH)P}_2)$RuCl$_2$Ru(\text{P(0)Ph}_2)_2$ | 76 |
| Table 4.1 | $\nu\text{(CS)}$ frequency ranges for the known types of transition metal $\text{CS}_2$ and thiocarbonyl complexes. | 103 |
| Table 4.2 | Analytical data for some ruthenium(II) carbonyl, thiocarbonyl and carbon disulphide complexes. | 122 |
| Table 4.3 | $^1\text{H}	ext{n.m.r.}$ spectral data for some ruthenium complexes. | 123 |
| Table 4.4 | $^{31}\text{P}	ext{n.m.r.}$ spectral data for some ruthenium complexes. | 125 |
| Table 5.1 | Selected bond lengths and bond angles of [Ru(S₂PPh₂)(PMe₂Ph)₃]⁺. | 139 |
| Table 5.2 | Analytical data for some ruthenium(II) dithioacid complexes. | 165 |
| Table 5.3 | $^{31}$Pn.m.r. spectral data for some ruthenium dithioacid complexes. | 167 |
| Table 5.4 | $^{1}$Hn.m.r. spectral data for some ruthenium dithioacid complexes. | 170 |
| Table 6.1 | Assignment of isomeric forms of (Ph₃P)Cl(SC)RuCl₃Ru(CS)(PPh₃)₂ to $^{31}$Pn.m.r. resonances. | 186 |
| Table 6.2 | Comparison of AB resonances for L₂(CO)RuCl₃RuCl₄ with those of Ru₂Cl₄(CO)L₄ and Ru₂Cl₄(CO)L'L₄ (L=PPh₃; L'=P(p-tol)_₃). | 198 |
| Table 6.3 | Selected bond lengths and bond angles for RuCl(SnCl₃)(CO)(PPh₃)₂(Me₂CO). | 202 |
| Table 6.4 | Analytical data for some ruthenium complexes. | 203 |
| Table 6.5 | $^{31}$Pn.m.r. spectral data for some ruthenium complexes. | 209 |
Table 7.1 Criteria for reversible, quasi-reversible and irreversible charge transfer processes. 214
SCHEMES

Scheme 1.1  Some reactions of 'RuCl₃·3H₂O'

Scheme 1.2  Mechanism of formation of Ru(CO)₃L₂
(L=PPh₃, PBU₃, PMePh₂)

Scheme 1.3  Mechanism for hydrogenation of olefins
by Ru(II) species.

Scheme 1.4  Mechanism for hydroformylation of
alkenes by Ru(CO)₃(PPh₃)₂.

Scheme 2.1  Original proposed mechanism for the
rearrangement of RuCl₂L₄ (L=tertiary phosphine).

Scheme 2.2  Intramolecular rearrangement of
[Ru₃Cl₅(P(OEt)Ph₂)₉]⁺ at 298K.

Scheme 2.3  Mechanism of rearrangement of
RuCl₂L₄ (L=tertiary phosphine, phosphinite, phosphonite).

Scheme 2.4  Mechanism of formation of [Ru₃Cl₅L₉]⁺

Scheme 2.5  Alternative pathway for rearrangement
of RuCl₂L₃ (L=tertiary phosphine)

Scheme 4.1  Stereochemistry of carbonyl substitution
reactions of RuCl₂(CO)₂(PMe₂Ph)₂.

Scheme 5.1  Mechanism for optical isomerisation of
Ru(S₂PMe₂)₂L₂.
Scheme 5.2  Mechanism of formation of
Os(S-S)₂(PMe₂Ph)₂ from OsCl₃(PMe₂Ph)₃.  136

Scheme 5.3  Possible rearrangements of
RuCl₂(S₂PMe₂)L₃ at 298K.  147

Scheme 5.4  Mechanism of formation of
[Ru(O₂COR)(PMe₂Ph)₄]⁺  153

Scheme 5.5  Mechanism of formation of Ru(S-S)₂L₂
from RuCl₂L₄ and RuCl₂L₃.  156

Scheme 6.1  Original proposed mechanism of formation
of Ru₂Cl₃(SnCl₃)(CO)₅.  179

Scheme 6.2  Several routes to the preparation of
Ru₂Cl₄L₂(PPh₃)₃ (L=CO, PF₃, Me₂NF₂).  180

Scheme 6.3  Coupling reaction of RuCl₂(PF₃)₂(PPh₃)₂
with RuCl₂(PPh₃)₃.  181

Scheme 6.4  Original mechanism proposed for formation
of Ru₂Cl₄(CS)(PPh₃)₄.  184

Scheme 6.5  Dimerisation of RuCl₂(CS)(PPh₃)₂MeOH.  189

Scheme 6.6  Mechanism of [RuCl₂(PPh₃)₂]₂CS₂ reaction.  191
A brief survey of the chemistry of ruthenium

Ruthenium was first discovered by Karl Karlovich Klaus in 1844. He named it after his native Russia or Ruthenia as it was then called. Ruthenium is very rare and its abundance in the earth's crust has been estimated at only $4 \times 10^{-4}$ p.p.m. The main sources are laurite (a mixture of osmium and ruthenium disulphide) found mainly in Borneo and the Transvaal, and platinum deposits found in the Urals, Columbia and Ethiopia. Ruthenium metal, which is silver-white in colour, is insoluble in all acids including aqua regia and resistant to oxygen up to a temperature of $600^\circ$C.

1.1 Oxidation states of ruthenium

Ruthenium exhibits a wide range of oxidation states from (VIII) to (-I). The 'normal' oxidation state, i.e. that for which the greatest diversity of complexes with "classical type" ligands is formed, is (III) and the least common states are (VII), (V), (I) and (-I). Small electronegative ligands such as fluoride and oxide are required to stabilize oxidation states (VIII) to (IV). Ru(VIII) and Ru(VII) are found only in oxycomplexes either with or without fluoride or hydroxide ligands. This is due to a combination of high electronegativity and the strong $\pi$ donor properties of the oxide ligand. Conversely, $\pi$ acceptor ligands such as cyanide, carbon monoxide and tertiary phosphines stabilize low oxidation states viz. Ru(II), (I) and (0). Ligands which are good $\sigma$ donors but which have no marked $\pi$ acceptor or $\pi$ donor properties, such as water and ammonia, are usually associated with Ru(III).

(a) Ru(VIII), Ru(VII), Ru(VI), Ru(V)

The only well characterised compound of Ru(VIII)($4d^0$) is the tetroxide $\text{RuO}_4^+$ ($T_d$ symmetry) which is a powerful oxidising agent. $\text{RuO}_4^+$
can react with pyridine$^2$ and PF$_3$ to form RuO$_4$.py$_2$ and RuO$_4$.PF$_3$ respectively, the structures of which are unknown. It is reduced by hydroxide ion to form RuO$_4^-$ which is, in turn, reduced to RuO$_4^{2-}$. Some fluoride complexes of Ru(VI) are also known e.g. RuF$_6^4$, made by direct fluorination of the metal, and RuOF$_4^{5}$.

The only known compounds of Ru(V) are the fluorides [RuF$_5$]$_4^{5}$, [RuF$_6$]$^-_{12}$ and [RuP$_6$]$^{2-}$. [RuF$_5$]$_4$ (1) consists of discrete tetrameric units with the Ru atoms lying at the corner of a square. The fluorine atoms are arranged around each Ru in a distorted octahedron and the Ru - F - Ru bridges are non linear.

\[ \text{(1)} \]

(b) Ru(IV)

Ru(IV) compounds are also not very common. [RuX$_6$]$^{2-}$ ions (X = F, Cl, Br) are all known although they decompose readily in aqueous solution, but of the neutral halides only RuF$_4$ has been isolated as a solid although RuCl$_4$ exists in the gaseous phase. The 'ruthenium red' complexes e.g. [RuO$_2$(NH$_3$)$_2$]$^{6+}$ are well known. These contain a linear Ru - O - Ru - O - Ru backbone with formally Ru(III); Ru(IV); Ru(III) oxidation states. A related complex K$_4$[Ru$_2$OCl$_{10}$] is prepared by reducing RuO$_4$ with HCl in the presence of KCl. The X-ray structure shows it to contain a linear Ru - O - Ru unit. Octahedral complexes of
Ru(IV) \((t_2g^4\) configuration) would be expected to be paramagnetic but the above compounds are diamagnetic\(^7\), and this is attributed to spin pairing via Ru - O - Ru \(\pi\) interactions.

Oxidative addition of tetra-chloro 1,2 benzoquinone to the Ru(II) species RuCl\(_2\)(PPh\(_3\))\(_3\) leads to formation of the six co-ordinate Ru(IV) monomeric species Ru\((\text{O}_2\text{C}_6\text{Cl}_4)\)(PPh\(_3\))\(_2\)Cl\(_2\). Similar reactions occur with 1,2 napthoquinone and 9,10 phenanthroquinone.\(^8\)

Until recently most Ru(IV) compounds have possessed six co-ordinate structures. However photolysis of Ru\((\text{S}_2\text{CNET}_2)\)_3 in degassed CHCl\(_3\) produces the seven co-ordinate diamagnetic RuCl\((\text{S}_2\text{CNET}_2)\)_3\(^9\), and an X-ray analysis shows the structure to be a distorted pentagonal bipyramid \((2)\). The corresponding Ru\((\text{S}_2\text{CNET}_2)\)_3NO\(^{10}\)

![Diagram](2)

is six co-ordinate with one of the diethylidithiocarbamate ligands monodentate. This complex, however, contains a Ru(II)\(d^6\) metal ion which has a strong preference for an octahedral configuration.

Recently, evidence has been obtained for ionic Ru(IV) species\(^{11}\) thought to be intermediates in the heterolytic splitting of molecular hydrogen by Ru(II) species, which is the initial step in the catalytic hydrogenation of alkenes (see later). The \([\text{RuH(L}_2\text{)}\text{MeOH}]^+\) ion \((L_2 = \text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPh}_2)\), prepared by treating \([\text{(cod)RuH(NH}_2\text{NMMe}_2)]\)\(\text{PF}_6\) with \(L_2\),
was reacted with $H_2$ to give the trihydro complex $[\text{RuH}_3(L_2)_2]^\text{PP}_6$. Subsequent treatment of the ionic trihydrido complex with $\text{Et}_3\text{N}$ converts it to $\text{RuH}_2(L_2)_2$ [1].

$$[\text{Ru}^{IV}_3\text{H}_3(L_2)_2]^+ \xrightarrow{+H^+} \text{RuH}_2(L_2)_2$$ [1]

This is the first example of the reductive elimination of $H^+$ from a relatively stable Ru(IV) hydrido complex.

(c) Ru(III), Ru(II)

The most common oxidation state of ruthenium is Ru(III) and there is a wide range of compounds known. Virtually all complexes, generally octahedral, are low spin $t_{2g}^5$ species with one unpaired electron and therefore paramagnetic ($\mu_{\text{eff}} \sim 1.8\text{B.M. at 300K}$). Exceptions are the dimeric $\text{Ru}_2(\text{OCOR})_4\text{Cl}$ ($R = \text{Me, Et}$) compounds which contain mixed Ru(II)/Ru(III) states and where magnetic measurements $^{12}$ indicate three unpaired electrons per dimer suggesting a high spin system. All four halides are known but the most stable is ruthenium trichloride which exists in both water soluble and water insoluble forms. The water soluble form of RuCl$_3$ can be obtained by prolonged action of HCl on RuO$_4$. This commercial product 'RuCl$_3\cdot 3\text{H}_2\text{O}' contains Ru(III) species such as RuCl$_3(\text{H}_2\text{O})_3$, polynuclear Ru(IV) oxy and hydroxy chloro species and sometimes the nitrosyl chloride $[\text{Ru(NO)}\text{Cl}_3]_n$. Due to its solubility in solvents such as water, methanol and acetone it is a useful starting material for the preparation of many Ru(III) and Ru(II) complexes. Some of these reactions are outlined in Scheme 1.1. Carbonylation of an ethanolic solution of 'RuCl$_3\cdot 3\text{H}_2\text{O}' gives a red solution which has been shown to contain several compounds including $[\text{Ru(CO)}_2\text{Cl}_2]_n$, $[\text{Ru(CO)}_3\text{Cl}_3]^{-}$ and RuCOCl$_3$. $^{13}$ Addition of various ligands $L$ to this red solution produces compounds of the type RuCl$_2$(CO)$_2$L$_2$ ($L = \text{py, PPh}_3, \text{AsPh}_3, \text{SbPh}_3$). $^{14}$
Although not as numerous as for Ru(II), there are a number of tertiary phosphine and arsine complexes of Ru(III). Refluxing RuCl₃·3H₂O' with L (L = PMe₂Ph, PET₂Ph, PBu₂Ph, PPh₃) for a short time in ethanol, containing HCl, gives mer-RuCl₃L₃ ¹⁵ RuCl₃(AsMePh₂)₃ ¹⁶ and RuCl₃(AsEt₂Ph)₃ ¹⁷ are also reported. Reaction of RuCl₃·3H₂O' with a stoichiometric amount of PPh₃ (or in the case of AsPh₃ an excess) in methanol produces RuCl₃(EPh₃)₂MeOH ¹⁴ (E = P, As), which then reacts with Ph₄AsCl.HCl to give anionic Ru(III) species Ph₄As[RuCl₄(EPh₃)₂] ¹⁸. Exchange reactions of Ph₄As[RuCl₄(EPh₃)₂] with other tertiary phosphine and phosphite ligands gives Ph₄As[RuCl₄L₂] (L = PMe₂Ph, PET₃, P(OPh)₃). RuCl₃(EPh₃)₂MeOH also reacts with a variety of ligands ¹⁹, ²⁰ to give species of the type RuCl₃(EPh₃)₂L (L = MeCN, acetone ¹⁴, THF, Me₂SO, CS₂), RuCl₃(EPh₃)L₂ (L = Me₂S, py ¹⁴; L₂ = bipy, o-phen) and RuCl₂(EPh₃)₂L₂ (L = CO, C₇H₈).

A fairly large number of Ru(III) ammine complexes are known viz. [Ru(NH₃)₆]Cl₃ ²¹, [Ru(NH₃)₅X]²⁺ (X = Cl, Br ²², OH, H₂O, NO₃ ²³), [Ru(NH₃)₄X₂]⁺ (X = Cl, Br) ²⁴, RuX₃(NH₃)₃ (X = Cl, Br) ²⁵. On heating in aqueous alkali in the presence of oxygen both the hexammine and the pentammines yield the 'ruthenium red' species [(NH₃)₅Ru - O - Ru(NH₃)₄ - O - Ru(NH₃)₅]⁶⁺ described previously.

The mechanism of reduction of Ru(III) ammine complexes to the
corresponding Ru(II) species has been extensively studied. $[\text{Ru(NH}_3^6]^{3+}$ is thought to be sufficiently inert to substitution in aqueous solution that electron transfer from the reductant to Ru(III) occurs by an outer sphere mechanism.\(^{26}\) In contrast, the reduction of $[\text{RuCl(NH}_3^5]^{2+}$ by Cr(II)\(^{27}\) is considered to proceed by an inner sphere mechanism involving a chloro bridged intermediate of the type $[[\text{NH}_3^5\text{Ru}^{II}\text{Cl} - \text{Cr}^{III}\text{H}_2\text{O}]^4$; this undergoes reversible electron transfer prior to decomposition to form the products. A recent paper\(^ {28}\) has suggested that the reduction of $[\text{RuX(NH}_3^5]^{2+}$ ($X = \text{Cl, Br, I}$) by uranium(III) also occurs by an inner sphere mechanism.

A variety of Ru(III) complexes containing oxygen and sulphur donor ligands can be prepared. $\text{Ru(acac)}_3$\(^ {29}\) and mer-$\text{RuCl}_3(\text{S}Et_2)_3$\(^ {30}\) are prepared by reaction of 'RuCl$_3\cdot3\text{H}_2\text{O}' with acetylacetone and diethylsulphide respectively. The oxidation of $\text{Ru(S}_2\text{CNR}_2)_3$ ($R = \text{Me, Et, benzyl}$) in the presence of BF$_3$ produces a diamagnetic Ru(III) complex $[\text{Ru}_2(S}_2\text{CNR}_2)_5]\text{BF}_4$\(^ {31}\)(3). An X-ray analysis has been carried out and shows the molecule to contain a metal-metal bond and three bridging dithiocarbamate groups which exhibit two different modes of bonding.

Ru(II) forms a large number of complexes with CO, tertiary phosphines and other $\pi$ acceptor ligands and these will be discussed in the following chapters. The compounds are diamagnetic ($t_{2g}^6$ configuration) and usually octahedral, although some examples of five co-ordinate species are known e.g. $\text{RuCl}_2(\text{PPh}_3)_3$ (see Page 18).
Unlike Ru(II) and Ru(III), Ru(I) is a relatively uncommon oxidation state and not many compounds are known. "RuX" (X = Cl, Br, I) are reported to have been prepared by the action of hypophosphorus acid on aqueous solutions of the respective trihalides. \([\text{Ru(CO)Br}]_n\) and \([\text{Ru(CO)}_x \text{I}]_n\) have also been synthesised. A nitrosyl complex \([\text{Ru(NO)}_2\text{I}]_n\) has been prepared by the action of nitric oxide on \([\text{Ru(CO)}_2\text{I}]_n\). It is diamagnetic and it was suggested that it is polymeric with halide bridges and metal-metal bonding. It reacts with amines, tertiary phosphines and arsines to produce compounds of empirical formulae \(\text{Ru(NO)}_2\text{I}_2\text{L}_2\) which would be expected to be paramagnetic \((t_2g^6 e_g^1)\) if monomers. However the compounds are only slightly paramagnetic which would suggest a dimeric structure with a metal-metal bond.

At ambient temperature, hydrochloric acid solutions of 'RuCl₃·3H₂O' (which contain both Ru(III) and Ru(IV) species) are rapidly reduced by hydrogen to Ru(III) and then slowly to Ru(II). At higher temperatures, further reduction occurs and the Ru(II) blue solution turns dark brown. This dark brown solution was thought to contain a Ru(I) species. It was later reported that hydrogenation of 'RuCl₃·3H₂O' in dimethylacetamide at 85°C also produces a brown solution and a brown solid, formulated as \(\text{Ru}_2\text{Cl}_3(\text{HDMA})\) (where HDMA indicates a protonated dimethylacetamide ligand), was isolated when the solution was cooled to liquid nitrogen temperature and benzene added. This compound was diamagnetic and therefore likely to contain a metal-metal bond.

A number of Ru(I) complexes containing carboxylate bridges have been prepared from the reaction of \(\text{Ru}_3(\text{CO})_{12}\) with carboxylic acids. Refluxing \(\text{Ru}_3(\text{CO})_{12}\) with excess carboxylic acids \(\text{RCO}_2\text{H}\) \((R = \text{H, Me, Et})\) give polymeric \([\text{Ru(CO)}_2(\text{RCO}_2)]_n\) compounds which then react with CO to produce \([\text{Ru(CO)}_3(\text{RCO}_2)]_2\). These are thought to have dimeric structures.
with bridging carboxylate groups and metal-metal bonds. Both the polymers and dimers react with tertiary phosphines, tertiary arsines, pyridine and methylcyanide to produce the dimeric complexes 

$$[\text{Ru}(\text{CO})_2(\text{RCO}_2\text{L})_2]$$ (4).

![Diagram of complex 4](image)

The addition of bulky tertiary phosphine ligands to the yellow solution, formed by treating 'RuCl$_3$$\cdot$3H$_2$O' with CO in 2-methoxyethanol for prolonged periods, produces orange diamagnetic Ru(I) complexes 

$$[\text{RuCl}(\text{CO})_2\text{L}]_2$$ (L = PPh$_2$Ph, PPh$_2$P-tol) (5). Treatment of 

$$[\text{RuCl}(\text{CO})_2(\text{PBu}_2\text{P-tol})_2]$$ with silver acetate then gives 

$$[\text{Ru(OOCMe)(CO)}_2(\text{PBu}_2\text{P-tol})_2].$$ In contrast reaction of less bulky ligands such as PMe$_2$Ph with the yellow solution gives the Ru(II) species RuCl$_2$(CO)$_2$(PMe$_2$Ph)$_2$.

![Diagram of complex 5](image)
The Ru(I) species $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^+$ has been observed in methanol solution. It was generated by reducing $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ by a method known as electron pulse radiolysis which involves the production of solvated electrons in liquids by means of an ionising radiation. However the Ru(I) species was unstable, disproportionating to give the original Ru(II) complex and a Ru(0) complex which readily decomposed to ruthenium metal i.e.

$$2[\text{Ru}(\text{NH}_3)_5\text{N}_2]^+ \rightarrow [\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+} + \text{Ru(0)}$$

(e) Ru(0)

There are now a fairly large number of Ru(0) compounds which for the purpose of this brief introduction can be conveniently divided into two groups

(i) Carbonyl complexes and their derivatives

(ii) Olefin and arene-olefin complexes.

The best known Ru(0) carbonyl complex was originally reported to be $\text{Ru}_2(\text{CO})_9$, but was later shown by X-ray analysis to be $\text{Ru}_3(\text{CO})_{12}$. The molecule has a $D_{3h}$ point group with the Ru atoms forming a triangle, and containing only terminal carbonyl groups (6). $\text{Ru}_3(\text{CO})_{12}$ reacts with
a wide variety of ligands \(^{41}\) to produce complexes of ruthenium in the zerovalent and higher oxidation states. Chlorine, bromine or iodine react with \(\text{Ru}_3(\text{CO})_{12}\) \(^{42}\) affording four types of complex: mononuclear \(\text{RuX}_2(\text{CO})_4\) \((X = \text{I}, \text{Br})\), binuclear \([\text{RuX}_2(\text{CO})_3]_2\) \((X = \text{I}, \text{Br}, \text{Cl})\), trinuclear \([\text{RuX}_2(\text{CO})_2]_3\) \((X = \text{Cl}, \text{Br})\) and polymeric \([\text{Ru(CO)}_2X_2]_n\) \((X = \text{I}, \text{Br}, \text{Cl})\).

Reaction with cyclohexa-1,3-diene and cycloocta-1,5-diene give the monomeric \(\text{Ru(CO)}_3(\text{diene})\) \(^{43}\) while refluxing \(\text{Ru}_3(\text{CO})_{12}\) in benzene or cyclohexane yields \(\text{Ru}_6(\text{CO})_{18}\) \(^{44}\).

\(\text{Ru}_3(\text{CO})_{12}\) reacts with \(\text{PPh}_3\) to give \(\text{Ru}_9(\text{CO})_9(\text{PPh}_3)_3\) \(^{45}\) which reacts further with more \(\text{PPh}_3\) to give the mononuclear species \(\text{Ru}_9(\text{CO})_3(\text{PPh}_3)_2\). This and related reactions of \(\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3\) have recently \(^{46}\) been studied and found to proceed by three kinetically distinct pathways. Reaction with \(\text{PBu}_3^n\) to give \(\text{Ru}_3(\text{CO})_9(\text{PBu}_3^n)_3\) proceeds by the reversible loss of \(\text{PPh}_3\). Replacement of the first \(\text{PPh}_3\) ligand by \(\text{PBu}_3^n\) must be the slowest step since the only product observed was \(\text{Ru}_3(\text{CO})_9(\text{PBu}_3^n)_3\) i.e.

\[
\begin{align*}
\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3 & \rightleftharpoons \text{Ru}_3(\text{CO})_9(\text{PPh}_3)_2 + \text{PPh}_3 & \text{... ... ... [2]} \\
\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_2 + \text{PBu}_3^n & \text{slow} \rightarrow \text{Ru}_3(\text{CO})_9(\text{PPh}_3)_2(\text{PBu}_3^n)
\end{align*}
\]

Reaction with \(\text{PPh}_3\), at values of \([\text{PPh}_3]\) sufficient to suppress step [2], proceeds by reversible loss of \(\text{CO}\) i.e.

\[
\begin{align*}
\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3 & \rightleftharpoons \text{Ru}_3(\text{CO})_8(\text{PPh}_3)_3 + \text{CO} & \text{... ... ... [3]} \\
\end{align*}
\]

followed by fragmentation and eventual formation of \(\text{Ru(CO)}_3(\text{PPh}_3)_2\). Reaction with \(\text{PPh}_3\), in the presence of sufficient \(\text{PPh}_3\) and \(\text{CO}\) to suppress steps [2] and [3], involves either sequential or concerted fission of two Ru - Ru bonds to form initially \(\text{Ru(CO)}_3(\text{PPh}_3_3\) and \(\text{Ru}_2(\text{CO})_6(\text{PPh}_3)_2\).

The photolysis of \(\text{Ru}_3(\text{CO})_{12}\) \(^{47}\) in the presence of \(\text{CO}\) produces \(\text{Ru(CO)}_5\), and in the presence of \(L\) \((L = \text{PPh}_3, \text{PBu}_3^n, \text{PMePh}_2)\) gives \(\text{Ru(CO)}_4L\) and some \(\text{Ru(CO)}_3L_2\). Reaction of \(\text{Ru(CO)}_4L\) with more \(L\) give \(\text{Ru(CO)}_3L_2\) and is thought to proceed by a dissociative mechanism.
(Scheme 1.2). The observed rate constant is given by

\[
\frac{k_1}{k_{-1}} \quad \text{Ru(CO)}_4L \xrightleftharpoons{k_2}{L} \quad \text{Ru(CO)}_3L + CO
\]

\[
L \downarrow k_2 \quad \text{Ru(CO)}_3L_2
\]

\[k_{obs} = \frac{k_1k_2[L]}{k_{-1}[CO] + k_2[L]}\]. At high ligand concentrations \(k_2[L] > k_{-1}[CO]\).

Therefore \(k_{obs}\) is independent of \(L\) and equal to \(k_1\). The usual steric acceleration for dissociative reactions is observed for the loss of CO from \(\text{Ru(CO)}_4L\), the rate constant decreasing in the order

\[\text{PPh}_3 > \text{PMePh}_2 > \text{PBu}_3^n\].

\(\text{Ru(CO)}_3(\text{PPh}_3)_2\) has been reported to undergo an oxidative addition reaction with MeI to give the Ru(II) species \(\text{Ru(CO)}_2\text{I(Me)}(\text{PPh}_3)_2\) but attempts to repeat this reaction by Mawby et al. were unsuccessful and instead \(\text{PPh}_3\text{Me[RU}_3(\text{CO})_2\text{PPh}_3]\) was obtained. However \(\text{Ru(CO)}_3(\text{PPh}_3)_2\) does react with thiocyanogen and selenocyanogen to give \(\text{Ru(CO)}_2(\text{PPh}_3)_2(\text{NCS})_2\) and \(\text{Ru(CO)}_2(\text{PPh}_3)_2(\text{NCS})_2\) respectively which contain N-bonded thiocyanato and selenocyanato ligands. Only thiocyanogen reacts with \(\text{Ru}_3(\text{CO})_12\) giving \([\text{Ru(CO)}_2(\text{CNS})_2]_n\) with bridging thiocyanato groups.

Oxidative addition reactions converting Ru(0)(d^8) complexes to Ru(II)(d^6) complexes play an important role in many homogeneous catalytic processes (see Page 15).

Ru(0) arene and arene-olefin complexes are usually obtained by reduction of Ru(II) and Ru(III) species. For example, reduction of \([\text{Ru(h}^6\text{C}_6\text{Me}_6)_2]^{2+}\) using sodium in liquid ammonia gives \(\text{Ru(h}^6\text{C}_6\text{Me}_6)_2\) whereas reduction of the corresponding \([\text{Ru(h}^6\text{C}_6\text{H}_6)_2]^{2+}\) yields \((\text{h}^4\text{C}_6\text{H}_6)\text{Ru(h}^6\text{C}_6\text{H}_6)_2\). Photolysis of a mixture of 'RuCl_3.3H_2O', 1,3,5-cyclooctatriene and isopropyl magnesium bromide produces
(h^6C_8H_{10})Ru(h^4C_8H_{10}) \ (7), \text{ where isomerisation of cyclooctatriene to bicyclo[4,2,0] octa-2,4-diene has occurred.}^{52}

1.2 Nitrosyl complexes of ruthenium

An interesting feature of ruthenium chemistry is the large number of nitrosyl compounds formed, a number greater than for any other element. Ruthenium nitrosyl complexes contain the group Ru-NO which has been found to be remarkably stable, being able to persist through a variety of substitution and redox reactions. As well as neutral compounds, anionic and cationic species are well characterised e.g. [Ru(OH)(NO_2)_4(NO)]^{2-},^{53} [Ru(NO)(diphos)_2]^+ \text{ and also cluster compounds e.g. Ru}_4(PPh_3)_4Cl_4(NO)_4.^{55} \text{ This is a tetramer in which the co-ordination geometry of each Ru atom is square pyramidal with two chlorine atoms and two phosphide groups in the basal plane and an NO group at the apex (8).}
The nitrosyl ligand can co-ordinate in several ways. Bent nitrosyl groups are considered as NO$^-$ and the bonding viewed primarily as $\sigma$ donation from an electron pair of the nitrogen atom to the metal. The majority of ruthenium nitrosyl complexes contain a linear co-ordinated nitrosyl group viewed as NO$^+$. The bonding of NO$^+$ is analogous to that of a carbonyl group, with a strong $\pi$ acceptor interaction between filled metal $d_\pi$ orbitals and empty $\pi^*$ NO levels. The complex $\left[\text{RuCl(NO)}_2(\text{PPPh}_3)_2\right]\text{PF}_6$ (9) has been shown by X-ray analysis$^{56}$ to contain both linear and bent nitrosyl groups. The Ru-N distance for the bent NO group is longer than that of the linear group consistent with the idea that the bent group co-ordinates as a $\sigma$ Lewis acid and the linear
group as a $\pi$ acid. X-ray structural studies have suggested that five co-ordinate ruthenium complexes containing a bent nitrosyl group possess a square pyramidal geometry e.g. $[\text{RuCl(NO)}_2(\text{PPh}_3)_2]\text{PF}_6$ whereas those containing a linear nitrosyl group exhibit a trigonal bipyramidal geometry e.g. $\text{RuH(NO)(PPh}_3)_3$ where the linear NO group is in an axial position, and $[\text{RuNO(diphos)}_2]\text{Cl}$ where it is in an equatorial position. However the particular stereochemistry adopted is more likely due to the oxidation state of the Ru rather than the mode of bonding of the NO group. Five co-ordinate Ru(II) complexes have been shown to prefer a square pyramidal geometry.

Ru(0)(d$^8$) complexes containing a nitrosyl group undergo oxidative addition reactions to form Ru(II)(d$^6$) species in which the Ru-NO group is usually retained. Thus, $[\text{Ru(CO)}_2\text{NO(PPh}_3)_2]\text{BPh}_4$ reacts with halogens to give mainly $\text{RuX}_3(\text{NO})(\text{PPh}_3)_2$, and $\text{RuCl(NO)(PPh}_3)_2$ reacts with a variety of ligands, e.g. halogens, acyl chlorides, to give Ru(II)(d$^6$) compounds containing NO. Furthermore, these reactions occur much more rapidly than for the corresponding isoelectronic carbonyls $\text{MCl(CO)(PPh}_3)_2$ (M = Rh, Ir).

Ruthenium also forms a number of dinitrogen species in which the N$_2$ group is bound in a linear manner. The most famous is $[\text{Ru(NH}_3)_5\text{N}_2]^{2+}$, the first dinitrogen species to be prepared. This was first obtained by reaction of 'RuCl$_3$·3H$_2$O' with hydrazine hydrate, and later shown to be formed by spontaneous reaction of $[\text{Ru(NH}_3)_5\text{H}_2\text{O}]^{2+}$ with molecular nitrogen in aqueous solution.

1.3 Ruthenium complexes as homogeneous catalysts

Many ruthenium complexes have been found to be effective homogeneous catalysts. Thus $\text{RuHCl(PPh}_3)_3$, $[\text{RuCl}_2\text{C}_6\text{H}_4\text{.}]_2$, and $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (in the presence of added PPh$_3$) catalyse the hydrogenation of alkenes. $\text{RuCl}_2(\text{PPh}_3)_3$ is also effective but only in
benzene-ethanol solutions where the active species is RuHCl(PPh₃)₃. Carboxylato tertiary phosphine complexes of ruthenium, e.g. RuH(CO₂Me)(PPh₃)₃, Ru₂O(CO₂Me)₄(PPh₃)₂, are active in acidic media and the catalytic species here is thought to be a Ru(II) cation with two triphenylphosphine ligands, the other sites being occupied by either solvent or alkene molecules. Studies of the homogeneous hydrogenation of maleic and fumaric acid in aqueous solution by Ru(II) chloride species show that the rate of hydrogenation can be represented by the expression

\[
\text{Rate} = k[H₂][\text{(olefin)}\text{Ru(II)}]
\]

and the mechanism shown in Scheme 1.3 was proposed. It includes

\[
\begin{align*}
\text{Ru}^{2+} & \xrightleftharpoons{\text{fast}} \text{olefin} \rightarrow [\text{Ru(olefin)}]^{2+} \\
[\text{(alkyl)Ru}]^{+} + H^+ & \rightarrow H_2 \rightarrow [\text{HRu(olefin)}]^{+} + H^+ \\
\end{align*}
\]

**Scheme 1.3 Mechanism for hydrogenation of olefins by Ru(II) species**

 heterolytic cleavage of H₂ followed by olefin insertion into a Ru-H bond and finally cleavage of the Ru-alkyl bond by H⁺.

Ru(CO)₃(PPh₃)₂ is a very effective homogeneous catalyst for the hydroformylation of alkenes. The mechanism suggested for this process (Scheme 1.4) involves oxidative addition of H₂ to Ru(CO)₃(PPh₃)₂ followed by binding of an alkene molecule. Ru(CO)₃(PPh₃)₂ has also been shown to promote the reaction of iodoalkanes with ethylene to produce higher molecular weight alkanes i.e. CH₃CH₂I + nCH₂ = CH₂ → CH₃CH₂(CH₂CH₂)n I.

The mechanism again involves oxidative addition to the Ru(0) species followed in this case by the formation of an alkyl radical by homolytic cleavage of the metal-carbon bond.
viz. \[ \text{RI} + \text{Ru(CO)}_3(\text{PPh}_3)_2 \rightarrow \text{Ru(CO)}_2(R)(I)(\text{PPh}_3)_2 + \text{CO} \]

\[ \text{Ru(CO)}_2(R)(I)(\text{PPh}_3)_2 \rightarrow R' + \text{RuI(CC)}_2(\text{PPh}_3)_2 \]

\[ R' + n\text{CH}_2 = \text{CH}_2 \rightarrow R(\text{CH}_2\text{CH}_2)_n. \]

During the course of this reaction \( \text{Ru(CO)}_3(\text{PPh}_3)_2 \) slowly converts to inactive \( \text{RuI}_2(\text{CO})_2(\text{PPh}_3)_2 \) formed probably by attack of \( \text{RuI}(\text{CO})_2(\text{PPh}_3)_2 \) on an iodoalkane.

Finally, complexes of ruthenium have recently been used as heterogeneous catalysts.\textsuperscript{70} Ruthenium acetate was chemically bonded to the surface of silica by reaction with \( (\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2 \) in benzene and found to be an effective catalyst for the hydrogenation of olefins and dienes.
Scheme 1.4  Mechanism for hydroformylation of alkenes by
Ru(CO)(PPh₃)₃
2.1 Introduction

The preparation of RuCl₂(PPh₃)₃ was first reported in 1966 by Stephenson and Wilkinson. Refluxing 'RuCl₃·3H₂O' with an excess of PPh₃ in methanol produced dark brown crystals of this complex which had independently been synthesised by Vaska, although no details of the preparation are available. An X-ray structural analysis was carried out, showing that the Ru lies close to the centre of a distorted square pyramid, containing trans phosphines and trans chlorides in the basal plane and a phosphine group at the apex (L = PPh₃). This represented the first X-ray analysis of a 5 co-ordinate d⁶ complex although several examples of this co-ordination number for Ru(II) compounds have since been established. RuCl₂(PPh₃)₄ can be prepared by shaking 'RuCl₃·3H₂O'

\[
\begin{align*}
\text{Ru} & \quad \text{Cl} \\
\text{L} & \quad \text{L}
\end{align*}
\]

with an excess of PPh₃ in methanol.

Spectrophotometric studies indicate that at 298K RuCl₂(PPh₃)₃ is 80% dissociated in benzene as shown in equation [1]

\[ \text{RuCl}_2(\text{PPh}_3)_3 \rightleftharpoons \text{RuCl}_2(\text{PPh}_3)_2 + \text{PPh}_3 \quad \ldots \quad [1] \]

and 100% dissociated in dma, in which partial ionisation also takes place (equation [2]). These observations have been supported by ³¹P n.m.r.

\[ \text{RuCl}_2(\text{PPh}_3)_2 \rightleftharpoons [\text{RuCl(PPPh}_3)_2]^+ + \text{Cl}^- \quad \ldots \quad [2] \]

studies except that the dissociated neutral product is reformulated
as the halide bridged dimer (2) \( (L = \text{PPh}_3) \) with the vacant co-ordination sites probably occupied by solvent molecules. \( \text{Reaction of } \text{RuCl}_3 \cdot 3\text{H}_2\text{O} \)

\[
\begin{align*}
\text{Ru} & \quad \text{Cl} \quad \text{Cl} \\
\text{L} & \quad \text{L} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

with \( \text{PPh}_3 \) for short periods\(^75\) in ethanol, isopropanol or benzyl alcohol, however, gives an insoluble black material of composition \([\text{RuCl}_2(\text{PPh}_3)_2]_n\), which is considered to be a chloride bridged polymer. Further reaction in ethanol and isopropanol then yields \( \text{RuCl}_2(\text{PPh}_3)_3 \), whereas in benzyl alcohol decarbonylation of the solvent occurs to give \( \text{RuCl}_2\text{CO(PPH}_3)_3 \).

\( \text{RuCl}_2(\text{P(p-tol)}_3)_4 \)\(^76\) and \( \text{RuCl}_2(L - L)_2 \)\(^77\) \( (L - L = \text{Et}_2\text{P(CH}_2)_2\text{PEt}_2, \) Me\(_2\text{P(CH}_2)_2\text{PMe}_2, \) Ph\(_2\text{P(CH}_2)_2\text{PPh}_2, \) Ph\(_2\text{PCH}_2\text{PPH}_2) \) have also been prepared from \( \text{RuCl}_3 \cdot 3\text{H}_2\text{O} \), while treatment with bulkier tertiary phosphine\(^78\) produces the formally mixed valence Ru(II); Ru(III) dimers \( \text{Ru}_2\text{Cl}_5\text{L}_4 \) \( (L = \text{P(n-Bu)}_3, \) P(n-Pr), P(n-pent),\) shown by X-ray analysis\(^79\) to contain a triple halide bridge (3). In addition, the double halide bridged Ru(III) dimers

\[
\begin{align*}
\text{R}_3\text{P} & \quad \text{Cl} \quad \text{Ru} \quad \text{Cl} \quad \text{Ru} \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{R}_3\text{P} & \quad \text{PR}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{PR}_3 & \quad \text{Cl} \quad \text{Ru} \quad \text{Cl} \quad \text{Ru} \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{PR}_3 & \quad \text{PR}_3 \\
\end{align*}
\]

\( \text{Formulated with square pyramidal stereochemistry rather than trigonal bipyramidal to conform to the established structure of } \text{RuCl}_2(\text{PPh}_3)_3 \) and other 5 five co-ordinate complexes.
[RuCl₃(PR₃)₂]₂ (4) are also formed. In contrast, the reaction of 'RuCl₃·3H₂O' with trialkyl-, dialkylaryl- and alkyldiaryl- phosphines in aqueous ethanol does not produce neutral monomeric species as would be expected by analogy with PPh₃, or Ru(III) species as above, but ionic Ru(II) dimers of the type [Ru₂Cl₃L₆]Cl (L = PMePh₂, PMe₂Ph, PEtPh₂, P₃MePh, P₃EtPh, P₃PrPh, PBu₂Ph); on addition of NaBPh₄ to these solutions [Ru₂Cl₃L₆]BPh₄ are produced. These complexes also contain a triple halide bridge (5) and do not react further with L to give RuCl₂L₄. However the neutral compounds RuCl₂L₄ (L = PMe₂Ph, PMePh₂, P₃MePh₂), RuCl₂L₃ (L = P₃EtPh₂), Ru₂Cl₄L₅ (L = P₃EtPh₂, PC₁Ph₂) have recently been obtained by reaction of RuCl₂(PPh₃)₄ with an excess of L in n-hexane or petroleum ether (b.p. 60 – 80°C). In polar solvents the reactions, in all cases, yield the ionic dimers [Ru₂Cl₃L₆]Cl. Thus, RuCl₂L₄ and RuCl₂L₃ have been found to rearrange in polar solvents and this has been studied by ³¹P n.m.r. spectroscopy. For example, RuCl₂(P₃EtPh₂)₃ in CDCl₃ rapidly forms Ru₂Cl₄(P₃EtPh₂)₅ which subsequently rearranges slowly to [Ru₂Cl₃(P₃EtPh₂)₆]Cl whereas refluxing RuCl₂(PPh₃)₄ with excess P₃EtPh₂ in ethanol for short periods produced a species exhibiting an AB₂ pattern in its ³¹P n.m.r. spectrum at low temperatures which was formulated as the dimeric complex [RuCl₂(P₃EtPh₂)₃]₂⁺ (c.f. [RuCl₃(PR₃)₂]²⁺). On warming the solution this species converted to RuCl₂(P₃EtPh₂)₃, Ru₂Cl₄(P₃EtPh₂)₅, [Ru₂Cl₃(P₃EtPh₂)₆]Cl and free P₃EtPh₂. Therefore on the basis of the above results and those previously obtained for RuCl₂(PPh₃)ₙ (n = 3,4), a general reaction scheme for the
rereangement of Ru(II) tertiary phosphine complexes was proposed (Scheme 2.1). Since RuCl₂(PMe₂Ph)₄ rapidly converted in solution to (5) (L = PMe₂Ph) and no intermediate products were observed, this was attributed to the short lifetime of such intermediates. The dissociative path (i) was only important when L is PPh₃ in which case the bulkiness of the ligands prevents path (ii). For the smaller tertiary phosphines it was postulated that association occurs to give the neutral dimer (6) which is unstable, transforming to regenerate either (1) by solvent cleavage, (5) by chloride loss, or (7) by phosphine loss. Compound (7) slowly but irreversibly converts to (5) in the presence of L.

The present work was carried out in order to ascertain if Scheme 2.1 is valid when L is tertiary phosphinite P(OR)Ph₂, tertiary phosphonite P(OR)₂Ph, or tertiary phosphite P(OR)₃ and thus establish the generality of such a scheme for a wider range of Group VB donor ligands. There has been an increasing interest in these alkoxy substituted phosphine ligands over the past few years and therefore a brief survey of ruthenium complexes containing tertiary phosphite, phosphonite or phosphinite groups with or without halide or hydride ligands is appropriate at this juncture.

