THE SYNTHESES AND REACTIONS OF
CARBONYL(PHOSPHINE)(THIOLATO)RUTHENIUM(II)
COMPLEXES

By

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ABSTRACT

The chemistry of homogeneous transition metal systems offer parallels to the reactions on the surfaces of industrial hydrodesulphurization catalysts. The reactions of several ruthenium complexes with sulphur-containing reagents are described, with an emphasis on the kinetics and mechanisms thereof. The complex Ru(CO)2(PPh3)3 (2), for example, reacts quickly with thiols and disulphides, producing cct-RuH(SR)(CO)2(PPh3)2 (9) and cct-Ru(SR)2(CO)2(PPh3)2 (14), respectively, although 2 fails to react with unstrained thioethers. Reactions of the related complex Ru(CO)2(PPh3)(dpm) (dpm=Ph2PCH2PPh2) are complicated by the lability of all of the three different ligands.

The two dihydrides cct-RuH2(CO)2(PPh3)2 (3) and RuH2(dpm)2, as a cis/trans mixture (7), react with thiols to produce the hydrido-thiolato complexes 9 and RuH(SR)(dpm)2 (13), respectively. The mechanisms appear to depend on the basicity of the hydride ligands; the more basic dihydride, 7, is probably protonated by the thiol, giving an unobserved molecular hydrogen intermediate, while 3 reacts by slow reductive elimination of H2. The same rate constant, rate law, and activation parameters are found for the reaction of 3 with thiols, CO or PPh3. The reaction of 3 with RSSR produces mostly 9, with small amounts of 14.

The complete characterization of several members of the series 9 and 14 is described, including the crystal structure of the p-thiocresolate example of each. The reactions of 9 with other thiols, P(C6H4pCH3)3, CO, RSSR, HCl, PPh3, and H2, are also reported. The first three of these reactions share the same rate law and rate constant, the common rate determining step probably being initial loss of PPh3. Some equilibrium constants for the exchange reactions of 9d (R=CH2CH3) with other thiols were determined, the Keq values increasing with the acidity of the incoming thiol.
The mercapto hydrogens of $9a$ and $14a\,(R=H)$ exchange with the acidic deuterons of added CD$_3$OD. The hydridic and ortho-phenyl hydrogens exchange more slowly, presumably by intramolecular processes.

Complex $14b\,(R=C_6H_4pCH_3)$ is unstable in the presence of light, exchanges phosphines rapidly with added P(C$_6H_4pCH_3$)$_3$, exchanges thiolate groups with added thiols, and is converted by high pressures of H$_2$ to a mixture of $9b$ and $3$.

Intermediates proposed for the mechanism of the thiol exchange reactions of $9$ and $14$ contain two or three thiolate groups sharing a proton. A related complex, [Ru(CO)$_2$(PPh$_3$)$_2$(μSEt)$_2$(μ3SEt)Na(THF)]$_2$, which contains three thiolate groups on a ruthenium centre sharing a sodium cation, was isolated from the reaction of cct-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ with sodium ethanethiolate. In acetone, $9b$ and $14b$ can be formed cleanly from cct-RuHCl(CO)$_2$(PPh$_3$)$_2$ and cct-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$, respectively, by reaction with p-thiocresolate.

Complex $3$ or cheaper analogues could be used as catalysts for the reduction of disulphides by H$_2$, or as recyclable reagents for the non-oxidative extraction of thiols from thiol-containing mixtures such as oil fractions. The chemistry described above will help to guide future researchers to systems that more closely parallel the processes occurring on the surfaces of industrial hydrodesulphurization catalysts.
to my family
TABLE OF CONTENTS

Abstract ii
List of Tables x
List of Figures xiii
List of Abbreviations xxii
Numerical Key to Ruthenium Complexes xxvii
Acknowledgements xxix

1 INTRODUCTION 1

1.1 Sulphur 2
  1.1.1 History and applications 2
  1.1.2 Natural occurrence 4
  1.1.3 Nomenclature of sulphur compounds 7
1.2 The extraction of sulphur from fossil fuels 8
  1.2.1 Reasons for sulphur extraction 8
  1.2.2 Sulphur extraction from petroleum 11
1.3 Reactions of sulphur-containing organics with transition metal complexes 22
  1.3.1 Reactions involving S-H bond cleavage 23
  1.3.2 Reactions involving S-S bond cleavage 27
  1.3.3 Reactions involving S-C bond cleavage 31