The preparation of RuX₂(P(OR)₃)₄ (X = Cl, Br, R = Ph, p-tol, p-ClC₆H₄; X = I, R = Ph) by reaction of RuX₂(PPh₃)₃ with P(OR)₃ in hexane, CH₂Cl₂ or ethanol was first described in 1970.⁸² Although a small amount of RuCl₂(P(O₂CC₆H₄Cl)₃)₄ was obtained, isolation of the corresponding trialkyl species was unsuccessful due to their high solubility. However yellow crystals of RuCl₂(P(OC₂H₄Cl)₃)₄ have recently been prepared⁸³ by refluxing 'RuCl₃·3H₂O' and NaBH₄ in P(C₂H₅)₃, and then further reaction with NaBH₄ and P(C₂H₅)₃ in ethanol yields RuH₂(P(OEt)₃)₄. Treatment of RuH(PPh₃)₃ (X = Cl, Br) with P(OR)₃ (R = Ph, p-tol), however, gives orthometallated species of the type RuX(P(CC₆H₃R')(OR)₂)(P(OR)₃)₃ ('R' = H, Me) (8),⁸²,⁸⁴ in which the ruthenium ion is σ-bonded to one of
Scheme 2.1 Original proposed mechanism for the rearrangement of $\text{RuCl}_2\text{L}_2$ ($\text{L}=$ tertiary phosphine)
the ortho-carbon atoms of a co-ordinated triaryl phosphite ligand. Such

\[
\begin{align*}
\text{Ru} & \quad \text{P(OC}_6\text{H}_4\text{R')}_3 \\
\text{P(OC}_6\text{H}_4\text{R')}_3 & \quad (X = \text{Cl}, \text{Br}; \\
\text{R'} & = \text{H, Me})
\end{align*}
\]

(8)

reactions involving the formation of a five-membered ring are termed "Intramolecular Aromatic Substitution" processes and often occur with triaryl phosphite ligands especially when placed in a \textit{cis} position to a hydrido group e.g. treatment of \text{RuH}_2(\text{PPh}_3)_4 with \text{P(OPh)}_3 gives \text{Ru(POPh)}_3\text{[(P(OC}_6\text{H}_4\text{)(OPh)})_2]}. 85

Cationic \text{[Ru(P(OMe)}_3\text{]}_6\text{]}\text{(BPh}_4\text{)}_2 can be prepared by the action of \text{P(OMe)}_3 on \text{[(C}_8\text{H}_12\text{)Ru(N}_2\text{H}_4\text{]}_4\text{]}\text{(BPh}_4\text{)}_2 in methanol, 86 whereas treatment of \text{[(C}_8\text{H}_12\text{)RuH(N(CH}_3\text{)}_2\text{NH}_2\text{]}_3\text{]}\text{(BPh}_4\text{)}_2 with \text{L (L = P(OEt)}_3\text{, P(OMe)}_2\text{Ph}) gives the pentakis species \text{[RuHL}_5\text{]}\text{BPh}_4; with \text{P(OPh)}_3\text{, (C}_8\text{H}_12\text{)Ru(P(OPh)}_3\text{]}}_2 is obtained, for which structure (9) containing two ortho-metallated phosphite groups has been proposed.

A wide range of cationic phosphite, phosphonite and phosphinite derivatives of ruthenium are formed by the reaction of \text{[RuX}_2\text{(C}_7\text{H}_8\text{)]}_n or

\[
\begin{align*}
\text{Ru} & \quad \text{P(OPh)}_2 \\
\text{P(OPh)}_2 & \\
\end{align*}
\]

(9)
RuCl₂(PPh₃)₃ with the appropriate ligand.⁸⁷,⁸⁸ Thus [Ru(P(OMe)₃)₆](BPh₄)₂ and [RuX(P(OMe)₃)₅]BPh₄ (X = Cl,Br) are precipitated by addition of NaBPh₄ to a reacted solution of [RuX₂(C₇H₈)]ₙ with P(OMe)₃ in methanol. Treatment of RuXCl(PPh₃)₃ in alcohol with P(OR)₃ affords [RuX(P(OR)₃)₅]⁺ (X = H, R = Me,Et; X = Cl, R = Et) whereas reaction of [RuBr₂(C₇H₈)]ₙ with P(0Et)₃ gives the triple halide bridged dimeric cation [Ru₂Br₃(P(0Et)₃)₆]⁺. The combination of bromide and triethyl phosphate is considered to inflict stereochemical restraints which are best satisfied by the 3:3 co-ordination adopted. The tertiary phosphonite and phosphinite ligands L (L = P(OR)₂Ph, P(OEt)₂Ph; R = Me,Et) are reported to react with [RuCl₂(C₇H₈)]ₙ in methanol (R = Me) or ethanol (R = Et) to afford the binuclear tri-μ-chloro cations [Ru₂Cl₃L₆]⁺ which were isolated as their tetraphenylborate salts. The bromo complex [RuBr₂(C₇H₈)]ₙ reacts with P(OEt)₂Ph and P(OEt)Ph₂ to give the corresponding tri-μ-bromo cations [Ru₂Br₃L₆]⁺ but with P(CMe)₂Ph in methanol [Ru(P(OMe)₂Ph)₆]²⁺, which is thought to be formed because of the smaller steric requirements of this ligand, is obtained.

Very recently,⁸⁹ the Ru(0) species Ru(P(OMe)₃)₅ has been prepared by the sodium amalgam reduction of RuCl₂(P(OMe)₃)₄ (made by a similar method to that of RuCl₂(P(OEt)₃)₄), in the presence of excess P(OMe)₃ in THF. Ru(P(OMe)₃)₅ has a trigonal bipyramidal stereochemistry (n.m.r. evidence) and in solution undergoes an intramolecular rearrangement process involving simultaneous exchange of a pair of axial with a pair of equatorial ligands.

By analogy with RuH₂(P(OEt)₃)₄⁺, a series of dihydrido complexes RuH₂L₄ (L = P(OMe)₃, P(O-iC₃H₇)₃, P(OMe)₂Ph, P(OEt)₂Ph, P(O-iC₃H₇)₂Ph, P(OMe)Ph₂) have been prepared by addition of NaBH₄ to a solution of 'RuCl₃·H₂O' in L.⁹⁰ These six co-ordinate species also undergo intramolecular rearrangements in solution. RuH₂L₄ (L = P(OMe)₃, P(OEt)₃, P(O-iC₃H₇)₃, P(OMe)Ph₂) exist entirely in a cis configuration whereas...
RuH₂L₄ (L = P(CMe)₂Ph, P(OEt)₂Ph, P(0-iC₃H₇)₂Ph) exist as a mixture of cis and trans isomers with ca 15%, 7.5% and 7.5% respectively of the trans isomer at room temperature in d⁸-toluene. At higher temperatures (60 - 150°C) the ligand resonance in the Hn.m.r. spectra of all the complexes broaden suggesting the onset of further rearrangements, but thermal decomposition occurs, by loss of hydrogen or by ligand dissociation, before the fast exchange limit is reached.

The Pn.m.r. and Hn.m.r. studies were unable to distinguish between two possible mechanisms for the rearrangement processes which averages the hydrido and L groups respectively. Mechanism A (Fig. 2.1) involves the shift of a hydride group from an occupied to a vacant face of a nearly regular tetrahedral arrangement of phosphorus atoms by traverse of a tetrahedral edge, whereas mechanism B (Fig. 2.2) consists of simultaneous motion of the hydrido groups from face positions to trans edge positions, with the trans intermediate sufficiently long-lived such that the hydrogens move with equal probability back to previously occupied faces or on to previously unoccupied faces. The ruthenium species exhibit a larger barrier to intramolecular rearrangement than their iron analogues. An X-ray structure of trans-RuH₂(P(OEt)₂Ph)₄ shows it to be a distorted octahedron with a flattened tetrahedron of phosphorus atoms and axial hydrido ligands whereas in cis-FeH₂(P(OEt)₂Ph)₄ the geometry is much nearer to tetrahedral than octahedral. These facts would therefore favour mechanism A.

Since RuH₂L₄ complexes are co-ordinatively saturated (18 electrons), the rate determining step for reactions at the metal centre is thought to be the dissociation of one of the ligands L to give a 16 electron species (equation [3]). In support of this, complexes containing tertiary phosphite ligands were found to be less reactive than the
Fig. 2.1  Model for mechanism A for rearrangement of RuH$_2$L$_4$ species.
Phosphorus atoms P$_1$, P$_2$, P$_4$ are in a nearly trigonal array about P$_3$-Ru-H$_1$ axis and the mechanism involves the motion of H$_2$, which is in the face between P$_1$, P$_2$, P$_3$, into the face between P$_1$, P$_4$, P$_3$ or between P$_2$, P$_3$, P$_4$.

Fig. 2.2  Model for mechanism B for rearrangement of RuH$_2$L$_4$ species.
corresponding tertiary phosphine species. Thus no evidence was found for the ligand exchange reaction (equation [4]) whereas under the same conditions RuH$_2$(PMePh$_2$)$_4$ and P(OMe)$_3$ exhibited substantial exchange. Similarly, RuH$_2$(PMePh$_2$)$_4$ reacted with CO under ambient conditions to give RuH$_2$(PMePh$_2$)$_3$CO whereas RuH$_2$(P(OR)$_3$)$_4$ (R = Me, Et, iC$_3$H$_7$) were unreactive.

2.2 Results and discussion

(a) Preparation of RuCl$_2$L$_3$-or-4 (L = P(OR)$_3$, P(OR)$_2$Ph, P(OR)Ph$_2$) by exchange reactions in non-polar solvents.

Before a study of their rearrangements in solution could be made the complexes RuCl$_2$L$_3$ or 4 (L = P(OR)$_3$, P(OR)$_2$Ph, P(OR)Ph$_2$) first had to be prepared. The most convenient method was analogous to that adopted for the synthesis of RuCl$_2$(P(0Ph)$_3$)$_4$ and RuCl$_2$L$_3$-or-4 (L' = PMePh$_2$, PMe$_2$Ph; n = 4; L' = P(Ph)$_2$; n = 3) viz, reaction of RuCl$_2$(PPh$_3$)$_3$ with L in a non-polar solvent. Thus, refluxing RuCl$_2$(PPh$_3$)$_3$ with P(OMe)$_3$ in hexane produces a yellow crystalline solid analysing for RuCl$_2$(P(CMe)$_3$)$_4$ (Table 2.1). The far infra-red spectrum (400-200 cm$^{-1}$) (Table 2.2) contains a strong band at 340 cm$^{-1}$ due to ν(RuCl) from trans chloride groups and bands at 306 cm$^{-1}$ and 295 cm$^{-1}$ due to ν(Ru-Cl) from chloride trans to phosphorus, while the $^{31}$P n.m.r. spectrum in CDCl$_3$ at both 213K and 298K (Table 2.4) consists of a singlet at 129.4 p.p.m. These results indicate that, unlike the corresponding dihydride, RuCl$_2$(P(OMe)$_3$)$_4$ exists as a mixture of trans(10) and cis(11) isomers in the solid state but rearranges rapidly to the trans isomer in solution. This is supported by the $^1$H n.m.r. spectrum, in CDCl$_3$ at 301K (Table 2.3),

$^\dagger$ All $^{31}$P n.m.r. spectra are proton noise decoupled.
which is a symmetrical "quintet" centred at 3.846 (Fig. 2.3). Very similar patterns have been obtained for trans-[Rh(P(OME)₃)₄XY]⁺₉⁴ (X = Y = Br; X = H, Y = Br; X = CH₃, Y = I) and [Rh(P(OME)₃-xPhₓ)₄]PF₆₉⁵ (x = 1, 2) where the ligands adopt a square planar configuration around the central atom. Such a pattern arises because of strong coupling between cis and trans phosphorus nuclei and is a limiting case for a spin system of the AA'AX''X'X₄₄ form.

\[
\begin{align*}
\text{(10)} & \quad \begin{array}{c}
\text{(MeO)}₃P \\
\text{Cl} \\
\text{P(OMe)}₃ \\
\text{Ru} \\
\text{P(OMe)}₃ \\
\text{Cl}
\end{array} \\
\text{(11)} & \quad \begin{array}{c}
\text{(MeO)}₃P \\
\text{Cl} \\
\text{P(OMe)}₃ \\
\text{Ru} \\
\text{P(OMe)}₃ \\
\text{Cl}
\end{array}
\end{align*}
\]

The corresponding exchange reaction between RuCl₂(PPh₃)₃ and P(OEt)₃ resulted only in the formation of a yellow oil. However RuCl₂(P(OMe)₂Ph)₄ was prepared by this method as yellow crystals and the far infra-red spectrum, containing bands at 324cm⁻¹, 308cm⁻¹ and 291cm⁻¹ again indicates the presence of both cis and trans isomers in the solid state. The ³¹Pn.m.r. spectrum, at 213K in CDCl₃ contains a singlet at 150.5p.p.m. due to the trans isomer and two triplets at 166.6p.p.m. and 149.4p.p.m. (Jₚₚ = 44.0Hz) due to the cis isomer. On warming to 298K the triplets disappear and do not reappear when the solution is recooled. Therefore, as for RuCl₂(P(OMe)₃)₄, an irreversible cis/trans isomerisation takes place in solution. In support of this conclusion the methyl resonance in the ¹Hn.m.r. spectrum at 301K in CDCl₃ is a similar pattern to that obtained for RuCl₂(P(OMe)₃)₄ (Fig. 2.3).

Reaction of RuCl₂(PPh₃)₃ with P(OR)Ph₂ (R = Me, Et) in hexane produces
Fig. 2.3

$^1$H n.m.r. spectrum of $\text{RuCl}_2\{\text{P(OMe)}_3\}_4$ in CDCl$_3$ at 301K
orange-brown crystals analysing closely for RuCl₂(P(OR)Ph₂)₃. The far infra-red spectrum contains a strong band at 337 cm⁻¹ (R = Me), 328 cm⁻¹ (R = Et) indicating the presence of trans chloride groups (Table 2.2). The complexes dissolve in all common polar solvents but are found to rapidly rearrange (see later). However they are soluble and stable in benzene or toluene and osmometric molecular weight measurements in benzene at 294K indicate that the complexes are monomeric (see experimental section). The ³¹P n.m.r. spectra in C₆D₆ at 298K show a sharp singlet at 149.5 p.p.m. (R = Me), 144.7 p.p.m. (R = Et), implying that the tertiary phosphinite groups are scrambling rapidly at this temperature. For RuCl₂(P(OEt)Ph₂)₃ in a (CD₃)₂CO/toluene mixture at 163K, the singlet broadens considerably and at 140K, two broad resonances at 167.3 and 141.1 p.p.m. of relative intensity 1:2 are found. These n.m.r. changes are concentration independent and reversible with temperature. Thus, although no spin-spin couplings are resolved (probably because of adverse viscosity effects at this temperature) these resonances can be ascribed respectively to the expected triplet and doublet pattern for the "frozen-out" RuCl₂(P(OEt)Ph₂)₃ structure. By analogy with RuCl₂(PPh₃)₃ and other five co-ordinate Ru(II) complexes, it is suggested that this is probably essentially square pyramidal in nature. The observed averaged position (146.5 p.p.m. at 193K in (CD₃)₂CO/toluene) and that calculated on the basis of the low temperature spectrum at 140K (149.3 p.p.m.) provides further support for the correctness of the above interpretation of this data.

The scrambling process causing equivalence of all the phosphinite groups of RuCl₂(P(OEt)Ph₂)₃ is much more facile than the corresponding process for RuCl₂(PPh₃)₃. This is due to two factors viz., the less bulky ligands and the fact that the resonances for the different phosphinite groups of RuCl₂(P(OEt)Ph₂)₃ are much closer to each other than are the PPh₃ groups in RuCl₂(PPh₃)₃. The ligand P(OMe)Ph₂ is less bulky than
either P(CEt)Ph₂ or PPh₃ and at 140K in (CD₃)₂CO/toluene the ³¹Pn.m.r. spectrum consists solely of a broad resonance at 147p.p.m. indicating that in this case scrambling of the ligands is still taking place at this temperature.

(b) **Rearrangement of monomeric species in polar solvents**

RuCl₂(P(OMe)₃)₄ remains stable in polar solvents and is recovered unchanged both after refluxing in methanol for six hours, or irradiating with ultraviolet light (low pressure Hg lamp). RuCl₂(P(OMe)₂Ph)₄ does not rearrange on leaving at room temperature in methanol but, after refluxing for 1 hour, a yellow conducting solution is obtained. Addition of NaBPh₄ produces a pale yellow solid whose ³¹Pn.m.r. spectrum at 298K in CDCl₃ contains a singlet at 168.7p.p.m., which agrees with that obtained for [Ru₂Cl₃(P(CMe)₂Ph)₆]BPh₄ (prepared by the method of Couch and Robinson), and also an AB₂ pattern (ν₁ = 159.56p.p.m., ν₂ = 170.38 p.p.m., Jₜ = 58.4Hz). On refluxing for a further hour the ³¹Pn.m.r. spectrum of the product still contains the singlet but no AB₂ pattern, which must therefore arise from an intermediate ionic product containing three phosphonite groups per Ru atom. Possibilities include [RuCl(P(CMe)₂Ph)₃S₂]BPh₄ or [RuCl(P(CMe)₂Ph)₃S₂(BPh₄)₂ (S = solvent), but it is impossible to differentiate further between these formulations because of the inability to separate this intermediate from the ionic dimer.

Dissolving RuCl₂(P(OMe)Ph₂)₃ in CH₂Cl₂ produces initially a bright yellow solution which gradually becomes paler and increases in conductivity reaching a maximum of 29μmho (specific conductivity) for a 10⁻³M solution after approximately four hours (Fig. 2.4), which corresponds to a 1:1 electrolyte. The addition of NaBPh₄ then precipitates [Ru₂Cl₃(P(CMe)Ph₂)₆]BPh₄. This rearrangement has also been studied by ³¹Pn.m.r. spectroscopy (Fig. 2.5). At 18³K in CH₂Cl₂/(CD₃)₂CO, the
The spectrum consists of a broad signal at 144 p.p.m. due to \( \text{RuCl}_2(\text{P(OMe)Ph}_2)_3 \) and a sharp singlet at 139.8 p.p.m. due to the rearranged product \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]^-\)Cl. As the temperature increases, the signal at 144 p.p.m. sharpens but simultaneously decreases in intensity while the signal at 139.8 p.p.m. increases and at 303K almost all of the monomer has been converted to the ionic species. The rearrangement is irreversible as cooling the mixture has no effect on the ratios observed at ambient temperature. No intermediate products were observed but an expansion of the spectrum when the sample was recooled to 213K showed a number of peaks at the base of the singlet at 139 p.p.m. (Fig. 2.6). After the sample was allowed to stand at room temperature for 48 hours, the spectrum, rerun at 213K, contained no resonance due to the monomer but the weak peaks at the base of the strong singlet were still present. These are attributed to a small amount of another rearrangement product and are discussed later.

Dissolving \( \text{RuCl}_2(\text{P(OEt)Ph}_2)_3 \) in \( \text{CH}_2\text{Cl}_2 \) also produces initially a bright yellow solution which slowly becomes paler. The conductivity increases reaching a maximum after 24 hours (Fig. 2.4). Again the rearrangement has been studied by \( ^{31}\text{Pn.m.r.} \) (Fig. 2.7) and although much slower follows a similar pattern to that of \( \text{RuCl}_2(\text{P(OMe)Ph}_2)_3 \) (viz. irreversible conversion of the monomer to an ionic species). However, there is one very important difference here in that the rearrangement product (A) is not the triple bridged ionic dimer, since the \( ^{31}\text{Pn.m.r.} \) spectrum at 213K is not a singlet but a complicated multiplet (Fig. 2.8) consisting of at least 20 lines. Leaving the sample in solution for 3-days and then rerunning the spectrum at 213K showed that all of the monomer had been converted to (A). On warming to 303K the multiplet collapses to a broad resonance centred at 135 p.p.m. which suggests that rapid scrambling of all the tertiary phosphinite groups is taking place at this temperature. Subsequent recooling to 213K gives the original sharp multiplet.
Fig. (2.4) Plot of conductivity vs. time for
\[ \text{RuCl}(\text{P(OR)Ph})_{2-3} \quad (R=\text{Me, Et}) \]

- Conductivity (\(\mu\text{mho}\))
- Time (hours)

**Specific Conductivity:**
- \(x = \text{RuCl}(\text{P(OMe)Ph})_{2} \)
- \(o = \text{RuCl}(\text{P(OEt)Ph})_{2} \)
Fig. 2.5  $^3$P$_{n.m.r.}$ spectra of $\text{RuCl}_2(P(OMe)\text{Ph}_2)_3$ in (CD$_3$)$_2$CO/CH$_2$Cl$_2$ at various temperatures.
Fig. 2.6 Expansion of $^{31}\text{P n.m.r.}$ spectrum of the rearrangement products of RuCl$_2$(P(OMe)Ph)$_2$ in (CD$_3$)$_2$Co/CH$_2$Cl$_2$ at 213K
$^{31}$P n.m.r spectra of RuCl$_2$(POEt)Ph$_3$ in (CD$_3$)$_2$CO/CH$_2$Cl$_2$ at various temperatures.

193K

213K

273K
Fig. 2.8  $^{31}$P n.m.r. spectrum of the ionic rearrangement product of $\text{RuCl}_2(\text{P(OEt)Ph}_3)_3$ in CDCl$_3$ at 213K

<table>
<thead>
<tr>
<th>Chemical Shift (p.p.m.)</th>
<th>Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>138.39</td>
<td></td>
</tr>
<tr>
<td>133.55</td>
<td></td>
</tr>
<tr>
<td>129.81</td>
<td></td>
</tr>
</tbody>
</table>
(Fig. 2.8) which remained unchanged even after a period of twelve weeks. The addition of NaBPh₄ or NH₄PF₆ precipitated a pale yellow solid, but addition of AsPh₄Cl,HCl gave no precipitate, implying that the phosphorus containing species present is only cationic in nature. This was verified by running the ³¹P n.m.r. spectrum in CDCl₃ at 213K of the tetraphenylborate salt which consisted of an identical multiplet to that reproduced in Fig. 2.8. Therefore (A) cannot be for example [Ru₂Cl₃(P(OEt)Ph₂)₆][RuCl₃(P(OEt)Ph₂)₃]. The reaction between [RuCl₂(C₇H₈)_n] and P(OEt)Ph₂ is reported to give, on addition of NaBPh₄, the ionic dimer [Ru₂Cl₃(P(OEt)Ph₂)₆]BPh₄. This reaction was repeated and the ³¹P n.m.r. spectrum of the product in CDCl₃ at 213K was found to be the same as that of the tetraphenylborate salt of (A). Samples of (A) with counterions BPh₄⁻ or PF₆⁻, prepared on several different occasions and run in a variety of different solvents ((CD₃)₂CO, CDCl₃, (CD₃)₂CO/CH₂Cl₂), always displayed the same ³¹P n.m.r. spectrum and line intensities at 213K, suggesting that the product is a single species and not a mixture.

The infra-red spectrum (4000-400cm⁻¹) of (A) (BPh₄⁻ salt) is identical with that of RuCl₂(P(OEt)Ph₂)₃ except for the additional bands due to the anion and therefore this suggests that no change in the tertiary phosphinite ligands can have occurred during the rearrangement process. P(OR)₃ groups are known to lose the R group to form P(O)Ph₂⁻ or P(OH)Ph₂ moieties but in each case significant changes in the infra-red spectrum are observed. The narrow range of chemical shifts (ca 10p.p.m.) in the ³¹P n.m.r. spectrum of (A) is also consistent with the non-formation of Ru-P(O)Ph₂ or Ru-P(OH)Ph₂ linkages. Furthermore

† For the complex (h⁵-C₅H₅)(FeC₆H₄OP(C₆H₅)₂P(OCC₆H₅)₃) the ³¹P chemical shifts of meta-metalled (200.0p.p.m.) and unmeta-metalled (164.4p.p.m.) phosphite ligands are substantially different.
no evidence for the formation of ethanol or ethylchloride was observed in the $^1$H n.m.r. spectrum or on a g.l.c. trace of a 3 day old solution of RuCl$_2$(P(OEt)Ph$_2$)$_3$ in CDCl$_3$ and also, apart from resonances due to BPh$_4^-$ and the solvent, the $^{13}$C n.m.r. spectrum of (A) in CDCl$_3$ was similar to that of RuCl$_2$(P(OEt)Ph$_2$)$_3$ in C$_6$D$_6$ (Table 2.5). The far infrared spectrum (400-200 cm$^{-1}$) of (A) (BPh$_4^-$ salt) (Fig. 2.9) contains bands at 314 cm$^{-1}$ and ca 260 cm$^{-1}$ indicating the presence of both terminal and bridging chloride groups.

As no free P(OEt)Ph$_2$ is observed in the $^{31}$P n.m.r. spectrum on rearrangement of RuCl$_2$(P(OEt)Ph$_2$)$_3$ to (A) in various solvents, (A) must contain three tertiary phosphinite groups per Ru atom. It has been shown to behave as a 1:1 electrolyte in both CH$_2$Cl$_2$ and acetone. (For detailed discussion of conductivity measurements and determination of electrolytic type see experimental section.) Furthermore the molecular weight of the BPh$_4^-$ salt in CHCl$_3$ was found to be 1350. Thus for a 1:1 electrolyte the actual molecular weight would be 2700. As a check on the validity of this assumption the molecular weight of [Ru$_2$Cl$_3$(P(OMe)Ph$_2$)$_3$]BPh$_4$ in CHCl$_3$ was found to be 1003; required for 1:1 electrolyte 967.

Therefore on the basis of this molecular weight data and all the spectroscopic evidence detailed earlier, compound (A) is formulated as containing the trimeric ruthenium(II) cation [Ru$_3$Cl$_5$(P(OEt)Ph$_2$)$_9$]$^+$. Analytical data (see Table 2.1) for various counterions is also reasonably consistent with this formulation. Two possible trimeric structures which fit most of the experimental observations are shown in Fig. 2.10. However the linear structure (b) can be readily eliminated on the basis that facile intramolecular scrambling of all P(OEt)Ph$_2$ groups in such a structure is impossible. However the closed structure (a) containing one terminal chloride group, one double chloride bridge, two single
chloride bridges and three P(OEt)Ph₂ groups per ruthenium is much more feasible when trying to explain the fluxional nature of (A).

Scheme 2.2 indicates how it is possible to rationalise the facile intramolecular scrambling process of P(OEt)Ph₂ groups observed in the 3¹P n.m.r. spectrum of (A) in terms of a structure such as (a). Thus in (Ia) terminal chloride (i) positioned on Ru(1) can form a bond with Ru(2) with the subsequent breaking of bond (s), to form (IIa) in which the terminal chloride is now on Ru(3) or bond (z) to form (IIIa) in which the chlorides (i) and (iii) have interconverted. Similarly (IIa) and (IIIa) can rearrange intramolecularly, and so on, with the result that all the phosphinite groups become equivalent when such rearrangement processes are sufficiently rapid on the n.m.r. time scale.

This is not the first example of a trimeric Ru(II) species. For example, a carbonylated solution of 'RuCl₃.3H₂O' in methanol treated with MeSCS.NEt₂ yields a small amount of yellow brown crystals whose structure (12) has been determined by X-ray analysis.⁹⁻
Fig. 2.10 Possible structures of $\text{[Ru}_3\text{Cl}_{3-5}(\text{P(OME)}_2\text{Ph})_{2-9}]^+$. 
Scheme 2.2  Intramolecular rearrangement of $[\text{Ru}_3\text{Cl}_5(P(\text{OEt})\text{Ph})_2]^{\dagger}$ at 298 K.
The Ru - Cl(vi) distances are longer than the Ru(4) or Ru(5) - Cl(vii) and the Ru ... Ru distances are ca 3.70Å which is too long for significant metal-metal interactions. Unfortunately extensive recrystallisation attempts on (A) have failed to produce crystals suitable for an X-ray structure determination which hopefully would have provided unequivocal confirmation of both the above formulation and the detailed structure.

On the basis of the structure postulated in Fig. 2.10a (assuming a regular octahedral geometry around each Ru ion) it might be expected that its $^{31}$P n.m.r. spectrum would consist of an $AB_2$ pattern arising from atoms $P_1$, $P_2$, $P_3$ superimposed on an $ABC$ pattern of twice the intensity arising from atoms $P_4$, $P_5$, $P_6$ and $P_7$, $P_8$, $P_9$. Several attempts have been made to fit such a theoretical pattern of lines to the observed pattern shown in Fig. 2.8 using the well known computer simulation program LAOCOON. Unfortunately to date, these attempts have not proved successful. For several reasons, however, this failure does not necessarily invalidate the correctness of the structure shown in Fig. 2.10a. First, as stated above, the theoretical n.m.r. pattern was formulated on the basis of a regular octahedral environment around each Ru ion, but it is quite likely that small deviations from regular geometry might occur, sufficient to destroy, for example, the postulated magnetic equivalence of the two $ABC$ sets or the equivalence of atoms $P_1$ and $P_3$ in the supposed $AB_2$ set. Thus, the expected $^{31}$P n.m.r. spectrum of structure (a) might more realistically be a supposition of three slightly different $ABC$ subsets i.e. 9 coupling constants and 9 chemical shifts would then be required to completely define this spin system. Another difficulty is the quality of the experimental spectrum. Thus, although 20 lines can be counted, the combination of narrow spectral width (ca 10p.p.m.), low temperature (producing some viscosity broadening) and complexity of
signals, imply that it is highly likely that many overlapping resonances are present (note a single ABC spin system can generate a maximum of 15 lines). Therefore, in this situation, insufficient unambiguous experimental information is available to completely solve this n.m.r. problem.

However although the structure is not proven by spectral analysis the wide range of chemical and spectroscopic evidence does strongly support the formulation of (A) as $[\text{Ru}_2\text{Cl}_5(\text{P(0Et)Ph}_2)_9]X\ (X = \text{Cl}^-, \text{BPh}_4^-, \text{PF}_6^-)$ with the structure shown in Fig. 2.10(a).

Finally the weak peaks appearing at the base of the singlet (Fig. 2.6) due to $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]\text{Cl}$ in the $^{31}\text{P}$n.m.r. spectrum of the rearrangement products $\text{RuCl}_2(\text{P(OMe)Ph}_2)_3$ (Fig. 2.6) correspond very closely to those in Fig. 2.8 and are therefore considered to arise from the presence of a small amount of $[\text{Ru}_3\text{Cl}_5(\text{P(OMe)Ph}_2)_9]\text{Cl}$.

(c) Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $L\ (L = \text{P(OR)}_3, \text{P(OR)}_2\text{Ph, P(OR)Ph}_2)$ in polar solvents.

Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with excess of $L\ (L = \text{P(OMe)}_3, \text{P(OMe)}_2\text{Ph})$ in methanol produces the previously known $[\text{Ru}_6]^2^+$ species readily isolated as $\text{BPh}_4^-$ salts. In contrast, refluxing $\text{RuCl}_2(\text{PPh}_3)_3$ with excess of $\text{P(OMe)Ph}_2$ in methanol for a short time gives a deep red solution which gradually, over a period of two hours, turns yellow in colour. Addition of Na$\text{BPh}_4$ to the yellow solution produces $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]\text{BPh}_4\ (^{31}\text{P}\text{n.m.r. evidence})$ but addition of Na$\text{BPh}_4$ to the initial red solution yields a red solid which analyses closely for $[\text{RuCl}(\text{P(OMe)Ph})_4]\text{BPh}_4$. The mull infra-red spectrum, in which there is no evidence of a co-ordinated solvent molecule, contains, in addition to bands due to $\text{P(OMe)Ph}_2$ and $\text{BPh}_4^-$, a band at 290cm$^{-1}$ attributed to $\nu(\text{Ru-Cl})$ of a chloride ion trans to phosphorus. The complex slowly rearranges to the ionic dimer in chlorinated solvents but is stable in acetone and therefore the $^{31}\text{P}$n.m.r. spectrum was studied in $(\text{CD}_3)_2\text{CO}$.
over a range of temperatures (Fig. 2.11). At 173K (Fig. 2.12) several resonances are observed viz. a singlet at 139.1 p.p.m. due to the presence of some \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]\text{BPh}_4\) in the sample, a singlet at 110.9 p.p.m. due to free \(\text{P(OMe)Ph}_2\), two multiplets at 157 and 140 p.p.m. and sharp resonances resembling two triplets centred at 123 p.p.m. As the solution is warmed the broad multiplets at 157 and 140 p.p.m. coalesce to a broad hump at 148 p.p.m. which on further warming sharpens up to a peak at 148.5 p.p.m. The resonance at 123 p.p.m. also collapses on warming and at 213K a broad peak at 124.0 p.p.m. is observed. At 333K the peaks at 148.5 and 124.0 p.p.m. have disappeared and a broad resonance at 136 p.p.m. has appeared. No change in the singlet due to free \(\text{P(OMe)Ph}_2\) occurs up to 213K but at 333K it has broadened considerably and shifted to higher frequency.

In the spectrum, obtained at 173K (Fig. 2.12), it appeared initially that the resonances at 157 and 140 p.p.m. on the one hand and at 123 p.p.m. on the other might arise from two different species. On examining the spectra at higher temperatures the observed coalescence of the multiplets at 157 and 140 p.p.m. to a resonance at 148 p.p.m. indicates that they arise from the same species and that each peak corresponds to the same number of P atoms in that species. However as the temperature is further raised the resonances at 148 and 123 p.p.m. coalesce to a resonance mid-way between them which implies that they also arise from the same species and correspond to the same number of P atoms. Cooling the solution restores the spectrum shown in Fig. 2.12. Hence it seems that the multiplets at 157, 140 and 123 p.p.m. in the spectrum at 173K are produced by P atoms in the ratio 1:1:2 respectively which arise from a single species which is likely to be \([\text{RuCl(P(OMe)Ph}_2)_4]\)^+. To obtain such a spectrum, two of the P atoms must be magnetically equivalent and the other two non-equivalent. Structures consistent with this requirement are (13a) with the sixth position of the octahedral complex in
Fig. 2.11  Pn.m.r. spectra of [RuCl(P(OMe)Ph₂)₂]BPh₄ in (CD₃)₂CO at various temperatures.

chemical shift (p.p.m.)
Fig. 2.11 (continued)

213K

138.5  124.0  112.9

148.5

333K

137.7

141.1  136  116

chemical shift (p.p.m.)
Fig. 2.12 $^{31}$P n.m.r. spectrum of $[\text{RuCl}(\text{POMePh})_2]_4$IBPh in (CD$_3$)$_2$CO at 173K

Chemical shift (p.p.m.)

- 157.0
- 140.0
- 139.1
- 122.3
- 124.4
- 110.9

chemical shift (p.p.m.)
solution occupied by a solvent molecule or (13b) with no co-ordinated solvent.

Unfortunately all attempts to reproduce the spectrum at 173K (Fig. 2.12) assuming an $ABC_2$ spin system and using computer simulation techniques have proved unsuccessful since no combination of chemical shift

\[
\begin{align*}
&\text{Ru} \\
&\text{Cl} \\
&P(\text{OMe})\text{Ph}_2 \\
&S
\end{align*}
\]

(13a)

\[
\begin{align*}
&\text{Ru} \\
&\text{Cl} \\
&P(\text{OMe})\text{Ph}_2 \\
&P(\text{OMe})\text{Ph}_2
\end{align*}
\]

(13b)

and coupling constant data can simulate the symmetrical pattern centred at 123 ppm. However, a precedent exists in the literature for the occurrence of unexpected $^{31}$P.n.m.r. spectra in a related complex at low temperature. Thus, for $\text{cis-FeH}_2(\text{P(OMe)}_2\text{Ph})_4$ (14) the $^{31}$P.n.m.r.

\[
\begin{align*}
&P(\text{OR})_2\text{Ph} \\
&\text{Fe} \\
&P(\text{OR})_2\text{Ph} \\
&\text{H} \\
&P(\text{OR})_2\text{Ph} \\
&\text{H} \\
&P(\text{OR})_2\text{Ph} \\
&(R = \text{Me, Et})
\end{align*}
\]

(14)

\[\dagger\]

The other two multiplets at 157 and 140 p.p.m. are much broader and it is difficult to tell whether or not they match the simulated spectra.
spectrum at 210K consists of the expected $A_2E_2$ pattern (Fig. 2.13).

However as the temperature is lowered the triplets broaden but at 187K they sharpen up again to more complex patterns with the lower frequency resonance sharpening up more quickly than the one at higher frequency. In fact, at 150K the shape of the lower frequency resonance is virtually identical to that observed in Fig. 2.12.

The explanation offered by Meakin et al is that the bulky P(OMe)$_2$Ph ligands interact in such a way as to reduce the symmetry of the molecule below that shown in (14) and that the ligand motions are sufficiently restricted such that the reduction of symmetry is maintained on the n.m.r. time scale at these low temperatures. In support of this interpretation, the solid state structure of FeH$_2$(P(OEt)$_2$Ph)$_4$ differs appreciably from the idealised $C_{2v}$ symmetry shown in (14) and this distortion is attributed more to interligand interactions than crystal packing effects.

By comparison of the spectra in Fig. 2.13 with those in Fig. 2.11, it seems probable that such a situation occurs for [RuCl(P(OMe)Ph)$_2$)$_4$]$^+$. In the latter case, a frozen-out $ABC_2$ spectrum is not observed at higher temperatures because of rapid intramolecular scrambling processes and at lower temperatures the equatorial phosphinite groups in (13a) (and $P_1$ and $P_2$ of 13b) are in different chemical environments so that two multiplets are observed in contrast to the one for the equatorial phosphonite groups of FeH$_2$(P(OMe)$_2$Ph)$_4$.

The equivalence of the equatorial tertiary phosphinite groups of [RuCl(P(OMe)Ph)$_2$)$_4$]$^+$ at 193K can be explained by invoking a dynamic equilibrium of the type

\[
\begin{align*}
\text{Cl} & \quad \text{Ru}^{+} & \quad \text{Cl} \\
\text{S} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{S} & \quad \text{Ru}^{+} & \quad \text{Cl} \\
\text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} \\
\end{align*}
\]
Fig. 2.13  $^{31}$P n.m.r. spectra of cis-FeH$_2$(P(OMe)$_2$Ph)$_2$ in 50%CH$_2$Cl$_2$-50%CHF$_2$Cl at various temperatures.
hence implying structure (13a) at 173 K. Loss of the solvent molecule occurs to form a 5 co-ordinate intermediate in which there is no facile overall rearrangement at this low temperature. Recombination of the solvent molecule trans to the other equatorial ligand then causes the two to become equivalent on the n.m.r. time scale. At higher temperatures rearrangement of the axial and equatorial phosphinite via a pseudorotation mechanism takes place in the 5 co-ordinate intermediate producing scrambling of all four phosphinite ligands. Some intermolecular exchange with free P(OMe)Ph₂ also starts to occur at higher temperatures suggesting an equilibrium of the type

\[
[RuCl(P(OMe)Ph₂)_4 S]^+ \rightleftharpoons [RuCl(P(OMe)Ph₂)_3 S₂]^+ + \text{P(OMe)Ph₂}
\]

is becoming of some importance and an additional resonance is observed at 141 p.p.m. which may possibly be due to the cation \([RuCl(P(OMe)Ph₂)_3 S₂]^+\). Furthermore, the addition of excess P(OMe)Ph₂ inhibits the formation of \([Ru₂Cl₃(P(OMe)Ph₂)_₆]^+\) in CH₂Cl₂ whereas the addition of Cl⁻ to an acetone solution of \([RuCl(P(OMe)Ph₂)_₄]^\text{EPH₄}\) causes a colour change from red to yellow and rerunning the spectrum at 298K shows that all the resonances except those due to \([Ru₂Cl₃(P(OMe)Ph₂)_₆]^\text{EPH₄}\) and free P(OMe)Ph₂ have disappeared. Finally conductivity measurements on an acetone solution of \([RuCl(P(OMe)Ph₂)_₄]^\text{EPH₄}\) indicate the presence of a 1:1 electrolyte.

Several examples of related five co-ordinate Ru(II) cations are already known. For example, treating RuH₂(PPh₃)₄ with (Ph₃C)PF₆ results in the abstraction of a hydride ion and the formation of \([RuC(P(Ph₃)₃P)₄]^\text{PF₆}^{99}\) as a red solid. ¹H n.m.r. evidence suggests that the molecule is almost tetrahedral and that the hydrogen on ruthenium traverses between tetrahedral faces rapidly enough to make all the tertiary phosphine groups equivalent on the n.m.r. time scale at room temperature. When \([RuH(PPh₃)₃]^{PF₆}₄\) is treated with smaller phosphorus containing ligands
the complexes \([\text{RuHL}_5]^+\) \((L = \text{PHPh}_2, \text{P(OMe)}_2\text{Ph}, \text{P(OEt)}_2\text{Ph})\) are obtained. Hence the formation of the unsaturated 16 electron cation \([\text{RuH(PPh}_3)_4]^+\) rather than the 18 electron species \([\text{RuHL}_5]^+\) is attributed to the large size of the triphenylphosphine ligand which prevents more than four of them acting as ligands on the same metal ion. This is probably the reason for the formation of \([\text{RuCl(P(OMe)Ph}_2)_4]^+\) rather than \([\text{RuCl(P(OMe)Ph}_2)_5]^+\). However a solution of \([\text{RuH(PPh}_3)_4]\text{PF}_6\) in \(\text{CH}_2\text{Cl}_2\) at 293K changes colour from red to green in a few hours and a pale yellow compound analysing for \([\text{RuH(PPh}_3)_3]\text{PF}_6\) is obtained. An X-ray structure shows one of the benzene rings of a PPh\(_3\) group to be \(\pi\)-bonded to the ruthenium thus resulting in an 18 electron system\(^{15}\). In this instance

\[
\begin{align*}
\text{PPh}_2 \\
\text{Ru}^+ \\
\text{Ph}_3\text{P} \\
\text{H} \\
\text{PPh}_3
\end{align*}
\]  \(\text{(15)}\)

the formation of a dimer is prohibited because of the steric constraints involved in accommodating three triphenylphosphine groups in one face.

The complex \([(\text{cod})\text{RuH(NH}_2\text{NMe}_2)_3]\text{PF}_6\) reacts with \(L_2\) \((L_2 = \text{bis(diphenylphosphino)propane, bis(diphenylphosphino)butane})\) in alcohol to produce the red 5 co-ordinated complexes \([\text{RuH(L}_2)_2]\text{PF}_6\).\(^{11}\) As the size of the ligands are reduced the tendency to form a sixth ligand increases such that for \(L_2 = (\text{PMe}_2\text{Ph})_2, (\text{PMePh}_2)_2\) or bis(diphenylphosphino)ethane, \([\text{RuH(L}_2)_2\text{MeOH}]\text{PF}_6\) complexes (which are also red) are formed. \([\text{RuH(L}_2)_2\text{MeOH}]\text{PF}_6\) then react with \(\text{H}_2\) at ambient temperatures and pressure to produce \([\text{RuH}_3(L_2)_2]^+\) cations \((L_2 = (\text{PMe}_2\text{Ph})_2)\) and
RuH₂(L₂)₂ (L₂ = (PMePh₂)₂).

Other examples of similar 5 co-ordinate cations are [RuX(dpp)₂]⁺ (X = Cl, Br; dpp = bis(diphenylphosphino)propane)¹⁰¹ which are formed by dissolving trans-RuX₂(dpp)₂ in 1,2 dichloroethane, the large crowding of the dpp ligands being such that elimination of a halide ion is favoured, and [Ru(S-S)L₃]BPh₄ (S-S = S₂PR₂, S₂CNR₂; L = PMe₂Ph, P(OMe)Ph₂, P(OEt)Ph₂) which will be discussed in Chapter 5.

The reaction between RuCl₂(PPh₃)₃ and P(OEt)Ph₂ in ethanol, as for P(OMe)Ph₂, produces initially a red solution which slowly turns yellow in colour. Addition of NaBPh₄ to the yellow solution gives [Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄ and from the red solution a red solid analysing for [RuCl(P(OEt)Ph₂)₄]BPh₄ is obtained. However the ³¹P n.m.r. spectra at various temperatures in (CD₃)₂CO (Fig. 2.14) contain several different features from those of [RuCl(P(OMe)Ph₂)₄]BPh₄. At 173K (Fig. 2.15) the spectrum contains a multiplet centred at 135p.p.m. due to the presence of some [Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄, a singlet at 110.1p.p.m. due to free P(OEt)Ph₂, and two triplets at 148.1p.p.m. and 119.0p.p.m. (Jₚₚ = 29.2Hz). As the temperature increases the triplets broaden and at 298K coalesce to a broad peak superimposed on the resonance at 135p.p.m. due to the trimer. The triplets, which reappear on cooling the solution to 173K must arise from the double chloride bridged dimer [Ru₂Cl₂(P(OEt)Ph₂)₈]²⁺ (16) since a monomer would, as in the case of [RuCl(P(OMe)Ph₂)₄]⁺, be expected to give a more complicated spectrum.
Fig. 2.14 $^{31}$Pnmr. spectra of $[\text{RuCl}_2(\text{P(OEt)Ph}_2)_2\text{BPPh}_3]_{2-2}^{2-8} \text{(CD)}_{2-42}^{32} \text{CO}$ at various temperatures.

173K

213K

298K
Fig. 2.15 $^{31}$Pnmr. spectrum of $[\text{RuCl}_2(\text{P(OME)Ph}_3)_2\text{BPh}_4]_2$ in $(\text{CD}_3)_2\text{CO}$ at 173K.

- 148.1 ppm
- 119.0 ppm
The presence of such a dimer in the solid state is suggested by a broad band at 270 cm\(^{-1}\) in the far infra-red spectrum which is not observed for \([\text{RuCl}(\text{P(OMe)Ph}_2)_4]^{+}\). However, the collapse and coalescence of the triplets at higher temperatures is not consistent with retention of this dimeric structure in solution and it would suggest that the dimer is cleaved to produce the monomer \([\text{RuCl}(\text{P(OEt)Ph}_2)_4]^{+}\) as the temperature is raised (c.f. the \(^{31}\text{P} \text{n.m.r.} \text{spectra of [RuCl(P(OMe)Ph}_2)_4]}^{+}\) (Fig. 2.11) and \([\text{Ru}_2\text{Cl}_2(P(\text{OEt})\text{Ph}_2)_8](\text{BPh}_4)_2\) (Fig. 2.14) at 213 K and above). Furthermore, conductivity measurements at 298 K in \((\text{CH}_3)_2\text{CO}\) indicate the presence of a 1:1 electrolyte. No evidence for exchange with free P(OEt)Ph\(_2\) is observed since the resonance at 110.1 p.p.m. remains sharp at all temperatures and no additional resonances which could be attributed to \([\text{RuCl}(\text{P(OEt)Ph}_2)_2]^{+}\) appear in the spectrum at 298 K. However, addition of excess P(OEt)Ph\(_2\) inhibits rearrangement to \([\text{Ru}_3\text{Cl}_5(P(\text{OEt})\text{Ph}_2)_9]^{+}\) \(\text{BPh}_4\) in \(\text{CH}_2\text{Cl}_2\) whereas addition of \(\text{Cl}^-\) to an acetone solution of \([\text{Ru}_2\text{Cl}_2(P(\text{OEt})\text{Ph}_2)_8](\text{BPh}_4)_2\) causes a colour change from red to yellow but the rearrangement is slower than for \([\text{RuCl}(\text{P(OMe)Ph}_2)_4]^{+}\).

(d) Mechanism of rearrangement of \(\text{RuCl}_2L_3\) or \(\text{RuCl}_4\) species

It seems evident from the results just described that the mechanism of rearrangement of the phosphinite and phosphonite complexes is different from that proposed earlier for the corresponding phosphine complexes (see Scheme 2.1). Thus, as outlined in Scheme 2.3 the complex \(\text{RuCl}_2L_3\) (Ib), formed in the case of \(L = \text{P(OMe)}_2\text{Ph}\) by dissociation of \(L\) from \(\text{RuCl}_2L_4\), loses a chloride ion to give the cation (IIb) as observed for \(L = \text{P(OMe)}_2\text{Ph}\). This species can then combine with \(\text{RuCl}_2L_3\) to produce the triple halide bridged cation (Vb). In Scheme 2.1 \([\text{Ru}_2\text{Cl}_3L_6]\) Cl was postulated to be formed by the initial coupling of two monomeric species to form a double bridged dimer followed by nucleophilic attack of a lone pair of a chloride ion on the adjacent Ru ion with concomitant
Scheme 2.3  Mechanism of rearrangement of RuCl₂L₄ (L=tertiary phosphine, phosphinite, phosphonite).

(N.B. in solution the vacant co-ordination sites are probably occupied by solvent molecules.)
loss of chloride i.e.

\[
\begin{array}{c}
\text{L} \quad \text{Cl} \\
\text{Ru} \quad \text{Cl} \\
\text{L} \quad \text{Cl}
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{L} \quad \text{Ru} \quad \text{Cl} \\
\text{L} \quad \text{Ru} \quad \text{Cl} \\
\text{L} \quad \text{L}
\end{array}
\]

However, evidence obtained for the formation of other triple bridged species (see Chapter 6) indicates that dissociation of chloride ion occurs prior to the coupling of the two monomers which directly form the triple bridged dimers (step 7).

For \( L = \text{P(0Et)Ph}_2 \) (and to some extent for \( L = \text{P(OMe)Ph}_2 \)) not \([\text{Ru}_2\text{Cl}_3\text{L}_6]^+\) but the ionic trimer \( \text{VIb} \) is formed. This can be explained in terms of the bulkiness of the ligand \( L \) which inhibits the accommodation of three such ligands in one face. Thus, reaction of \([\text{RuClL}_3]^+ \) (IIb) with \( \text{RuCl}_2\text{L}_3 \) (Ib) might produce a double chloride bridged cation (17), in which the vacant co-ordination site is probably occupied by a solvent molecule. Further reaction of (17) with \( \text{RuCl}_2\text{L}_3 \) could than produce the trimeric cation \([\text{Ru}_3\text{Cl}_5\text{L}_9]^+ \) (Scheme 2.4).
Evidence for the existence of an equilibrium between $[\text{RuCl}_4\text{L}_4]^+$ (IVb) and $[\text{RuCl}_3\text{L}]^+$ (IIb) has already been discussed (see Page 53) and is supported by the addition of excess L ($L = \text{P(OR)}\text{Ph}_2$) to a fresh solution of RuCl$_2$L$_3$ in CH$_2$Cl$_2$ (which contains $[\text{RuCl}_3\text{L}]^+$) to produce the red colouration of (IVb). This equilibrium is stable in the absence of Cl$^-$ but in the presence of Cl$^-$ step (2) occurs to produce RuCl$_2$L$_3$ and subsequent combination of this with IIb gives the ionic dimer and/or trimer. As previously noted, $[\text{RuCl}_4\text{L}_4]^+$ for $L = \text{P(OMe)}\text{Ph}_2$ exists at low temperature as the dimer (VIIb).

Attempts to prepare the tetrakis species RuCl$_2$(P(OR)Ph$_2$)$_4$ by refluxing RuCl$_2$(P(OR)Ph$_2$)$_3$ with excess P(OR)Ph$_2$ in benzene were unsuccessful although the $^{31}$P n.m.r. spectra of the resultant solution did show several small peaks at the base of the singlet due to RuCl$_2$(P(OR)Ph$_2$)$_3$ suggesting that small amounts of other species had been produced.

The stability of RuCl$_2$L$_4$ ($L = \text{P(OMe)}_3$, P(OMe)$_2$Ph) to rearrangement is largely attributed to the small size of the ligands L compared with P(OR)Ph$_2$. This allows at least four of the ligands to be accommodated...
quite easily around the Ru atom as reflected by the fact that in polar solvents with an excess of L, \([\text{RuL}_6]^{2+}\) are produced. Hence, there is little or no driving force to produce a tris species by loss of L, although in the case of \(\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4\) such a species is produced on heating. Similar results have been obtained for the dissociation of L from \(\text{NiL}_4\) species \(^{102}\) where the steric effects were expressed in terms of ligand cone angles, the order of dissociation being

\[
\text{P(OMe)}_3 < \text{P(OMe)}_2\text{Ph} < \text{P(OMe)}\text{Ph}_2 < \text{PPh}_3
\]

In view of the above mechanism (Scheme 2.3) the reaction between \(\text{RuCl}_2(\text{PPh}_3)_3\) and excess \(\text{PEtPh}_2\) in ethanol, reported earlier to give \([\text{RuCl}_2(\text{PEtPh}_2)_3]^{1/2}\) \(^{73}\) was repeated. Addition of \(\text{NaBPh}_4\) to the yellow solution obtained produced a yellow solid exhibiting a \(\text{^31P} n.m.r.\) spectrum, in \(\text{CDCl}_3\) at 213K, containing in addition to a singlet due to

\([\text{Ru}_2\text{Cl}_3(\text{PEtPh}_2)_6]^{\text{BPh}_4}\), an identical \(\text{AB}_2\) pattern to that originally obtained. Hence the product is ionic and therefore likely to be \([\text{RuCl}(\text{PEtPh}_2)_3\text{S}_2]^+ (S = \text{solvent})\). Thus it seems probably that formation of \([\text{Ru}_2\text{Cl}_3\text{L}_6]^+\) from \(\text{RuCl}_2\text{L}_3\) (\(\text{L} = \text{PEtPh}_2\)) or \(\text{RuCl}_2\text{L}_4\) (\(\text{L} = \text{PMe}_2\text{Ph}, \text{PMePh}_2\)) follows a similar pathway to that outlined in Scheme 2.3. However to make the scheme completely general a few additional steps are necessary (Scheme 2.5). \(\text{RuCl}_2\text{L}_3\) can, in the case of bulky phosphines, lose L to give \(\text{RuCl}_2\text{L}_2\) which is then able to dimerise to form \([\text{RuCl}_2\text{L}_2]_2\) (\(\text{L} = \text{PPh}_3\)) or combine with \(\text{RuCl}_2\text{L}_3\) to produce the neutral triple bridged complexes \(\text{Ru}_2\text{Cl}_4\text{L}_5\) (\(\text{L} = \text{PEtPh}_2\) etc.) which in the presence of L slowly rearranges to \([\text{Ru}_2\text{Cl}_3\text{L}_6]\)\text{Cl}. For the more nucleophilic \(\text{P(OR)}_3\), \(\text{P(OR)}_2\text{Ph}\) and \(\text{P(OR)}\text{Ph}_2\) ligands no evidence for the formation of the neutral triple bridged dimers \(\text{Ru}_2\text{Cl}_4\text{L}_5\) has been observed (but see Chapter 3).
Scheme 2.5 Alternative pathway for rearrangement of RuCl₂L₃

(L = tertiary phosphine)
2.3 Experimental

Microanalyses were by B.M.A.C., A. Bernhardt, West Germany and the University of Edinburgh Chemistry department. Molecular weights were determined on a Mechrolab Vapour Pressure osmometer (model 301A) calibrated with benzil. Infra-red spectra were recorded in the region 4000-2500 cm\(^{-1}\) on Perkin Elmer 457 and 225 grating spectrometers using Nujol mulls on caesium iodide plates and in the region 400-2000 cm\(^{-1}\) on a Beckman RIIC IR 720 far infra-red spectrometer using pressed polythene discs. \(^1\)H n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable temperature attachment and \(^13\)C n.m.r. spectra on a Varian CFT-20 spectrometer operating at 20 MHz (\(^13\)C chemical shifts are quoted in p.p.m. to high frequency of TMS). \(^31\)P n.m.r. spectra (proton noise decoupled) were recorded on a Varian Associates XL-100 spectrometer operating in the Pulse and Fourier Transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m. to high frequency of \(85\%\) \(\text{H}_3\text{PO}_4\). Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Conductivity vs concentration data were obtained over a range of concentrations \((2 \times 10^{-3} \text{dm}^{-3} \text{mol. to } 5 \times 10^{-3} \text{dm}^{-3} \text{mol.})\). A plot of \(\Lambda\) (equivalent conductance) against \(C^{\frac{1}{2}}\) (concentration in equivalents dm\(^{-3}\)) is a straight line which when extrapolated to \(C^{\frac{1}{2}} = 0\) gives \(\Lambda_0\). A subsequent plot of \(\Lambda_0 - \Lambda_c\) vs. \(C^{\frac{1}{2}}\) yields a straight line whose slope is \((A + \omega B \Lambda_0)\) from the equation \(\Lambda_0 - \Lambda_c = (A + \omega B \Lambda_0)C^{\frac{1}{2}}\) where \(\Lambda_0, \Lambda_c\) are equivalent conductances at concentrations zero and \(c\) respectively, \(A\) and \(B\) are constants depending on the dielectric constant and viscosity of the solvent, temperature and ionic charges and \(\omega = 0.586\) for univalent electrolytes and is a function of the ionic charges and mobilities for more highly charged electrolytes. Therefore in a particular solvent at a particular temperature the slope
is a function of the ionic charge. The slope obtained for various samples are compared with those obtained for known 1:1 electrolytes.

**Materials:**
- Ruthenium trichloride trihydrate (Johnson Matthey);
- triphenylphosphine (Aldrich);
- trimethylphosphite (Fisons);
- dimethylphenylphosphonite, methyldiphenylphosphinite, ethyldiphenylphosphinite (Maybridge);
- sodium tetraphenylborate (BDH);
- ammonium hexafluorophosphate (Alfa). All reactions were carried out in degassed solvents under a nitrogen atmosphere. RuCl$_2$(PPh$_3$)$_3$ was prepared as described earlier.$^{14}$

**Dichlorotetakis(trimethylphosphite)ruthenium(II):**
- RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OMe)$_3$ (0.4cm$^3$) in hexane (20cm$^3$) for 1 hour. The solution was cooled and the yellow crystals obtained were filtered off and recrystallised from CH$_2$Cl$_2$/hexane (0.63g, 45%), m.p. 145-147°C.

**Dichlorotetakis(dimethylphenylphosphonite)ruthenium(II):**
- RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OMe)$_2$Ph (0.4cm$^3$) in hexane (20cm$^3$) for 3 hours to give yellow crystals which were filtered off and recrystallised from CH$_2$Cl$_2$/hexane (0.125g, 75%); m.p. 158-160°C.

**Dichlorotris(ethyldiphenylphosphinite)ruthenium(II):**
- RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OEt)Ph$_2$ (0.2cm$^3$) in hexane (20cm$^3$) for 3 hours. The resultant orange-brown solid was filtered off and washed with hexane (0.168g, 95%); m.p. 164-166°C; Mol. wt. in C$_6$H$_6$ at 294K: 834 (Required 820). The corresponding bromide was prepared similarly from RuBr$_2$(PPh$_3$)$_4$.

**Dichlorotris(ethyldiphenylphosphinite)ruthenium(II):**
- RuCl$_2$(PPh$_3$)$_3$ and P(OEt)Ph$_2$ (0.160g, 66%); m.p. 155-157°C; mol. wt. in C$_6$H$_6$ at 294K: 925 (Required 862). The corresponding bromide was prepared from RuBr$_2$(PPh$_3$)$_4$.

**Hexakis(dimethylphenylphosphonite)ruthenium(II) (tetraphenylborate):**
- RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OMe)$_2$Ph (0.4cm$^3$) in methanol.
(20cm$^3$) for 3 hours to give a very pale yellow solution which was cooled and NaBPh$_4$ (0.25g) added. A white solid precipitated which was filtered off and recrystallised from CH$_2$Cl$_2$-MeOH to give colourless crystals of the complex; m.p. 209-211°C.

[Chlorotetrakis(methylidiphenylphosphinite)ruthenium(II)] tetraphenylborate:-

RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OMe)Ph$_2$ (0.2cm$^3$) in methanol (20cm$^3$) for 5 minutes to give a deep red solution. The solution was filtered to remove any unreacted starting material. NaBPh$_4$ (0.25g) was then added and the precipitated solid filtered off and recrystallised from (CH$_3$)$_2$CO/MeOH to give a small amount of a red solid; m.p. 96-98°C; Conductivity in (CH$_3$)$_2$CO at 303K:- slope of graph = 140 (for [Ru$_2$Cl$_3$(P(OMe)Ph$_2$)$_6$]BF$_4$ slope = 155).

{Di-µ-chlorobis[tetrakis(ethylidiphenylphosphinite)ruthenium(II)]} tetraphenylborate was prepared similarly by reacting RuCl$_2$(PPh$_3$)$_3$ with P(OEt)Ph$_2$ in ethanol. m.p. 91-93°C; conductivity in (CH$_3$)$_2$CO at 303K:- slope of graph 175.

[Tri-µ-chlorohexakis(methylidiphenylphosphinite)diruthenium(II)] tetraphenylborate:-

RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OMe)Ph$_2$ (0.2cm$^3$) in MeOH (20cm$^3$) for 3 hours to give a yellow solution. Addition of NaBPh$_4$ (0.2g) produced a pale yellow solid which was filtered off and recrystallised from CH$_2$Cl$_2$-MeOH. m.p. 202-204°C. The above complex is also obtained by adding NaBPh$_4$ to a solution of RuCl$_2$(P(OMe)Ph$_2$)$_3$ dissolved in MeOH.

[Tri-µ-chlorohexakis(dimethylphenylphosphonite)diruthenium(II)] tetraphenylborate:-

RuCl$_2$(P(OMe)$_2$Ph)$_4$ (0.2g) was refluxed in MeOH (30cm$^3$) for 3 hours to give a yellow solution. Addition of NaBPh$_4$ precipitated a very pale yellow solid which was filtered off and washed with MeOH. m.p. 186-188°C.
RuCl$_2$(PPh$_3$)$_3$ (0.2g) was refluxed with P(OEt)Ph$_2$ (0.2cm$^3$) in EtOH (20cm$^3$) for 4 hours to give a pale yellow solution. Addition of NaBPh$_4$ (0.2g) precipitated the complex as a pale yellow solid which was filtered off and washed with EtOH. Attempts to recrystallise the complex resulted only in the formation of oils; m.p. 174-176°C; conductivity in (CH$_3$)$_2$CO at 303K: slope = 140. The corresponding hexafluorophosphate salt was obtained by addition of NH$_4$PF$_6$ to the pale yellow solution.
Table 2.1

Analytical data for some ruthenium complexes containing tertiary phosphite, phosphinite and phosphonite ligands.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found %</th>
<th>Calculated %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C  H  Cl</td>
<td>P  C  H  Cl</td>
</tr>
<tr>
<td>$\text{RuCl}_2 (\text{P(OMe)}_3)_4$</td>
<td>21.6 5.4</td>
<td>21.6 5.4</td>
</tr>
<tr>
<td>$\text{RuCl}_2 (\text{P(OMe)}_2 \text{Ph})_4$</td>
<td>45.0 5.2</td>
<td>45.0 5.2</td>
</tr>
<tr>
<td>$\text{RuCl}_2 (\text{P(OMe)}\text{Ph}_2)_3$</td>
<td>56.5 4.6 8.7</td>
<td>57.0 4.7 8.7</td>
</tr>
<tr>
<td>$\text{RuBr}_2 (\text{P(OMe)}\text{Ph}_2)_3$</td>
<td>50.2 4.3</td>
<td>51.4 4.3</td>
</tr>
<tr>
<td>$\text{RuCl}_2 (\text{P(OEt)}\text{Ph}_2)_3$</td>
<td>58.1 5.2 8.1</td>
<td>58.3 5.2 8.2</td>
</tr>
<tr>
<td>$\text{RuBr}_2 (\text{P(OEt)}\text{Ph}_2)_3$</td>
<td>54.5 4.7</td>
<td>53.0 4.7</td>
</tr>
<tr>
<td>$[\text{Ru(PO\text{Me})}_2 \text{Ph}_2]_6 (\text{BF}_4)_2$</td>
<td>65.2 6.0</td>
<td>65.5 6.0</td>
</tr>
<tr>
<td>$[\text{RuCl(PO\text{Me})_2 Ph}_2)_4 B\text{Ph}_4$ a</td>
<td>68.3 5.3 3.6</td>
<td>69.1 5.4 2.7</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_2 (\text{PO\text{Et Ph}_2})_8 (\text{BF}_4)_2$ a</td>
<td>69.6 5.8 2.6</td>
<td>69.8 5.8 2.6</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3 (\text{PO\text{Me Ph}_2})_6 B\text{Ph}_4$</td>
<td>63.6 5.1</td>
<td>63.6 5.1</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3 (\text{PO\text{Me Ph}_2})_6 B\text{Ph}_4$</td>
<td>52.3 5.3</td>
<td>52.4 5.2</td>
</tr>
<tr>
<td>$[\text{Ru}_3\text{Cl}_5 (\text{PO\text{Et Ph}_2})_9 B\text{Ph}_4$</td>
<td>60.1 5.2 6.3 8.7</td>
<td>62.7 5.2 6.3 9.7</td>
</tr>
<tr>
<td>$[\text{Ru}_3\text{Cl}_5 (\text{PO\text{Et Ph}_2})_9 \text{PF}_6$</td>
<td>54.2 5.0</td>
<td>56.1 5.1</td>
</tr>
</tbody>
</table>

a - analytical data were obtained for recrystallised product (see experimental section) whereas $^{31}$P n.m.r. and $^1$H n.m.r. spectroscopic data were obtained on product before recrystallisation which also contains some of the rearranged starting material.
### Table 2.2

**Far infra-red spectra (400-200 cm\(^{-1}\)) of some ruthenium complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bands (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{RuCl}_2(\text{P(OMe)}_3)_4)</td>
<td>340s, 306s, 295s, 284m, 274m, 260w, 250w, 210s</td>
</tr>
<tr>
<td>(\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4)</td>
<td>324s, 308m, 291s, 257sh, 214s</td>
</tr>
<tr>
<td>(\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3)</td>
<td>337s, 290s, 280sh</td>
</tr>
<tr>
<td>(\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_3)</td>
<td>328s, 298w, 286s, 272m, 253m, 234m, 214m</td>
</tr>
<tr>
<td>(\left[\text{RuCl}_3(\text{P(OMe)}\text{Ph}_2)_6\right]\text{BPh}_4)</td>
<td>295s, 260bs, 228w</td>
</tr>
<tr>
<td>(\left[\text{RuCl}_5(\text{P(OEt)}\text{Ph}_2)_9\right]\text{BPh}_4)</td>
<td>314m, 288(^a), 272(^a), 256(^a), 242(^a)</td>
</tr>
<tr>
<td>(\left[\text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4\right]\text{BPh}_4)</td>
<td>290, 275sh</td>
</tr>
<tr>
<td>(\left<a href="%5Ctext%7BBPh%7D_4">\text{Ru}_2\text{Cl}_2(\text{P(OEt)}\text{Ph}_2)_8\right</a>_2)</td>
<td>270sb</td>
</tr>
</tbody>
</table>

s - strong  m - medium  w - weak  b - broad  sh - shoulder

\(^a\) - superimposed on broad band centred at approximately 260 cm\(^{-1}\)
Table 2.3

$^1$H n.m.r. data for some ruthenium complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp.(K)</th>
<th>$^5$ value</th>
<th>Ph</th>
<th>$CH_2$</th>
<th>$CH_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}_3)_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td></td>
<td></td>
<td></td>
<td>3.84$^a$</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.2(m)</td>
<td></td>
<td></td>
<td>3.45$^a$</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3$</td>
<td>C$_6$D$_6$</td>
<td>301</td>
<td>7.7(m), 6.92</td>
<td></td>
<td></td>
<td>2.90$^b$</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_3$</td>
<td>C$_6$D$_6$</td>
<td>301</td>
<td>7.7(m), 6.90</td>
<td>3.40$^c$</td>
<td>0.78(t)</td>
<td>$J_{\text{HH}}$ = 7Hz</td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4]^+\text{BPh}_4$</td>
<td>(CD$_3$)$_2$CO</td>
<td>301</td>
<td>7.2(m), 6.8$^d$</td>
<td></td>
<td></td>
<td>3.15$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_2(\text{P(OEt)}\text{Ph}_2)_8]^+\text{BPh}_4$</td>
<td>(CD$_3$)$_2$CO</td>
<td>301</td>
<td>7.2(m), 6.8$^d$</td>
<td>3.40$^c$</td>
<td>1.25(t)</td>
<td>$J_{\text{HH}}$ = 7Hz</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph}_2)_6]^+\text{BPh}_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.1(m), 6.9$^d$</td>
<td></td>
<td></td>
<td>2.95$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}_2\text{Ph})_6]^+\text{BPh}_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.2(m), 7.0$^d$</td>
<td></td>
<td></td>
<td>3.45$^a$</td>
</tr>
<tr>
<td>$[\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph}_2)_9]^+\text{BPh}_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.3(m)$^e$, 7.0$^d$</td>
<td>2.96$^c$</td>
<td>1.18(t)</td>
<td>$J_{\text{HH}}$ = 7Hz</td>
</tr>
</tbody>
</table>

$^a$ - symmetrical "quintet". $^b$ - 'pseudo-triplet' (for origin of such a pattern see Appendix 1)
$c$ - broad . $^d$ - multiplet due to BPh$_4^-$. $^e$ - ratio of Ph:Et = 28:9 (Required 26:9)

(t) - triplet . (m) - multiplet.
Table 2.4

$^{31}$P n.m.r. data for some ruthenium complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp.(K)</th>
<th>Position (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}_3)_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>129.43(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4$</td>
<td>CDCl$_3$</td>
<td>213</td>
<td>150.49(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3$</td>
<td>C$_6$D$_6$</td>
<td>298</td>
<td>149.51(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_3$</td>
<td>C$_6$D$_6$</td>
<td>298</td>
<td>144.67(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}_3\text{Ph})_6\text{BPh}_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>138.65(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_6\text{BPh}_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>168.68(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_9\text{BPh}_4$</td>
<td>CDCl$_3$</td>
<td>213</td>
<td>135(m)</td>
</tr>
<tr>
<td>$\text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4\text{BPh}_4$</td>
<td>(CD$_3$)$_2$CO</td>
<td>173</td>
<td>157(m) 140(m) 123(m)</td>
</tr>
<tr>
<td>$\text{RuCl}(\text{P(OEt)}\text{Ph}_2)_8\text{BPh}_4$</td>
<td>(CD$_3$)$_2$CO</td>
<td>173</td>
<td>148.1(t) 119.0(t) ($J_{PP} = 32.5$Hz)</td>
</tr>
</tbody>
</table>

s - singlet t - triplet m - multiplet
a - approximate temperature
b - broad
c - assignment of triplet and doublet based on the average position at higher temperatures
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp.(K)</th>
<th>Position (p.p.m.)</th>
<th>Ph</th>
<th>CH₂</th>
<th>CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl₂(P(OMe)Ph₂)₃</td>
<td>C₆D₆</td>
<td>318</td>
<td>134.33</td>
<td>-</td>
<td>54.83</td>
<td></td>
</tr>
<tr>
<td>RuCl₂(P(OEt)Ph₂)₃</td>
<td>C₆D₆</td>
<td>318</td>
<td>134.33</td>
<td>64.47</td>
<td>16.11</td>
<td></td>
</tr>
<tr>
<td>[Ru₂Cl₃(P(OMe)Ph₂)₆]BPh₄</td>
<td>CDCl₃</td>
<td>318</td>
<td>136.5, 125.4, 121.3</td>
<td>-</td>
<td>55.21</td>
<td></td>
</tr>
<tr>
<td>[Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄</td>
<td>CDCl₃</td>
<td>318</td>
<td>136.5, 125.5, 121.4</td>
<td>64.5</td>
<td>16.0</td>
<td></td>
</tr>
</tbody>
</table>

a - due to BPh₄

Table 2.5

1³C n.m.r. data for some ruthenium complexes
CHAPTER 3

Pyrolysis of complexes of the type \([\text{Ru}_2\text{Cl}_3\text{L}_6]\) \(X = \text{BF}_4^-, \text{Cl}^-, \text{SCN}^-, \text{CN}^-, \text{S}_2\text{PMe}_2^-\) and \([\text{Ru}_3\text{Cl}_7\text{L}_9]\) \(X = \text{P(OMe)Ph}_2\)

3.1 Introduction

No evidence for neutral Ru(II) dimeric or anionic complexes \(\text{Ru}_2\text{Cl}_4\text{L}_5\) or \([\text{Ru}_2\text{Cl}_3\text{L}_6][\text{RuCl}_3\text{L}_3]\) \((L = \text{P(OR)Ph}_2, \text{P(OR)}_2\text{Ph})\) was obtained from the exchange reactions of \(\text{RuCl}_2(\text{PPh}_3)_3\) with \(L\) and the subsequent rearrangements of the products in solution (see Chapter 2). However, the compound \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6]X\) \((X = \text{Cl}^-)\) has been shown to convert to \(\text{Ru}_2\text{Cl}_4(\text{PET}_2\text{Ph})_5\) by pyrolysis at 393K in \(n\)-propyl propionate or methyl acetate.\(^{104}\) Pyrolysis in acetone or methyl acetate at 333K \((X = \text{Cl}^-)\) produced \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6][\text{RuCl}_3(\text{PET}_2\text{Ph})_3]\)\(^{105}\) and for \(X = \text{SCN}^-, \text{CN}^-\) complexes in which the thiocyanate and cyanide groups were thought to be present in the anion. Therefore it was in an attempt to obtain analogous species containing tertiary phosphinite or phosphonite ligands that the following pyrolysis reactions were carried out.

3.2 Results and discussion

The yellow solution, obtained from the reaction of \([\text{RuCl}_2(\text{C}_7\text{H}_8)]_n\) with \(\text{P(OMe)Ph}_2\)\(^{88}\) (or the rearrangement of \(\text{RuCl}_2(\text{P(OMe)Ph}_2)_3\)) in methanol, which contains \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]\)\(^-\) was reduced in volume and pyrolysed at 393K for 12 hours. The resulting bright yellow crystals \((1)\) were shown by e.s.r. and magnetic measurements to be diamagnetic and the far infra-red spectrum \((400-2000\text{ cm}^{-1})\) contained only a broad band at 260\text{ cm}^{-1}, indicating the presence of a triple chloride bridge and no terminal chlorides. The infra-red spectrum \((4000-4000\text{ cm}^{-1})\) revealed extra features not present in the spectrum of \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]\)\(^{+}\) \(\text{BF}_4^+\) viz, a broad band at 3250\text{ cm}^{-1} and strong bands at 1090, 920 and 855\text{ cm}^{-1} suggesting the presence of \(\text{Ph}_2\text{POH}\) and \(\text{Ph}_2\text{PO}^-\) groups\(^{106}\) in addition to \(\text{P(OMe)Ph}_2\). The same compound is obtained by pyrolysis at 333K for 48 hours.
Although a full elemental analysis of (1) was obtained, it proved too insoluble for n.m.r. spectroscopy or molecular weight measurements and too involatile for mass spectroscopy. Therefore an X-ray structure determination was undertaken, the results of which are shown in Fig. 3.1 and Table 3.1.

Unlike the expected neutral dimer Ru₂Cl₄(P(OMe)Ph₂)₅, the product contains two methyldiphenylphosphinite groups and four other oxyphosphorus ligands. The diamagnetism of the compound and the long Ru...Ru distance (3.425Å), which indicate no direct metal-metal interaction, suggest a Ru(II) complex. One half of the molecule contains two P(OMe)Ph₂ and one P(OH)Ph₂ group and interatomic distances suggest that a proton on O(1) interacts primarily with O(5), whereas the other half of the molecule must formally contain one Ph₂PO⁻ group and two Ph₂P(OH) groups. The most plausible arrangement is to place protons on O(2) and O(4) both of which interact with the negative charge on O(3) (Fig. 3.2).

Fig. 3.2 Proposed molecular structure of Ru₂Cl₃(P(O)Ph₂)(P(OH)Ph₂)₃(P(OMe)Ph₂)₂
Fig. 3.1  Structure of $(\text{P(OMe)Ph}_2)_2(\text{P(OH)Ph}_2)\text{RuCl}_3$.

$\text{Ru}[\text{P(OH)}_{22}(\text{Ph}_2\text{PO})]_2$. 
Table 3.1

Selected bond lengths of \( \text{(P(OMe)Ph}_2\text{)}_2\text{(P(OH)Ph}_2\text{)}\text{RuCl}_3\text{Ru(P(0)Ph}_2\text{)}(\text{P(OH)Ph}_2\text{)}_2 \)

Estimated standard deviations are: Ru-Cl 0.015, Ru-P 0.018, P-O 0.05, P-C 0.07 and O-C 0.09 Å.

<table>
<thead>
<tr>
<th>Bond Length(Å)</th>
<th>Bond Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1) - Cl(1)</td>
<td>2.454</td>
</tr>
<tr>
<td>Ru(1) - Cl(2)</td>
<td>2.484</td>
</tr>
<tr>
<td>Ru(1) - Cl(3)</td>
<td>2.471</td>
</tr>
<tr>
<td>Ru(1) - P(1)</td>
<td>2.258</td>
</tr>
<tr>
<td>Ru(1) - P(2)</td>
<td>2.277</td>
</tr>
<tr>
<td>Ru(1) - P(3)</td>
<td>2.226</td>
</tr>
<tr>
<td>O(1) ... O(5)</td>
<td>2.66</td>
</tr>
<tr>
<td>O(1) ... O(6)</td>
<td>2.92</td>
</tr>
<tr>
<td>O(5) ... O(6)</td>
<td>3.05</td>
</tr>
<tr>
<td>Ru(1) ... Ru(2)</td>
<td>3.425</td>
</tr>
</tbody>
</table>

\( M = 1549; \) monoclinic plates; \( a = 13.19(1) \text{Å}, \) \( b = 21.98(2) \text{Å}, \)
\( c = 24.98(2) \text{Å}; \) space group \( P2_1/C; \) \( Z = 4; \) \( D_c = 1.49 \text{gcm}^{-3} \)
Two other examples of X-ray structures containing Ph₂POHCPPh₂ ligands are known. Hydrolysis of MX₂(Ph₂PCCF₃)₂ (M = Pd, Pt; X = Cl, Br, SCN) yields M₂X₂(P(OH)Ph₂)₂(P(O)Ph₂)₂¹⁰⁹ and prolonged reaction of M(S-S)₂ with P(OMe)Ph₂ (M = Pd S=S = -S₂PPh₂, -S₂CNEt₂; M = Pt S=S = -S₂PMe₂, -S₂CNEt₂) gives M(S-S)(P(OH)Ph₂)(P(O)Ph₂).¹¹⁰ The X-ray structures of Pd₂(SCN)₂(P(OH)Ph₂)₂(P(O)Ph₂)₂¹⁰⁹(2) and Pd(S₂PMe₂)(P(OH)Ph₂)(P(O)Ph₂) (3)¹¹⁰ contain short O..O distances (2.42 and 2.41Å respectively) indicating the existence of symmetrical hydrogen bonds between the Ph₂PO moieties.

Pd₂X₂(P(O)Ph₂)₂(P(O)Ph₂) (X = Cl, Br) have been prepared by reacting K₂PdX₄ with Ph₂PCL or Ph₂HPO in water¹¹¹, and further reaction with NaOH or AgNO₃ yields the phosphinato bridged polymer Pd(P(O)Ph₂)₂. In contrast treatment of PtCl₂ with Ph₂HPO gives PtCl(P(O)Ph₂)₁¹¹ (4) whose infra-red spectrum contains a broad band at 2280cm⁻¹ assigned to hydrogen bonded OH, three P-O stretches in the region 880-970cm⁻¹ but no evidence for terminal P=O or free P-OH. Further reaction with
AgOPPh$_2$ yields Pt(P(0)Ph$_2$)$_2$(P(OH)Ph$_2$)$_2$ (5) where the infra-red spectrum contains no v(OH) band indicative of a symmetrical hydrogen bond.

Hydrolysis of Pt(P(OR)Ph$_2$)$_4$ (R = Me, Bu) also gives Pt(P(0)Ph$_2$)$_2$(P(OH)Ph$_2$)$_2$ as well as PtH(P(0)Ph$_2$)(P(OH)Ph$_2$) and PtH(P(0)Ph$_2$)(P(OH)Ph$_2$)$_2^{112}$.

[Ru$_2$Cl$_3$(P(OMe)Ph$_2$)$_6$]BF$_4$ was recovered unchanged after pyrolysis for long periods, but for [Ru$_2$Cl$_3$(P(OMe)Ph$_2$)$_6$]X (X = SCN$^-$, CN$^-$, S$_2$PM$_2$) pyrolysis gave products not containing X$^-$ and with infra-red spectra and elemental analysis identical to (1). This suggests that the first step is nucleophilic attack of X$^-$ on a co-ordinated alkoxy group to give a Ph$_2$PO$^-$ group and RX, followed by stepwise hydrolysis of the P(OMe)Ph$_2$ groups, the partially hydrolysed product precipitating out because of its insolubility.

Attack of nucleophiles on co-ordinated tertiary phosphite, phosphinite and phosphonite ligands attached to cobalt$^{113}$ to give P(C)Ph$_2^-$ has
previously been demonstrated, but no evidence has been obtained for hydrolysis of such ligands while co-ordinated to a metal. In all other species containing Ph₂POOHPh₂ ligands the P(OH)Ph₂ group is thought to be formed by hydrolysis of free P(OR)Ph₂,¹¹⁰,¹¹² for which there is n.m.r. evidence, followed by subsequent attachment to the metal. However ³¹P n.m.r. evidence shows that there is no facile dissociation of P(OMe)Ph₂ from [Ru₂Cl₃(P(OMe)Ph₂)₆]Cl in solution, although in the case of Ru₂Cl₃(P(O)Ph₂)(P(OMe)Ph₂)₅ this may occur. Nevertheless due to the high temperature required for the formation of (1) it seems quite likely that hydrolysis of some co-ordinated P(OMe)Ph₂ groups does occur.

Pyrolysis of the yellow solution obtained from the reaction of [Ru₂Cl₃(C₇H₈)] and P(oEt)Ph₂ (or the rearrangement of RuCl₂(P(OEt)Ph₂)₃) in ethanol also gave an insoluble crystalline yellow solid (6) whose infra-red spectrum contains all the additional features obtained previously as well as bands characteristic of P(OEt)Ph₂. Compound (6) analyses well for P(OEt)Ph₂ but as the starting material in this case is known not to be the triple chloride bridged dimer, but a trimer (see Chapter 2) the mechanism of formation must involve cleavage of Ru-Cl bonds in addition to formation of Ph₂PO⁻ and Ph₂POH. However due to the insolubility of (6) the structure can only be determined by an X-ray analysis. Some preliminary studies have been carried out¹¹⁴ which show that the crystals are orthorhombic with space group Fddd and cell dimensions a = 26.01Å, b = 43.79Å, c = 24.56Å. Photographs indicate a substantially disordered structure and the calculated density indicates half a molecule per asymmetric unit (Dc = 1.50gcm⁻³ for Z = 16) suggesting that the molecules are distorted about a two fold axis of symmetry. Pyrolysis of [Ru₃Cl₅(P(OEt)Ph₂)₉]X

† The ³¹P n.m.r. spectra of these species are identical to that of [Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄ (Fig. 2.8 Page 37) and they have been wrongly formulated as [Ru₂Cl₃(P(OEt)Ph₂)₆]X in ref. 107.
(X = SCN⁻, CN⁻, S₂PMe₂) also gave (6) and pyrolysis of the yellow solution containing [Ru₃Cl₅(P(OEt)Ph₂)]⁺ in the presence of excess LiBr gave a yellow crystalline solid (7) analysing well for (P(OEt)Ph₂)₂(P(OH)Ph₂)RuBr₃Ru(P(OH)Ph₂)₂(P(0)Ph₂). Attempts to make (1), (6) or (7) undergo further reaction, e.g. halide bridge cleavage, were unsuccessful as was pyrolysis of [Ru₂Cl₅(P(OMe)₂)₂]Cl which gave only unchanged starting material. This is consistent with results obtained for the rate of nucleophilic attack on the R groups of P(OR)₂Ph which was found to be ca 20 times slower than for P(OR)Ph₂.¹¹³

† Compound (6) is also obtained if PClPh₂ is refluxed with RuCl₂(PPh₃)₃ in aqueous ethanol whereas in hexane³ Ru₂Cl₄(PClPh₂)₅ is formed.
3.3 Experimental

Microanalyses, infra-red spectra and melting points were obtained as in Chapter 2. Magnetic measurements were made on a Faraday balance by Dr. G. Hunter of Dundee University and e.s.r. spectra were run by Dr. R.M. Paton. \([\text{RuCl}_2(C_7H_8)]_n\) was prepared by a standard method.\(^{115}\)

def-tri-\(\mu\)-chloro-h-diphenylphosphinito-bis(diphenylphosphinous acid)-ac-bis(methyldiphenylphosphinite)diruthenium(II)\(^{\dagger}\) (1): (a) \([\text{RuCl}_2(C_7H_8)]_n\) (0.22g) was refluxed with an excess of \(\text{P(OMe)Ph}_2\) (0.50cm\(^3\)) in methanol (10cm\(^3\)) for 4h under nitrogen to give a yellow solution. The solution was filtered to remove any unchanged starting material and then concentrated to a volume of ca 5cm\(^3\). This solution was then pyrolysed in an evacuated sealed tube at 120°C for 12h. The bright yellow crystals were filtered off, washed with methanol and diethyl ether and dried in vacuo, m.p. 285°C (Found: C, 56.6; H, 4.5; Cl, 6.5; P, 13.0; Ru, 11.0. Calc. for \(C_{74}H_{69}Cl_3O_6P_6Ru_2\): C, 57.4; H, 4.5; Cl, 6.9; P, 12.0; Ru, 13.0%)

(b) \([\text{RuCl}_2(\text{P(OMe)Ph}_2)_3\] was dissolved in MeOH and the solution pyrolysed as above to give yellow crystals of (1).

(c) \([\text{RuCl}_2(C_7H_8)]_n\) (0.22g) and \(\text{P(OMe)Ph}_2\) (0.5cm\(^3\)) were refluxed in methanol for 4h. An aqueous solution of KSCN was then added and the mixture allowed to stand for several days during which time the yellow solid \([\text{tri-}\(\mu\)-chlorohexakis(methyldiphenylphosphinite)diruthenium(II)]\) thiocyanate was deposited. \([\nu(\text{CN}) 2020\text{cm}^{-1}\] (Found: C, 56.6; H, 4.6; N, 0.6; Calc. for \(C_{79}H_{78}Cl_3N_6P_6Ru_2S\): C, 57.0; H, 4.7; N, 0.8%).