2. GENERAL EXPERIMENTAL PROCEDURES 34

2.1 Materials 34
2.2 Equipment and techniques 35
2.2.1 Reaction conditions
2.2.2 Spectroscopy and chromatography
2.2.3 Kinetic measurements
2.2.4 Data handling for kinetic experiments

2.3 Syntheses of the precursor complexes
2.3.1 \textit{cct-}RuCl_2(CO)_2(PPh_3)_2
2.3.2 Ru(CO)_2(PPh_3)_3
2.3.3 \textit{cct-}RuH_2(CO)_2(PPh_3)_2
2.3.4 \textit{cct-}RuH(Cl)(CO)_2(PPh_3)_2
2.3.5 \textit{cis-} and \textit{trans-}RuCl_2(dpm)_2
2.3.6 \textit{cis-} and \textit{trans-}RuH_2(dpm)_2
2.3.7 An attempted new synthesis of RuH_2(dpm)_2: the synthesis of trans-RuH(\eta_1BH_4)(dpm)_2

3. THE REACTIONS OF RUTHENIUM COMPLEXES WITH THIOLS

3.1 The reaction of Ru(CO)_2(PPh_3)_3 with H_2S and thiols
3.2 The characterization of RuH(ER)(CO)_2(PPh_3)_2
3.3 The reaction of RuH_2(CO)_2(PPh_3)_2 with H_2S and thiols
3.4 The reaction of RuH_2(dpm)_2 with H_2S and thiols
3.5 The thiol exchange reactions of \textit{cct-}RuH(SR)(CO)_2(PPh_3)_2
3.6 The slower reaction of RuH(SR)(CO)_2(PPh_3)_2 with H_2S and thiols
3.7 The reaction of RuH(SH)(dpm)_2 with H_2S
3.8 The thiol exchange reactions of \textit{cct-}Ru(SR)_2(CO)_2(PPh_3)_2
3.9 The reactions of other carbonyl(phosphine)ruthenium(0) complexes with H_2S and thiols
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.10</td>
<td>Experimental details</td>
<td>138</td>
</tr>
<tr>
<td>4.</td>
<td>REACTIONS OF CARBONYL (PHOSPHINE) RUTHENIUM COMPLEXES WITH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DISULPHIDES, THIOETHERS, AND RELATED REAGENTS</td>
<td>152</td>
</tr>
<tr>
<td>4.1</td>
<td>The reactions of Ru(CO)₂(PPh₃)₃ with disulphides</td>
<td>152</td>
</tr>
<tr>
<td>4.2</td>
<td>The characterization of cct-Ru(SR)₂(CO)₂(PPh₃)₂</td>
<td>158</td>
</tr>
<tr>
<td>4.3</td>
<td>The reaction of cct-RuH₂(CO)₂(PPh₃)₂ (3) with disulphides</td>
<td>168</td>
</tr>
<tr>
<td>4.4</td>
<td>The reaction of cct-RuH(SR)(CO)₂(PPh₃)₂ with disulphides</td>
<td>170</td>
</tr>
<tr>
<td>4.5</td>
<td>The reactions of carbonyl (phosphine) ruthenium complexes with strained cyclic thioethers</td>
<td>170</td>
</tr>
<tr>
<td>4.6</td>
<td>The non-reactions of carbonyl (phosphine) ruthenium complexes with unstrained thioethers</td>
<td>172</td>
</tr>
<tr>
<td>4.7</td>
<td>The reactions of carbonyl (phosphine) ruthenium complexes with other neutral sulphur-containing reagents</td>
<td>172</td>
</tr>
<tr>
<td>4.8</td>
<td>Experimental details</td>
<td>173</td>
</tr>
<tr>
<td>5.</td>
<td>THE METATHESIS REACTIONS OF CHLORORUTHENIUM COMPLEXES WITH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THIOLATE SALTS</td>
<td>180</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>180</td>
</tr>
<tr>
<td>5.2</td>
<td>The reactions of cct-RuCl₂(CO)₂(PPh₃)₂ with sodium thiolates</td>
<td>182</td>
</tr>
<tr>
<td>5.3</td>
<td>The characterization of [Ru(SEt)₃(CO)₂(PPh₃)Na(THF)]₂</td>
<td>188</td>
</tr>
<tr>
<td>5.4</td>
<td>The reactions of other ruthenium chloro complexes with sodium thiolates</td>
<td>212</td>
</tr>
<tr>
<td>5.5</td>
<td>Experimental details</td>
<td>213</td>
</tr>
</tbody>
</table>
6. THE REACTIONS OF THIOLATO RUTHENIUM(II) COMPLEXES WITH NON-SULPHUR-CONTAINING REAGENTS