\([\text{P(OMe)Ph}_2)_3\text{RuCl}_3\text{Ru(OMe)Ph}_2)_3\]SCN (0.2g) was then pyrolysed in n-propylpropionate (5cm\(^3\)) at 120°C to give (1). In a similar fashion pyrolysis of \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6\]X (X = CN\(^-\), \(\text{S}_2\text{PMe}_2\)) gave (1).

\(\dagger\) Following the suggestion in ref. 112, the term diphenylphosphinite has been used to describe P-bonded \(\text{Ph}_2\text{PO}^-\) rather than the previously used diphenylphosphinate.
def-tri-μ-chloro-h-diphenylphosphinito-bgi-tris(diphenylphosphinous acid)-ac-bis(ethyldiphenylphosphinite)diruthenium(II) (6):-(a) Prepared as for (1) by reaction of [RuCl₂(C₇H₈)]ₙ and P(OEt)Ph₂ in ethanol followed by concentration and pyrolysis at 120°C for 12 hours. m.p. 225°C (Found: C, 57.3; H, 4.6; Cl, 6.7; P, 11.9; Calc. for C₇₆H₇₃Cl₃O₆P₆Ru₂: C, 57.9; H, 4.6; Cl, 6.7; P, 11.8%)

(b) RuCl₂(P(OEt)Ph₂)₃ was dissolved in ethanol and the solution pyrolysed as above to give (6).

(c) [RuCl₂(C₇H₈)]ₙ was refluxed with an excess of P(OEt)Ph₂ in ethanol under nitrogen for 4h to give a yellow solution. An aqueous solution of KSCN was added and the mixture allowed to stand for several days during which time the yellow solid [Ru₃Cl₅(P(OEt)Ph₂)₉(SCN)] was deposited [ν(CN) 2020cm⁻¹] (Found: C, 58.2; H, 5.1; N, 0.8; Calc. for C₁₂₇H₁₃₅Cl₅NO₉P₉Ru₃: C, 58.4; H, 5.2; N, 0.9%).

In a similar fashion pyrolysis of [Ru₃Cl₅(P(OEt)Ph₂)₉]ₓ (x = CN⁻, S₂PH₂) gave (6).

def-tri-μ-bromo-h-diphenylphosphinito-bgi-tris(diphenylphosphinous acid)-ac-bis(ethyldiphenylphosphinite)diruthenium(II) (7):-[RuCl₂(C₇H₈)]ₙ (0.22g) was refluxed with an excess of P(OEt)Ph₂ (0.5cm³) for 4h in ethanol to give a yellow solution. This was reduced in volume and an excess of LiBr (0.25g) added. The mixture was then pyrolysed at 120°C for 12h and the resulting yellow crystals filtered off and washed with ethanol and diethyl ether, m.p. 220°C (Found: C, 52.9; H, 4.3; Br, 13.9; P, 11.4; Calc. for C₇₆H₇₃Br₃O₆P₆Ru₂: C, 53.4; H, 4.3; Br, 14.0; P, 10.9%)
Chapter 4

Exchange reactions of RuCl₄Y(PPh₃)₄ with L (L = P(OR)Ph₂, P(OR)₂Ph; Y = CO, CS) and reactions of RuCl₂L₃ or 4 with carbon monoxide and carbon disulphide.

4.1 Introduction

Due to the success of the exchange reactions of RuCl₂(PPh₃)₃ with excess L to produce RuCl₂(P(OR)Ph₂)₃ (R = Me, Et) and RuCl₂(P(OMe)₂Ph)₄ (see Chapter 2), attempts have been made to prepare complexes of the type Ru₂Cl₄YL₄ (Y = CO, CS; L = P(OR)Ph₂, P(OR)₂Ph) by means of direct exchange between Ru₂Cl₄Y(PPh₃)₄ (1) and excess L. The results obtained have led to an investigation of the reactions of RuCl₂L₃ or 4 with CO and CS₂.

![Chemical Reaction](image)

(1) (Y = CO, CS)

4.2 Results and discussion

(a) Carbonyl complexes

Treating Ru₂Cl₄(CO)(PPh₃)₄ prepared by reaction of RuCl₂(CO)(PPh₃)₂ dm with RuCl₂(PPh₃)₃ (1:1 molar ratio)¹¹⁶ (see Chapter 6) with an excess of P(OMe)Ph₂ in C₆H₆ under reflux produces after 1 hour a bright yellow solution which, on addition of light petroleum (b.p. 60-80°C), yields a yellow solid (A). The $^{31}$P n.m.r. spectrum of (A) at 298K in C₆D₆ contains a singlet at 149.8 p.p.m. due to RuCl₂(P(OMe)Ph₂)₃ and a doublet and triplet at 114.9 and 136.4 p.p.m. respectively ($J_{PP} = 29.6$Hz), thought to arise
from RuCl₂(CO)(P(OMe)Ph₂)₃ since the mull infra-red spectrum contains a band at 1972 cm⁻¹ (ΔCO). Clearly, in addition to ligand exchange, bridge cleavage has also taken place as in equation [1]. The reaction was

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Ph}_3\text{P} - \text{Ru} - \text{Cl} - \text{Ru} - \text{PPh}_3 & + \text{excess L} \rightarrow \text{RuCl}_2\text{L}_3\text{or4} \\
\text{Ph}_3\text{P} & \quad \text{Cl}
\end{align*}
\]

repeated using a 1:4 molar ratio of Ru₂Cl₄(CO)(PPh₃)₄ to P(OMe)Ph₂ which gave the same products together with much unreacted starting material, thus indicating that the first step in this reaction is that of bridge cleavage. Unfortunately, chromatographic techniques failed to separate the two compounds and fractional recrystallisation proved impossible as it was found that both species rearranged in polar solvents.

However, a pure sample of RuCl₂(CO)(P(OMe)Ph₂)₃ could be obtained by bubbling CO through a solution of RuCl₂(P(OMe)Ph₂)₃ in cold C₆H₆. The i.r. spectrum, as for (A), contains a CO absorption band at 1972 cm⁻¹. In addition bands at 312 and 286 cm⁻¹, consistent with \(\nu(\text{RuCl})\) vibrations from a chloride \textit{trans} to CO and a chloride \textit{trans} to phosphorus respectively, appear in the far infra-red spectrum. The \(^{31}\text{Pn.m.r.}\) spectrum exhibits an identical doublet and triplet pattern to that found for solid (A) while the \(^{1}\text{Hn.m.r.}\) spectrum at 301K in C₆D₆ consists of a 1, 2, 1 triplet at 3.196 and a doublet at 2.845 of intensity ratio 2:1. These results are consistent with structure (2) containing \textit{cis} chloride groups and two magnetically equivalent and one non-equivalent tertiary phosphinite groups. The methyls of the \textit{trans}-P(OMe)Ph₂ groups give rise to the triplet at 3.198 in the \(^{1}\text{Hn.m.r.}\) spectrum (see Appendix 1) and the
Similarly, treatment of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$ with an excess of P(OEt)$_2$Ph$_2$ produces a mixture of RuCl$_2$(P(OEt)$_2$Ph)$_3$ and RuCl$_2$(CO)(P(OEt)$_2$Ph)$_3$ which could not be separated. However, like RuCl$_2$(CO)(P(OMe)$_2$Ph)$_3$, RuCl$_2$(CO)(P(OEt)$_2$Ph)$_3$ can be prepared by reaction of RuCl$_2$(P(OEt)$_2$Ph)$_3$ with CO in benzene. The $^{31}$P n.m.r. (Table 4.3), infra-red ($\nu$(CO) $1980$cm$^{-1}$, $\nu$(RuCl) $302$, $279$cm$^{-1}$) and $^1$H n.m.r. spectra (Table 4.2) are also consistent with structure (2).

Reaction of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$ with excess P(OMe)$_2$Ph produces, as expected, a mixture of RuCl$_2$(CO)(P(OMe)$_2$Ph)$_3$ and RuCl$_2$(P(OMe)$_2$Ph)$_4$. However, in this case, the complexes do not rearrange readily in polar solvents and recrystallisation from CH$_2$Cl$_2$/MeOH produces initially white crystals of RuCl$_2$(CO)(P(OMe)$_2$Ph)$_3$ and later yellow crystals of RuCl$_2$(P(OMe)$_2$Ph)$_4$ are deposited. The infra-red spectrum contains bands at $1985$cm$^{-1}$ due to $\nu$(CO) and at $305$ and $280$cm$^{-1}$ due to $\nu$(RuCl) vibrations. The $^{31}$P n.m.r. spectrum in C$_6$D$_6$ at 298K contains a doublet and triplet at 143.9 and 157.4p.p.m. respectively ($J_{PP} = 37.3$Hz), while the $^1$H n.m.r. spectrum under the same conditions contains two 1, 2, 1 triplets at 3.94$\delta$ and 3.69$\delta$ and a doublet at 3.61$\delta$ in the intensity ratio 1:1:1. Such a spectrum is consistent with the structure shown in Fig. 4.1. The methyl groups (a) and (b) are magnetically inequivalent and give rise to the two

$^+$ Note that this is the same isomer as found for RuCl$_2$(CO)(P(OR)Ph)$_3$ (2).
triplets whereas the methyl groups (c) which are equivalent give rise to the doublet.

The reaction of CO with RuCl$_2$(P(OMe)$_2$Ph)$_4$ in cold CH$_2$Cl$_2$ or benzene produced only unreacted starting material. In this case there is no vacant site to accommodate the CO molecule and hence a Ru-P bond must first be broken for the formation of RuCl$_2$(CO)(P(OMe)$_2$Ph)$_3$ to occur. Thus, passing CO through a refluxing solution of RuCl$_2$(P(OMe)$_2$Ph)$_4$ in benzene produces mainly RuCl$_2$(CO)(P(OMe)$_2$Ph)$_3$ in the same isomeric form as obtained above (spectroscopic evidence) but several other CO absorption bands in the i.r. spectrum and the appearance of a large number of much weaker resonances in the $^{31}$P n.m.r. spectrum of the product suggest also the formation of other isomeric forms and/or dicarbonyl complexes RuCl$_2$(CO)$_2$L$_2$ (L = P(OR)Ph$_2$, P(OR)$_2$Ph; R = Me, Et) have been previously prepared by addition of excess L to a carbonylated solution of 'RuCl$_3$·3H$_2$O' in 2-methoxyethanol. For these complexes, spectroscopic data indicated structure (3) containing cis carbonyls, cis chlorides and trans L groups. Treating [RuCl$_2$(CO)$_2$]$_n$ with
excess L in alcohols however produced mixtures of the dicarbonyl and

![Diagram](3)

monocarbonyl species RuCl₂(CO)₂L₂ and RuCl₂(CO)L₃ respectively, but the only monocarbonyl complex to be isolated in a pure state was RuCl₂(CO)(P(OEt)Ph₂)₃. Spectroscopic data indicated that the product had the same isomeric form as that obtained by reaction of CO with RuCl₂(P(OEt)Ph₂)₃. Subsequent reaction of the monocarbonyl complexes with CO in boiling C₆H₆ then produced the dicarbonyl species.¹¹⁷

Addition of excess L to the red solution, obtained by passing CO through a solution of 'RuCl₃·3H₂O' in boiling ethanol, produces the analogous RuCl₂(CO)L₃³⁸,⁸⁰ (L = PMe₂Ph, P₂Et₂Ph, PPr₂Ph, PBu₂Ph) while prolonged shaking of an ethanolic suspension of [Ru₂Cl₃(P₂Et₂Ph)₆]Cl with CO gives RuCl₂(CO)(P₂Et₂Ph)₃.¹⁷ On the basis of ¹H n.m.r. evidence³⁸ RuCl₂(CO)(PMe₂Ph)₃ prepared from the red solution was assigned configuration (4) whereas the same species prepared by action of CO on

![Diagram](4)
[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl} has configuration (2). \text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3 can also be prepared by the direct reaction of \text{RuCl}_2(\text{PMe}_2\text{Ph})_4 with \text{CO}, and was shown by $^{31}\text{P}$ n.m.r. studies to be, in this case, a mixture of the two isomers (2) and (4).

The complex \text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2 (all \text{trans} isomer) reacts under mild conditions with a wide range of ligands $L'$ to give monosubstituted $L'$ products \text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2L'^{\dagger}$. In the case, where $L'$ is a phosphorus donor ligand, the initial product has configuration (5) but on heating in solution this rearranges to an isomer of structure (6).

\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2 (all \text{cis} isomer) reacts also with a variety of ligands $L'$ to give products \text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2L' assigned structure (7). When $L'$ is $\text{P(OMe)}_n\text{Ph}_{3-n}$ ($n = 1, 2, 3$) heating isomer (7) in solution produces (6). All these observations are compatible with Scheme 4.1. The all \text{trans} isomer loses CO to form a five co-ordinate intermediate (8), and since on the basis of the principle of microscopic reversibility a ligand with a large \text{trans} labilising effect should also be kinetically \text{trans} directing, the kinetically preferred direction of attack on (8) should be \text{trans} to CO rather than \text{trans} to $\text{Cl}^-$. Hence ligands $L'$ which bind strongly to ruthenium(II) (e.g. phosphorus donor ligands) will form products of structure (5) initially, although these may rearrange to the more thermodynamically stable isomer (6) on heating. Ligands which bind less strongly will form products (6) directly. The stereochemistry of the reactions of the all \text{cis} isomer is also kinetically controlled. Initial formation of isomer (7) is attributed to loss of the carbonyl ligand opposite to the \text{trans} labilising $\text{PMe}_2\text{Ph}$ ligand giving intermediate (9).

$^{\dagger}$In accordance with the scheme given in reference 119, these five co-ordinate intermediates are written with trigonal bipyramidal structures. However, most known five co-ordinate ruthenium(II) compounds are essentially square pyramidal in structure as recently predicted by various theoreticians.
Scheme 4.1 Stereochemistry of carbonyl substitution reactions of RuCl₂(CO)₂(PMe₂Ph)₂.
This will pick up L' preferentially trans to PMe₂Ph rather than trans to chloride giving (7).

(b) Thiocarbonyl complexes

The first examples of transition metal thiocarbonyl complexes, trans-RhX(CS)(PPh₃)₂ and RhX₂(CS)(PPh₃)₂ (X = Cl, Br) were synthesised by Baird and Wilkinson in 1966. Since then, the relatively few thiocarbonyl complexes prepared have been restricted to Group VIII metals and manganese.

The reaction of RuCl₂(PPh₃)₃ with CS₂ produces three species viz. [RuCl₂(CS₂)(PPh₃)₂]Cl, [RuCl₂(CS)(PPh₃)₂]₂ (10) and Ru₂Cl₄(CS)(PPh₃)₄ (1) (Y = CS) and the mechanism of this reaction is discussed later in Chapter 6. When the dimer (10) is treated with excess Ph₄AsCl,HCl in acetone, conversion to Ph₄As[RuCl₃(CS)(PPh₃)₂]₂(acetone) occurs. This compound was not sufficiently soluble for ¹H or ³¹P n.m.r. studies but a strong band at 320cm⁻¹ appears in the infra-red spectrum characteristic of a trans RuCl₂ grouping, consistent with structure (11a) or (11b). In contrast the triple bridged dimer (1; Y = CS) reacts with Ph₄AsCl,HCl to give a neutral mixed Ru(II)/Ru(III) dimer Ru₂Cl₅(CS)(PPh₃)₅ (12). Shaking (10) in acetone produces a small amount of Ru₂Cl₄(CS)₂(PPh₃)₃ (13) whereas reacting the complex with L (L = CO, py) cleaves the halogen bridge to produce RuCl₂(CS)L(PPh₃)₂.
As for Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$, reactions of Ru$_2$Cl$_4$(CS)(PPh$_3$)$_4$ (1) with P(OR)Ph$_2$ give an inseparable mixture of RuCl$_2$(CS)(P(OR)Ph$_2$)$_3$ and RuCl$_2$(P(OR)Ph$_2$)$_3$ (R = Me, Et). However RuCl$_2$(CS)(P(OR)Ph$_2$)$_3$ can be obtained pure by treating [RuCl$_2$(CS)(PPh$_3$)$_2$]$_2$ (10) with P(OR)Ph$_2$. For RuCl$_2$(CS)(P(CMe)Ph$_2$)$_3$ the $^{31}$P.n.m.r. spectrum at 298K in C$_6$D$_6$ contains a triplet and doublet at 131.9 and 115.8 p.p.m. respectively ($J_{PP} = 29.7$Hz) and absorptions at 1275 cm$^{-1}$ ($\nu$(CS)) and 315 cm$^{-1}$ (chloride trans to CO).
and 286 cm\(^{-1}\) (chloride trans to phosphorus) are present in the infra-red spectra. The \(^1\)H n.m.r. spectrum in \(\text{CDCl}_3\) at 301 K consists of a triplet at 3.23 s and doublet at 3.14 s in the intensity ratio 2:1. Similar spectral data are obtained for \(\text{RuCl}_2(CS)(P(\text{OEt})\text{Ph}_2)_3\) (Tables 4.2 and 4.3) which, as for the corresponding carbonyl complexes is consistent with structure (2) \((Y = \text{CS})\).

The mixture produced in the reaction between \(\text{Ru}_2\text{Cl}_4(CS)(\text{PPh}_3)_4\) and excess \(\text{P(OMe)}_2\text{Ph}\) can be separated by recrystallisation from \(\text{CH}_2\text{Cl}_2/\text{MeOH}\) to give white crystals of \(\text{RuCl}_2(CS)(\text{P(OMe)}_2\text{Ph})_3\). The spectral data is again in agreement with structure (2), the \(^{31}\)P n.m.r. spectrum in \(\text{C}_6\text{D}_6\) at 298 K, in this case, displaying an AB\(_2\) pattern (Fig. 4.2).

Similar exchange reactions of \(\text{Ru}_2\text{Cl}_4(Y(\text{PPh}_3)_4\) with excess \(\text{PMe}_2\text{Ph}\) were carried out elsewhere\(^{118}\) and analogous results involving cleavage of the triple chloride bridge and replacement of \(\text{PPh}_3\) groups (equation [1]) were obtained. Wilkinson et al\(^{122}\) have reported that reaction of \([\text{RuCl}_2(CS)(\text{PPh}_3)_2]_2\) with \(\text{L} - \text{L}\) \((\text{L} - \text{L} = 2,2'\text{-bipyridyl}, 1,10\text{-phenanthroline})\) in benzene or ethanol produced \(\text{RuCl}_2(\text{PPh}_3)_2(\text{L-L})\) and the fate of the thiocarbonyl group was not established. However, at that time, the formation of the triple bridged dimer, from the reaction of \(\text{RuCl}_2(\text{PPh}_3)_3\) with \(\text{CS}_2\), was not recognised and \('[\text{RuCl}_2(CS)(\text{PPh}_3)_2]_2\',\) prepared by concentration of the solution after filtering off \([\text{RuCl}(\eta\text{CS}_2)(\text{PPh}_3)_3]\)\(_2\text{Cl}\), was likely to have contained a fairly high percentage of \(\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4\) \((1; Y = \text{CS})\). Hence, in view of the above results, reaction of the latter with \(\text{L-L}\) would be expected to yield some \(\text{RuCl}_2(\text{PPh}_3)_2(\text{L-L})\) (equation [2])

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \quad \text{Ph}_3\text{P} \\
\text{Ph}_3\text{P} & \quad \text{Ru} \quad \text{Cl} \quad \text{Ru} \quad \text{PPh}_3 \\
\text{CS} & \quad \text{PPh}_3 \\
+ 2(\text{L} - \text{L}) & \rightarrow \text{RuCl}_2(\text{PPh}_3)_2(\text{L-L}) \\
+ \text{RuCl}_2(CS)(\text{PPh}_3)_2(\text{L-L})
\end{align*}
\]
Fig. 4.2  31P n.m.r. spectrum of \( \text{RuCl}_2(\text{CS})(\text{P(OMe)}_2\text{Ph})_2 \text{ at } 298K \) in \( \text{C}_6\text{D}_6 \).
(c) **Rearrangement of RuCl₂YL₃ complexes in polar solvents**

As noted previously, difficulties arose when trying to separate mixtures of RuCl₂Y(P(OR)Ph₂)₃ and RuCl₂(P(OR)Ph₂)₃ because of the rearrangement of both species in polar solvents. The rearrangement of RuCl₂(P(OR)Ph₂)₃ has already been fully discussed (see Chapter 2). Dissolving RuCl₂Y(P(OMe)Ph₂)₃ (Y = CO, CS) in methanol and adding NaN₃ produced colourless crystals analysing well for [RuCl₂Y(P(OMe)Ph₂)₃]BF₄ (Table 4.1). The Mull i.r. spectra contain no evidence of co-ordinated solvent molecules but bands at ca 300 cm⁻¹ are attributed to v(RuCl) vibrations. The ³¹P n.m.r. spectra at both 213K and 298K consist of a singlet indicating monomeric structures in which all the tertiary phosphinite groups are equivalent. Possibilities to explain this equivalence include a trigonal bipyramidal structure such as (14) (but see footnote on page 88) or more likely a square pyramidal or weakly solvated octahedral structure such as (15) in which facile scrambling of the axial and equatorial phosphinite ligands renders them equivalent on the n.m.r. time-scale. This conclusion is supported by the ¹H n.m.r. spectra at 301K which exhibit a single broad resonance at 2.975. Furthermore, for each compound, conductivity measurements in CH₂Cl₂ are consistent with the presence of a 1:1 electrolyte in solution.

Dissolving RuCl₂Y(P(OEt)Ph₂)₃ in EtOH containing NaN₃ also slowly deposits colourless crystals analysing for [RuCl₂Y(P(OEt)Ph₂)₃]BF₄.
However, in contrast to \( \text{[RuCl}_2\text{Y(P(OMe)Ph}_2\text{)}_3\text{]}_{\text{BrPh}} \text{4} \) the \(^{31}\text{P n.m.r.} \) spectra at 213K display complicated multiplet patterns at ca 118 p.p.m. (see Fig. 4.3, \( \text{Y = CO} \)). These spectra are not entirely consistent with monomeric structures† where at 213K intramolecular scrambling would still be expected to occur, by analogy with the \( \text{P(OMe)Ph}_2 \) results, and therefore the presence of dimers at this temperature is probable. Moreover the complexity of the n.m.r. patterns suggest the presence of more than one isomer. The possible isomers of \([\text{Ru}_2\text{Cl}_2\text{Y}_{\text{2}}(\text{P(OEt)Ph}_2\text{})_{\text{6}}\text{]}_{\text{2+}}\) are shown in Fig. 4.4.

For \( \text{Y = CO} \) cooling the sample to 198K causes the resonance at 120.02 p.p.m. (Fig. 4.3) to decrease in intensity while the remainder of the spectrum remains unchanged, but on warming to 298K the entire multiplet collapses to a single resonance at 119 p.p.m. These results strongly indicate that the resonance at 120.02 p.p.m. is due to the monomer \([\text{RuCl(CO)(P(OEt)Ph}_2\text{)}_3\text{]}_{\text{3+}}\) which becomes increasingly more important as the temperature is raised and the dimer breaks down. Indeed conductivity measurements at 298K in CH\(_2\)Cl\(_2\) (see experimental section) are reasonably consistent with the presence of a 1:1 electrolyte. However the presence of a dimeric structure in the solid state for both \( \text{Y = CO} \) and \( \text{Y = CS} \) is substantiated by the presence of a broad band at 270 cm\(^{-1}\) in their far infra-red spectra.

The behaviour of \([\text{Ru}_2\text{Cl}_2(\text{CO})_{\text{2}}(\text{P(OEt)Ph}_2\text{)}_{\text{6}}\text{]}_{\text{2+}}\) is analogous to that found for \([\text{Ru}_2\text{Cl}_2(\text{P(OEt)Ph}_2\text{)}_{\text{6}}\text{]}_{\text{2+}}\) (see Chapter 2) and this ability of the P(OEt)Ph\(_2\) complexes to form dimeric species, compared with the corresponding P(OMe)Ph\(_2\) complexes which appear to exist entirely as monomers, must be due to an electronic effect rather than a steric effect since the

†The possibility of frozen-out monomeric structures at this temperature (due to the bulkier P(OEt)Ph\(_2\) groups) seems unlikely in view of the fact that the \(^{31}\text{P n.m.r.} \) spectrum of \( \text{RuCl}_2(\text{P(OEt)Ph}_2\text{)}_3 \) even at 213K is still a sharp singlet (see Chapter 2)
Fig. 4.3 $^{31}$P n.m.r. spectrum of $[\text{RuCl}(\text{CO})(\text{P(OEt)Ph})_1\text{ (BPh)}_{2-3-2}\text{ (BPh)}_{4-2}]$ in CDCl$_3$ at 213K.
smaller P(OMe)Ph₂ complexes would be expected to dimerise preferentially.

Several examples of ruthenium(II) double bridged dimers containing CO groups have been previously reported although none of these are cationic in nature. For example, one of the products obtained from the reaction of [Ph₃(PhCH₂)P][Ru(C₇H₈)(CO)Cl₃] with 2 moles of PPh₃ is [Ru(CO)Cl₂(PPh₃)₂]₂ (16), analogous to [Ru(CS)Cl₂(PPh₃)₂]₂ (10) the only double halide bridged ruthenium(II) dimer containing CS groups prior to the above work. Treating Ru₂Cl₄(PEt₂Ph)₅ with CO in diethyl ether produces a white complex formulated as Ru₂Cl₄(CO)(PEt₂Ph)₅, for which two isomeric forms were detected (17a) and (17b). Finally, during the isomerisation of all trans RuCl₂(CO)₂(PPh₂Ph)₂,¹¹⁹ which proceeds by loss

\[
\text{(16)}
\]

\[
\text{(17a)} \quad \text{(17b)}
\]

† The exact isomeric form of this compound is not known
Fig. 4.4 Possible isomers of \([\text{Ru}_2\text{Cl}_2(Y)\text{P}_5]^{2+}\) (P: P(OEt)Ph2).
of CO, a solid (18) is deposited, which is produced by dimerisation of the five co-ordinate intermediate RuCl₂(CO)(PMe₂Ph)₂.

\[
\begin{align*}
\text{PhMe₂P} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{PMe₂Ph} \\
\text{Ru} & \quad \text{CO} & \quad \text{PhMe₂P} & \quad \text{Cl} & \quad \text{PMe₂Ph}
\end{align*}
\]

This tendency of RuCl₂Y(P(OR)Ph₂)₃ to readily lose a chloride ion in methanol to generate apparently five co-ordinate monomeric cations [RuClY(P(OEt)Ph₂)₃]⁺ or six co-ordinate dimeric cations [Ru₂Cl₂Y₂(P(OEt)Ph₂)₆]²⁺ is unusual but not without precedent. Thus, recently MX₂(Ph₂P(CH₂)₃PFPh₂)₂ (M = Ru, Os X = Cl, Br) were shown to lose a halide ion in boiling alcohol to give the five co-ordinate cations [MX(dppe)₂]⁺ isolated as PF₆⁻ or BPh₄⁻ salts. Steric effects are clearly important here since the corresponding compounds with the smaller diphosphines Ph₂P(CH₂)nPFPh₂ (n = 1, 2) show no tendency to lose halide ion. Similarly, when RuCl₂Y(P(OMe)₂Ph)₃ is dissolved in methanol no cationic complexes are generated which can be attributed to the smaller steric requirements of the tertiary phosphonite groups. It is interesting to note, however, that much milder conditions are required for conversion to cationic species in the present work compared to the diphos work where boiling under reflux for long periods was required.

(d) Reactions of RuCl₂L₃ (L = PEtPh₂, P(OR)Ph₂) and RuCl₂L₄ (L = PMe₂Ph, PMePh₂, P(OMe)₂Ph) with CS₂

The reaction of RuCl₂(PPh₃)₃ with CS₂ as already stated earlier produces [RuCl(CS₂)(PPh₃)₃]Cl, [RuCl₂(CS)(PPh₃)₂]₂ and Ru₂Cl₄(CS)(PPh₃)₄.
Therefore, as previous attempts to prepare Ru$_2$Cl$_4$(CS)L$_4$ (L = P(OR)Ph$_2$, P(OMe)$_2$Ph, PMe$_2$Ph), by exchange reactions with Ru$_2$Cl$_4$(CS)(PPh$_3$)$_4$ had failed, it was considered of interest to find out if they could be obtained instead by direct reaction of RuCl$_2$L$_3$ or 4 with CS$_2$.

In addition to its important role in the formation of thiocarbonyl complexes however, carbon disulphide can co-ordinate to transition metals to form four distinctly different types of complexes which are first briefly discussed below.

(a) $\eta^1$CS$_2$ complexes

The reaction of RuX$_2$(PPh$_3$)$_3$ (X = Cl,Br) with PPh$_3$ in refluxing CS$_2$ gives a high yield of the ionic species [RuX($\eta^1$CS$_2$)(PPh$_3$)$_3$]$^+$ where the CS$_2$ group is bonded to the metal through both the carbon atom and one of the sulphur atoms. Several cationic $\eta^1$CS$_2$ complexes of rhodium, isolable as their tetraphenylborate salts have been prepared. For example reaction of RhCl(PPh$_3$)$_3$ with CS$_2$ and PPh$_3$ in methanol yields [Rh(PPh$_3$)$_3$(CS$_2$)($\eta^1$CS$_2$)]$^+$ (20) which also contains an S-bonded CS$_2$ group which is readily lost to give a stable cation. Addition of CS$_2$ to trans-RhCl(CO)(PPh$_3$)$_2$ and PPh$_3$ in methanol produces a blue solution and subsequent treatment of this blue solution with NaBPh$_4$ results in the

\[ \text{[Rh(PPh$_3$)$_3$(CS$_2$)($\eta^1$CS$_2$)]}^+ \]

\[ \text{[Rh(PPh$_3$)$_3$(CS$_2$)]} \]

The isomeric form of this complex is not known and two possibilities are presented.
precipitation of \([\text{Rh}(\text{CO})(\text{PPh}_3)_3(\eta^1\text{CS}_2)](\text{BPh}_4)\).

\[ \begin{array}{c}
\text{Ph}_3\text{P} \\
\text{Rh} \\
\text{Ph}_3\text{P} \\
\text{C} \equiv \text{S} \\
\text{S} \\
\text{S}
\end{array} \]

\[ (20) \]

(b) \textit{S}-bonded complexes

Examples of \textit{S}-bonded complexes are \([\text{Rh}(\text{PPh}_3)_3(\text{CS}_2)(\eta^1\text{CS}_2)]^+ \) (20) above and \(\text{RhCl}(\text{PPh}_3)_2(\text{SCS})(\eta^1\text{CS}_2)\) prepared by treating \(\text{RhCl}(\text{PPh}_3)_3\) with \textit{CS}_2.

(c) \textit{Complexes with bridging CS}_2 \textit{groups}

Reaction of \(\text{K}_2[\text{Co(CN)}_5]\) with \textit{CS}_2 produces \(\text{K}_6[\text{Co-CS}_2\text{Co(CN)}_5]\), the structure of which is uncertain and has been reported independently as (21a)\(^{126}\) in which only one sulphur atom is attached to a metal atom and (21b)\(^{127}\) where both sulphur atoms are bonded to metal atoms.

\[ \text{K}_6[\text{Co-CS}_2\text{Co(CN)}_5] \quad \text{(21a)} \]
\[ \text{K}_6[\text{Co-CS}_2\text{Co(CN)}_5] \quad \text{(21b)} \]

(d) \textit{CS}_2 \textit{insertion complexes}

The insertion of a \textit{CS}_2 molecule into an \(M-X\) bond (\(M = \text{transition metal}; X = \text{H, alkyl, aryl, amine, alkoxide}\)) can lead to a wide variety of dithio compounds (Scheme 4.2). An example of insertion into an \(\text{Rh-H}\) bond occurs in the reaction between \(\text{RhH(CO)(PPh}_3)_3\) and \textit{CS}_2\(^{128}\) which leads to the formation of \([\text{Rh(CO)(PPh}_3)_2\text{CS}_2]_2\text{S} \) (22) formed by the coupling together of two molecules of the insertion product.
Scheme 4.2 Insertion reactions of $\text{CS}_2$

$\text{Rh(CO)(PPh}_3)_2(\sigma\text{CS}_2)(\text{CSSH})$ with elimination of $\text{H}_2\text{S}$. Only one example of insertion of $\text{CS}_2$ into a metal-halogen viz. $[\text{Pt(PPh}_3)_2(\text{SSCF})]\text{HF}_2$, formed by reaction of $[\text{PtF(PPh}_3)_3]\text{HF}_2$ with $\text{CS}_2$\textsuperscript{129} is known. The crystal structure of the complex shows the dithiocarbic ligand to be co-ordinated through the two sulphur atoms.

Infra-red spectroscopy provides the best means of distinguishing
between the various types of bonding and the frequency ranges for the CS stretching absorptions for the different types of complexes are shown in Table 4.1.

### Table 4.1 \( \nu(\text{CS}) \) frequency ranges for the known types of transition metal \( \text{CS}_2 \) and thiocarbonyl complexes

<table>
<thead>
<tr>
<th>Type of complex</th>
<th>( \nu(\text{CS})(\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M-S = C = S} )</td>
<td>1520-1503</td>
</tr>
<tr>
<td>( \text{M-CS}_2\text{-M} )</td>
<td>980, 840c</td>
</tr>
<tr>
<td>( \text{M}_2\text{S}_2\text{CX}^d )</td>
<td>1267-815e, 780-612f</td>
</tr>
<tr>
<td>( \text{M}\text{-CS} )</td>
<td>1381-1193</td>
</tr>
</tbody>
</table>

- \( \nu(\text{C} = \text{S}) \) out of ring vibration
- \( \nu(\text{C} = \text{S}) \) in ring vibration
- c - data only available for one complex viz. \( \text{K}_6[(\text{CN})_5\text{CoCS}_2\text{Co(CN)}_5] \)
- d - \( X = \text{H}, \text{alkyl, aryl, amine} \)
- e - \( \nu(\text{CS}_2) \) asymm
- f - \( \nu(\text{CS}_2) \) sym

When \( \text{RuCl}_2(\text{PMe}_2\text{Ph})_4 \) is refluxed in \( \text{CS}_2 \) a purple solution is produced, which on cooling deposits a purple solid which gives a highly conducting solution in acetone. The infra-red spectrum contains a weak band at 1130 cm\(^{-1}\) consistent with a \( \pi \)-bonded \( \text{CS}_2 \) group. The \( ^{31}\text{Pn.m.r.} \) spectrum in CDCl\(_3\) at 298K (Fig. 4.5) contains a sharp singlet at 20.65 p.p.m. due to \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\)Cl and three sets of multiplets constituting an \( \text{ABC}_2 \) pattern \( \nu_A = 19.43\text{p.p.m.}, \nu_B = 15.71\text{p.p.m.}, \nu_C = 15.36\text{p.p.m.} \).
\[ \nu_C = 12.48 \text{p.p.m.}, \quad J_{AB} = 3.83 \text{Hz}, \quad J_{AC} = -14.75 \text{Hz}, \quad J_{BC} = 31.66 \text{Hz} \] 
(The calculated spectrum for such a set of parameters is shown in Fig. 4.6). The species giving rise to this pattern is almost certainly the ionic complex \([\text{Ru}(\text{CS}_2)(\text{PMe}_2\text{Ph})_4]^{2+}\) (23).†

\[
\begin{array}{c}
\text{PhMe}_2\text{P} \\
\text{PhMe}_2\text{P} \\
\text{Ru} \\
\text{PMe}_2\text{Ph} \\
\text{PMe}_2\text{Ph} \\
\text{S} \\
\end{array}
\]

\[ 2^+ \]

Similarly, reaction of \(\text{RuCl}_2(\text{PMePh}_2)_4\) with \(\text{CS}_2\) produces a blue-purple conducting solid and spectroscopic and conductivity data on this is consistent with the formulation \([\text{Ru}(\text{CS}_2)(\text{PMePh}_2)_4]\text{Cl}_2\). The \(^{31}\text{P}\) n.m.r. spectrum in \(\text{CDCl}_3\) at 298K (Fig. 4.7) is also an \(\text{ABC}_2\) pattern. \(\nu_A = 12.96 \text{p.p.m.}, \nu_B = 10.66 \text{p.p.m.}, \nu_C = 6.84 \text{p.p.m.}, \quad J_{AB} = 9.67 \text{Hz}, \quad J_{AC} = 28.36 \text{Hz}, \quad J_{BC} = 4.78 \text{Hz}\) (see Fig. 4.8 for the calculated spectrum).

A related complex containing four tertiary phosphine groups \([\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]\text{PF}_6\) has been synthesised, as an orange complex, from the reaction between \(\text{CS}_2\) and \([\text{RuH}(\text{PMe}_2\text{Ph})_5]\text{PF}_6\).† This complex undergoes an unusual rearrangement reaction in methanol to give a purple compound \([\text{Ru}(\text{S}_2\text{C(H)PMe}_2\text{Ph})(\text{PMe}_2\text{Ph})_3]\) (24) shown by X-ray analysis to contain a phosphonium betaine group. However under sterically favourable conditions the \(\text{PMe}_2\text{Ph}\) group can be transferred back onto the Ru atom. Thus,

† Attempts to separate this complex from the ionic dimer were unfortunately unsuccessful and hence a good elemental analysis could not be obtained.
31P nmr spectrum of [Ru(h(CS$_2$)PMe$_3$)$_2$Ph$_2$]Cl$_2$ in CDCl$_3$ at 298 K

chemical shift (ppm)
Line width $= 1\text{ Hz}$.

\[
\begin{align*}
J_{AB} &= 3.83, \\
J_{AC} &= 14.75, \\
J_{BC} &= 31.66\text{ Hz}, \\
J_A &= 19.43, \\
J_B &= 15.71, \\
J_C &= 12.48 \text{ ppm}
\end{align*}
\]

Fig. 4.6. Calculated AB$_2$C spectrum for parameters.
reaction of (24) with L = P(OMe)₃ yielded $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_2L_2]\text{PF}_6$
whilst with the larger phosphinite $L' = \text{P(OMe)}_2\text{Ph}_2$,
$[\text{Ru}(\text{S}_2\text{C(H)PMe}_2\text{Ph})(\text{PMe}_2\text{Ph})L'_2]\text{PF}_6$ was obtained.

The complex $[\text{Ru}(\eta\text{CS}_2)(\text{PMePh}_2)_4]\text{Cl}_2$ does not rearrange in methanol
at ambient temperatures since addition of $\text{NaBPh}_4$, to a solution of the
complex dissolved in methanol, precipitates a dark blue complex whose
$^{31}\text{P n.m.r.}$ spectrum is identical to that in Fig. 4.7. However for
$[\text{Ru}(\eta\text{CS}_2)(\text{PMe}_2\text{Ph})_4]\text{Cl}_2$ dissolved in methanol the precipitated $\text{BPh}_4^-$ salt
exhibits a different $^{31}\text{P n.m.r.}$ spectrum (Fig. 4.9) to that of the start-
ing material. Most of the spectrum is very similar to that shown in Fig.
4.5 except that the multiplet at ca 20p.p.m. (Fig. 4.5) is no longer pre-
sent although additional signals now occur at ca 16p.p.m. This indicates
that the environment of one of the $\text{PMe}_2\text{Ph}$ groups, which was originally
trans to either the C or S of the $\text{CS}_2$ group, has changed but that none
of the other chemical shifts nor the coupling constants have altered very
much. Furthermore, apart from additional bands due to the anion no sig-
nificant changes are observed in the infra-red spectrum.

By analogy with the recent work of Ashworth and Singleton,¹³⁰ one
explanation of this change in methanol might be the facile transfer of a
$\text{PMe}_2\text{Ph}$ group to the $\eta\text{CS}_2$ group. However, if this was true some changes
would surely occur in the coupling constants exhibited by the other three
Fig. 4.7. $^{31}$P n.m.r. spectrum of $[\text{Ru} \eta^1\text{CS}_2 \{\text{PMePh}_2\}_4]\text{Cl}_2$ at 298K in CDCl$_3$.
Fig. 4.8. Calculated ABC$_2$ spectrum for parameters

$\nu_A = 12.96$, $\nu_B = 10.66$, $\nu_C = 6.84$ p.p.m.

$J_{AB} = 9.67$, $J_{AC} = 28.36$, $J_{BC} = 4.78$ Hz.

line width = 2.5 Hz.
Fig 4.9 $^{31}$P n.m.r. spectrum of the rearrangement product of $[\text{Ru}(\text{CS}_2)(\text{PMe}_2\text{Ph})_4]^{2+}$ in CDCl$_3$ at 298K.
PMe₂Ph groups and a bigger chemical shift change in the transferred PMe₂Ph group would be expected. Formation of species such as [Ru(SCS)(PMe₂Ph)₄MeOH]²⁺ with an S-bonded CS₂ group can also be discounted because of the similarity of the i.r. spectra of the two complexes.

The only other possibility appears to be the formation of a CS₂ bridged species such as (25) where it would be expected that the chemical shift of the PMe₂Ph groups trans to the co-ordinated sulphur atom would be the most affected compared to that in compound (23). A reasonable mechanism of formation of (25) would involve the generation of the solvated intermediate (26) followed by rapid dimerisation which might account for the inability of the corresponding PMePh₂ cation (which contains a lower trans effect ligand) to rearrange in methanol under these mild conditions.
When RuCl$_2$(PETPh$_2$)$_3$ is refluxed in CS$_2$ a red-pink solid is produced which analyses for [RuCl(η-CS$_2$)(PETPh$_2$)$_3$]Cl.CS$_2$ (27). The infra-red spectrum contains a strong band at 1515 cm$^{-1}$ which as for [RuCl(η-CS$_2$)(PPh$_3$)$_3$]Cl.CS$_2$ is associated with a CS$_2$ solvate. This is proven by dissolving the complex in CH$_2$Cl$_2$ and reprecipitating with light petroleum (b.p. 60-80°C) to give a product analysing for [RuCl(η-CS$_2$)(PETPh$_2$)$_3$]Cl whose i.r. spectrum no longer contains the band at 1515 cm$^{-1}$. Bands at 1115 and 995 cm$^{-1}$ attributed to η-CS$_2$ are also present. The $^{31}$P n.m.r. spectrum in CDCl$_3$ at 298K consists of an AMX pattern (Fig. 4.10) $\nu_X = 41.1$ p.p.m., $\nu_M = 34.0$ p.p.m., $\nu_X = 9.2$ p.p.m., $J_{AM} = 28.9$ Hz, $J_{AX} = 3.7$ Hz, $J_{MX} = 9.2$ Hz, consistent with the above formulation with each PETPh$_2$ trans to a different atom (27). In view of this it seems probable that the corresponding triphenylphosphine complex [RuCl(η-CS$_2$)(PPh$_3$)$_3$]Cl also exists in the same isomeric form (19b).