6.1 The reactions of cct-RuH(SR)(CO)2(PPh3)2 (9)  
6.1.1 P(C₆H₄pCH₃)₃  
6.1.2 CO  
6.1.3 PPh₃  
6.1.4 H₂  
6.1.5 Acids  
6.1.6 CD₃OD

6.2 The reactions of cct-Ru(SR)₂(CO)₂(PPh₃)₂ (14)  
6.2.1 Light  
6.2.2 P(C₆H₄pCH₃)₃  
6.2.3 H₂  
6.2.4 CD₃OD

6.3 Experimental details

7. GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Potential applications for the complexes in sulphur chemistry  
7.2 Parallels to surface chemistry  
7.3 Conclusions  
7.4 Recommendations for future research

8. REFERENCES
| APPENDIX 1 | Summary of crystallographic data | 282 |
| APPENDIX 2 | Atomic coordinates for cct-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (9b) | 284 |
| APPENDIX 3 | Atomic coordinates for cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b) | 288 |
| APPENDIX 4 | Atomic coordinates for [(CO)$_2$(PPh$_3$)Ru(SEt)$_3$Na(THF)]$_2$ (21) | 294 |
| APPENDIX 5 | Kinetic data | 298 |
LIST OF TABLES

1.1 Estimated concentrations of selected sulphur compounds identified in Wasson, Texas, crude oil 5
1.2 Nomenclature of compounds containing sulphur, carbon and hydrogen 9
1.3 Canadian nationwide emissions of sulphur oxides, in 1972 12

2.1 Fragments detected in the FAB/mass spectrum of RuH(BH4)(dpm)2 55
2.2 1H NMR data for trans-RuH(X)(dpm)2 55

3.1 £P{1H} and 1H NMR data for cct-RuH(ER)(CO)2(PPh3)2 complexes in C6D6 at 200°C and 300 MHz 67
3.2 FT-IR data for cct-RuH(ER)(CO)2(PPh3)2 complexes in Nujol, HCB, or CH2Cl2 at room temperature 67
3.3 Selected bond lengths (Å) with estimated standard deviations in parentheses, for RuH(SC6H4pCH3)(CO)2(PPh3)2 (9b) 73
3.4 Selected bond angles (°) with estimated standard deviations in parentheses, for RuH(SC6H4pCH3)(CO)2(PPh3)2 (9b) 73
3.5 £P{1H} and 1H NMR data for RuH(SEt)(CO)2L2 73
3.6 Kinetic data for the reaction ofRuH2(CO)2(PPh3)2 (3) with various reagents in C6D6 at 260°C 85
3.7 NMR data for Ru(X)(Y)(dpm)2 complexes 96
3.8 Published pKa values for selected thiols in aqueous solution 106

4.1 NMR spectroscopic data for complexes of the series cct-Ru(SR)(SR')(CO)2(PPh3)2 159
4.2 Selected bond lengths (Å) for cct-Ru(SC6H4pCH3)2(CO)2(PPh3)2 (14b) 166
4.3 Selected bond angles (°) for cct-Ru(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(14b)}

4.4 Selected bond lengths (Å) for cct-Ru(SH)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(14a)}

4.5 Selected bond angles (°) for cct-Ru(SH)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(14a)}

5.1 Fragments detected in the FAB-Mass spectrum of cct-RuCl(SEt)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}

5.2 NMR and IR spectral data for Ru(X)(SEt)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}

5.3 Fragments detected in the FAB-Mass spectrum of [(CO)\textsubscript{2}(PPh\textsubscript{3})Ru(SCH\textsubscript{2}CH\textsubscript{3})\textsubscript{3}Na(THF)]\textsubscript{2}

5.4 Selected bond lengths (Å) for 21

5.5 Selected bond angles (°) for 21

A2.1 Final atomic coordinates (fractional) and B(eq) \textit{(9b)}

A2.2 Calculated hydrogen coordinates and B(iso) \textit{(9b)}

A3.1 Final atomic coordinates (fractional) and B(eq) \textit{(14b)}

A3.2 Calculated hydrogen coordinates and B(iso) \textit{(14b)}

A4.1 Final atomic coordinates (fractional) and B(eq) \textit{(21)}

A4.2 Calculated hydrogen coordinates and B(iso) \textit{(21)}

A5.1 The reaction of cct-RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(3)} with p-thiocresol

A5.2 The reaction of cct-RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(3)} with ethanethiol

A5.3 The reaction of cct-RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(3)} with carbon monoxide

A5.4 The reaction of cct-RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(3)} with triphenyl phosphine

A5.5 The reaction of cct-RuH(SCH\textsubscript{2}CH\textsubscript{3})(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(9d)} with thiophenol at 22°C

A5.6 The reaction of cct-Ru(SH)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} \textit{(14a)} with thiophenol at 25°C

A5.7 The reaction of Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3} \textit{(2)} with p-tolyl disulphide (RSSR) at 25°C
A5.8  The reaction of $cct$-$\text{RuH}$(SR)(CO)$_2$(PPh$_3$)$_2$ (9) with P(C$_6$H$_4$pCH$_3$)$_3$ (L') at 45°C  
A5.9  The reaction of $cct$-$\text{RuH}$(SR)(CO)$_2$(PPh$_3$)$_2$ (9) with 1 atm carbon monoxide

300

301
# LIST OF FIGURES

1.1 The spirit of sulphur ................................................................. 3
1.2 The dependence of sulphur content of three crude oils on the fraction distilled 5
1.3 An overview of a petroleum refinery, emphasizing the placement of desulphurization units ................................................................. 13
1.4 Hydroprocessor flow plan ............................................................. 14
1.5 The dependence of the HDS activity of the transition metal sulphides on their heat of formation ................................................................. 16
1.6 Transition metal complexes exhibiting different modes of thiophene coordination 18
1.7 The Lipsch-Schuit mechanism for thiophene HDS ........................................... 20
1.8 The Angelici mechanism for thiophene HDS ........................................... 21

2.1 Anaerobic UV/vis. cell ................................................................. 37
2.2 Constant pressure gas uptake apparatus .............................................. 39
2.3 FAB mass spectrum of RuH(BH₄)(dpm)₂ in p-nitrobenzyl alcohol 56
2.4 ¹H NMR spectrum of RuH(BH₄)(dpm)₂ under H₂ at 20°C, 300 MHz 57
2.5 ¹H NMR (300 MHz) spectra of RuH(BH₄)(dpm)₂ in C₆D₅CD₃ below ambient temperatures 59
2.6 FT-IR spectra of HCB mulls of a) RuH(BH₄)(dpm)₂ and b) RuD(BD₄)(dpm)₂ (88% deuteration) 61

3.1 ¹H NMR spectrum of cct-RuH(SEt)(CO)₂(PPh₃)₂ (9d) in C₆D₆ at 20°C and 300 MHz 65
3.2 ¹H NMR spectrum of cct-RuH(SCH₂Ph)(CO)₂(PPh₃)₂ (9e) in C₆D₆ at 20°C and 300 MHz 66
3.3 FT-IR spectrum of cct-RuH(SR)(CO)₂(PPh₃)₂ (9) in HCB where a) R=Me and
b) R=Ph.

3.4 $^{13}$C($^1$H) NMR spectrum of $cct$-RuH(SEt)(CO)$_2$(PPh$_3$)$_2$ (9d) in CD$_2$Cl$_2$

3.5 X-ray crystallographic structure of $cct$-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (9b)

3.6 Stereo-view of the structure of $cct$-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (9b)

3.7 Relationship between the $^{31}$P NMR chemical shift and the Ru-P bond length of thiolato-phosphine ruthenium complexes

3.8 The UV/vis. spectra of $cct$-RuH(ER)(CO)$_2$(PPh$_3$)$_2$ in THF at room temperature, where ER = SC$_6$H$_4$CH$_3$ (9b), SCH$_3$ (9c), or SeC$_6$H$_5$ (9h). The spectra of Ru(CO)$_2$(PPh$_3$)$_3$ (2) and RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) are included for comparison