Dissolving [RuCl(η-CS$_2$)(PETPh$_2$)$_3$]Cl.CS$_2$ in methanol produces a highly conducting purple solution which on standing for several hours gradually turns blue in colour and eventually goes green, the latter change being most likely due to oxidation to a Ru(III) species. However addition of NaBPh$_4$ to the purple solution produces a purple solid (28) analysing reasonably well for [Ru(η-CS$_2$)Cl(PETPh$_2$)$_3$]BPh$_4$. However, although the $^{31}$P n.m.r. spectrum at 298K in CDCl$_3$ is an AMX pattern (Fig. 4.11) the parameters $\nu_A = 44.64$ p.p.m., $\nu_M = 29.03$ p.p.m., $\nu_X = 16.35$ p.p.m., $J_{AM} = 28.0$ Hz, $J_{AX} = 3.5$ Hz, $J_{MX} = 11.3$ Hz are different from that of (27). A new band at 850 cm$^{-1}$ also appears in the infra-red spectrum which could possibly be due to bridging CS$_2$ groups (see Table 4.1) but the $^1$H n.m.r. spectra of both (27) and (28) are broad and no significant difference could be detected. One possible explanation of the above results is the formation of a dimer with bridging CS$_2$ groups and three PETPh$_2$ groups on

† The difference in chemical shifts is too large to be due solely to the different anion
Fig. 4.10. $^{31}$Pnmr. spectrum of $[\text{RuCl}([\text{CS}_2])(\text{PEtPh}_2)_3]\text{Cl}$ in CDCl$_3$ at 298K.
Fig. 4.11. $^{31}$P n.m.r. spectrum of $[\text{RuCl}(\text{CS$_2$})(\text{PETPh$_2$})_2\text{][BPh$_4$}]_2$ in CDCl$_3$ at 298K.
each Ru ion. Each of the three tertiary phosphine groups is in a different chemical environment which means that the bridging group must bond through C and S. As for the corresponding \([\text{Ru}(\text{CS}_2)(\text{PMe}_2\text{Ph})_4]_2(\text{BPh}_4)_4\)

\[
\begin{array}{c}
\text{Cl} \\
\text{S} \\
\text{C} \\
\text{Ru} \\
\text{S} \\
\text{C} \\
\text{Cl}
\end{array}
\]

(27)

\[
\begin{array}{c}
\text{Cl} \\
\text{S} \\
\text{C} \\
\text{Ru} \\
\text{S} \\
\text{C} \\
\text{Cl}
\end{array}
\]

(28)

Solvolysis of (27) followed by ready dimerisation to give (28) appears to be a reasonable method of formation. Unfortunately no solid could be obtained from the blue solution formed on further rearrangement of (28).

After filtering off \([\text{RuCl} (\eta\text{CS}_2)(\text{PETPh}_2)_3]\text{Cl}\cdot\text{CS}_2\) formed in this reaction between \(\text{RuCl}_2(\text{PETPh}_2)_3\) and \(\text{CS}_2\), an orange solution remained which on standing deposited a non-conducting orange solid. Its infra-red spectrum contains a strong band at \(1295\text{cm}^{-1}\) attributed to \(\nu(\text{CS})\) vibrations while its \(^{31}\text{P n.m.r.}\) spectrum at \(298\text{K}\) in CDCl\(_3\) (Fig. 4.12) consists predominantly of a singlet at \(49.17\text{p.p.m.}\) and an AB pattern centred at \(36.79\text{p.p.m.}\) (\(J_{AB} = 35.7, \Delta_{AB} = 84.1\text{Hz}\)) attributed to the triple bridged dimer \(\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PETPh}_2)_3\) (29). The spectrum also contains weaker resonances at \(43.35\text{p.p.m.}\) (singlet) due to the starting material \(\text{RuCl}_2(\text{PETPh}_2)_3\) and other signals at \(48.42\) (singlet), \(37.75\) (singlet).

\[\text{See Appendix 2 for analysis of an AB type spectrum}\]

\[\text{There are three possible isomeric forms of this complex which are shown for the corresponding } \text{Ru}_2\text{Cl}_4(\text{L})_2(\text{PPh}_3)_3 \text{ in Fig. 6.2, but it is not possible to tell from the above data which isomer of } \text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PETPh}_2)_3 \text{ is formed}\]
Fig. 4.12 $^{31}$P n.m.r. spectrum of $\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PEtPh}_2)_3$ in CDCl$_3$ at 298K.
and 18 p.p.m. (multiplet) the origins of which are unknown.

The attempted reactions of $\text{RuCl}_2(P(\text{OR})\text{Ph}_2)_3$ ($R = \text{Me, Et}$) and $\text{RuCl}_2(P(\text{OMe})_2\text{Ph})_4$ with $\text{CS}_2$ were not very successful. $\text{RuCl}_2(P(\text{OMe})_2\text{Ph})_4$ remained completely unchanged whereas with $\text{RuCl}_2(P(\text{OR})\text{Ph}_2)_3$ orange solids were obtained whose $^{31}\text{P\,n.m.r.}$ spectra in $\text{CDCl}_3$ at 298K contained complicated multiplet patterns in the region 138-145 p.p.m. and strong resonances due to $\text{RuCl}_2(P(CR)\text{Ph}_2)_3$ and the rearrangement products of $\text{RuCl}_2(P(CR)\text{Ph}_2)_3$ (see Chapter 2).

However, although the reactions of $\text{RuCl}_2L_3$ or $4 \ (L = \text{tertiary phosphine})$ compounds with $\text{CS}_2$, unlike the reaction of $\text{RuCl}_2(P\text{Ph}_3)_3$, have produced only one dimeric neutral complex containing a thiocarbonyl group viz. $\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PETPh}_2)_3$, a number of interesting carbon disulphide complexes including possibly some bridged carbon disulphide complexes have been prepared by this route.
4.3 Experimental

General experimental techniques were as for Chapter 2. The calculated spectra were obtained by first gaining approximate values to the parameters using the SIMEQ computer program in conjunction with the XL-100 spectrometer, and then refining the values obtained using the LAOCCON computer program. Using the refined parameters the spectra were plotted out on the XL-100 spectrometer using a line width corresponding to the observed spectrum.

Materials:— carbon monoxide (Air Products), carbon disulphide (Fisons). RuCl₂(CS)(PPh₃)₂¹²¹, Ru₂Cl₄(CS)(PPh₃)₄¹²¹, cis-RuCl₂(PMe₂Ph)₄⁷³ and RuCl₂(PMe₃H)(PPh₃)₄⁷³ were prepared by standard literature methods and RuCl₂(PMe₂Ph)₄⁷⁸ was prepared by a procedure analogous to that of cis-RuCl₂(PMe₂Ph)₄. All reactions were carried out in degassed solvents and, apart from carbonylation reactions, under an atmosphere of nitrogen.

Dichlorocarbonyltris(methylidiphenylphosphinite)ruthenium(II):— carbon monoxide gas was bubbled through a solution of RuCl₂(P(OMe)Ph₂)₃ in benzene for 1 minute. The resulting pale yellow solution was reduced in volume and light petroleum (b.p. 60-80°C) added. A pale yellow solid precipitated which was filtered off and washed with light petroleum (b.p. 60-80°C); i.r. spectrum ν(co) 1972 cm⁻¹; far i.r. spectrum 312, 266, 275, 233 cm⁻¹; m.p. 128-130°C. A similar method was used to prepare Dichlorocarbonyltris(ethylidiphenylphosphinite)ruthenium(II) from RuCl₂(P(OEt)Ph₂)₃ as a white solid; i.r. spectrum ν(co) 1980 (strong) 1935 cm⁻¹ (weak); far i.r. spectrum 302, 272, 260, 238 cm⁻¹; m.p. 203-205°C.

Dichlorocarbonyltris(dimethylphenylphosphonite)ruthenium(II):— The complex Ru₂Cl₄(CO)(PPh₃)₄ (0.2g) was refluxed with excess P(OMe)₂Ph (0.4 cm³) in benzene (30 cm³) for 1 hour. The resulting yellow solution was reduced

† Proposed ν(RuCl) are underlined
in volume to ca 10cm$^3$ and light petroleum (b.p. 60-80°C) added. The yellow solid which precipitated was filtered off and recrystallisation from CH$_2$Cl$_2$/MeOH produced initially colourless crystals of the complex; i.r. spectrum $\nu$(CO) 1985cm$^{-1}$, $\nu$(RuCl) 305, 280cm$^{-1}$. The remaining yellow solution deposited after several days yellow crystals of RuCl$_2$(P(OMe)$_2$Ph)$_4$. Similarly Dichlorothiocarbonyltris(dimethylphenylphosphonite)ruthenium(II) was prepared as colourless crystals from Ru$_2$Cl$_4$(CS)(PPh$_3$)$_4$; i.r. spectrum $\nu$(CS) 1305cm$^{-1}$, $\nu$(RuCl) 312, 274cm$^{-1}$; m.p. 149-151°C.

Dichlorothiocarbonyltris(methyldiphenylphosphinite)ruthenium(II):- The complex [RuCl$_2$(CS)(PPh$_3$)$_2$]$_2$ (0.2g) was refluxed with P(OMe)Ph$_2$ (0.3cm$^3$) in benzene (30cm$^3$) for 1 hour. The resulting yellow solution was reduced in volume to ca 10cm$^3$ and light petroleum (b.p. 60-80°C) added to precipitate the complex as a yellow solid which was filtered off, washed with light petroleum (b.p. 60-80°C) and dried in vacuo; i.r. spectrum $\nu$(CS) 1275cm$^{-1}$; far i.r. spectrum 315, 286, 272, 233cm$^{-1}$; m.p. 110-112°C. Similarly Dichlorothiocarbonyltris(ethyldiphenylphosphinite)ruthenium(II) was prepared as a yellow solid; i.r. spectrum $\nu$(CS) 1295cm$^{-1}$; far i.r. spectrum 305, 260, 265cm$^{-1}$.

[Chlorocarbonyltris(methyldiphenylphosphinite)ruthenium(II)tetrphenylborate:- The complex RuCl$_2$(CO)(P(OMe)Ph$_2$)$_3$ (0.2g) was dissolved in methanol (15cm$^3$) containing NaBF$_4$ (0.2g). After 24 hours white crystals of the complex were deposited; i.r. spectrum $\nu$(CO) 1975cm$^{-1}$, $\nu$(RuCl) 303cm$^{-1}$; m.p. 193-195°C; conductivity at 298K in CH$_2$Cl$_2$: slope = 148 (for [Ru$_2$Cl$_3$(P(OMe)Ph)$_2$]$_6$BF$_4$ slope = 165). In the same way [Chlorothiocarbonyltris(methyldiphenylphosphinite)ruthenium(II)tetrphenylborate was prepared as white crystals; i.r. spectrum $\nu$(CS) 1285, $\nu$(RuCl) 301cm$^{-1}$; m.p. 174-176°C; conductivity at 298K in CH$_2$Cl$_2$: slope = 156.
Bis(chlorocarbonyltris(ethyldiphenylphosphinite)ruthenium(II)) tetraphenylborate: The complex RuCl₂(CO)(P(CEt)Ph₂)₃ (0.2g) was dissolved in ethanol (15cm³) containing NaBPh₄ (0.2g). Over a period of 3 days white crystals of the complex were deposited; i.r. spectrum ν(CO) 1960cm⁻¹; far i.r. spectrum 270, 282, 263, 256; m.p. 198-200°C; conductivity in CH₂Cl₂ at 298K: slope = 198. Likewise RuCl₂(CS)(P(OEt)Ph₂)₃ dissolved in ethanol containing NaBPh₄ produces [Bis(chlorothiocarbonyltris(ethyldiphenylphosphinite)ruthenium(II))] tetraphenylborate; i.r. spectrum ν(CS) 1285cm⁻¹, ν(RuCl) 270cm⁻¹; m.p. 112-114°C.

Refluxing RuCl₂(PMe₂Ph)₄ (0.2g) in CS₂ (20cm³) for 12 hours produces a purple solid containing [(²²-carbodisulphide)tetrakis(dimethylphenylphosphine)ruthenium(II)] chloride; i.r. spectrum: ν(CS₂) 1132cm⁻¹; and [Ru₂Cl₃(PMe₂Ph)₆]Cl.

[(²²-carbodisulphide)tetrakis(methylidiphenylphosphine)ruthenium(II)] chloride: Refluxing RuCl₂(PMePh₂)₄ (0.2g) in CS₂ (20cm³) for 2 hours produced the complex as a blue-purple solid which was filtered off; m.p. 187-189°C; i.r. spectrum: ν(CS₂) 1110, 985cm⁻¹; conductivity in acetone at 295K: slope = 450 (for [Ru(C₆H₆)(H₃)₃PF₆] slope = 350)

[(²²-carbodisulphide)chlorotris(ethyldiphenylphosphine)ruthenium(II)] chloride. carbodisulphide: Shaking RuCl₂(PEtPh₂)₃ (0.2g) in CS₂ (20cm³) for 1 hour produces the complex as a red-pink solid which was filtered off; m.p. 170-172°C; i.r. spectrum: ν(CS₂) 1515, 1115, 995cm⁻¹. Dissolving the complex in CH₂Cl₂ and reprecipitating with light petroleum (b.p. 60-80°C) gives [RuCl(²²-carbodisulphide)(PEtPh₂)₃]Cl. Refluxing RuCl₂(PEtPh₂)₃ in CS₂ for 3 hours produces a small amount of the above complex which was filtered off leaving an orange solution. On standing for 2 days, or

† superimposed on the broad band at 270cm⁻¹
alternatively by addition of light petroleum (b.p. 60-80°C), an orange solid was precipitated, consisting mainly of tri-μ-chloro-bis(thiocarbonyl)chlorotris(ethyldiphenylphosphine)diruthenium(II); i.r. spectrum ν(CS) 1295 cm⁻¹.

[di-μ-carbondsulphidebis(chlorotris(ethyldiphenylphosphine)ruthenium(II))]-tetraphenylborate: The complex [Ru(μ-CS₂)(PET₂)₃]Cl was dissolved in MeOH to give a purple solution. The addition of NaBPh₄ precipitated the complex as a purple solid which was filtered off; m.p. 120-122°C; i.r. spectrum: ν(CS₂) 1115, 980 (broad), 850 (broad).
Table 4.1

Analytical data for some ruthenium(II) carboxyl, thiocarboxyl and carbon disulphide complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found %</th>
<th>Calculated %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>RuCl₂CO(P(OMe)Ph₂)₃</td>
<td>56.4</td>
<td>4.5</td>
</tr>
<tr>
<td>RuCl₂CO(P(OEt)Ph₂)₃</td>
<td>57.8</td>
<td>5.1</td>
</tr>
<tr>
<td>RuCl₂CO(P(OMe)₂Ph)₃</td>
<td>42.3</td>
<td>4.5</td>
</tr>
<tr>
<td>RuCl₂CS(P(OMe)Ph₂)₃</td>
<td>56.0</td>
<td>4.6</td>
</tr>
<tr>
<td>RuCl₂CS(P(OEt)Ph₂)₃</td>
<td>57.1</td>
<td>5.0</td>
</tr>
<tr>
<td>RuCl₂CS(P(OMe)₂Ph)₃</td>
<td>41.4</td>
<td>4.6</td>
</tr>
<tr>
<td>[RuCl₂CC(P(OMe)Ph₂)₃]BPh₄</td>
<td>67.6</td>
<td>5.3</td>
</tr>
<tr>
<td>[RuCl₂CC(P(OEt)Ph₂)₃]₂(BPh₄)₂</td>
<td>68.8</td>
<td>5.6</td>
</tr>
<tr>
<td>[RuCl₂CS(P(OMe)Ph₂)₃]BPh₄</td>
<td>66.9</td>
<td>5.2</td>
</tr>
<tr>
<td>[RuCl₂CS(P(OEt)Ph₂)₃]₂(BPh₄)₂</td>
<td>67.9</td>
<td>5.5</td>
</tr>
<tr>
<td>[Ru(ηCS₂)(PMePh₂)₄]Cl₂</td>
<td>58.6</td>
<td>4.6</td>
</tr>
<tr>
<td>[RuCl(ηCS₂)(PETPh₂)₃]Cl.CS₂</td>
<td>55.1</td>
<td>4.7</td>
</tr>
<tr>
<td>[RuCl(ηCS₂)(PETPh₂)₃]Cl</td>
<td>57.1</td>
<td>5.0</td>
</tr>
<tr>
<td>[RuCl(CS₂)(PETPh₂)₃]₂(BPh₄)₂</td>
<td>66.3</td>
<td>5.4</td>
</tr>
<tr>
<td>Complex</td>
<td>Pha</td>
<td>CH₂</td>
</tr>
<tr>
<td>---------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>RuCl₂CO(P(OMe)Ph₂)₃</td>
<td>C₆D₆</td>
<td>301</td>
</tr>
<tr>
<td>RuCl₂CO(P(OEt)Ph₂)₃</td>
<td>CDCl₃</td>
<td>301</td>
</tr>
<tr>
<td>RuCl₂CO(P(OMe)₂Ph)₃</td>
<td>CDCl₃</td>
<td>301</td>
</tr>
<tr>
<td>RuCl₂CS(P(OMe)Ph₂)₃</td>
<td>CDCl₃</td>
<td>301</td>
</tr>
<tr>
<td>RuCl₂CS(P(OEt)Ph₂)₃</td>
<td>CDCl₃</td>
<td>301</td>
</tr>
<tr>
<td>RuCl₂CS(P(OMe)₂Ph)₃</td>
<td>CDCl₃</td>
<td>301</td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Temp(K)</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>[RuCl(CO)(P(OMe)Ph$_2$)$_3$]BPh$_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="BPh$_4$">Ru$_2$Cl$_2$(CO)$_4$(P(OEt)Ph$_2$)$_6$</a>$_2$</td>
<td>CDCl$_3$</td>
<td>301</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RuCl(CS)(P(OMe)Ph$_2$)$_3$]BPh$_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a - multiplet between stated values

b - due to the protons of mutually trans phosphinite or phosphonite ligands
c - due to the protons of the phosphinite or phosphinite group trans to Cl
d - doublet
e - multiplet due to BPh$_4^-$
g - broad

N = J$_{PH}$ + J$_{PH'}$ (see Appendix 1)
### Table 4.3

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp(K)</th>
<th>Position (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl₂CO(P(OMe)Ph₂)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>138.45(t) Jₚₚ = 29.6Hz 114.92(d)</td>
</tr>
<tr>
<td>RuCl₂CO(P(OEt)Ph₂)₃</td>
<td>CDCl₃</td>
<td>298</td>
<td>135.42(t) Jₚₚ = 30.0Hz 115.05(d)</td>
</tr>
<tr>
<td>RuCl₂CO(P(OMe)₂Ph)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>157.42(t) Jₚₚ = 37.3Hz 143.97(d)</td>
</tr>
<tr>
<td>RuCl₂CS(P(OMe)Ph₂)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>131.91(t) Jₚₚ = 29.7Hz 115.80(d)</td>
</tr>
<tr>
<td>RuCl₂CS(P(OEt)Ph₂)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>130.01(t) Jₚₚ = 29.7Hz 112.71(d)</td>
</tr>
<tr>
<td>RuCl₂CS(P(OMe)₂Ph)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>AB₂ ωₐ = 152.59 ωₐ = 143.43 Jₚₚ = 35.7Hz</td>
</tr>
<tr>
<td>[RuCl₂CO(P(OMe)Ph₂)₃]BF₄</td>
<td>CDCl₃</td>
<td>213</td>
<td>125.43(s)</td>
</tr>
</tbody>
</table>

3¹Pn.m.r. spectral data for some ruthenium complexes
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp(K)</th>
<th>Position (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl(ηCS₂)(P(OEt)Ph₂)₃]₂(BPh₄)₂</td>
<td>CDCl₃</td>
<td>213</td>
<td>120.02(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>122.7 - 115.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RuCl(ηCS₃)(P(OMe)Ph₂)]BPh₄</td>
<td>CDCl₃</td>
<td>213</td>
<td>123.02(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RuCl(ηCS₃)(P(OEt)Ph₂)]₂(BPh₄)₂</td>
<td>CDCl₃</td>
<td>213</td>
<td>120.0 - 114.4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(ηCS₂)(PMε₂Ph₄)]Cl₂</td>
<td>CDCl₃</td>
<td>298</td>
<td>ABC₂ pattern ( \mathbf{J}_A = 19.43 ),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \mathbf{J}_B = 15.71, \mathbf{J}_C = 12.48 \text{p.p.m.} ) ;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \mathbf{J}<em>{AB} = 3.83, \mathbf{J}</em>{AC} = -14.75, \mathbf{J}_{BC} = 31.66 \text{Hz} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Position due to inequivalence of the Cl ligands.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp(K)</th>
<th>Position (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{RuCl}(\text{CS}_2)(\text{PEtPh}_2)_3]_2(\text{BPh}_4)_2)</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>AMX pattern $J_A = 44.6$, $J_M = 29.0$, $J_X = 16.3\text{ p.p.m.}$; $J_{AM} = 28.0$, $J_{AX} = 3.5$, $J_{MX} = 11.3\text{ Hz}$</td>
</tr>
<tr>
<td>(\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PEtPh}_2)_3)</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>49.17(s) $\text{AB pattern } 36.79$ [$J_{AB} = 35.7$, $S_{AB} = 84.1\text{ Hz}$]</td>
</tr>
</tbody>
</table>

s - singlet  t - triplet  d - doublet  a - multiplet ranging over values stated
Chapter 5

Reaction of RuCl₂L₃ or 4 (L = PR₂Ph₂, PR₂Ph, P(OR)₂Ph₂, P(OR)₂Ph) with some dithioacid ligands

5.1 Introduction

The dithioacid ligands used for the work presented in this chapter are N, N disubstituted dithiocarbamates (S₂CNR₂), O-substituted dithiocarbonates (xanthates)(S₂COR) and P, P disubstituted phosphinodithiocarbonates (S₂PR₂). These ligands are able to co-ordinate to metals in several different ways. Thus apart from acting as a simple counter anion they may act as a unidentate ligand i.e.

![Unidentate Ligand Diagram]

or by donation of a lone pair from the unco-ordinated sulphur atom form a bidentate or bridging ligand i.e.

![Bidentate Ligand Diagram]

Occasionally a further two electrons may be donated to another metal atom to form a five electron donor ligand bridging either two or three metal atoms i.e.

![Five Electron Donor Ligand Diagram]
For Pt and Pd diphenylphosphinodithioate complexes, bidentate, ionic and unidentate co-ordination can be distinguished on the basis of infra-red spectroscopy\textsuperscript{131} and the same method of distinction has also been applied to Ru complexes\textsuperscript{132}. Thus bidentate co-ordination is characterised by two bands at 603 and 570 cm\textsuperscript{-1}, unidentate (645 and 540 cm\textsuperscript{-1}) and ionic (650 and 560 cm\textsuperscript{-1}). Similarly for \(\text{S}_2\text{PMe}_2\), bidentate co-ordination is identified by a band in the region 570-585 cm\textsuperscript{-1}, unidentate (600 cm\textsuperscript{-1}) and ionic (610 cm\textsuperscript{-1}); in this instance the lower energy band (ca 500 cm\textsuperscript{-1}) is usually masked by strong ligand vibrations.

N, N dialkyldithiocarbamate complexes exhibit a band of medium intensity in the region 1480-15550 cm\textsuperscript{-1} (i.e. between the ranges for C-N and C=N). This band has been assigned\textsuperscript{133} to a C-N stretching mode where the CN bond order is between 1 and 2 due to a resonance of the type

\[
\begin{align*}
\text{M} & \leftrightarrow \text{M} \\
\text{C=N} & \leftrightarrow \text{C=N} \\
\text{S} & \leftrightarrow \text{S}
\end{align*}
\]

In the infra-red spectra of N, N dialkyldithiocarbamate derivatives of Cr(III), Fe(III), Rh(III) and Ni(II)\textsuperscript{133} the C=N frequencies are higher for the dimethyl derivative than for the diethyl derivative. This is believed to be due to an increase in the \(\pi\) bond character due to the stronger inductive effect of a methyl group. Other characteristic infra-red bands of N, N dialkyldithiocarbamate complexes occur at ca 1150 cm\textsuperscript{-1}, ca 990 cm\textsuperscript{-1} and ca 360 cm\textsuperscript{-1} assigned\textsuperscript{134} to \(\nu\text{NC}_2\), \(\nu\text{C--S}\) and \(\nu\text{M--S}\) respectively. The number of C--S stretching frequency bands has been claimed to be indicative of the bonding mode of the ligand\textsuperscript{135} such that if the ligand is functioning as a bidentate ligand a single band near 990 cm\textsuperscript{-1} is present while a doublet is found if it is unidentate. For \(\text{SCNMe}_2\) the
position of $\nu(CN)\)occurring below 1500 cm$^{-1}$ if the ligand is unidentate, and between 1500-1530 cm$^{-1}$ if it is bidentate, has also been used as a guide to the mode of co-ordination.\textsuperscript{136}

Quite a large number of ruthenium complexes containing the above mentioned dithiocarbinate ligands are already known. Thus the Ru(III) complexes Ru(S-S)$)_3$ ($S-S = \text{S}_2\text{CNR}_2$,\textsuperscript{137} $\text{S}_2\text{PR}_2$\textsuperscript{138}), containing three bidentate ligands, have been prepared by the reaction of 'RuCl$_3$.3H$_2$O' with Na(S-S). Oxidation of Ru(S$_2$CNEt$_2$)$_3$ with BF$_3$ under aerobic conditions produces a diamagnetic compound originally formulated as [Ru(S$_2$CNEt$_2$)$_3$]BF$_4$\textsuperscript{139} but shown by X-ray analysis\textsuperscript{31} to be the dimeric species [Ru$_2$(S$_2$CNEt$_2$)$_5$]BF$_4$ (1). The diamagnetism is a result of spin pairing, via the Ru-Ru bond, of two low spin Ru(III) d$^5$ ions. As previously mentioned in Chapter 1 photolysis of Ru(S$_2$CNEt$_2$)$_3$ in CH$_2$Cl$_2$ or CHCl$_3$ yields the novel 7 co-ordinate complex RuCl(S$_2$CNEt$_2$)$_3$.\textsuperscript{9} The corresponding Ru(NO)(S$_2$CNEt$_2$)$_3$ prepared by action of NO on Ru(S$_2$CNEt$_2$)$_3$ is six co-ordinate\textsuperscript{10} and was the first complex to be isolated containing a unidentate dithiocarbamate ligand.

A series of recent papers by Raston and White describe the X-ray structures of several ruthenium complexes containing dithiocarbamate ligands. Thus, as for Ru(S$_2$CNEt$_2$)$_3$ the crystal structure of Ru(S$_2$CN(CH$_2$)$_4$O)$_3$\textsuperscript{140} shows it to contain three symmetrically co-ordinated bidentate ligands. Two derivatives of ruthenium di-isopropylidithiocarbamate viz. [Ru$_2$(S$_2$CNPr$_2^+$)$_5$]Cl.5C$_6$H$_5$ and [Ru$_2$(S$_2$CPPr$_2^+$)$_5$][Ru$_2$Cl$_6$].2CHCl$_3$,
obtained by dissolving Ru\((S_2CNPr_2)_3\) in CHCl\(_3\) and recrystallisation of the products from chloroform - cyclohexane or benzene, were found to have structure (2)\(^{141}\) an isomeric form of structure (1). Treatment of the red solution, obtained by carbonylation of a solution of RuCl\(_3\cdot\text{H}_2\text{O}\)

\[
\begin{align*}
\text{RuCl}_2\text{(PPh}_3\text{)}_3 \text{ reacts with Na}(S-S) (\text{"S-S = } S_2\text{CNR}_2, \text{"S}_2\text{COR, } S_2\text{PR}_2) \text{ to give Ru}(S-S)_2\text{(PPh}_3\text{)}_2. \text{ Similar reactions of RuCl}_2\text{(PETPh}_2\text{)}_3, \\
\text{[RuCl}_3\text{(PMePh}_2\text{)}_6\text{]} \text{ and } \text{mer-RuCl}_3\text{(PMe}_2\text{Ph)}_3 \text{ with excess Na}_2\text{PR}_2 \text{ (R = Me, Et, Ph) in ethanol produce Ru}(S_2\text{PR}_2)_2\text{L}_2 \text{ and for mer-RuCl}_3\text{(PMe}_2\text{Ph)}_3 \text{ treatment with Na}_2\text{CNMe}_2 \text{ gives Ru}(S_2\text{CNMe}_2)_2\text{(PMe}_2\text{Ph)}_2. \text{ The complexes Ru}(S_2\text{PR}_2)_2\text{L}_2 \text{ react with CO under mild conditions to form the monocarboxyl}
\end{align*}
\]
species Ru(S-S)$_2$LCO and undergo ligand exchange reactions with other phosphorus ligands of greater basicity enabling formation of mixed ligand complexes of the type Ru(S-S)$_2$LL' to be achieved. ($L = \text{PMe}_2\text{Ph}$, $PF_3$, $L' = \text{P(0Ph)}_3$)

The $^1$H n.m.r. spectrum of Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$ changes with temperature. At low temperature (253K) the spectrum is consistent with the cis structure presented in Fig. 5.1, but at higher temperatures (338K) methyl groups (a) and (b) become equivalent as do groups (c) and (d).

![Diagram of cis-Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$](image)

**Fig. 5.1** Diagramatic representation of cis-Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$

This was attributed to the rapid interconversion, at this temperature, of optical isomers and was found to be a general feature of complexes of the type Ru(S$_2$PMe$_2$)$_2$L$_2$. However the rate of inversion depended upon $L$ the order being $PF_3 > \text{PMe}_2\text{Ph} > \text{P(OMe)}_3 > \text{PMe}_2\text{Ph} > \text{P(0Ph)}_3 \gg$ diphos.

† In support of this Ru(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)$_2$ has been shown by X-ray analysis to have a cis configuration.\textsuperscript{144}
The mechanism proposed (Scheme 5.1) involves five steps viz

(i) attack of solvent to form a seven co-ordinate intermediate.
(ii) rupture of a metal-sulphur bond trans to L. 
(iii) exchange of bidentate and unidentate ligands.
(iv) reattack of the free sulphur atom in such a position that when the solvent is expelled the attacking sulphur atom becomes trans to L.

Finally, due to their similarity with several of the ruthenium complexes isolated in the following work, it seems appropriate to discuss in this introduction the products obtained from the reactions of mer-OsCl$_3$(PMe$_2$Ph)$_3$ with dithiocarbamidyl ligands.$^{145}$ Thus refluxing mer-OsCl$_3$(PMe$_2$Ph)$_3$ (4) with NaS$_2$CNMe$_2$ produced Os(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_2$ (5) whereas shaking the mixture for a short time gave OsCl(S$_2$CNMe$_2$)(PMe$_2$Ph)$_3$ (6). This then reacted with more NaS$_2$CNMe$_2$ to give (5) but not in such a high yield as from (4) suggesting the existence of two separate reaction pathways. Refluxing mer-OsCl$_3$(PMe$_2$Ph)$_3$ with NaS$_2$PMe$_2$ yielded Os(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$ (7), but in this case shaking the mixture produced the Os(III) species OsCl$_2$(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$ (8) which on standing in a non-polar solvent, such as benzene, gave [OsCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$]$^+$ (9) and OsCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$ (10) but in polar solvents, such as acetone, produced (9) but not (10). On the basis of these results a reaction scheme for the formation of Os(S-S)$_2$(PMe$_2$Ph)$_2$ ("S-S = S$_2$CNMe$_2$, S$_2$PMe$_2")$ from mer-OsCl$_3$(PMe$_2$Ph)$_3$ was suggested (Scheme 5.2). This invoked two separate pathways, one involving reduction to Os(II) at a fairly early stage of the reaction and the other involving reduction to Os(II) only at the last step. However treatment of mer-OsCl$_3$(PMe$_2$Ph)$_3$ with KS$_2$COEt produced only OsCl(S$_2$COEt)(PMe$_2$Ph)$_3$ (11) which did not react further with KS$_2$COEt.

† Hence the rate dependence of L, due to the varying trans influence of L (the extent to which L weakens the bond trans to itself in the equilibrium state of the complex)
Scheme 5.1 Mechanism for optical isomerisation of \[ \text{Ru}(S_{2}PMe_{2})_{2}L_{2} \]
This was considered to be due to the strong reducing nature of \( S_2 COEt \) which caused reduction to Os(II) before \([\text{OsCl}(S_2 COEt)(\text{PMe}_2 \text{Ph})_3]^{1+}\) could react with more \( S_2 COEt \) and once formed (11) did not readily isomerise (evidence of isomerisation of (6) to (12) was obtained for \( \text{OsCl}(S_2 \text{CNMe}_2)(\text{PMe}_2 \text{Ph})_3 \)) and hence no further reaction could take place.

No intermediates of this type were isolated or detected in the formation of \( \text{Ru}(S-S)_2 L_2 \) reported elsewhere (\( S-S = S_2 \text{PR}_2 \), \( L = \text{PPh}_3 \), \( \text{PMe}_2 \text{Ph} \), \( \text{PMePh}_2 \), \( \text{PETPh}_2 \); \( S-S = S_2 \text{COR} \), \( L = \text{PPh}_3 \); \( S-S = S_2 \text{CNR}_2 \), \( L = \text{PMe}_2 \text{Ph} \)) but in the following work the reactions of \( \text{RuCl}_2 L_4 \) (\( L = \text{POEtPh}_2 \), \( \text{PMe}_2 \text{Ph} \), \( \text{PMePh}_2 \)) and \( \text{RuCl}_2 L_3 \) (\( L = \text{PETPh}_2 \), \( \text{P(OR)Ph}_2 \); \( R = \text{Me,Et} \)) with dithioc acid ligands have been studied with the purpose of characterising such reaction intermediates.

5.2 Results and discussion

(a) Diphenyl and dimethylphosphinodithioate complexes

Prolonged reflux of \( \text{RuCl}_2 (\text{PO(OR)Ph})_2 \) (\( R = \text{Me,Et} \)) with \( \text{NaS}_2 \text{P'Me}_2 \) in alcohol produces a brown solution from which for \( R = \text{Me} \) no solid could be isolated but where \( R = \text{Et} \) a small amount of red-brown crystals analysing for \( \text{Ru}(S_2 \text{P'Me}_2)_2 (\text{PO(OR)Ph})_2 \) (13) (Table 5.2) were obtained. The infrared spectrum of (13) contains a band at 588 cm\(^{-1}\) indicating bidentate co-ordination of the dithioc acid group and the \( ^{31}\text{P} \) n.m.r. spectrum in CDCl\(_3\) at 303 K (Table 5.3) consists of two triplets at 140.76 and 86.70 p.p.m. due to the phosphinite and dithioc acid groups respectively. The \( ^1\text{H} \) n.m.r. spectrum at 301 K contains a doublet at 1.43\( \delta \) due to the methyl groups of \( S_2 \text{P'Me}_2 \) and resonances at 3.35 and 1.20\( \delta \) due to \( \text{P(OR)Ph}_2 \). Unfortunately at lower temperatures the spectrum becomes very broad and the isomeric form of (13) could not be determined. Similarly prolonged reaction of \( \text{cis-RuCl}_2 (\text{PMe}_2 \text{Ph})_4 \) with \( \text{NaS}_2 \text{P'Me}_2 \) produces yellow crystals shown by \( ^{31}\text{P} \) n.m.r. and \( ^1\text{H} \) n.m.r. spectroscopy to be identical to that obtained from \( \text{mer-RuCl}_3 (\text{PMe}_2 \text{Ph})_3 \) viz. \( \text{cis-Ru}(S_2 \text{P'Me}_2)_2 (\text{PMe}_2 \text{Ph})_2 \).
Scheme 5.2 Mechanism of formation of Os(S-S)₂(PMe₂Ph)₂ from mer-OsCl₃(PMe₂Ph)₃ (compounds in dotted brackets were not isolated.)
However shaking RuCl$_2$(PMe$_2$Ph)$_4$ or RuCl$_2$(P(OR)Ph$_2$)$_3$ in methanol (R = Me) or ethanol (R = Et) with NaS$_2$P'R'R (R' = Me,Ph) for a short time produces red conducting solutions which on addition of NaBP$_4$ precipitate red solids analysing closely for [Ru(S$_2$P'R'R$_2$)$_2$L$_3$]BP$_4$ (L = P(OR)Ph$_2$ (14), L = PMe$_2$Ph (15)). The infra-red spectra of (14) and (15) contain a band ca 580 cm$^{-1}$ consistent with bidentate co-ordination of the dithioacid group and conductivity measurements in acetone indicate 1:1 electrolytes. The latter result suggests a monomeric structure in solution and is supported by molecular weight measurements on [Ru(S$_2$P'Me$_2$)(PMe$_2$Ph)$_3$]BP$_4$ in CHCl$_3$ (see experimental section). The presence of a monomeric structure in the solid state is confirmed by a preliminary X-ray analysis of [Ru(S$_2$P'Me$_2$)(PMe$_2$Ph)$_3$]BP$_4$ the results of which are shown in Fig. 5.2 and Table 5.1. The cation has a distorted square pyramidal geometry, as expected for a five co-ordinate Ru(II) complex, with the equatorial phosphine groups and the dithioacid ligand lying below the basal plane.

The $^{31}$P n.m.r. spectrum of [Ru(S$_2$P'Me$_2$)(PMe$_2$Ph)$_3$]BP$_4$ in CDCl$_3$ at 298K (Fig. 5.3) consists of a doublet at 32.36 ppm ($J_{PP} = 3.6$ Hz) due to the phosphine groups which, because of intramolecular scrambling, are equivalent at this temperature and equally coupled to the phosphorus of $^7$S$_2$P'Me$_2$, and a quartet at 110.31 ppm due to P' (coupled to the three phosphine groups). Under similar conditions the $^1$H n.m.r. spectrum (Fig. 5.4) contains a doublet ($J_{PP} = 13$ Hz) due to the methyl groups of $^7$S$_2$P'Me$_2$ (equivalent due to scrambling of the phosphines) and a 'pseudo-triplet' due to the methyl groups of PMe$_2$Ph. Neither the $^{31}$P n.m.r. nor the $^1$H n.m.r. spectra change on cooling to 213K indicating that facile scrambling is still taking place at this temperature.

If RuCl$_2$(P(OR)Ph$_2$)$_3$ or RuCl$_2$(PMe$_2$Ph)$_4$ are shaken with NaS$_2$P'Me$_2$ in benzene, however, in each case a yellow non conducting solid analysing

$^\dagger$ for origin of 'pseudo-triplet' see Appendix 1
Fig. 5.2. X-ray structure of [Ru(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)$_3$]$^+$. 
Table 5.1

Selected bond lengths and bond angles of $[\text{Ru}(\text{S}_2\text{Ph}_2)(\text{PMe}_2\text{Ph})_3]^+$

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru - S₁</td>
<td>2.436</td>
</tr>
<tr>
<td>Ru - S₂</td>
<td>2.463</td>
</tr>
<tr>
<td>Ru - P₁</td>
<td>2.313</td>
</tr>
<tr>
<td>Ru - P₂</td>
<td>2.293</td>
</tr>
<tr>
<td>Ru - P₄</td>
<td>2.196</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cell dimensions

\[
\begin{align*}
    a &= 9.840(6)\text{Å} \\
    b &= 17.231(7)\text{Å} \\
    c &= 33.63(4)\text{Å}
\end{align*}
\]
Fig. 5.3. $^{31}$P n.m.r. spectrum of $[\text{Ru}(\text{S}_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3]\text{BPh}_4$ in CDCl$_3$ at 298K.
Fig. 54. $^1$Hnmr. spectrum of $[\text{Ru}(S_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3]\text{BPh}_4$ in CDCl$_3$ at 301 K.
for $\text{RuCl}(\text{S}_2\text{PMe}_2)L_3$ ($L = \text{P(OR)Ph}_2$ (16), $\text{PMe}_2\text{Ph}$ (17)) is obtained. Complexes (16) and (17) are fairly stable in $\text{CHCl}_3$ or $\text{CH}_2\text{Cl}_2$ but in methanol or ethanol a red solution, containing $[\text{Ru}(\text{S}_2\text{P'Me}_2)L_3]^{\dagger}$ is formed immediately on dissolving the yellow solids. The infra-red spectra of (16) and (17) contain a band at ca 600 cm$^{-1}$ which, although outside the normal range is considered to arise from a bidentate $\text{S}_2\text{PMe}_2$ ligand.

The $^{31}\text{P}$ n.m.r. spectrum of $\text{RuCl}(\text{S}_2\text{P'Me}_2)(\text{PMe}_2\text{Ph})_3$ (17) at 213 K in $\text{CDCl}_3$ (Fig. 5.5) consists of a resonance resembling an unsymmetrical quartet at 93.9 p.p.m. due to the phosphorus atom of $\text{S}_2\text{P'Me}_2$ and an $\text{AB}_2$ pattern ($v_A = 20.38$, $v_B = 16.06$ p.p.m., $J_{AB} = 33.0$ Hz) due to the $\text{PMe}_2\text{Ph}$ groups. At 298 K the $\text{AB}_2$ resonance broadens and a singlet at 21.16 p.p.m. appears due to $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ formed presumably by the decomposition of (17). The $^1\text{H}$ n.m.r. spectrum at 233 K in $\text{CDCl}_3$ (Fig. 5.6) contains two doublets at 1.19$\delta$ and 2.17$\delta$ respectively which both collapse at the same $^{31}\text{P}$ frequency (viz 95.5 p.p.m.) indicating that they arise from the methyl groups of $\text{S}_2\text{P'Me}_2$. There is also a doublet at 1.60$\delta$ (decoupling $^{31}\text{P}$ frequency = 19.5 p.p.m.) and a broad resonance at 1.86$\delta$, due to the methyls of the phosphine groups. At 298 K only a broad resonance at 1.70$\delta$ is observed as, on one hand, all the $\text{PMe}_2\text{Ph}$ groups and, on the other, the methyls of $\text{S}_2\text{P'Me}_2$ become equivalent. Two geometries are possible.

$^\dagger$ Some decomposition occurs to form $[\text{Ru}_2\text{Cl}_3L_6]\text{Cl}$

$^\ddagger$ For analysis of an $\text{AB}_2$ spectrum see Appendix 2

$^\oplus$ The irradiation frequencies are different from the frequencies of the $^{31}\text{P}$ nuclei obtained from the Fourier transform spectrum (Fig. 5.5) because the former are obtained from the HA-100 spectrometer (with Schlumberger FS 30 frequency synthesiser attachment) whereas the latter were directly measured on the XL 100 spectrometer and these have slightly different reference frequencies.
Fig. 5.5. $^{31}$P n.m.r. spectrum of RuCl($\text{S}_2\text{PMe}_2$)(PMe$_2$Ph)$_3$ in CDCl$_3$ at 213K.
for \((17)\) (Fig. 5.7) viz. \((17a)\) in which the chloride is trans to a sulphur atom of the bidentate group, or \((17b)\) in which the chloride is trans to a tertiary phosphine group. However the low temperature \(^1\text{Hn.m.r}\) spectrum is only consistent with one of these. For \((17a)\) the methyl groups \((a)\) and \((b)\) attached to \(\text{S}_2\text{P'}\text{Me}_2\) are equivalent whereas in \((17b)\) they are inequivalent. Therefore, as two doublets are observed \((17b)\) must be correct. The doublet at 1.60s originates from the methyl groups \((c)\) and \((d)\) attached to \(\text{PMe}_2\text{Ph}\) trans to Cl whereas the resonance at 1.88s (two overlapping 'pseudo-doublets') is due to the methyls on the two \(\text{PMe}_2\text{Ph}\) groups trans to the dithioacid ligand.

The equivalence of all the tertiary phosphine methyl groups and also \(\text{Me}(a)\) and \(\text{Me}(b)\) at higher temperatures is quite feasible for such a six co-ordinate structure since the bidentate group can also act as a unidentate ligand forming a five co-ordinate intermediate. The dangling sulphur atom can then reattack to form the original isomer or a different one (Scheme 5.3).

Reaction between \(\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4\) and \(\text{NaS}_2\text{P'R}_2\) \((R = \text{Me,Ph})\) under all these conditions, however, produces in both cases \(\text{Ru(S}_2\text{P'}\text{Me}_2\text{)}_2(\text{P(OMe)}_2\text{Ph})_2\). The \(^1\text{Hn.m.r}\) spectrum at 301K of \(\text{Ru(S}_2\text{P'Me}_2\text{)}_2(\text{P(OMe)}_2\text{Ph})_2\) exhibits a 'pseudo-triplet' at 3.60s and a broad resonance at 1.88s. As the temperature is lowered the 'pseudo-triplet' splits into two and the broad resonance sharpens up until at 213K the spectrum contains two 'pseudo-triplets' (decoupling to two singlets at the same \(^{31}\text{P}\) frequency) at 3.42s and 3.58s respectively and two doublets (also decoupling at the same \(^{31}\text{P}\) frequency) at 1.71s and 2.12s respectively. This low temperature spectrum in which the methyl groups of \(\text{S}_2\text{P'Me}_2\) are inequivalent is consistent with a cis configuration. Rearrangement at higher temperatures is likely to occur via a mechanism similar to that established for \(\text{Ru(S}_2\text{P'Me}_2\text{)}_2(\text{PMe}_2\text{Ph})_2\)^{132} (see Scheme 5.1).

\[^{132}\text{for origin of 'pseudo-doublet' see Appendix 1}\]
Fig. 5.7 Possible geometries for RuCl(S₂PMe₂)(PMe₂Ph)₃.
Scheme 5.3 Possible rearrangements of RuCl(S₂PMe₂)L₃ at 298K.
(b) O-substituted dithiocarbonate complexes

Shaking RuCl₂(P(OR)₂Ph)₃ (R = Me, Et) or RuCl₂(PMe₂Ph)₄ with excess KS₂COMe in methanol produces yellow non-conducting solids analyzing for Ru(S₂COMe)₂L₃ (L = P(OR)₂Ph (18), L = PMe₂Ph (19)). The infra-red spectra contain several bands in the region 1000-1200 cm⁻¹ indicating the presence of co-ordinated S₂COMe groups and the ³¹P n.m.r. spectra in CDCl₃ at 298K, exhibiting an AB₂ pattern (Fig. 5.8 L = PMe₂Ph) confirms the presence of three L groups. The ¹H n.m.r. spectrum of (19) in CDCl₃ at 301K (Fig. 5.9) contains two resonances at 3.92 and 3.65 due to the methyl groups of the xanthate ligands indicating the presence of both monodentate and bidentate xanthate ligands. The spectrum also contains a 'pseudo-triplet' and doublet in the intensity ratio 2:1 assigned to the methyl groups of the tertiary phosphine ligands. The doublet is obtained from the PMe₂Ph group trans to the monodentate dithioacid ligand and the 'pseudo-triplet' from the two cis PMe₂Ph groups, each trans to a sulphur of the bidentate ligand.

Heating Ru(S₂COMe)₂(P(OMe)₂Ph)₃ under reflux in CH₂Cl₂, in the presence of KS₂COMe, produces orange-yellow crystals analyzing for Ru(S₂COMe)₂(P(OMe)₂Ph)₂ (20). The ³¹P n.m.r. spectrum in CDCl₃ at 298K consists of a singlet at 146.51 p.p.m. while the ¹H n.m.r. contains a singlet at 3.71 due to the S₂COMe groups and a 'pseudo-triplet' at 3.22 from the PMe₂Ph groups suggesting a cis configuration.

An intractable yellow oil is obtained from the reaction between RuCl₂(P(OMe)₂Ph)₄ and excess KS₂COMe but shaking RuCl₂L₄ (L = PMePh₂) and RuCl₂L₃ (L = PEtPh₂) with excess KS₂COMe in alcohol produces Ru(S₂COMe)₂L₂. For Ru(S₂COMe)₂(PMePh)₂ the ³¹P n.m.r. and ¹H n.m.r. spectra at both 218K and 298K are consistent with a cis configuration. However for Ru(S₂COMe)₂(PEtPh₂)₂ the ³¹P n.m.r. spectrum at 218K in CDCl₃ consists of two singlets, of equal intensity, at 50.32 and 44.31 p.p.m. As
Fig. 5.8. $^{31}$P n.m.r. spectrum of $\text{Ru(S}_2\text{COMe})_2(\text{PMe}_2\text{Ph})_3$ at 298K in CDCl$_3$. 

Chemical shift (p.p.m.)

10.28

6.84
Fig 5.9 $^1$H-n.m.r. spectrum of Ru(S$_2$COMe)$_2$(PMe$_2$Ph)$_3$ in CDCl$_3$ at 301K.
the temperature is raised the singlet at 44.31 p.p.m. increases at the expense of the other, thus implying conversion from one species to the other. This process is irreversible as recooling the mixture does not change the intensities of the signals. The $^1$Hn.m.r. spectrum in CDCl$_3$ at 301K which contains resonances at 3.72δ and 3.85δ from S$_2$COMe, also suggests the presence of two species. The most likely explanation is the presence of both the cis and trans isomers, one of which is more stable at higher temperatures than the other. A similar situation arises for Ru(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_2$ where both cis and trans isomers are formed from reaction of mer-RuCl$_3$(PMe$_2$Ph)$_3$ with NaS$_2$CNR$_2$ in methanol. On warming in solution the trans isomer irreversibly converts to the cis isomer.

(c) N, N disubstituted dithiocarbamate complexes

Reacting RuCl$_2$(PMe$_2$Ph)$_4$ with excess NaS$_2$CNR$_2$ (R = Me, Et) for a very short time in ethanol produces pale yellow conducting solutions which on addition of NaBPh$_4$ precipitate white solids analysing for [Ru(S$_2$CNR$_2$)(PMe$_2$Ph)$_4$]BPh$_4$ (21). Conductivity measurements in CH$_2$Cl$_2$ are consistent with 1:1 electrolytes while the infra-red spectra contain a band at ca 1500 cm$^{-1}$ confirming the presence of a co-ordinated dithiocarbamate ligand and molecular weight measurements in CHCl$_3$ support a monomeric structure (21). The $^{31}$Pn.m.r. spectra in CDCl$_3$ at 298K consist of two triplets one arising from P$_A$ and P$_B$ and the other from P$_C$ and P$_D$. The $^1$Hn.m.r. spectrum of [Ru(S$_2$CNMe$_2$)(PMe$_2$Ph)$_4$]BPh$_4$ in CDCl$_3$ at 301K contains a singlet at 2.37δ, 'pseudo-triplet' at 1.76δ and triplet at 1.27δ

† The resonance at 3.85δ is more intense and therefore most likely originates from the same species as the singlet at 44.31 p.p.m. in the $^{31}$Pn.m.r. spectrum.

† The methyl and methylene resonances in the $^1$Hn.m.r. spectrum are complex and it is not possible to determine which isomeric form is predominant.
in the intensity ratio 1:2:2 arising from the methyl groups of the
dithioacid ligand (equivalent due to the symmetry of the molecule), the
cis phosphine groups ($P_A$ and $P_B$) and the trans phosphine groups ($P_C$ and
$P_D$) respectively.

Ashworth and Singleton$^{147}$ have recently prepared a similar species
viz. $[\text{Ru(O}_2\text{COR})'(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ (22) by reacting $[\text{RuH(PhMe}_2\text{Ph})_5]\text{PF}_6$ with $\text{CO}_2$

in methanol or ethanol. The mechanism of formation of (22) is thought
to occur by insertion of $\text{CO}_2$ into an intermediate containing a
Ru-alkoxide bond (Scheme 5.4).

The reaction between $\text{RuCl}_2(\text{PMe}_2\text{Ph})_4$ and $\text{NaS}_2\text{CNMe}_2$ in benzene, how-
ever produces a bright yellow non conducting solid analysing for
$\text{Ru(S}_2\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_3$ (23). The $^{31}\text{P n.m.r.}$ spectrum in $\text{CDCl}_3$ at 298K
exhibits an $AB_2$ pattern $J_A = 14.19$, $J_B = 11.48$ p.p.m., $J_{AB} = 29.5$Hz and the
The 1H n.m.r. spectrum under the same conditions contains two singlets at 3.49 and 2.90 due to the unidentate and bidentate \( S_2CNMe_2 \) groups respectively, two overlapping 'pseudo-doublets' at 1.96 arising from the two

\[
\text{Ru-H + ROH} \rightarrow \text{Ru-OR + H}_2
\]

Scheme 5.4 Mechanism of formation of \([\text{Ru(O}_2\text{COR})(\text{PMe}_2\text{Ph})_4]^+\)

phosphine groups trans to bidentate \( S_2CNMe_2 \) and a doublet at 1.07 from the phosphine ligand trans to the unidentate group.

\( \text{Ru(S}_2\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_3 \) is also deposited as yellow crystals on prolonged reaction of \( \text{RuCl}_2(\text{PMe}_2\text{Ph})_4 \) with \( \text{NaS}_2\text{CNMe}_2 \) in methanol. The reaction presumably does not yield \( \text{Ru(S}_2\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_2 \) (c.f. reaction of mer-
\( \text{RuCl}_3(\text{PMe}_2\text{Ph})_3 \)) because of the insolubility of \( \text{Ru(S}_2\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_3 \) in methanol.

Shaking \( \text{RuCl}_2(\text{P(OMe)Ph}_2)_3 \) with \( \text{NaS}_2\text{CNR}_2 \) (R = Me, Et) in ethanol produces a mixture of two species the major one of which is

\( \text{Ru(S}_2\text{CNR}_2)_2(\text{P(OMe)Ph}_2)_2 \) (24). The \(^{31}\text{P n.m.r. spectra}\) in \( \text{CDCl}_3 \) at 298K are singlets while the \(^1\text{H n.m.r. spectra}\) contain a 'pseudo-triplet' due to the phosphinite ligands and two resonances due to the dithiocarbamate groups which therefore indicates a cis stereochemistry. The other species is a small amount of \([\text{Ru(S}_2\text{CNR}_2)(\text{P(OMe)Ph}_2)_3]^+\) (25) trapped out by addition of \( \text{NaBPh}_4 \).

When the above reaction with \( \text{NaS}_2\text{CNMe}_2 \) is carried out in benzene a yellow solid analysing closely for \( \text{Ru(S}_2\text{CNMe}_2)_2(\text{P(OMe)Ph}_2)_3 \) is obtained. The \(^{31}\text{P n.m.r. spectrum}\) in \( \text{CDCl}_3 \) at 218K contains a broadened resonance
at ca 144 p.p.m. considered to arise from the latter and a sharp singlet at 147.57 p.p.m. due to Ru(S$_2$CNMe$_2$)$_2$(P(OMe)Ph)$_2$ suggesting that some conversion has taken place. Unfortunately the $^1$H n.m.r. spectrum obtained was virtually identical to that of (24) except for weak resonances at 2.968 and 2.828.

As for the other dithioacid ligands treatment of RuCl$_2$L$_4$ (L = PMePh$_2$, P(OMe)$_2$Ph) and RuCl$_2$L$_3$ (L = PEtPh$_2$) with Na$_2$S$_2$CNR$_2$ (R = Me, Et) under all conditions gives only Ru(S$_2$CNR$_2$)$_2$L$_2$. All the $^{31}$P n.m.r. spectra consist of a singlet except those of Ru(S$_2$CNMe$_2$)(PEtPh$_2$)$_2$ which contained two singlets the higher frequency signals decreasing in intensity as the temperature is raised from 213K to 298K. This suggests as for Ru(S$_2$COMe)$_2$(PEtPh$_2$)$_2$ an irreversible isomerisation, shown for Ru(S$_2$CNMe$_2$)$_2$(PEtPh$_2$)$_2$ to be from the trans to the cis isomer by the relative intensities of the three methyl resonances of the dithiocarbamate groups in the $^1$H n.m.r. spectrum at 301K, two of which are of equal intensity and much more intense than the third.

The $^1$H n.m.r. spectra of the remaining complexes are all consistent with a cis stereochemistry. The methylene resonance of Ru(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$ is an unsymmetrical pattern of at least 11 lines centred at ca 3.55 the spacing between each line being ca 7 Hz (Fig. 5.10). Such a pattern is due to the magnetic inequivalence of the methylene protons of S$_2$CNMe$_2$ which are each split by the CH$_3$ group ($J_{IH} = 7$ Hz) resulting in four overlapping quartets.

(d) Proposed mechanism for formation of Ru(S-S)$_2$L$_2$ from RuCl$_2$L$_3$ or 4

In view of the above results, in which several intermediates produced in the formation of Ru(S-S)$_2$L$_2$ have been isolated, a general reaction scheme for the formation of Ru(S-S)$_2$L$_2$ is proposed (Scheme 5.5).
Fig. 5.10. Methylene region of $^1$H n.m.r. spectrum of $[\text{Ru}(\text{S}_2\text{CNEt}_2)_2(\text{PMePh}_2)_2]$ in CDCl$_3$ at 301K.
Scheme 5.5 Mechanism of formation of Ru(S-S)\textsubscript{2}L\textsubscript{2} from RuCl\textsubscript{2}L\textsubscript{4} and RuCl\textsubscript{2}L\textsubscript{3}.

\[ \text{(I)} \]
\[ \text{(II)} \]
\[ \text{(III)} \]
\[ \text{(IV)} \]
\[ \text{(V)} \]
\[ \text{(VI)} \]

\* (21) \( S-S=S_2\text{CNR}_2 \) \( L=\text{PMe}_2\text{Ph} \)

\textit{cis} isomer for \( L=\text{PMe}_2\text{Ph} \)

\textit{trans} isomer for \( L=\text{P(OMe)}_2\text{Ph} \)

\*\* For \( L=\text{P(OR)}\text{Ph}_2 \) chlorides, are \textit{trans} to each other.

\( \text{(VII)} \)
Thus for RuCl₂L₃ (II) the initial step is replacement of one of the chloride ions by a dithiaoacid ligand to give the proposed intermediate (III) followed by rapid attack of the dangling sulphur atom on the vacant co-ordination site to produce (IV). Complex (IV) is stable in benzene when \( ^\text{-}S-S = ^\text{-}S_2\text{PR}_2 \) but in alcohol it loses chloride ion and converts to the cation (V) which can then react with more Na\( ^\text{-}S_2\text{PR}_2 \) to give (VI). However (IV) is not stable in benzene in the presence of stronger nucleophiles such as \( ^\text{-}S_2\text{COR} \) and \( ^\text{-}S_2\text{CNR}_2 \) which replace the chloride ion to produce (VI) although in polar solvents for \( ^\text{-}S-S = ^\text{-}S_2\text{CNR}_2 \) the initial step in this process is the formation of the cation (V). The final step in this mechanism is then attack of the free sulphur atom with the subsequent loss of L to give (VII).

For RuCl₂L₄ (I) the reaction with Na\( ^\text{-}S_2\text{PR}_2 \) follows the same path as that of RuCl₂L₃ and it seems reasonable therefore to assume that loss of an L group occurs prior to reaction with the dithiaoacid ligand. However reaction with Na\( ^\text{-}S_2\text{CNR}_2 \) in alcohol produces the cationic species (VIII) containing four L groups which is probably formed by the rapid attack of the more nucleophilic dithiocarbamate ligand on RuCl₂L₄, which takes place prior to loss of L. Subsequent loss of L and reaction with more dithiocarbamate ligand yields (VI) which, because of its insolubility in alcohol, is precipitated out and further reaction does not occur. Treatment of RuCl₂(PMe₂Ph)₄ with K\( ^\text{-}S_2\)COMe produces only (VI) and therefore as (VI) is formed by both pathways it is not possible to determine which one is operative in this case.

The isolation of several intermediate products in the reactions of RuCl₂(PMe₂Ph)₄ and RuCl₂(P(OR)Ph)₂ (R = Me, Et) with dithiaoacid ligands as opposed to the corresponding reactions of RuCl₂L₄ (L = PMePh₂, P(OMe)₂Ph) and RuCl₂L₃ (L = PETPh₂), which yield only Ru(S-S)₂L₂, is a reflection of the stronger Ru-P bonds in the former complexes. Hence
the last step of the mechanism, which involves the cleavage of a Ru-P bond, is slow so that the intermediate complexes containing three phosphorus donor groups, although they are presumably less thermodynamically stable than Ru(S=S)$_2$L$_2$ (VII), are fairly long lived and can easily be isolated. On the other hand, for complexes containing weaker Ru-P bonds, the tendency to lose an L group is much greater and any intermediates are unstable and quickly rearrange to form the product (VII).
5.3 Experimental

General experimental methods were as in Chapter 2 and heteronuclear decoupling experiments were carried out on the HA 100 spectrometer using a radio frequency field provided by the Schlumberger FS30 frequency synthesiser.

Materials: Sodium dimethyl- and ammonium diphenylphosphinodithioates and potassium O-methyldithiocarbonate were prepared by standard literature methods; NaS₂CNMe₂·2H₂O, NaS₂CNEt₂·3H₂O (Ralph Emmanuel). All reactions were carried out in degassed solvents under an atmosphere of nitrogen.

Diaryl(alkyl)phosphinodithioate complexes.

Chloro(dimethylphosphinodithioato)tris(dimethylphenylphosphine)ruthenium(II) : RuCl₂(PMe₂Ph)₄ (0.2g) and NaS₂PMe₂ (0.2g) were shaken in benzene (20cm³) for 1 hour. The yellow solution obtained was filtered to remove unreacted NaS₂PMe₂ and the benzene removed to give the complex as yellow crystals which were washed with water and dried in vacuo; i.r. spectrum: 600cm⁻¹ (S₂PMe₂); m.p. 178-180°C; mol.wt. in CHCl₃ 744 (required 775).

Chloro(dimethylphosphinodithioat o)tris(methyldiphenylphosphinite)ruthenium(II) : RuCl₂(P(OMe)Ph₂)₃ (0.2g) and NaS₂PMe₂ (0.2g) were shaken in benzene (20cm³) for 1 hour. The resultant yellow solution was filtered and reduced in volume to ca 5cm³. The addition of light petroleum (b.p. 60-80°C) precipitated a yellow solid which was filtered off, washed with water and dried in vacuo; i.r. spectrum: 595cm⁻¹ (S₂PMe₂); m.p. 91-93°C. In a similar manner, Chloro(dimethylphosphinodithioato)tris(ethyldiphenylphosphinite)ruthenium(II) was
prepared from RuCl$_2$(P(OEt)Ph)$_2$; i.r. spectrum: 595 cm$^{-1}$ ($S_2$PMe$_2$); m.p. 116-118°C.

[(Dimethylphosphinodithioato)tris(dimethylphenylphosphine)-
ruthenium(II)] tetraphenylborate: RuCl$_2$(PMe$_2$Ph)$_4$ (0.2g) and NaS$_2$PMe$_2$ (0.2g) were shaken in methanol (20 cm$^3$) for 5 minutes to give a red solution which was filtered to remove unreacted NaS$_2$PMe$_2$. A solution of NaBPh$_4$ (0.2g) in MeOH (5 cm$^3$) was added and the red crystals formed were filtered off and washed with water and diethyl ether; i.r. spectrum: 580 cm$^{-1}$ ($S_2$PMe$_2$); m.p. 149-151°C; mol. wt. in CHCl$_3$ 492 (required 479); conductivity in (CH$_3$)$_2$CO at 298K: - slope of graph = 192. Similarly reaction with NaS$_2$PPh$_2$ produced red crystals of [(Diphenyl-
phosphinodithioato)tris(dimethylphenylphosphine)ruthenium(II)]
tetraphenylborate; i.r. spectrum: 570 cm$^{-1}$ ($S_2$PPh$_2$); m.p. 160-162°C.

[(Dimethylphosphinodithioato)tris(methyl(diphenylphosphinite)-
ruthenium(II)] tetraphenylborate; i.r. spectrum: 580 cm$^{-1}$ ($S_2$PMe$_2$); m.p. 184-186°C; conductivity in (CH$_3$)$_2$CO at 298K: - slope of graph = 215; and [(Diphenylphosphinodithioato)tris(methyl(diphenyl-
phosphinite)] ruthenium(II)] tetraphenylborate; i.r. spectrum: 570 cm$^{-1}$ ($S_2$PPh$_2$); m.p. 150-152°C; were prepared as red-brown

† For a 1:1 electrolyte: molecular weight measured is half of actual molecular weight.

‡ See page 64.
and orange-brown solids respectively by shaking $\text{RuCl}_2(P(\text{OMe})\text{Ph}_2)_3$ with $\text{Na}_2\text{S}_2\text{PMe}_2$ in methanol for 5 minutes followed by addition of $\text{NaBPh}_4$ in methanol to the resultant red solution. Similarly $[(\text{dimethylphosphinodithioato})\text{tris(ethylidiphenylphosphinite)}]\text{ruthenium(II)}$ tetraphenyloborate; i.r. spectrum $580\text{cm}^{-1}$ ($\text{S}_2\text{PMe}_2$); m.p. 116-118°C; and $[(\text{diphenylphosphinodithioato})\text{tris(ethyl-diphenylphosphinite)}]\text{ruthenium(II)}$ tetraphenyloborate; $570\text{cm}^{-1}$ ($\text{S}_2\text{PPh}_2$); m.p. 174-176°C; were prepared as red-brown and orange-brown solids respectively.

$\text{Bis(dimethylphosphinodithioato)}\text{bis(ethylidiphenylphosphinite)}\text{ruthenium(II)}$: $\text{RuCl}_2(P(\text{OEt})\text{Ph}_2)_3$ (0.2g) and $\text{Na}_2\text{S}_2\text{PMe}_2$ (0.2g) were refluxed in ethanol (20cm³) for 2 hours to give a brown solution. On standing for 3 days the solution deposited a small amount of the complex as yellow brown crystals which were filtered off; i.r. spectrum: $588\text{cm}^{-1}$ ($\text{S}_2\text{PMe}_2$); m.p. 230°C.

$\text{Bis(dimethylphosphinodithioato)}\text{bis(dimethylphenylphosphonite)}\text{ruthenium(II)}$: $\text{RuCl}_2(P(\text{OMe})\text{Ph}_2)_4$ (0.2g) and $\text{Na}_2\text{PMe}_2$ (0.2g) were refluxed in methanol (40cm³) for 1 hour to give a bright yellow solution which was reduced in volume to ca. 15cm³. On standing for 1 hour yellow crystals were deposited. These were filtered off, washed with water and dried in vacuo; i.r. spectrum: $580\text{cm}^{-1}$ ($\text{S}_2\text{PMe}_2$); m.p. 207-209°C; mol. wt. in $\text{CH}_2\text{Cl}_2$ 688 (required 691). Similarly $\text{Bis(diphenylphosphinodithioato)}\text{bis(dimethylphenylphosphonite)}\text{ruthenium(II)}$; m.p. 211-213°C; was prepared by reaction of $\text{RuCl}_2(P(\text{OMe})\text{Ph}_2)_4$ with $\text{Na}_2\text{PPh}_2$.

$\text{O-substituted dithiocarbonate complexes.}$

$\text{Bis(O-methyl dithiocarbonate)}\text{tris(dimethylphenylphosphine)}\text{ruthenium(II)}$: $\text{RuCl}_2(P\text{Me}_2\text{Ph})_4$ (0.2g) and $\text{K}_2\text{S}_2\text{COMe}$ (0.2g)
were shaken in methanol (30cm\(^3\)) for two hours during which
time lemon-yellow crystals of the complex were deposited. These
were filtered off and washed with water and diethyl ether;
m.p. 123-125\(^o\)C; mol.wt. in CHCl\(_3\) 726 (required 729). Both
\textit{Bis(0-methylidithiocarbonato)tris(methylidiphenylphosphinite)-
ruthenium(II)}; m.p. 111-113\(^o\)C; and \textit{Bis(0-methylidithiocarbonato)-
tris(ethylidiphenylphosphinite)ruthenium(II)}; m.p. 106-108\(^o\)C;
were prepared similarly from RuCl\(_2\)(P(OMe)Ph\(_2\))\(_3\) and RuCl\(_2\)(P(OEt)Ph\(_2\))
respectively.

\textit{Bis(0-methylidithiocarbonato)bis(methylidiphenylphosphinite)-
ruthenium(II)}: Ru(S\(_2\)COMe)\(_2\)(P(OMe)Ph\(_2\))\(_3\) (0.2g) was refluxed
in CH\(_2\)Cl\(_2\) (20cm\(^3\)) containing KS\(_2\)COMe (0.05g) for 1 hour to
give an orange-yellow solution. Methanol (10cm\(^3\)) was added
and the CH\(_2\)Cl\(_2\) allowed to evaporate off slowly over a period
of 2 days. The orange crystals obtained were filtered off;
m.p. 85-87\(^o\)C.

\textit{Bis(0-methylidithiocarbonato)bis(methylidiphenylphosphinite)-
ruthenium(II)}: RuCl\(_2\)(PMe\(_2\)Ph\(_4\)) (0.2g) and KS\(_2\)COMe (0.2g)
were shaken in methanol for 12 hours. The bright yellow solid
obtained was filtered off and washed with water and diethyl
ether; m.p. 163-165\(^o\)C. The complex \textit{Bis(0-methylidithiocarbon-
ato)bis(ethylidiphenylphosphinite)ruthenium(II)} was prepared
similarly as a yellow solid from RuCl\(_2\)(PETPh\(_2\))\(_3\); m.p. 147-149\(^o\)C.
N,N disubstituted dithiocarbamate complexes

\[
[(\text{Dimethyldithiocarbamato})\text{tetrakis(dimethylphenylphosphine)}-\text{ruthenium(II)}] \text{tetraphenyloborate} \; \text{RuCl}_2(\text{PMe}_2\text{Ph})_4 (0.2\text{g})
\]
was shaken in methanol (30cm\(^3\)) with NaS\(_2\text{CNMe}_2\) (0.2g) for 5 minutes. The solution was filtered and NaBPh\(_4\) (0.2g) added. The white precipitate was filtered off and washed with methanol and diethyl ether; m.p. 154-156\(^\circ\)C; conductivity in CH\(_2\text{Cl}_2\) slope 185; mol. wt. in CHCl\(_3\) 612 (required 546); \(\nu(\text{C-N}) \; 1525\text{cm}^{-1}\). The complex \([(\text{diethyldithiocarbamato})\text{-tetrakis(dimethylphenylphosphine)}\text{ruthenium(II)}] \text{tetraphenyloborate} \;
\nu(\text{C-N}) \; 1492\text{cm}^{-1}\); was prepared similarly using NaS\(_2\text{CNMe}_2\). Bis(dimethyldithiocarbamato)tris(dimethylphenylphosphine)-ruthenium(II) \; \text{RuCl}_2(\text{PMe}_2\text{Ph})_3 (0.2g) and NaS\(_2\text{CNMe}_2\) (0.2g) were shaken in benzene (20cm\(^3\)) for 1 hour. The resulting yellow solution was reduced in volume to ca. 5cm\(^3\) and light petroleum (b.p. 60-80\(^\circ\)C) added to precipitate a yellow solid which was filtered off; mol. wt. in CHCl\(_3\) 683 (required 755); \(\nu(\text{C-N}) \; 1510\text{cm}^{-1}\). An analogous method was used to prepare Bis(dimethyldithiocarbamato)tris(methylidiphenylphosphinite)-ruthenium(II) from RuCl\(_2\)(P(OMe)Ph\(_2\))\(_3\); m.p. 95-97\(^\circ\)C; \(\nu(\text{C-N}) \; 1500\text{cm}^{-1}\)(broad).

\[
[(\text{Dimethyldithiocarbamato})\text{tris(methylidiphenylphosphinite)}-\text{ruthenium(II)}] \text{tetraphenyloborate} \; \text{RuCl}_2(\text{P(OMe)Ph}_2)_3 (0.2g)
\]
and NaS\(_2\text{CNMe}_2\) (0.2g) were shaken in methanol (20cm\(^3\)) for 10 minutes to give an orange solution. The addition of NaBPh\(_4\) (0.2g) produced an orange-pink solid which was filtered off leaving a yellow filtrate. The solid was recrystallised from CH\(_2\text{Cl}_2\)/MeOH. Initially yellow crystals of

\[\text{[Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6\text{]}\text{BPh}_4\] (identified by \(^1\)H n.m.r.) were deposited but on further standing the remaining red solution
gave red crystals of the complex; \( \nu(C-N) 1510\text{cm}^{-1} \). The yellow filtrate on slowly evaporating to half its volume produced orange-yellow crystals of \( \text{Bis(dimethylthiocarbamato)bis(methyl diphenylphosphinite)ruthenium(II)} \); m.p. 194-196°C; \( \nu(C-N) 1510\text{cm}^{-1} \). Similarly reaction with \( \text{NaS}_2\text{CNEt}_2 \) produced \( \text{[(Diethylthiocarbamato)tris(methyl diphenylphosphinite)ruthenium(II)} \) tetrphenylborate as red crystals; \( \nu(C-N) 1480\text{cm}^{-1} \); and \( \text{Bis(diethylthiocarbamato)bis(methyl diphenylphosphinite)ruthenium(II)} \) as yellow crystals; m.p. 170-172°C; \( \nu(C-N) 1482\text{cm}^{-1} \).

\( \text{Bis(dimethylthiocarbamato)bis(dimethylphenylphosphonite)ruthenium(II)} \) : \( \text{RuCl}_2(\text{P(OME)}_2\text{Ph})_4 \) (0.2g) and \( \text{NaS}_2\text{CNMe}_2 \) (0.2g) were refluxed in methanol for 1 hour. The solution was filtered and the solvent allowed to evaporate off slowly to give yellow crystals of the complex; m.p. 178-180°C; \( \nu(C-N) 1520\text{cm}^{-1} \). Reaction with \( \text{NaS}_2\text{CNEt}_2 \) yielded yellow crystals of \( \text{Bis(diethylthiocarbamato)bis(dimethylphenylphosphonite)ruthenium(II)} \); m.p. 125-127°C; \( \nu(C-N) 1482\text{cm}^{-1} \).

The complexes \( \text{Bis(dimethylthiocarbamato)bis(methyl diphenylphosphinite)ruthenium(II)} \); m.p. 229-231°C; \( \nu(C-N) 1515\text{cm}^{-1} \); \( \text{Bis(diethylthiocarbamato)bis(methyl diphenylphosphinite)ruthenium(II)} \); m.p. 84-86°C; \( \nu(C-N) 1485\text{cm}^{-1} \); \( \text{Bis(dimethylthiocarbamato)bis(ethyl diphenylphosphinite)ruthenium(II)} \); m.p. 133-135°C; \( \nu(C-N) 1515\text{cm}^{-1} \) and \( \text{Bis(diethylthiocarbamato)bis(ethyl diphenylphosphinite)ruthenium(II)} \); m.p. 152-154°C; \( \nu(C-N) 1480\text{cm}^{-1} \) were all obtained as yellow solids by shaking \( \text{RuCl}_2(\text{PMePh}_2)_4 \) (0.2g) and \( \text{RuCl}_2(\text{PETPh}_2)_3 \) (0.2g) respectively with \( \text{NaS}_2\text{CNMe}_2 \) (0.2g) and \( \text{NaS}_2\text{CNEt}_2 \) (0.2g) in methanol (30cm³). The complexes were filtered off and washed with water and diethyl ether.
Table 5.2

Analytical data for some ruthenium(II) dithiocarbamates.

<table>
<thead>
<tr>
<th>Complex</th>
<th>% Found</th>
<th>% Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>RuCl(S₂PMe₂)(P(OMe)Ph₂)₃</td>
<td>55.5</td>
<td>5.0</td>
</tr>
<tr>
<td>RuCl(S₂PMe₂)(P(OEt)Ph₂)₃</td>
<td>55.5</td>
<td>5.4</td>
</tr>
<tr>
<td>RuCl(S₂PMe₂)(PMe₂Ph)₃</td>
<td>46.6</td>
<td>5.7</td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>65.1</td>
<td>5.4</td>
</tr>
<tr>
<td>[Ru(S₂PPh₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>68.2</td>
<td>5.2</td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)(P(OEt)Ph₂)₃]BPh₄</td>
<td>64.9</td>
<td>5.6</td>
</tr>
<tr>
<td>[Ru(S₂PPh₂)(P(OEt)Ph₂)₃]BPh₄</td>
<td>68.9</td>
<td>5.3</td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>62.3</td>
<td>6.1</td>
</tr>
<tr>
<td>[Ru(S₂PPh₂)(PMe₂Ph)₃]BPh₄</td>
<td>66.3</td>
<td>5.8</td>
</tr>
<tr>
<td>Ru(S₂PMe₂)₂(P(OEt)Ph₂)₂</td>
<td>46.8</td>
<td>5.2</td>
</tr>
<tr>
<td>Ru(S₂PMe₂)₂(P(OMe)Ph₂)₂</td>
<td>53.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Ru(S₂PPh₂)₂(P(OMe)Ph₂)₂</td>
<td>51.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OMe)Ph₂)₃</td>
<td>52.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OEt)Ph₂)₃</td>
<td>53.9</td>
<td>5.1</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PMe₂Ph)₃</td>
<td>45.6</td>
<td>5.3</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PMePh₂)₂</td>
<td>50.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PEtPh₂)₂</td>
<td>51.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OMe)Ph₂)₂</td>
<td>49.1</td>
<td>4.3</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₄]BPh₄</td>
<td>65.3</td>
<td>6.3</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>65.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(PMe₂Ph)₃</td>
<td>47.5</td>
<td>5.9</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P(OMe)Ph₂)₃</td>
<td>53.8</td>
<td>5.2</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>64.7</td>
<td>5.2</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>65.6</td>
<td>5.4</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P(OMe)Ph₂)₂</td>
<td>50.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Complex</td>
<td>% Found</td>
<td></td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CN&lt;sub&gt;E&lt;/sub&gt;2) &lt;sub&gt;2&lt;/sub&gt;(P(OMe)Ph&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>52.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CNMe&lt;sub&gt;2&lt;/sub&gt;) &lt;sub&gt;2&lt;/sub&gt;(P(OMe)&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>37.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CN&lt;sub&gt;E&lt;/sub&gt;2) &lt;sub&gt;2&lt;/sub&gt;(P(OMe)&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>42.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CNMe&lt;sub&gt;2&lt;/sub&gt;) &lt;sub&gt;2&lt;/sub&gt;(PMePh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>51.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CN&lt;sub&gt;E&lt;/sub&gt;2) &lt;sub&gt;2&lt;/sub&gt;(PMePh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>52.9</td>
<td>5.5</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CNMe&lt;sub&gt;2&lt;/sub&gt;) &lt;sub&gt;2&lt;/sub&gt;(PETPh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>53.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Ru(S&lt;sub&gt;2&lt;/sub&gt;CN&lt;sub&gt;E&lt;/sub&gt;2) &lt;sub&gt;2&lt;/sub&gt;(PETPh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>57.1</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Table 5.3

$^{31}$P n.m.r. spectral data for some ruthenium dithiocarbamate complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp (K)</th>
<th>chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl$(S_2PMe_2)(PMe_2Ph)_3$</td>
<td>CDCl$_3$</td>
<td>213</td>
<td>AB$<em>2$ pattern ($J_A = 20.38$, $J_B = 16.06$ $J</em>{AB} = 33.0$ Hz)</td>
</tr>
<tr>
<td>RuCl$(S_2PMe_2)(P(OMe)Ph_2)_3$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>139.67$^{a,e}$, 96.65$^{b,e}$</td>
</tr>
<tr>
<td>RuCl$(S_2PMe_2)(P(OEt)Ph_2)_3$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>143.42$^{a,e}$, 109.38$^{b,e}$</td>
</tr>
<tr>
<td>[Ru$(S_2PMe_2)(PMe_2Ph)_3]$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>110.31(q)$^{b}$, 32.36(d)$^{a}$ $J_{PP} = 3.6$ Hz</td>
</tr>
<tr>
<td>[Ru$(S_2PPh_2)(PMe_2Ph)_3]$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>104.26$^{b,e}$, 32.29$^{a,e}$</td>
</tr>
<tr>
<td>[Ru$(S_2PMe_2)(P(OMe)Ph_2)_3]$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>144.85(d)$^{a}$, 111.58(q)$^{b}$ $J_{PP} = 4.4$ Hz</td>
</tr>
<tr>
<td>[Ru$(S_2PPh_2)(P(OMe)Ph_2)_3]$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>144.95$^{a,e}$, 103.96$^{b,e}$</td>
</tr>
<tr>
<td>[Ru$(S_2PMe_2)(P(OEt)Ph_2)_3]$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>141.53(d)$^{a}$, 109.90(q)$^{b}$ $J_{PP} = 4.7$ Hz</td>
</tr>
<tr>
<td>[Ru$(S_2PPh_2)(P(OEt)Ph_2)_3]$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>141.39(d)$^{a}$, 102.52(q)$^{b}$ $J_{PP} = 4.2$ Hz</td>
</tr>
<tr>
<td>Ru$(S_2PMe_2)_2(P(OEt)Ph_2)_2$</td>
<td>CDCl$_3$</td>
<td>303</td>
<td>140.76(t)$^{a}$, 86.70(t)$^{b}$ $J_{PP} = 6.0$ Hz</td>
</tr>
<tr>
<td>Ru$(S_2PMe_2)_2(P(OMe)Ph_2)_2$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>170.54(t)$^{a}$, 88.83(t)$^{b}$ $J_{PP} = 6.8$ Hz</td>
</tr>
<tr>
<td>Ru$(S_2PPh_2)_2(P(OMe)Ph_2)_2$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>170.97(t)$^{a}$, 89.47(t)$^{b}$ $J_{PP} = 6.3$ Hz</td>
</tr>
<tr>
<td>Ru$(S_2COMe)_2(PMe_2Ph)_3$</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>AB$<em>2$ pattern ($J_A = 7.62$, $J_B = 10.61$ $J</em>{AB} = 30.3$ Hz)</td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Temp (K)</td>
<td>chemical shift (p.p.m.)</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>---------</td>
<td>----------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OMe)Ph₂)₃</td>
<td>CDCl₃</td>
<td>298</td>
<td>AB₂ pattern (ν₀ = 136.70, ν₁ = 138.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>J_AB = 35.0Hz)</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OEt)Ph₂)₃</td>
<td>CDCl₃</td>
<td>298</td>
<td>AB₂ pattern (ν₀ = 132.64, ν₁ = 135.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>J_AB = 34.8Hz)</td>
</tr>
<tr>
<td>Ru(S₂COMe)₆(P(OMe)Ph₂)₂</td>
<td>CDCl₃</td>
<td>298</td>
<td>146.51(s)</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PMePh₂)₂</td>
<td>CDCl₃</td>
<td>218</td>
<td>30.89(s)</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PEtPh₂)₂</td>
<td>CDCl₃</td>
<td>218</td>
<td>50.32(s) 44.31(s)</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₄]BPh₄</td>
<td>CDCl₃</td>
<td>298</td>
<td>5.02(t) -3.68(t) JPP = 27.0Hz</td>
</tr>
<tr>
<td>[Ru(S₂CNET₂)(PMe₂Ph)₄]BPh₄</td>
<td>CDCl₃</td>
<td>298</td>
<td>5.12(t) -3.32(t) JPP = 26.0Hz</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(PMe₂Ph)₃</td>
<td>CDCl₃</td>
<td>298</td>
<td>AB₂ pattern ν₀ = 14.19, ν₁ = 11.48, J_AB = 29.5Hz</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P(OMe)Ph₂)₃</td>
<td>CDCl₃</td>
<td>218</td>
<td>143.8e</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>CDCl₃</td>
<td>218</td>
<td>145.47(s)</td>
</tr>
<tr>
<td>[Ru(S₂CNET₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>CDCl₃</td>
<td>218</td>
<td>145.54(s)</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P(OMe)Ph₂)₂</td>
<td>CDCl₃</td>
<td>298</td>
<td>147.57(s)</td>
</tr>
<tr>
<td>Ru(S₂CNET₂)₂(P(OMe)Ph₂)₂</td>
<td>CDCl₃</td>
<td>298</td>
<td>148.37(s)</td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Temp (K)</td>
<td>chemical shift (p.p.m.)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>---------</td>
<td>----------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(PMePh₂)₂</td>
<td>CDCl₃</td>
<td>298</td>
<td>31.40(s)</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P₂EtPh₂)₂</td>
<td>CDCl₃</td>
<td>218</td>
<td>54.42(s)</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P₂EtPh₂)₂</td>
<td>CDCl₃</td>
<td>218</td>
<td>54.11(s)</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P(OMe)₂Ph₂)</td>
<td>CDCl₃</td>
<td>298</td>
<td>176.15(s)</td>
</tr>
<tr>
<td>Ru(S₂CNEt₂)₂(P(OMe)₂Ph₂)</td>
<td>CDCl₃</td>
<td>298</td>
<td>176.64(s)</td>
</tr>
</tbody>
</table>

a - resonance due to the phosphine, phosphinite or phosphonite ligands

b - resonance due to the dithiophosphinato group

c - multiplet resembling unsymmetrical quartet

e - broad

f - decreases in intensity as the temperature is raised

g - increases in intensity as the temperature is raised

(d) - doublet  (t) - triplet

(q) - quartet  (s) - singlet
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp (K)</th>
<th>$\delta$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$</td>
<td>CDC$_3$</td>
<td>233</td>
<td>7.28 - 7.36(m)${}^a$, 1.60(d)${}^b$ (J$_{PH}$ = 8Hz), 1.88$^{b,e}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.17(d)$^c$, 1.19(d)$^d$ (J$_{PH}$ = 12.5Hz)</td>
</tr>
<tr>
<td>RuCl(S$_2$PMe$_2$)(P(OMe)Ph$_2$)$_3$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.1 - 7.6(m)$^a$, 3.20$^{b,e}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.36(d)$^c$ (J$_{PH}$ = 12Hz)</td>
</tr>
<tr>
<td>RuCl(S$_2$PMe$_2$)(POE)Ph$_2$)$_3$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.2 - 7.4(m)$^a$, 1.25(t)$^b$ (J$_{HH}$ = 7Hz), 3.36$^{b,e}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.52(d)$^c$ (J$_{PH}$ = 12Hz)</td>
</tr>
<tr>
<td>[Ru(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$]BPh$_4$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.2 - 7.5(m)$^a$, 6.96(m)$^f$, 1.37$^{b,g}$ (N = 6Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.82(d)$^c$ (J$_{PH}$ = 13Hz)</td>
</tr>
<tr>
<td>[Ru(S$_2$PMe$_2$)(P(OMe)Ph$_2$)$_3$]BPh$_4$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.2 - 7.5(m)$^a$, 6.98(m)$^f$, 3.12$^{b,g}$ (N = 11.5Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.44(d)$^c$ (J$_{PH}$ = 12.5Hz)</td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Temp (K)</td>
<td>$\delta$ value</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>[Ru($S_2$PMe$_2$)(P(OEt)Ph$_2$)$_3$]BPh$_4$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.2 - 7.5(m)$^a$ 6.94(m)$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.19(t)$^b$ 3.40$^b,e$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.36(d)$^c$ ($J_{PH} = 13$Hz)</td>
</tr>
<tr>
<td>Ru($S_2$PMe$_2$)$_2$(P(OEt)Ph$_2$)$_2$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>6.8 - 7.5(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.3$^b,e$, 1.20(t)$^b$ $J_{HH} = 7$Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.43(d)$^c$ ($J_{PH} = 12$Hz)</td>
</tr>
<tr>
<td>Ru($S_2$PMe$_2$)$_2$(P(OMe)$_2$Ph)$_2$</td>
<td>CDC$_3$</td>
<td>213</td>
<td>7.70(m)$^a$, 7.36(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.42$^b,e$, 3.58$^b,e$ ($N = 12$Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.71(d)$^c$, 2.12(d)$^c$ ($J_{PH} = 13$Hz)</td>
</tr>
<tr>
<td>Ru($S_2$COMe)$_2$(PMe$_2$Ph)$_3$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.3 - 7.6(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.83$^b,e$ ($N = 8$Hz), 1.19(d)$^b$ ($J_{PH} = 7.5$Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.92(s)$^c$, 3.65(s)$^c$</td>
</tr>
<tr>
<td>Ru($S_2$COMe)$_2$(P(OMe)Ph$_2$)$_3$</td>
<td>CDC$_3$</td>
<td>301</td>
<td>7.0 - 7.6(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.22$^b,e$ ($N = 11$Hz), 3.10(d)$^b$ ($J_{PH} = 10.5$Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.46(s)$^c$, 3.33(s)$^c$</td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Temp (K)</td>
<td>δ value</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------</td>
<td>----------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OEt)Ph₂)₃</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.1 - 7.5(m)ₐ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.0 - 3.4(m)₁, 1.31(t)ᵇ, 1.26(m)ᵇ, j</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.33(s)ᶜ, 2.96(s)ᶜ</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(P(OMe)Ph₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.1 - 7.4(m)ₐ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.22ᵇ, 9 (N = 11Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.71(s)ᶜ</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PMePh₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.18(m)ₐ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.88ᵇ, 9 (N = 7.5Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.81(s)ᶜ</td>
</tr>
<tr>
<td>Ru(S₂COMe)₂(PEtPh₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.18(m)ₐ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.3ᵇ, e, 0.6(m)ᵇ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.85(s)ᶜ, 3.72(s)ᶜ</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph₄)BPh₄]</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.45(m)ₐ, 7.14(m)ₐ, 7.00(m)ᵢ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.76ᵇ, 9 (N = 6.5Hz), 1.17(t)ᵇ (N = 5Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.37ᶜ(s)</td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Temp (K)</td>
<td>$\delta$ value</td>
</tr>
<tr>
<td>---------------------------------------------------</td>
<td>---------</td>
<td>----------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>[Ru(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_4$]BPh$_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.44(m)$^a$, 7.14(m)$^a$, 6.98(m)$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.72$^{b, g}$ N = 6.5Hz, 1.27(t)$^b$ (N = 5Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.90(q)$^c$, 0.82(t)$^c$ (J$_{HH}$ = 7Hz)</td>
</tr>
<tr>
<td>Ru(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_3$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.31(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.96$^{b, e}$, 1.07(d) (J$_{PH}$ = 8Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.49(s)$^c$, 2.90(s)$^c$</td>
</tr>
<tr>
<td>Ru(S$_2$CNMe$_2$)$_2$(P(OMe)Ph$_2$)$_2$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.2 - 7.6(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.30$^{b, g}$ (N = 11Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.02(s)$^c$, 3.10(s)$^c$</td>
</tr>
<tr>
<td>Ru(S$_2$CNMe$_2$)$_2$(P(OMe)Ph$_2$)$_2$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.2 - 7.6(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.22$^{b, g}$ (N = 11Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.60(q)$^c$, 3.44(q)$^c$, 1.09(t)$^c$, 1.06(t)$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(J$_{HH}$ = 7Hz)</td>
</tr>
<tr>
<td>Ru(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>7.1 - 7.4(m)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.78$^{b, g}$ (N = 4Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.57$^{c, l}$, 1.07(t)$^c$ (J$_{HH}$ = 7Hz)</td>
</tr>
</tbody>
</table>
Table 5.4 (contd.)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp (K)</th>
<th>δ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(S₂CNMe₂)₂(P₂Et₂Ph₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.0 - 7.4(m)ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.50ᵇ,r, 2.10ᵇ,r, 0.56(m)ᵇ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.11(s)ᶜ, 2.91(s)ᶜ, 2.72(s)ᶜ,n</td>
</tr>
<tr>
<td>Ru(S₂CNEt₂)₂(P₂Et₂Ph₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.0 - 7.4(m)ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.50ᵇ,r, 2.10ᵇ,r, 0.50(m)ᵇ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.1 - 3.9ᶜ,c, 1.1ᶜ,p</td>
</tr>
<tr>
<td>Ru(S₂CNMe₂)₂(P₂OMe₂Ph₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>7.3(m)ᵃ, 7.5(m)ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.48(t)ᵇ, 3.61(t)ᵇ (N = 7.5Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.04(s)ᶜ, 2.91(s)ᶜ</td>
</tr>
</tbody>
</table>

a - due to phenyl groups(s) of phosphorus donor ligand(s)
b - due to proton(s) of the phosphorus donor ligand(s)
c - due to proton(s) of the dithioacid ligand(s)
d - doublet
e - broad resonance
f - due to BF₄⁻
g - 'pseudo-triplet' (see Appendix 1)
Table 5.4 (contd.)

i - overlapping quartets

j - containing at least one triplet

l - unsymmetrical multiplet consisting of at least 11 lines

m - multiplet

n - less intense than the other two singlets and therefore due to the less stable isomer

o - consisting of several overlapping quartets

p - at least two triplets at 1.01 and 1.18 are observed

r - symmetrical multiplet consisting of at least 7 lines

\[ N = J_{PH} + J_{PH'} \]  (see Appendix 1)
Syntheses of some triple bridged complexes of ruthenium and determination of their mechanism of formation

6.1 Introduction

Many Ru(II) dimers containing a triple halide bridge have been mentioned in the previous chapters. These include \([L_3RuCl_3RuL_3]Y\) prepared by reacting \('RUCl_3.3H_2O'\) with \(L (Y = \text{Cl}^-; L = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PETPh}_2, \text{PET}_2\text{Ph}, \text{PPr}_n\text{Ph}, \text{PBu}_n\text{Ph})\) in ethanol or 2-methoxyethanol, or by addition of \(\text{NaBPh}_4\) to a solution of \([\text{RuCl}_2\text{C}_7\text{H}_8I]\) refluxed with \(L (Y = \text{BPh}_4^-; L = \text{P(OMe)}_2\text{Ph}, \text{P(OMe)}_2\text{Ph})\). Pyrolysis of \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6]\)Cl yields \((\text{PET}_2\text{Ph})_2\text{ClRuCl}_3(\text{PET}_2\text{Ph})_3\) and \([((\text{PET}_2\text{Ph})_3\text{RuCl}_3(\text{PET}_2\text{Ph})_3)_2\text{Cl}]\), whereas one of the products obtained from reacting \(\text{RuCl}_2(\text{PPH}_3)_3\) with \(\text{CS}_2\) is \((\text{PPH}_3)_2(\text{CS})\text{RuCl}_3(\text{PPH}_3)_2\). X-ray structures of these three triple chloride bridged species have been determined and the \(\text{Ru}---\text{Ru}\) distances found to be 3.36\(\AA\), 3.44\(\AA\) and 3.37\(\AA\) respectively. This is in contrast to \((\text{PBu}_3)_2\text{ClRuCl}_3(\text{PBu}_3)_2\), a mixed Ru(II)/Ru(III) triple chloride bridged dimer formed by treating \('RUCl_3.3H_2O'\) with the bulkier \(\text{PBu}_3^n\), where the \(\text{Ru}---\text{Ru}\) distance is now 3.12\(\AA\).

The metal-metal interaction in tri-\(\mu\)-chloro diruthenium complexes has been examined qualitatively. All interactions with the terminal ligands are ignored and only the electrons not taking part in the Ru-Cl and Ru-L bonding are considered. The local symmetry at each metal is approximately \(C_3\) and three orbitals which do not participate in the ligand bonding, \(d_{xy}, d_{yz}\) and \(d_{xz}\) form the irreducible representations \(A_1\) and \(E\). Hybrid atomic orbitals of functional form \(\psi(A_1) = \frac{1}{\sqrt{3}}(d_{xy} + d_{yz} + d_{xz})\), \(\psi(E) = \frac{1}{\sqrt{6}}(d_{xy} - d_{yz})\) and \(\psi(E) = \frac{1}{\sqrt{6}}(2d_{xz} - d_{xy} - d_{yz})\) are formed on each metal atom. The \(\psi(0)\) orbital is maximum along the \(\text{Ru}---\text{Ru}\) inter-nuclear line and overlap between the two \(A_1\) orbitals is considered to
result in strong metal-metal bonding and antibonding orbitals. The \( \psi_1(E) \) orbitals are not maximum along the internuclear line and overlap will therefore not be as great as between the \( A_1 \) orbitals (Fig. 6.1).

This situation applies to all molecules of the type \([\text{Ru}_2\text{Cl}_3\text{A}_n\text{L}_{6-n}]^m\) where \( A \) is an anionic terminal ligand, \( L \) is a neutral terminal ligand and \( m \) is the charge. The two metal atoms contain 16-3-n-m electrons

\[
\begin{align*}
\text{A}_1^+ \\
\text{E}^* \\
d_{xy},d_{yz},d_{xz} \\
\text{E} \\
d_{xy},d_{yz},d_{xz} \\
\text{A}_1
\end{align*}
\]

\[\text{Ru(1)} \quad \text{Ru(1)-Ru(2)} \quad \text{Ru(2)}\]

Fig. 6.1 Schematic Representation of metal bonding orbitals in tri- -chloro-diruthenium complexes

which do not contribute to \( \sigma \) bonding and which therefore reside in metal orbitals. The species \([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6]^+, \text{Ru}_2\text{Cl}_4(\text{PET}_2\text{Ph})_5\) and \( \text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4\) each contain 12 electrons which completely fill the \( A_1 \) and \( E \) molecular orbitals, and the Ru --- Ru distances correlate with a bond order of zero. In paramagnetic \( \text{Ru}_2\text{Cl}_5(\text{PBu}^\text{N})_3 \) the eleven electrons fail to fill all 6 orbitals and the observed distance of 3.12\( \AA \) corresponds to a bond order of 0.5. However an X-ray structure\(^{151}\) of \((\text{CO})_3\text{RuCl}_3\text{Ru(SrCl}_3\text{)(CO})_2\) (2) prepared by treating \( \text{Ru}_3(\text{CO})_{12} \) with \( \text{SnCl}_4\)\(^{152}\) shows this molecule (which contains 12 electrons, completely filling all
6 orbitals) to have a metal-metal distance of only 3.157 Å. In this case it is suggested that electron density is withdrawn from the M-M antibonding orbitals into the terminal ligand π orbitals, thus increasing the Ru-Ru bond order from zero.

The reaction between \( \text{Ru}_3(\text{CO})_{12} \) and \( \text{SnCl}_4 \) to produce \( \text{Ru}_3 \text{Cl}_3 \text{Ru}(\text{SnCl}_3)(\text{CO})_2 \) \(^{(2)}\) \(^{152} \) was carried out at high temperature. The same reaction at room temperature gives \( \text{ClRu}_3(\text{CO})_{12}(\text{SnCl}_3) \) which is thought to have a linear structure \(^{(1)}\) analogous to \( \text{ClOs}_3(\text{CO})_{12} \text{AuPPh}_3 \). \(^{154} \)

At higher temperatures, \( \text{Ru}_2 \text{Cl}_3(\text{SnCl}_3)(\text{CO})_5 \) was thought to be formed by cleavage of \( \text{ClRu}_3(\text{CO})_{12}(\text{SnCl}_3) \) to give \( \text{RuCl}(\text{SnCl}_3)(\text{CO})_4 \) which then dimerises and loses \( \text{SnCl}_2 \). An intramolecular rearrangement involving loss of \( \text{CO} \) then forms the product (Scheme 6.1).

Several synthetic routes to triple chloro bridged complexes of Ru(II) have been described by Nixon and Head \(^{154} \) (Scheme 6.2). Treatment of \( \text{RuH}_2 \text{L}(\text{PPh}_3)_3 \) \( (L = \text{CO}, \text{PF}_3) \) with gaseous HCl; displacement of acetone and \( \text{PPh}_3 \) by \( L \) \( (L = \text{PF}_3) \) from the di-μ-chloro complex \( [\text{RuCl}_2(\text{PPh}_3)_2-\text{acetone}]_2 \); treatment of \( \text{RuCl}_2(\text{PPh}_3)_3 \) with \( L \) \( (L = \text{PF}_3, \text{Me}_2 \text{NPF}_2) \) and the thermal decomposition of complexes \( \text{RuCl}_2 \text{L}(\text{PPh}_3)_2 \text{dma} \) all yield \( \text{PPh}_3)_2 \text{LRuCl}_3 \text{RuClL(PPh}_3)_2 \) \((3)\) which can then react with excess \( L \) \( (L = \text{PF}_3) \) to give \( \text{cis-RuCl}_2 \text{L}_2(\text{PPh}_3)_2 \). The triple chloro bridged complex \( \text{PPh}_3)_2(\text{PF}_3)_2 \text{LRuCl}_3 \text{RuClL(PPh}_3)_2 \) is obtained from the reaction of a 2:1 mixture of \( \text{RuCl}_2(\text{PPh}_3)_3 \) and \( \text{PF}_3 \), while heating under reflux a 1:1 mixture of \( \text{RuCl}_2(\text{PPh}_3)_3 \) and \( \text{cis-RuCl}_2(\text{PF}_3)_2(\text{PPh}_3)_2 \) in acetone yields \((3)\) (Scheme 6.3). This reaction presumably involves a tertiary phosphine ligand.
Scheme 6.1 Original proposed mechanism of formation of

$\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_5$
Scheme 6.2 Several routes to the preparation of Ru$_2$Cl$_4$L$_2$(PPh$_3$)$_3$

Transfer. Compound (3) can exist as three geometric isomers (Fig. 6.2) and $^{19}$F n.m.r. studies have shown that all three are formed in the above reactions.

The complex (PPh$_3$)$_2$ClRuCl$_3$Ru(N$_2$)(PPh$_3$)$_2$ $^{155}$ is formed by treating RuCl$_2$(PPh$_3$)$_4$ in THF with N$_2$ under pressure. It reacts further with N$_2$B$_{10}$H$_{18}$S(CH$_3$)$_2$ to form (PPh$_3$)$_2$ClRuCl$_3$Ru(PPh$_3$)$_2$N$_2$B$_{10}$H$_{18}$S(CH$_3$)$_2$.

Heating the double chloro bridged species [RuCl$_2$(C$_6$H$_6$)$_2$] in water gives an orange solution which, on treatment with NH$_4$PF$_6$ precipitates [(C$_6$H$_6$)$_2$RuCl$_3$Ru(C$_6$H$_6$)]PF$_6$. $^{156}$ Recently, $^{157}$ this complex has been obtained in much higher yield by shaking [RuCl$_2$(C$_6$H$_6$)$_2$] with an excess of NH$_4$PF$_6$ in methanol, while reaction of [RuCl$_2$(arene)$_2$] with aqueous NaOH gives the triple hydroxy bridged species [(arene)Ru(OH)$_3$Ru(arene)]Cl.3H$_2$O.
Scheme 6.3  Coupling reaction of RuCl(PF3)(PPh3) with RuCl2(PPh3)2.  

Fig. 6.2 The geometric isomers of 
(PPh3)3ClRuClRu(L(PPh3))32 (L=PF3, CO)
(arene = C\textsubscript{6}H\textsubscript{6}, h\textsubscript{6}C\textsubscript{6}Me\textsubscript{3}H\textsubscript{3}).

The carbonyl complex \[\{(\text{PPh}_3)_2\text{(CO)}\text{RuCl}_3\text{RuCl(\text{PPh}_3)}_2\}\text{Me}_2\text{CO}^{116}\] was obtained by reacting \(\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{dmf}\) (prepared by carbonylation of \(\text{RuCl}_2(\text{PPh}_3)_3\) in \text{dmf}^{168}\) with \(\text{RuCl}_2(\text{PPh}_3)_3\) (1:1 molar ratio) in acetone, and this reaction has been extended\(^{158}\) to synthesise mixed halide bridged species \[\{(\text{PPh}_3)_2\text{BrRuBrCl}_2\text{Ru(CO)(PPh}_3)_2\}\text{Me}_2\text{CO}\] and \[\{(\text{PPh}_3)_2\text{ClRuClBr}_2\text{Ru(CO)(PPh}_3)_2\}\text{Me}_2\text{CO}\. The compound \(\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{dmf}\) was converted to \(\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{MeOH}\), by recrystallisation from methanol, which in hot \(\text{CH}_2\text{Cl}_2\) dimerised to give \((\text{PPh}_3)\text{Cl(CO)}\text{RuCl}_3\text{Ru(CO)(PPh}_3)_2\text{Cl}\), for which there are three possible geometric isomers (Fig. 6.2) and \(31\text{Pn.m.r. studics}^{158}\) showed all three to be present. This compound can also be obtained by treating \(\text{RuHCl(CO)(PPh}_3)_3\) or \(\text{RuH}_2(\text{CO)(PPh}_3)_3\) with \(\text{HCl}\). When \(\text{RuCl}_2(\text{CO)(PPh}_3)_2\text{MeOH}\) was treated with an equimolar amount of \(\text{PPh}_3\) in a polar solvent a small amount of \[\{(\text{PPh}_3)_2(\text{CO)}\text{RuCl}_3\text{Ru(CO)(PPh}_3)_2\}\text{X} (X = \text{Cl})\] was obtained. The same product \((X = \text{BPh}_4^-)\) resulted from the reaction of \((\text{PPh}_3)_2\text{ClRuCl}_3\text{Ru(CO)Cl(PPh}_3)_2\) isomeric mixture with \(\text{PPh}_3\) and \(\text{NaBPh}_4\) in a polar solvent.

Corresponding reactions using \(\text{RuCl}_2(\text{PETPh}_2)_3\) as the starting material have been attempted.\(^{81}\) Thus, reaction of \(\text{RuCl}_2(\text{PETPh}_2)_3\) with \(\text{CO}\) in \text{dmf} yielded \(\text{RuCl}_2(\text{CO})(\text{PETPh}_2)_2\text{dmf}\) which coupled with \(\text{RuCl}_2(\text{PETPh}_2)_3\) to give some \((\text{PETPh}_2)_2(\text{CO)}\text{RuCl}_3\text{RuCl(PETPh}_2)_2\) \((31\text{Pn.m.r. evidence})\) but at the same time side reactions take place.\(^{\dagger}\) Free \(\text{PETPh}_2\) liberated during the formation of the dimer reacts with \(\text{RuCl}_2(\text{CO})(\text{PETPh}_2)_2\text{dmf}\) to give \(\text{[RuCl}_2(\text{CO)(PPh}_3)_2\text{]}_2\) isomers \(\text{(See Ref. 115)}\)

\(\dagger\) reported in an earlier publication to be a mixture of \(\text{[RuCl}_2(\text{CO)(PPh}_3)_2\text{]}_2\) isomers \(\text{(See Ref. 115)}\)

\(\ddagger\) This reaction has been repeated and shown by \(31\text{Pn.m.r.}\) to result in the same isomeric mixture as found previously

\(\ddagger\) These side reactions do not occur in the \(\text{PPh}_3\) case due to the bulkiness of the ligand which inhibits formation of \(\text{RuCl}_2(\text{CO)(PPh}_3)_3\) or associative rearrangements of \(\text{RuCl}_2(\text{PPh}_3)_3\).
RuCl₂(CO)(PETPh₂)₃ and also RuCl₂(PETPh₂)₃ itself rearranges to (PETPh₂)₃RuCl₃RuCl(PSTPh₂)₂. Similarly shaking RuCl₂(CO)(PETPh₂)₂dmf in CH₂Cl₂ yields as well as the isomeric mixture of (PETPh₂)(CO)RuCl₃Ru(CO)(PETPh₂)₂ some RuCl₂(CO)(PETPh₂)₃ and a small amount of [(PETPh₂)₂(CO)RuCl₃Ru(CO)(PETPh₂)₂]Cl.

6.2 Determination of mechanism of formation of (PPh₃)₂(CS)RuCl₃RuCl(PPh₃)₂.

The reaction of RuCl₂(PPh₃)₃ with CS₂ gives three major products viz. [RuCl(ηCS₂)(PPh₃)₃]Cl (4), [RuCl₂(CS)(PPh₃)₂]₂ (5) and Ru₂Cl₄(CS)(PPh₃)₄ (6). The formation of (6) was originally thought to occur by the initial formation of a five co-ordinate intermediate RuCl₂(CS)(PPh₃)₂ (7), by loss of SPPh₃ from [RuCl(ηCS₂)(PPh₃)₃]Cl (4) which then dimerises to (5), followed by an intramolecular rearrangement involving displacement of a thiocarbonyl group by a chloride (Scheme 6.4). However prolonged refluxing of (5) in CS₂, acetone, benzene or chloroform failed to produce any of (6). Therefore it was considered that the formation of (6) might occur by direct reaction of RuCl₂(CS)(PPh₃)₂ (7) with unreacted RuCl₂(PPh₃)₃ but this was not proved although good evidence for the feasibility of such a mechanism was obtained from the formation of the analogous (PPh₃)₂(CO)RuCl₃RuCl(PPh₃)₂ by reaction of RuCl₂(CO)(PPh₃)₂dmf with RuCl₂(PPh₃)₃ (1:1 molar ratio) in acetone. Therefore the following work was carried out in order to determine the mechanism of formation of (6).

Results and discussion

Reaction of Ru₂Cl₄(CS)₂(PPh₃)₄ (5) with refluxing dmf gives RuCl₂(CS)(PPh₃)₂dmf. The infra-red spectrum contains ν(CS) at 1275cm⁻¹ and ν(Ru-Cl) at 325cm⁻¹ while the ³¹Pn.m.r. spectrum at 303K in CDCl₃ consists of a singlet at 30.2p.p.m. These observations indicate a structure with trans phosphines and trans chlorides (8).
Scheme 6.4  Original mechanism proposed for formation of Ru$_2$Cl$_4$(CS)(PPh$_3$)$_4$. 

-184-
Reaction of RuCl₂(CS)(PPh₃)₂ dmf with RuCl₂(PPh₃)₃ in refluxing acetone (1:1 molar ratio) gives the triple chloride bridged species Ru₂Cl₄(CS)(PPh₃)₄ (6), whose ³¹P n.m.r. spectrum at 303K in CDCl₃ contains two AB patterns at 48.3 p.p.m. (δₐ�� = 94.0, Jₓᵧ = 37.4 Hz) and 36.1 p.p.m. (δₐオープ = 54.9, Jₓᵧ = 24.6 Hz) respectively. Converting RuCl₂(CS)(PPh₃)₂ dmf to RuCl₂(CS)(PPh₃)₂ MeOH, by recrystallisation from methanol, and then shaking this complex in CH₂Cl₂ produces a yellow crystalline solid analysing closely for [Ru₂Cl₄(CS)(PPh₃)₃]0.5CH₂Cl₂ (9). A very small amount of this complex (Me₂CO solvate) has been prepared previously by shaking (5) in degassed Me₂CO for several days.¹²¹ The ³¹P n.m.r. spectrum in CDCl₃ at 303K is not very helpful, consisting of two strong broad peaks at 48.1 and 37.7 p.p.m. (relative intensity 1:2) and weaker peaks also of relative intensity 1:2 at 50.3 and 35.6 p.p.m. However at 213K the ³¹P n.m.r. spectrum is better resolved (Fig. 6.3) and the assignment of the three possible isomers to the various resonances is given in Table 6.1. A good indication that an isomeric mixture of (9) has been produced was obtained by its reaction with NaBPh₄ and PPh₃ in CH₂Cl₂ which gave a high yield of
[(PPh₃)₂(SC)RuCl₂Ru(CS)(PPh₃)₂]BPh₄ (10). The $^{31}$P.n.m.r. spectrum in CDCl₃ at 213K consists of a sharp quartet centred at 37.5 p.p.m. ($\delta_{AB} = 86.8$, $J_{AB} = 27.0$ Hz). A small amount of this cation along with the Ru₂Cl₄(CS)₂(PPh₃)₃ isomeric mixture was also found when RuCl₂(CS)(PPh₃)₂MeOH was shaken in ethanol with an equimolar amount of PPh₃ for several hours.

Therefore on the basis of the above results and those obtained previously for the corresponding CO system which are very similar, it is evident that the formation of these triple chloride bridged species occurs by the direct coupling together of two monomeric species and not through a double bridged intermediate. For RuCl₂(CS)(PPh₃)₂MeOH which contains both trans phosphines and trans chlorides the dimerisation product is Ru₂Cl₄(CS)₂(PPh₃)₃ (9) accompanied by loss of PPh₃ (Scheme 6.5). In the presence of excess PPh₃ in polar solvents some dimerisation can occur with loss of chloride to give

$$ [(PPh₃)₂(SC)RuCl₂Ru(CS)(PPh₃)₂]BPh₄ (10). $$

However in the [RuCl₂(PPh₃)₃]-CS₂ system, where very little Ru₂Cl₄(CS)₂(PPh₃)₃ is formed, it is reasonable to infer that the 'RuCl₂(CS)(PPh₃)₂' intermediate will initially have cis-PPh₃ groups. Support for this comes from the X-ray structure of RuCl₂(PPh₃)₃ which shows that the apical Ru-P bond is considerably shorter than the basal Ru-P bonds, together with the structure of its dissociation product [RuCl₂(PPh₃)₂]₂ shown by $^{31}$P.n.m.r. studies to contain cis-PPh₃ groups. Therefore a likely structure for the five co-ordinate intermediate in the
FIG. 63

Pnmr spectrum of Ru(CO)(CS)(PP)₃ in CDCl₃ at 213K.
Table 6.1

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$^{31}$P n.m.r. (CDCl$_3$ at 213K) δ/p.p.m.</th>
<th>Singlet</th>
<th>AB position</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Ph$_3$P—Ru—Cl—Ru—CS—PPh$_3$</td>
<td>49.7</td>
<td>37.0[$\delta_{AB}$ 15.0Hz] [$J_{AB}$ 26.0Hz]</td>
<td></td>
</tr>
<tr>
<td>B. Ph$_3$P—Ru—Cl—Ru—PPh$_3$</td>
<td>51.8</td>
<td>35.8[$\delta_{AB}$ 71.4Hz] [$J_{AB}$ 26.0Hz]</td>
<td></td>
</tr>
<tr>
<td>C. Ph$_3$P—Ru—Cl—Ru—PPh$_3$</td>
<td>50.9</td>
<td>41.2[$\delta_{AB}$ 52.0Hz] [$J_{AB}$ 26.9Hz]</td>
<td></td>
</tr>
</tbody>
</table>

†The resonances are assigned on the basis of the $\delta_{AB}$ values which are expected to be larger for isomers in which one PPh$_3$ is eclipsed by a PPh$_3$ group and the other by a CS or Cl (isomers B and C). Therefore it is possible to distinguish isomer A, where one PPh$_3$ group is eclipsed by CS and the other by Cl, but not between isomers B and C.
Scheme 6.5 Dimerisation of $\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\text{MeOH}$
[RuCl₂(PPh₃)₃]⁻-CS₂ system is (11) formed by elimination of SPPh₃ from either [Ru(CS₂)Cl(PPh₃)₃]Cl and/or RuCl₂(PPh₃)₃SCS (Scheme 6.6). Complex (11) can then undergo two competing reactions viz. (i) coupling with unchanged RuCl₂(PPh₃)₃ to give (6) in which prior dissociation of one of the trans-PPh₃ groups of RuCl₂(PPh₃)₃ occurs. (ii) self dimerisation without phosphine loss to give (5). Small amounts of Ru₄Cl₄(CS)₂(PPh₃)₃ (9) and [Ru₂Cl₂(CS)₂(PPh₃)₄]Cl (10) are obtained probably because of isomerisation of (11) to the trans isomer (8) and subsequent dimerisation as in Scheme 6.5.

The reason why five co-ordinate complexes (or six co-ordinate solvates) with trans-PPh₃ groups dimerise to triple chloride bridge complexes with PPh₃ loss whereas those with cis-PPh₃ groups form double bridged dimers without PPh₃ loss is attributed to the high trans influence of PPh₃ and the consequent electronic instability of trans-Ru(PPh₃)₂ compared to cis-Ru(PPh₃)₂ arrangements. Evidence for this comes from the isolation of [RuCl₂(CO)(PMe₂Ph)₂]₁₁₉ from a solution thought to contain RuCl₂(CO)(PMe₂Ph)₂ with cis-PMe₂Ph groups. The driving force for all these rearrangements is presumably the high stability of six co-ordinate Ru(II) complexes containing triple halide bridges.

6.3 Preparation of L₂YRuCl₃RuClL'₂ (L = L' = P(p-tol)₃, Y = CO,CS)
L = PPh₃, L' = P(p-tol)₃, Y = CO)

The complexes Ru₂Cl₄YL₄ (L = PPh₃, Y = CO,CS; L = PETPh₂, Y = CO) are now well characterised. To extend the range of such species Ru₂Cl₄YL₄ (L' = P(p-tol)₃) have been prepared and attempts made to synthesise Ru₂Cl₄(CO)L₂L'₂ (L = PPh₃, L' = P(p-tol)₃).

Results and discussion

Reaction of RuCl₃.3H₂O with P(p-tol)₃ in methanol, reported to give RuCl₂(P(p-tol)₃)₄,⁷⁶ repeatedly produced dark purple crystals of the tris
Scheme 6.6 Mechanism of $[\text{RuCl}_2(\text{PPh}_3)_3] - \text{CS}_2$ reaction.
species RuCl$_2$(P(p-tol)$_3$)$_3$. The $^{31}$P.n.m.r. spectrum in CH$_2$Cl$_2$/C$_2$D$_6$CO at 190K consists of a doublet at 25.05p.p.m. and a triplet at 74.34p.p.m. ($J_{PP} = 28.0$Hz) plus a weak singlet at 28.8p.p.m. due to OP(p-tol)$_3$. As the temperature is raised the doublet and triplet collapse and at 298K coalesce to a broad singlet at 39.9p.p.m. These results along with the infra-red spectrum which contains a band at $\sim 320\text{cm}^{-1}$ due to trans chlorides, indicate a structure similar to that of RuCl$_2$(PPh$_3$)$_3$ (12) which is undergoing rapid intramolecular exchange of P(p-tol)$_3$ groups at ambient temperature.

When RuCl$_2$(P(p-tol)$_3$)$_3$ was refluxed in CS$_2$, for a short time, a red solution was obtained, but in contrast to the analogous reaction of RuCl$_2$(PPh$_3$)$_3$ no [RuCl($\eta$CS$_2$)(P(p-tol)$_3$)$_3$]Cl was deposited. Addition of light petroleum (b.p. 60-80°C), however, precipitated a pink solid analysing closely for the double chloro bridged complex [RuCl$_2$(CS)(P(p-tol)$_3$)$_2$]$_2$. The infra-red spectrum contains a band at $1290\text{cm}^{-1} (\nu_{CS})$ and the $^{31}$P.n.m.r. spectrum in CDCl$_3$ at 298K consists of a strong singlet at 29.54p.p.m. due to the latter complex, with weaker singlets at 28.51p.p.m. due to OP(p-tol)$_3$ and 42.46p.p.m., possibly due to a different isomeric form of [RuCl$_2$(CS)(P(p-tol)$_3$)$_2$]$_2$, for which there is both a cis (13) and a trans isomer (14). The remaining solution

† The reason for this is probably the high pH of the commercial 'RuCl$_3$·3H$_2$O' used which favours formation of the tris species
on standing for 6 hours deposited an orange solid whose $^{31}$P n.m.r. spectrum in CDCl$_3$ at 298K displays two quartets at 47.59 ($J_{AB} = 39.7$, $\delta_{AB} = 80.9$Hz) and 34.61ppm ($J_{AB} = 25.1$, $\delta_{AB} = 74.9$Hz) (Fig. 6.4) and this is due to the triple chloro bridged species

$\text{(P(p-tol)$_3$)$_2$(SC)RuCl}_3\text{RuCl(P(p-tol)$_3$)$_2$.}$

Treatment of RuCl$_2$(P(p-tol)$_3$)$_3$ with CO in dmf produces RuCl$_2$(CO)(P(p-tol)$_3$)$_2$dmf, whose infra-red spectrum contains $\nu_{CO} = 1935$cm$^{-1}$, $\nu_{Ru-Cl} = 340$cm$^{-1}$ and a broad band at 1645cm$^{-1}$ due to co-ordinated dmf, and whose $^{31}$P n.m.r. spectrum at 298K in CDCl$_3$ is a singlet at 32.3ppm. Therefore RuCl$_2$(CO)(P(p-tol)$_3$)$_2$dmf has an analogous structure to RuCl$_2$(P(p-tol)$_3$)$_3$ with trans phosphines and trans chlorides. Coupling of RuCl$_2$(CO)(P(p-tol)$_3$)$_2$dmf with RuCl$_2$(P(p-tol)$_3$)$_3$ (1:1 molar ratio) yields as expected the triple chloride bridged dimer $(\text{P(p-tol)$_3$)$_2$(CO)Ru}_{3}$. Cl$_3\text{RuCl(P(p-tol)$_3$)$_2.}$ The $^{31}$P n.m.r. spectrum at 298K in CDCl$_3$ contains two quartets at 47.64 ($J_{AB} = 38.8$, $\delta_{AB} = 73.0$Hz) and 38.84ppm ($J_{AB} = 25.1$, $\delta_{AB} = 97.5$Hz), which are assigned as for Ru$_2$Cl$_4$(CS)(P(p-tol)$_3$)$_4$ (Fig. 6.4). Recrystallisation of RuCl$_2$(CO)(P(p-tol)$_3$)$_2$dmf from MeOH yields RuCl$_2$(CO)(P(p-tol)$_3$)$_2$MeOH and shaking the latter in CH$_2$Cl$_2$ produces a yellow brown solid analysing for Ru$_2$Cl$_4$(CO)$_2$(P(p-tol)$_3$)$_3$. The $^{31}$P n.m.r. spectrum at 298K in CDCl$_3$ (Fig. 6.5) indicated the presence of the three possible isomers.
An attempt to synthesise $\text{L}_2\text{ClRuCl}_3\text{Ru(CO)L}_2'$ by means of coupling $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{RuCl}_2(\text{CO})(\text{P(p-tol)}_3)_2\text{dmf}$ resulted in the isolation of an orange solid whose $^{31}\text{P n.m.r.}$ spectrum in $\text{CHCl}_3/\text{C}_6\text{D}_6$ (Fig. 6.6) shows a large number of resonances in the region 46-50 p.p.m. containing several AB patterns. However these are difficult to assign as the product is obviously a mixture. During the coupling process dissociation of $\text{PPh}_3$ from $\text{RuCl}_2(\text{PPh}_3)_3$ occurs, which can then displace $\text{P(p-tol)}_3$ from the postulated initially formed product $(\text{PPh}_3)_2\text{ClRuCl}_3\text{Ru(CO)(P(p-tol)}_3)_2$ to give in addition $(\text{PPh}_3)_2\text{ClRuCl}_3\text{Ru(CO)(P(p-tol)}_3)_n(\text{PPh}_3)_2-n$ ($n = 0, 1$). This side reaction should not occur in the reaction between $\text{RuCl}_2(\text{P(p-tol)}_3)_3$ and $\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{dmf}$ and indeed an orange solid analysing for $\text{Ru}_2\text{Cl}_4(\text{CO})(\text{PPh}_3)_2(\text{P(p-tol)}_3)_2$ is obtained. Its $^{31}\text{P n.m.r.}$ spectrum displays two AB patterns at 48.0 ($J_{AB} = 34.2$, $\delta_{AB} = 83.2$ Hz) and 40.23 p.p.m. ($J_{AB} = 25.1$, $\delta_{AB} = 99.1$ Hz) respectively as expected for $(\text{P(p-tol)}_3)_2\text{ClRuCl}_3\text{Ru(CO)(PPh}_3)_2$ (see Table 6.2).

Finally the attempted coupling reactions of $\text{RuCl}_2(\text{CO})\text{L}_2\text{dmf}$ ($\text{L} = \text{PPh}_3$, $\text{P(p-tol)}_3$) with $\text{RuCl}_2\text{L}_3'$ ($\text{L}' = \text{P(OMe)Ph}_2$, $\text{P(OEt)Ph}_2$) were completely unsuccessful. However considering the mechanism of formation of triple halide bridged ruthenium dimers suggested earlier this can now be explained by the fact that, unlike $\text{RuCl}_2\text{L}_3$ ($\text{L} = \text{PPh}_3$, $\text{P(p-tol)}_3$), $\text{RuCl}_2\text{L}_3'$ does not dissociate $\text{L}$ in solution and hence the formation of $\text{L}_2(\text{CO})\text{RuCl}_3\text{RuCl}_2'$ cannot occur. In polar solvents $\text{RuCl}_2\text{L}_3'$ can dissociate $\text{Cl}^-$, but then rapidly self-dimerise or trimerise to give $[\text{Ru}_2\text{Cl}_3\text{L}_6]'\text{Cl(L}^0\text{P(OMe)Ph}_2\text{)}$ or $[\text{Ru}_3\text{Cl}_5\text{L}_9]'\text{Cl(L}^0\text{P(OEt)Ph}_2\text{)}$. Hence the reaction products obtained in acetone were unreacted $\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{dmf}$, $\text{Ru}_2\text{Cl}_4(\text{CO})_2(\text{PPh}_3)_3$, due to the self-dimerisation of $\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{dmf}$, and the rearranged product of $\text{RuCl}_2\text{L}_3'$. 
Fig 6.4 $^{31}$P n.m.r. spectrum of $\text{Ru}_2\text{Cl}_4(\text{CS})(\text{P}(\text{p-tol}))_3$ in CDCl$_3$ at 298K.

Resonances assigned by analogy with $\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_3$. 

Chemical shift (p.p.m.)
Fig. 6.5 Pn.m.r. spectrum of Ru$_2$Cl$_4$(CO)$_2$(P(p tolyl)$_3$)$_3$ in CDCl$_3$ at 298K.

Isomer $\circ$ 50.49(s) 41.54(q)

$J_{AB}$ 25.5, $\delta_{AB}$ 24.3 Hz

Isomer $\times$ 51.25(s) 40.01(q)

$J_{AB}$ 24.9, $\delta_{AB}$ 132.6 Hz

Isomer $\Delta$ 52.18(s) 38.91(q)

$J_{AB}$ 26.1, $\delta_{AB}$ 170.2 Hz

† Isomers assigned as in Table 6.1
Fig. 6.6  $^{31}$P nmr. spectrum of reaction product, from coupling of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{RuCl}_2(\text{CO})(\text{P}(\text{p-tol})_3)_2$ dmf, in CDCl$_3$ at 298K.
Table 6.2

Comparison of AB resonances for $L_2$(CO)RuCl$_3$RuClL'$_2$ with those of $\text{Ru}_2\text{Cl}_4$(CO)L$_4$ and $\text{Ru}_2\text{Cl}_4$(CO)L'$_4$ ($L = \text{PPh}_3$, $L' = \text{P(p-tol)}_3$)

<table>
<thead>
<tr>
<th>AB position (ppm)</th>
<th>$\delta_{AB}$ (Hz)</th>
<th>$J_{AB}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)P(2)</td>
<td>48.0</td>
<td>97.7</td>
</tr>
<tr>
<td>P(3)P(4)</td>
<td>40.3</td>
<td>74.2</td>
</tr>
<tr>
<td>P(3)P(4)</td>
<td>47.6</td>
<td>73.0</td>
</tr>
<tr>
<td>P(3)P(4)</td>
<td>38.8</td>
<td>97.5</td>
</tr>
<tr>
<td>P(1)P(2)</td>
<td>48.0</td>
<td>83.2</td>
</tr>
</tbody>
</table>

(c.f. P(1)P(2) resonance of B)

(c.f. P(3)P(4) resonance of A)
6.4 Synthesis and rearrangement of $[\text{RuCl(SnCl}_3)(\text{CO})(\text{PPh}_3)_2\text{acetone}]$ acetone.

Treatment of the red solution, obtained from carbonylation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in EtOH, with a mixture of anhydrous tin(II) chloride and triphenylphosphine in the presence of acetone, is reported\textsuperscript{14} to give a species analysing for $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_3(\text{Me}_2\text{CO})_2$. Warming this complex in benzene gave an acetone soluble species analysing for $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_4$. In order to determine whether either of these species contain a triple halide bridge these reactions were repeated.

Results and discussion

Addition of $\text{SnCl}_2$ and $\text{PPh}_3$ to the red solution produced lemon yellow crystals whose infra-red spectrum contains a band at 1957 cm\textsuperscript{-1} due to $\nu_{\text{CO}}$ bands at 1701 and 1661 cm\textsuperscript{-1} due to free and co-ordinated acetone respectively and a strong band at 300 cm\textsuperscript{-1} due to $\nu_{\text{Sn-Cl}}$\textsuperscript{†}. The analysis figures obtained were very similar to those previously reported\textsuperscript{14} and for the original proposed formulation there are two possible structures viz. a triple chloro bridged dimer (15) and a double chloro bridged dimer (16) (or isomers of these compounds). However, the $^{31}\text{P}$ n.m.r. spectrum in $\text{C}_6\text{D}_6$ at 303 K showed only one $\text{PPh}_3$ resonance at 35.4 p.p.m. plus two broad, weak signals arising from $^{117}\text{Sn}$ and $^{119}\text{Sn}$ satellites ($J_{\text{PSn}} = 250$ Hz) which is not compatible with either structure (15) or (16).

Therefore, an X-ray structural determination of the product was

\textsuperscript{†}For $[\text{Me}_4\text{N}]_4[\text{RhCl}_2(\text{SnCl}_3)_4]$ the Sn-Cl stretches occur at 363 and 336 cm\textsuperscript{-1} and for $[\text{Et}_4\text{N}]_3[\text{Pt}(\text{SnCl}_3)_5]$ at 336 cm\textsuperscript{-1}.
undertaken to establish its formulation and to ascertain its detailed geometry. The results are shown in Fig. 6.7 and Table 6.3. The molecule deviates only very slightly from \( C_\text{2(h)} \) symmetry; the maximum deviation of the atoms Ru, Sn, Cl(1), Cl(2), O(1), C(1), O(2), C(39), C(40) and C(41) from their best plane is 0.02Å. Within this plane the short Ru-C(1) bond is reflected in the large Sn-Ru-C(1) and Cl(1)-Ru-C(1) angles. Conversely, both PPh\(_3\) groups are substantially tilted away from the bulky SnCl\(_3\) group. Within the SnCl\(_3\) group, the in-plane Sn-Cl(2) bond is significantly shorter than the two out-of-plane bonds, and the distortion from \( C_\text{3v}(3m) \) local symmetry is marked in the angles.

The compound is monomeric, and not dimeric as originally suggested, and, with trans PPh\(_3\) groups and a co-ordinated solvent molecule, is very similar to RuCl\(_2\)(Y)(PPh\(_3\))\(_2\) \( (Y = CO, CS \hspace{1em} S = \text{dmf, MeOH}) \) and is therefore expected to undergo similar dimerisations.

Warming \([\text{RuCl}_3(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2]_{\text{acetone}}\) acetone in benzene gave on addition of light petroleum (b.p. 60-80°C) a pale yellow solid analysing closely for Ru\(_2\)Cl\(_3\)(SnCl\(_3\))(CO)\(_2\)(PPh\(_3\))\(_3\) \( (17) \). The infra-red spectrum contains \( \nu_{\text{CO}} \) 1975 cm\(^{-1}\), \( \nu_{\text{Sn-Cl}} \) 320 cm\(^{-1}\) and no bands due to acetone. However

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Cl} & \quad \text{SnCl}_3 \\
\text{OC} & \quad \text{Ru} & \quad \text{Cl} & \quad \text{Ru} & \quad \text{PPh}_3 \\
\text{Ph}_3\text{P} & \quad \text{Cl} & \quad \text{CO}
\end{align*}
\]

\( (17) \) is not very stable in solution, readily eliminating another molecule of SnCl\(_2\) to give some (PPh\(_3\))Cl(CO)RuCl\(_3\)Ru(CO)(PPh\(_3\))\(_2\). The \( ^{31}\text{P n.m.r.} \) spectrum in C\(_6\)D\(_6\) at 298K consists of a singlet at 53.17 p.p.m. and AB pattern at 41.41 p.p.m. \( (J_{\text{AB}} = 25.9, \delta_{\text{AB}} = 66.1 \text{Hz}) \) due to an isomer

\[\ddagger \text{not } \text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_4 \text{ as originally suggested}\]
Fig 6.7. X-ray structure of RuCl(SnCl$_3$)(CO)(PPh$_3$)$_2$ acetone.
Table 6.3  
Some selected bond lengths and bond angles  
for RuCl(SnCl$_3$)(CO)(PPh$_3$)$_2$(Me$_2$CO)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length A</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru - Sn</td>
<td>2.59</td>
<td>Sn - Ru - C$_1$</td>
</tr>
<tr>
<td>Ru - Cl$_1$</td>
<td>2.41</td>
<td>Sn - Ru - P</td>
</tr>
<tr>
<td>Ru - P$_1$</td>
<td>2.39</td>
<td>Sn - Ru - O$_2$</td>
</tr>
<tr>
<td>Ru - P$_2$</td>
<td>2.40</td>
<td>Cl - Ru - P</td>
</tr>
<tr>
<td>Ru - C$_1$</td>
<td>1.79</td>
<td>Cl - Ru - O$_2$</td>
</tr>
<tr>
<td>Ru - O$_2$</td>
<td>2.19</td>
<td>Cl - Ru - C$_1$</td>
</tr>
</tbody>
</table>

$^+$The first figure refers to P$_1$, the second to P$_2$. 
of (PPh₃)Cl(CO)RuCl₃Ru(CO)(PPh₃)₂⁺ plus a singlet at 49.9 p.p.m. with ¹¹⁷Sn and ¹¹⁹Sn satellites (J<sub>PSn</sub> = 270 Hz) and AB pattern at 40.7 p.p.m. (J<sub>AB</sub> = 25.5, S<sub>AB</sub> = 183.1 Hz) due to (17).

Unlike the formation of Ru₂Cl₄(Y₂(PPh₃))₃ (Y = CO, CS) only one isomer of Ru₂Cl₃(SnCl₃)(CO)₂(PPh₃)₃ is formed presumably because of the steric constraints imposed by SnCl₃⁻. Furthermore on loss of SnCl₂ only one isomer of Ru₂Cl₄(CO)₂(PPh₃)₃ is obtained indicating that the 3 isomers, obtained previously are formed during the coupling process and not via subsequent isomerisation of Ru₂Cl₄(CO)₂(PPh₃)₃.

In view of the above results it seems likely that the formation of (CO)₃RuCl₃Ru(SnCl₃)(CO)₂ (Scheme 6.1, Page 179) does not occur by rear- rangement of the double bridged dimer but by direct coupling of two RuCl(SnCl₃)(CO)₄ monomers involving loss of both CO and SnCl₂.

† The resonances obtained do not correspond to those assigned to the same isomer of Ru₂Cl₄(CO)₂(PPh₃)₃ (ref. 158) suggesting that the original assignment of singlets to AB patterns is wrong and thus the singlet at 53.2 and AB pattern at 40.8 p.p.m. belong to the same isomer, most likely that in which the unique PPh₃ group is eclipsed by CO.
6.5 Experimental

General experimental techniques and materials were as for previous chapters. Tri-p-tolylphosphine was prepared by Linda Scott.

(a) Thiocarbonyl complexes.

**Dichloro(NN-dimethylformamide)thiocarbonylbis(triphenylphosphine)ruthenium(II)**: The complex \( \text{[Ru(CS)Cl}_2(PPh}_3)_2 \) (0.2g) was heated under reflux in NN-dimethylformamide (15cm³) for 3 hours. The resulting yellow solution was reduced in volume and diethyl ether added to precipitate the pale yellow solid; m.p. 168-170°C; \( \nu(CS) \) 1275cm⁻¹, \( \nu(CO) \) (dmf) 1640cm⁻¹, \( \nu(RuCl) \) 325cm⁻¹.

**Tri-\( \mu \)-chloro-\( \alpha \)-chloro-\( \mu \)-thiocarbonyl-tetrakis(triphenylphosphine)diruthenium(II)**: The complexes RuCl₂(PPh₃)₃ (0.19g) and Ru(CS)Cl₂(dmf)(PPh₃)₂ (0.16g) were heated under reflux for 4 hours in acetone (30cm³). On cooling the solution, the red solid was deposited together with some unchanged Ru(CS)Cl₂(dmf)(PPh₃)₂. Proof of formation of (6) was obtained from the \( ^{31} \)P n.m.r. spectrum of the products in CDCl₃ at 298K.

**Dichloro(methanol)thiocarbonylbis(triphenylphosphine)ruthenium(II)**: The complex Ru(CS)Cl₂(dmfaPPh₃)₂ was recrystallised from hot CH₂Cl₂-MeOH to give yellow crystals which were washed with methanol; m.p. 182-184°C; i.r. spectrum: \( \nu(CS) \) 1280cm⁻¹ (co-ordinated methanol), \( \nu(CS) \) 1280cm⁻¹, \( \nu(RuCl) \) 332cm⁻¹.

**Tri-\( \mu \)-chloro-\( \alpha \)-chloro-\( \mu \)-dithiocarbonyl-tris(triphenylphosphate)diruthenium(II)-dichloromethane(2/1)**: The complex Ru(CS)Cl₂(MeOH)(PPh₃)₂ was dissolved in CH₂Cl₂ and light petroleum (b.p. 60-80°C) was added. The yellow solution was placed on a water bath and the CH₂Cl₂ allowed to evaporate off slowly over a period of 24 hours to give yellow crystals which were filtered off and washed with diethyl ether;
Tri-μ-chloro-bis(thiocarbonyl-bis(triphenylphosphine))ruthenium(II) tetraphenyloborate: The Ru₂(CS)₂Cl₄(PPh₃)₃ isomeric mixture (0.08g), Na₂BPh₄ (0.022g) and PPh₃ were shaken in CH₂Cl₂ (20cm³) for 48 hours. The orange-yellow solution was evaporated to dryness and triturated with methanol to give an orange-yellow solid which was washed with water, methanol and diethyl ether; m.p. 118-120°C; ν(CS) 1290cm⁻¹.

(b) Tri-p-tolylphosphine complexes

Dichlorotris(tri-p-tolylphosphine)ruthenium(II): The complex 'RuCl₃·3H₂O' (0.5g) was refluxed with P(p-tol)₃ (2.5g) in methanol (25cm³) for 16 hours. The dark purple crystals obtained were filtered off and washed with diethyl ether; ν(RuCl) 320cm⁻¹; m.p. 138-140°C.

Dichlorocarbonylbis(tri-p-tolylphosphine)dimethylformamide) ruthenium(II): Carbon monoxide gas was bubbled through a suspension of RuCl₂(P(p-tol)₃)₃ (0.4g) in dmf (4cm³) for several minutes to give a yellow solution. Diethyl ether (5cm³) was added and the solution shaken for 1 hour. The resulting yellow solid was filtered off and dried in vacuo; ν(CO) 1955, ν(RuCl) 340, ν(CO)(dmf) 1645cm⁻¹; m.p. 173-175°C.

Tri-μ-chloro-a-μ-carbonyl-tetrakis(tri-p-tolylphosphine)-diruthenium(II): RuCl₂(P(p-tol)₃)₂ (0.1g) and RuCl₂(CO)(P(p-tol)₃)₂dmf (0.08g) were refluxed together in ethanol (20cm³) for 6 hours to give an orange solution. On cooling an orange solid formed which was filtered off and dried in vacuo; ν(CO) 1975cm⁻¹; m.p. 155-157°C.
Tri-μ-chloro-a-chloro-g-carbonyl-bc-bis(tri-p-tolylphosphine)-
ihi-bis(triphenylphosphine)diruthenium(II) was obtained
similarly from RuCl₂(P(p-tol)₃)₃ and RuCl₂(CC)(PPh₃)₂ dmf;
ν(CO) 1975 cm⁻¹. Tri-μ-chloro-a-chloro-bg-carbonyl-tris(tri-
phenylphosphine)diruthenium(II):- The complex
RuCl₂(CO)(P(p-tol)₃)₂MeOH (prepared by recrystallisation of
RuCl₂(CO)(P(p-tol)₃)₂ dmf from methanol) was shaken in CH₂Cl₂
for 4 days. The resultant solution was reduced in volume
and light petroleum (b.p. 60-80 °C) added to precipitate the
complex as a yellow brown solid; ν(CO) 1960 cm⁻¹.
Di-μ-chlorobis[chlorothiocarbonylbis(trip-tolylphosphine)-
ruthenium(II) :- The complex RuCl₂(P(p-tol)₃)₃ (0.25g) was
refluxed in CS₂ (15 cm³) for 5 minutes to give a red solution
which was cooled, filtered and then reduced in volume to
ca. 5 cm⁻¹. Addition of light petroleum (b.p. 60-80 °C) precip-
itated a pink solid which was filtered off and dried in vacuo;
ν(CS) 1290 cm⁻¹. The remaining solution on standing for 6
hours deposited Tri-μ-chloro-a-chloro-g-thiocarbonyltetra-
(tri-p-tolylphosphine)diruthenium(II) as an orange solid
which was filtered off and dried in vacuo; ν(CS) 1292 cm⁻¹;
m.p. 160-162 °C.

(c) Tin complexes
[Acetone(carbonyl)chloro(trichlorostannato)bis(triphenyl-
phosphine)ruthenium(II)]acetone(1/1):- The "red solution"
(made from 0.5g RuCl₃.3H₂O (15 cm³) was treated with 1.5g
of anhydrous SnCl₂ in ethanol (5 cm³) followed by 1.0g of
PPh₃ in acetone (20 cm³). To the resulting yellow-brown
solution was added a further 20 cm$^3$ of acetone and the solution allowed to stand overnight to deposit lemon-yellow crystals which were washed with acetone, diethyl ether and air-dried. $\nu$(CO) 1957 cm$^{-1}$; $\nu$(CO)(acetone) 1701, 1661 cm$^{-1}$; $\nu$(SnCl) 300 cm$^{-1}$. Tri-$\mu$-chloro-$\mu$-(dicarbonyl)-b-(trichlorostannato)tris(tri-phenylphosphine)diruthenium(II); The complex $[\text{Ru(Me}_2\text{CO})\text{CO(Cl)(SnCl}_3)(P\text{Ph}_3)_2]\text{Me}_2\text{CO}$ was dissolved in warm benzene. After two hours, the solution was reduced in volume and the pale yellow powder precipitated with light petroleum (b.p. 60-80°C); mol. wt. in CHCl$_3$ 1090 (required 1376); $\nu$(CC) 1975 cm$^{-1}$(broad), $\nu$(SnCl) 320 cm$^{-1}$.
Table 6.4

Analytical data for some ruthenium complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>% Found</th>
<th>% Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>RuCl₂(CS)(PPh₃)₂dmf</td>
<td>57.5</td>
<td>4.5</td>
</tr>
<tr>
<td>RuCl₂(CS)(PPh₃)₂MeOH</td>
<td>57.8</td>
<td>4.5</td>
</tr>
<tr>
<td>[Ru₂Cl₄(CS)₂(PPh₃)₃]⁺CH₂Cl₂</td>
<td>52.7</td>
<td>3.7</td>
</tr>
<tr>
<td>[Ru₂Cl₄(CS)₂(PPh₃)₄]BPh₄</td>
<td>66.5</td>
<td>4.6</td>
</tr>
<tr>
<td>RuCl₂(P(p-tol)₃)₃</td>
<td>69.7</td>
<td>5.8</td>
</tr>
<tr>
<td>RuCl₂(CO)(P(p-tol)₃)₂dmf</td>
<td>62.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Ru₂Cl₄(CO)(P(p-tol)₃)₄</td>
<td>63.1</td>
<td>5.3</td>
</tr>
<tr>
<td>Ru₂Cl₄(CO)(P(p-tol)₃)₂(P(p-tol)₃)₂</td>
<td>67.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Ru₂Cl₄(CS)₂(P(p-tol)₃)₄</td>
<td>62.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Ru₂Cl₄(CS)(P(p-tol)₃)₄</td>
<td>64.2</td>
<td>5.4</td>
</tr>
<tr>
<td>RuCl₃(SnCl₃)(CO)(PPh₃)₂⁻(acetone)₂</td>
<td>49.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Ru₂Cl₃(SnCl₃)(CO)₂(PPh₃)₃</td>
<td>47.2</td>
<td>3.3</td>
</tr>
</tbody>
</table>
### Table 6.5

31P n.m.r. spectral data for some ruthenium complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp (K)</th>
<th>Solvent</th>
<th>Chemical shift (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\text{dmf}$</td>
<td>303</td>
<td>CDCl$_3$</td>
<td>30.2(s)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\text{MeOH}$</td>
<td>303</td>
<td>CDCl$_3$</td>
<td>30.7(s)</td>
</tr>
<tr>
<td>$\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PPh}_3)_3$</td>
<td>213</td>
<td>CDCl$_3$</td>
<td>49.7(s) 37.0(q)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(J$<em>{AB}$ = 26.0; δ$</em>{AB}$ = 15.0Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>51.8(s) 35.8(q)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(J$<em>{AB}$ = 26.0; δ$</em>{AB}$ = 71.4Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50.9(s) 41.2(q)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(J$<em>{AB}$ = 26.0; δ$</em>{AB}$ = 52.0Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48.9, 37.3(s)</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{CS})_2(\text{PPh}_3)_4]\text{BPh}_4$</td>
<td>213</td>
<td>CDCl$_3$</td>
<td>37.5(q) (J$<em>{AB}$ = 27.0; δ$</em>{AB}$ = 86.8Hz)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{P}(\text{p-tol})_3)_3$</td>
<td>190</td>
<td>CH$_2$Cl$_2$/C$_2$D$_6$CO</td>
<td>74.34(t), 25.05(d) (J$_{PP}$ = 28.0Hz)</td>
</tr>
<tr>
<td>$\text{RuCl}_2(\text{CO})(\text{P}(\text{p-tol})_3)_2\text{dmf}$</td>
<td>298</td>
<td>CDCl$_3$</td>
<td>32.3(s)</td>
</tr>
<tr>
<td>$\text{Ru}_2\text{Cl}_4(\text{CO})(\text{P}(\text{p-tol})_3)_4$</td>
<td>298</td>
<td>CDCl$_3$</td>
<td>47.64(q) (J$<em>{AB}$ = 38.8; δ$</em>{AB}$ = 73.0Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>38.84(q) (J$<em>{AB}$ = 25.1; δ$</em>{AB}$ = 97.5Hz)</td>
</tr>
<tr>
<td>Complex</td>
<td>Temp (K)</td>
<td>Solvent</td>
<td>Chemical shift (p.p.m.)</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>----------</td>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ru₂Cl₄(CO)₂(P(p-tol)₃)₃</td>
<td>298</td>
<td>CDCl₃</td>
<td>50.49(s) 41.54(q) (Jₐₙ = 25.5; δₐₙ = 24.3Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>51.25(s) 40.01(q) (Jₐₙ = 24.9; δₐₙ = 133.6Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>52.18(s) 38.91(q) (Jₐₙ = 26.1; δₐₙ = 170.2Hz)</td>
</tr>
<tr>
<td>[RuCl₂(CS)(P(p-tol)₃)₂]₂</td>
<td>298</td>
<td>CDCl₃</td>
<td>29.54(s)</td>
</tr>
<tr>
<td>Ru₂Cl₄(CS)(P(p-tol)₃)₄</td>
<td>298</td>
<td>CDCl₃</td>
<td>47.59(q) (Jₐₙ = 37.9; δₐₙ = 80.9Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>34.61(q) (Jₐₙ = 25.1; δₐₙ = 74.9Hz)</td>
</tr>
<tr>
<td>Ru₂Cl₄(CO)(PPh₃)₂(P(p-tol)₃)₂</td>
<td>298</td>
<td>CDCl₃</td>
<td>48.0(q) (Jₐₙ = 34.2; δₐₙ = 83.2Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40.2(q) (Jₐₙ = 25.1; δₐₙ = 99.1Hz)</td>
</tr>
<tr>
<td>RuCl(SnCl₃)(CO)(PPh₃)₂(acetone)₂</td>
<td>303</td>
<td>C₆D₆</td>
<td>35.38(t) 2JₚSn = 250Hz</td>
</tr>
<tr>
<td>Ru₂Cl₃(SnCl₃)(CO)₂(PPh₃)₃</td>
<td>303</td>
<td>CDCl₃</td>
<td>49.9(t) 2JₚSn = 270Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40.7(q) (Jₐₙ = 25.5; δₐₙ = 18.3Hz)</td>
</tr>
</tbody>
</table>
Chapter 7

Some preliminary polarographic studies on ruthenium(II) triple bridged dimeric complexes

7.1 Introduction

In recent years there has been a lot of interest in the oxidation and reduction of Ru(II) and Ru(III) compounds using electrochemical techniques especially for the synthesis of mixed valence Ru(II)/Ru(III) dimeric species. For example, the cations \( [(\text{NH}_3)_5 \text{Ru}^{II} \text{L} \text{Ru}^{II} \text{Cl}(\text{bipy})_2]^3^+ \) (L=pyrazine, 4,4'-bipyridine, trans,2bis(4-pyridyl)ethylene, 1,2bis(4-pyridyl)ethane) undergo two, reversible, one-electron oxidations. Spectral and electrochemical data indicate that the initial site of oxidation in the one electron oxidised dimers

\( [(\text{NH}_3)_5 \text{RuLRuCl}(\text{bipy})_2]^4^+ \) is localised largely on the pentaammine end giving \( [(\text{NH}_3)_5 \text{Ru}^{III} \text{L} \text{Ru}^{II} \text{Cl}(\text{bipy})_2]^4^+ \) which can be prepared on a large scale by stoichiometric oxidation using either \( \text{Br}_2 \) or Ce(IV) salts. A further one electron oxidation then produces the Ru(III)/Ru(III) dimer \( [(\text{NH}_3)_5 \text{Ru}^{III} \text{L} \text{Ru}^{III} \text{Cl}(\text{bipy})_2^2 \)

Related mixed valence dimeric cations such as

\( [(\text{NH}_3)_5 \text{Ru(pyrazine)} \text{Ru(\text{NH}_3)_5}]^{5^+} \quad \text{and} \quad [(\text{bipy})_2 \text{ClRu(pyrazine)} - \text{Ru(bipy)_2Cl}]^{3^+} \quad \text{have also been characterised and their redox properties investigated by electrochemical methods.}

The following work describes some polarographic studies on the compounds (PPh\(_3\))\(_2^\text{Y} \text{RuCl}_3 \text{RuCl(PPh}_3\)_2 (Y=CO, CS) and \( [\text{L}_3 \text{RuCl}_3 \text{RuL}_3^\text{X}] (X=\text{BPh}_4, \text{L}=\text{P(OMe)}_2\text{Ph}; X=\text{SCN}, \text{L}=\text{PMs}_2\text{Ph}) \) and subsequent attempts to generate the products on a preparative scale by chemical methods. Before this, however, the polarographic method and especially the techniques of cyclic
Voltammetry and a.c. polarography are briefly described.

Polarography is an electrochemical method of analysis involving an electrolysis of short duration at a dropping mercury electrode, or other microelectrode, such that the currents are very small and the changes produced by polarographic electrolysis are normally not measurable; hence the polarographed solution can be recovered virtually unchanged. The microelectrode is polarised to different potentials by a voltage applied from an outside source between it and a reference electrode. By plotting the currents obtained when the applied voltage is gradually altered a current-voltage curve is produced.

Two of the more modern techniques of polarography are alternating current (a.c.) polarography and cyclic voltammetry, both of which, for the most part, provide access to the same information. Both techniques deal with three parameters, current, potential and time.

(a) **Cyclic voltammetry**

Consider a redox couple, the oxidant form of which is present in a solution containing an excess of supporting electrolyte (present to prevent the migration of charged species in the presence of an electric field). A stationary working electrode is employed, the potential of which is varied at a finite rate as a linear function of time. After reaching the required value the potential is then brought back to zero at the same rate. A current-potential curve

† A very full description of the technique is given in ref. 162
similar to that in Fig. 7.1 is obtained (except for irreversible processes where there is no reverse wave), which provides four measurable parameters; the net current \( i_p \) and potential \( E_p \) at the peak of the cathodic response, and the corresponding parameters \( i_a \) and \( E_a \) for the anodic response. These parameters can be used to determine whether the charge transfer process (i.e., transfer of electron to species at electrode) is reversible, quasi-reversible or irreversible. If the charge transfer is "reversible" the process occurs at a significantly more rapid rate than the rate of diffusion. A reaction in which the transfer process is governed 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". The criteria for each of these three types are tabulated in Table 7.1.

Fig. 7.1 Example of a cyclic voltammetric curve

\[ E_p^c \] at the peak of the cathodic response, and the corresponding parameters \( i_p^c \) and \( E_p^c \) for the anodic response. These parameters can be used to determine whether the charge transfer process (i.e., transfer of electron to species at electrode) is reversible, quasi-reversible or irreversible. If the charge transfer is "reversible" the process occurs at a significantly more rapid rate than the rate of diffusion. A reaction in which the transfer process is governed 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". The criteria for each of these three types are tabulated in Table 7.1.
Table 7.1 Criteria for reversible, quasi-reversible and irreversible charge transfer processes.

<table>
<thead>
<tr>
<th>Type</th>
<th>Conditions</th>
</tr>
</thead>
</table>
| Reversible    | $E_p$ is independent of $J$.  
$E_{p}^{c}-E_{p}^{a}=59/n$ mV at 25°C and is independent of $J$.  
$i_p/J^{1/2}$ (current function) is independent of $J$.  
i$_{p}^{a}/i_{p}^{c}$ is unity and independent of $J$. |
| Quasi-reversible | $E_p$ shifts with $J$.  
$E_{p}^{c}-E_{p}^{a}$ increases as $J$ increases.  
$i_p/J^{1/2}$ is independent of $J$.  
i$_{p}^{a}/i_{p}^{c}$≠1. |
| Irreversible  | $E_p$ shifts with $J$.  
i$_{p}^{a}/J^{1/2}$ is constant with scan rate.  
There is no current on the reverse scan. |

$J$ is the sweep rate in volts sec$^{-1}$.  
n=number of electrons involved in oxidation or reduction process.
(b) a.c. polarography

To obtain an a.c. polarogram, a d.c. potential is applied to the electrode and is varied as a function of time, and at the same time a potential periodic in time, such as a sine wave, is also applied to the electrode. The net alternating current is monitored as a function of d.c. potential to give a typical polarogram such as shown in Fig. 7.2 where the current oscillations are the result of the dropping mercury electrode. Two parameters are of use namely, the peak magnitude of the a.c. current and the d.c. potential at this peak which is related to the standard potential of the redox couple. These two parameters coupled again with variations in time provide the means of characterising the nature of the charge transfer processes, but since the same information is more easily obtained from cyclic voltammetry this is not considered further here.

7.2 Results and discussion

The a.c. polarogram of (Ph₃P)₂ClRuCl₃Ru(CO)(PPh₃)₂ in CH₂Cl₂ and supporting electrolyte TBAP(tetramethylammonium-
perchlorate) (anodic scan) exhibits a peak at 0.56V while the cathodic scan contains a peak at -1.6V (Fig. 7.3). However the cathodic cyclovoltammogram (Fig. 7.4) indicates that there is no current produced on the return scan and hence that the reduction is irreversible. In contrast, the anodic cyclovoltammogram (Fig. 7.5) is consistent with a reversible oxidation since $E^a_p$ and $E^c_p$ do not vary with the scan rate. Furthermore $E^a_p - E^c_p = 60$ mV indicating a one electron process. Similar results have been obtained for $(\text{Ph}_3\text{P})_2\text{ClRuCl}_3\text{Ru(CS)(PPh}_3)_2$; reversible oxidation potential at 0.55V and irreversible reduction potential at -1.48V.

Since the replacement of CO by CS has very little effect on the oxidation potential, this suggests that the oxidation site is localised largely on the $(\text{Ph}_3\text{P})_2\text{ClRu}$ end of the molecule i.e.

$$(\text{Ph}_3\text{P})_2\text{ClRu}^{II}_3\text{Ru}^{II}(\text{PPh}_3)_2 \overset{e^-}{\rightarrow} ((\text{PPh}_3)_2\text{ClRu}^{III}_3\text{Ru}^{II}(\text{PPh}_3))$$

This seems likely since this end of the molecule is the harder base end and would therefore be expected to be the site from which an electron is preferentially lost.

Unfortunately, attempts to isolate pure samples of the mixed Ru(II)/Ru(III) dimeric cations $[\text{Ru}_2\text{Cl}_4\text{Y}(\text{PPh}_3)_4]^+$ have, to date, been unsuccessful. Thus, although oxidation of methylene chloride solutions of $\text{Ru}_2\text{Cl}_4\text{Y}(\text{PPh}_3)_4$ with either I$_2$ or Ce$^{IV}$ salts (1:2 molar ratio) causes a colour change from red to greenish-brown and brown conducting solids were isolated, the cathodic cyclovoltammograms of the products each contain several reduction waves indicating the presence
Fig. 7.3 A.C. polarograms of \( \text{Ru}_2\text{Cl}_4(\text{CO})(\text{PPh}_3)_4 \) (scan rate 20mV/sec)

anodic scan

\[
\begin{array}{c}
\begin{array}{c}
0 \quad +0.2 \quad +0.4 \quad +0.6 \quad +0.8 \\
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
-0.2 \quad -0.4 \quad -0.6 \quad -0.8 \quad -1.0 \\
\end{array}
\end{array}
\]

\(2 \mu \text{A}\)

\[
\begin{array}{c}
\begin{array}{c}
-1.2 \quad -1.4 \quad -1.6 \quad -1.8 \\
\end{array}
\end{array}
\]

cathodic scan
Fig. 7.4 Cyclic voltammogram of $\text{Ru}_2\text{Cl}_4\text{(CO)}(\text{PPh}_3)_4$.

Scan rate: 200 mV/sec

cathodic scan
anodic scan

Fig. 7.5
Cyclic voltammogram of RuCl₂(CO)(PPh₃)₃₄⁻

scan rates
- 100mV/sec
- 20mV/sec

current [µA]

20µA
of mixtures and this is supported by variable analytical data. In fact, generating the mixed valence dimers in CH₂Cl₂ electrochemically and recording the cathodic cyclovoltammograms at various intervals of time reveals that the complexes are very unstable at room temperature, only existing for a short period of time. At lower temperatures, electrochemical studies indicate that the species are much more stable and therefore it may be possible to isolate them in a pure state by working at low temperatures.

Further oxidation of 

\[ [(\text{Ph}_3P)_2\text{ClRuCl}_3\text{Ru(CO)(PPh}_3)_2]\]

occurs at 1.08V to produce presumably 

\[ [(\text{Ph}_3P)_2\text{ClRuCl}_3\text{Ru(CO)(PPh}_3)_2]^{2+}\]

however this process is irreversible (see Fig. 7.6) and the Ru(III)/Ru(III) cation is unstable on the electrochemical time scale and probably undergoes rapid decomposition by solvent interaction. Consistent with the latter observation are the oxidation potentials for the related compounds 

\[ [\text{L}_3\text{RuCl}_3\text{RuL}_3]X \]

(\(X=\text{BF}_4^-, \text{L}=\text{P}[(\text{OMe})\text{Ph}_2]; \text{X}=\text{SCN}^-, \text{L}=\text{PMe}_2\text{Ph}\)) which are 0.3V higher (0.85V for \(\text{L}=\text{P}[(\text{OMe})\text{Ph}_2]\) and 0.95V for \(\text{L}=\text{PMe}_2\text{Ph}\)) than those for \(\text{Ru}_2\text{Cl}_3\text{(PPh}_3)_4\) and are also irreversible (see Fig. 7.7). Stable complexes of the type 

\[ [\text{L}_3\text{RuCl}_3\text{RuL}_3]^{2+}\]

have however been isolated for \(\text{L}=\text{H}_2\text{O}\) and \(\text{NH}_3\). Spectrophotometric titration of the blue cation 

\[ [(\text{NH}_3)_3\text{ClRuCl}_3\text{Ru(NH}_3)_3]^{2+}\]

with Ce⁴⁺ produces yellow 

\[ [(\text{NH}_3)_3\text{ClRuCl}_3\text{Ru(NH}_3)_3]^{3+}\]

and on further standing the solution deposits \(\text{RuCl}_3\text{(NH}_3)_3\). Similarly 

\[ [(\text{H}_2\text{O})_3\text{ClRuCl}_3\text{Ru(H}_2\text{O}_3)]^{2+}\]

undergoes a reversible oxidation at 0.55V to produce 

\[ [(\text{H}_2\text{O})_3\text{ClRuCl}_3\text{Ru(H}_2\text{O}_3)]^{3+}\]

This difference in behaviour compared to the tertiary phosphine and phosphinite compounds is presumably due to the hardness of the aqua and ammine ligands.
Fig. 7.6 Cyclic voltammogram of Ru$_2$Cl$_4$(CO)(PPh$_3$)$_4$ - anodic scan to potentials > 0.6 V.

Scan rates:
- Dashed line: 50 mV/sec
- Solid line: 20 mV/sec

Current (μA)

Potential (V vs. Hg)
Fig. 7.7 Cyclic voltammogram of \([\text{Ru}_2\text{Cl}_3\{(\text{P(OMe)}\text{Ph}_2)_6\}]\text{BPh}_4\).

anodic scan

scan rate
200mV/sec

100μA

potential (volts)
7.3 **Experimental**

All measurements were made with a three electrode Princeton Applied Research model 170 instrument at the University of Stirling, on ca $3 \times 10^{-3}$ moles dm$^{-3}$ solutions in degassed CH$_2$Cl$_2$ with supporting electrolyte [Bu$_4$N][ClO$_4$] (0.5 mole dm$^{-3}$). For cyclic voltammetry, potentials were measured at a stationary Pt electrode with reference to a Ag/AgCl electrode and scan speeds varied from 50 to 500mV/sec. The potentials for a.c. polarography were measured at a dropping mercury electrode with reference to a Ag/AgCl electrode at a scan speed of 20mV/sec.
Appendix I

Characteristics of the $X_n$ n.m.r. spectra of systems of the $X_nAA'X'_n$ type.

The system $X_nAA'X'_n$ represents a situation where the nuclei which are chemically and structurally equivalent are not magnetically equivalent and the resultant n.m.r. spectrum of $X$ is a second order system. In dealing with this system the assumption is made that coupling between nuclei $X$ and $X'$ is zero and hence only three nuclear magnetic parameters affect the spectrum viz. $J_A$, the coupling constant between $A$ and $A'$, and the two types of coupling constant between an $A$ or $A'$ nucleus and an $X$ or $X'$ nucleus, $J_{AX} (= J_{A'X'})$ and $J_{AX'} (= J_{A'X'})$. The total matrix representation of the Hamiltonian can be divided into three sub-matrices (i), (ii) and (iii). Sub-matrices (i) and (ii) give rise to an intense doublet symmetrically disposed about $\sqrt[2]{\chi}$ with a splitting of $N$ where $N = |J_{AX} + J_{AX'}|$. The third sub-matrix gives rise to a number of lines symmetrically placed about $\sqrt[2]{\chi}$ within this doublet. The exact pattern of lines and their intensities depends upon the value of $L/|J_A|$ where $L = |J_{AX} - J_{AX'}|$ (see Fig. A.1). There may be a total of $2n+1$ pairs of lines symmetrically placed about $\sqrt[2]{\chi}$ and half the total intensity lies in the doublet of separation $N$, whereas the remaining intensity is spread over the remaining $2n$ pairs of lines.

There are two limiting cases giving rise to "deceptively-

†A fuller description of the system including equations for the various energy levels is given in ref. 169.
Fig. A.1 Variation of the X spectrum of an $X_3^2AA'X_3^2$ system with changes in $L/|J_A|$.

Simple" spectra.

(A) $|J_A| \gg L$, giving approximately an $A_2^2X_{2n}$ spectrum. In this case the inner lines fall very close to $v_X$ and since they comprise half of the total intensity, the spectrum has the appearance of a 1,2,1 triplet. Such a situation often arises in complexes containing trans tertiary phosphine, phosphinite or phosphonite groups e.g. RuCl$_2$(CO)(P(OMe)Ph$_2$)$_3$ (1), where the trans phosphorus atoms are strongly coupled such that $2J_{PlP2} \gg |3J_{PlH} - 5J_{PlH'}|$ and the signal observed in
the $^1$H n.m.r. spectrum is a 1,2,1 triplet. As the difference between the size of $J_{PP}$ and $|3J_{PH} - 5J_{PH'}|$ decreases the central line broadens and becomes less intense and the resultant spectrum is usually termed a 'psuedo-triplet'. This often occurs when two chemically equivalent tertiary phosphine, phosphinite or phosphonite groups are cis to each other, in which case, the coupling between the phosphorus atoms is: usually weaker than in the trans case.

(3) $J \rightarrow 0$ giving approximately an $X_n A M$ spectrum. Here the inner part of the spectrum consists of (for $J=0$) two lines whose separation is $L$. Thus the whole X spectrum consists of four lines with spacings $N$ and $L$. In many cases it may be impossible to resolve the $L$ doublet from the $N$ doublet and there is effectively two uncoupled $X_n A$ systems giving a single doublet in the X spectrum. In the situation where $J_{PP}$ is small but non-zero the inner lines decrease in intensity and additional signals appear (see Fig. A.1(a)). The appearance of such a spectrum is often a rather broad doublet termed a 'psuedo-doublet'.
Appendix 2

Analysis of AB and AB$_2$ spin systems in n.m.r. spectroscopy.

a) AB spin system

When $J/\Delta\nu$ is large for a two spin system the system is designated AB and consists of four lines, symmetrically spaced about the centre of the spectrum $\frac{3}{2}(\nu_A + \nu_B)$, the inner two lines being more intense than the other two. $J$ is given.

Fig. A.2 Schematic representation of an AB spectrum

by the doublet spacing as in Fig. A.2, and the spacing of the doublet centres by $(\Delta\nu_2^2 + J^2)^{1/2}$. where $\Delta\nu$ (the chemical shift difference usually termed $\delta$) = $[(\nu_1 - \nu_4)(\nu_2 - \nu_3)]^{1/2}$.

b) AB$_2$ spin system

A system of two magnetically equivalent nuclei coupled to a third constitutes an AB$_2$ system, which consists of a total of 9 lines, although the ninth line, appearing beyond all the others, on the B side of the spectrum, is usually very weak and not often observed (see Fig. A.3). The chemical shift of nucleus A, $\nu_A$, is given by line 3 and the chemical shift of nucleus B, $\nu_B$, is given by the mean of lines 5 and 7. The magnitude of $J_{AB}$ can be calculated from the expression.
\[ J_{AB} = \frac{1}{3} [(\nu_3 - \nu_6) + (\nu_4 - \nu_1)] \]

**Fig. A.3 Schematic representation of an AB\(_2\) spectrum**

In many spectra it is difficult to resolve lines 5 and 6 and this may lead to uncertainty in the values of \( J_{AB} \) and \( \nu_B \). Also, when the value of \( J_{AB}/\Delta \nu > 1 \), line 1 becomes very weak.

If either of the above occurs then the spectrum may be analysed by:

- either (A) Fitting the observed spectrum to a plot of the calculated positions such as may be found in Appendix D, section 1, of ref. 165.
- or (B) Using the value of \( J_A \) and the approximate value for \( J_B \) and compiling a table of values for \( \nu_n, \nu_A, \nu_B \) where \( \nu_n \) is the frequency of lines 1 to 8.

\[ \frac{\nu_n - \nu_A}{\nu_A - \nu_B} \]

Then by fitting the values obtained to the graph on page 70 of ref. 166 an approximate value for \( J/\Delta \nu \) can be found. A more precise analysis can then be be obtained by computer simulation or by
comparison of the observed spectrum with the values for line positions and intensities tabulated in Appendix D of ref. 167.
## Appendix 3

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>acac</td>
<td>acetylacetone</td>
</tr>
<tr>
<td>B.M.</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>bipy</td>
<td>bipyridyl</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>ca.</td>
<td>circa</td>
</tr>
<tr>
<td>dma</td>
<td>dimethylacetamide</td>
</tr>
<tr>
<td>dmf</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>dpp</td>
<td>bis(diphenylphosphino)propane</td>
</tr>
<tr>
<td>e.s.r.</td>
<td>electron spin resonance</td>
</tr>
<tr>
<td>g.l.c.</td>
<td>gas liquid chromatography</td>
</tr>
<tr>
<td>i.r.</td>
<td>infra-red</td>
</tr>
<tr>
<td>mol.wt.</td>
<td>molecular weight</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>pent</td>
<td>pentyl</td>
</tr>
<tr>
<td>phen</td>
<td>phenanthroline</td>
</tr>
<tr>
<td>p.p.m.</td>
<td>parts per million</td>
</tr>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>Td</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
</tr>
<tr>
<td>tol</td>
<td>tolyl</td>
</tr>
<tr>
<td>viz.</td>
<td>namely</td>
</tr>
</tbody>
</table>
REFERENCES

1. O. RUFF, E. VIDIC; Z. Anorg. Allgem. 1924, 136, 49
2. Y. KODA; Inorg. Chem. 1963, 2, 1306
24. K. GLEU, W. BREUEL; Z. Anorg. Allgem. Chem. 1938, 237, 197, 335,
G. T. MORGAN, F. H. BURSTALL; J. Chem. Soc. 1936, 43
25. A. JOLY; Compt. Rend. 1891, 114, 291; 1892, 115, 1299
33. R. J. IRVING, P. G. LANE; J. Chem. Soc. (A) 1966, 161
34. B. HUI, B. R. JAMES; Chem. Comm. 1969, 198
38. J. M. JENKINS, M. S. LUPIN, B. L. SHAW; J. Chem. Soc. (A) 1966, 1787
41. M.I. BRUCE, F.G.A. STONE; Angew. Chem. (Int.Ed) 1968, 1, 427


44. F. PIACENTI, M. BIANCHI, E. BENEDETTI; Chem. Comm. 1967, 775


60. O. GANDOLFI, B. GIOVANNITTI, M. GHEDINI, G. DOLCETTI; J. Organometal. Chem. 1976, 104, 541
64. A. C. HINZE; Rec. Trav. Chim. 1973, 22, 543
74. K. G. CAULTON; J. Amer. Chem. Soc. 1974, 96, 3005
K. G. CAULTON, P. R. HOFFMAN; J. Amer. Chem. Soc. 1975, 97, 4221
76. W. H. KNOTH; J. Amer. Chem. Soc. 1972, 94, 104
78. J. K. NICHOLSON; Angew. Chem. Int. Ed. 1967, 6, 264
80. M. S. LUPIN, B. L. SHAW; J. Chem. Soc. (A) 1968, 741
86. J.J. HOUGH, E. SINGLETON; Chem. Comm. 1972, 371
95. L.M. HAINES; Inorg. Chem. 1971, 10, 1685
96. PI CHANG KONG, D.M. ROUNDHILL; Inorg. Chem. 1972, 749
100. G. WILKINSON; Chem. Comm. 1974, 327


114. R.O.GOULD; Private Communication


118. P.W.ARMIT; Unpublished results


120. M.C.BAIRD, G.WILKINSON; Chem. Comm. 1966, 267


130. T.V. ASHWORTH, E. SINGLETON; Chem. Comm. 1976, 875
133. F.A. COTTON, J.A. MCCLEVERTY; Inorg. Chem. 1964, 3, 1398
136. C. O'CONNOR, J. D. GILBERT, G. WILKINSON; J. Chem. Soc. (A) 1969, 84
137. L. MALATESTA; Gazz. Chim. It. 1938, 68, 195
139. L.R. GAHAN, M.J. O'CONNOR; Chem. Comm. 1974, 68
146. C.L. JONES; Private Communication
147. T.V. ASHWORTH, E. SINGLETON; Chem. Comm. 1976, 204
149. N.W. ALCOCK, K.A. RASPIN; J. Chem. Soc. (A) 1968, 2108
153. C.W. BRADFORD, R.S. NYHOLM; Chem. Comm. 1968, 867
159. R.W. CALLAHAN, G.M. BROWN, T.J. MEYER; J. Amer. Chem. Soc. 1974, 96, 7829
164. E.E. MERCER, L.W. GRAY; J. Amer. Chem. Soc. 1972, 94, 6426
166. J.D. ROBERTS; "An Introduction to Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectroscopy" Butterworths London 1972
Post Graduate Courses Attended.

"Aspects of Nuclear Magnetic Resonance Spectroscopy"  
by Dr. R. K. Harris.

"Aspects of Platinum Metal Chemistry"  
by Dr. T. A. Stephenson

"General Aspects of Vibrational Spectroscopy"  
by Dr. S. Cradock

"Optical Properties of Transition Metal Complexes"  
by Dr. T. A. Stephenson

"Chemical Aspects of Oil Product Research"  
Shell U.K.

E.R.C.C. Computing Course.


Departmental and Research Seminars and Colloquia.