3.9 $^1$H NMR spectra acquired during the reaction of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$

(3) with H$_2$S in C$_6$D$_6$

3.10 Plot absorbance at 400 nm versus time during the reaction of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with ethanethiol in THF at 26°C

3.11 Logarithmic plot of absorbance at 400 nm for the reaction of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with ethanethiol in THF at 26°C

3.12 Dependence of the $pseudo$-first order rate constant on the concentration of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) for the reaction with ethanethiol in THF at 26°C

3.13 Dependence of the $pseudo$-first order rate constant on the thiol concentration for the reaction of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with ethanethiol in THF at 26°C

3.14 Logarithmic plot of absorbance at 400 nm versus time for the reaction of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) and $p$-thiocresol in THF at 26°C

3.15 Dependence of the $pseudo$-first order rate constant on the concentration of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) for the reaction with $p$-thiocresol in THF at 26°C

3.16 Dependence of the $pseudo$-first order rate constant on thiol concentration for the reaction of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with $p$-thiocresol in THF at 26°C

3.17 Eyring plot for the reactions of $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with several reagents
3.18 Logarithmic plot of absorbance at 350 nm versus time for the *pseudo-*first order reaction of *cct*-RuH2(CO)2(PPh3)2 (3) with CO in THF at 26°C

3.19 Logarithmic plot of absorbance at 400 nm versus time for the *pseudo-*first order reaction of *cct*-RuH2(CO)2(PPh3)2 and PPh3 in THF at 26°C

3.20 a) 1H NMR spectra (hydride region) for the reaction of *cis-* and *trans*-RuH2(dpm)2 with H2S in C6D6 at 25°C and 300 MHz

b) 1H NMR spectra (methylene region) for the reaction of *cis-* and *trans*-RuH2(dpm)2 with H2S in C6D6 at 25°C and 300 MHz

3.21 1H NMR spectra (hydride region) for the reaction of RuH2(dpm)2 with PhCH2SH in C6D6 at 25°C

3.22 1H NMR spectrum (300 MHz) of a sample of RuH(SPh)(dpm)2 prepared *in situ* from RuH2(dpm)2 and thiophenol in C6D6

3.23 a) 31P{1H} NMR spectrum of a sample of RuH(SPh)(dpm)2 (13) prepared *in situ* from RuH2(dpm)2 and thiophenol in toluene-d8

b) Simulated spectrum for *cis-*13b

3.24 Time dependence of concentrations during the reaction of RuH2(dpm)2 with thiophenol in C6D6 at 25°C

3.25 Time dependence of the concentration of *cis*-RuH2(dpm)2 (*cis*-7) in the reaction with thiols in C6D6 at 25°C

3.26 The 1H NMR spectrum (hydride region) acquired during the reaction of RuH2(dpm)2 with *p*-toluenesulphonic acid

3.27 1H NMR spectra acquired during the reaction of *cct*-RuH(SEt)(CO)2(PPh3)2 with thiophenol in C6D6 at 22°C

3.28 Time dependence of concentrations during the reaction of *cct*-RuH2(CO)2(PPh3)2 with PhSH and EtSH in C6D6 at 36°C

3.29 Logarithmic plot of concentrations versus time for the *pseudo-*first order reaction of *cct*-RuH(SEt)(CO)2(PPh3)2 and PhSH in C6D6 at 22°C
3.30 Dependence of the pseudo-first order rate constant on [PhSH] for the reaction with cct-RuH(SEt)(CO)2(PPh3)2 in C6D6 at 22°C

3.31 1H NMR spectra (hydride region) acquired during the reaction of cct-RuH(SH)(CO)2(PPh3)2 (9a) with H2S in C6D6 at 60°C

3.32 a) 1H NMR spectra (hydride region) acquired during the reaction of RuH(SH)(dpm)2 (13a) with H2S in C6D6 at 60°C

b) 1H NMR spectra (methylene region) acquired during the reaction of RuH(SH)(dpm)2 (13a) with H2S in C6D6 at 60°C

3.33 Logarithmic plot of concentration of trans-RuH(SH)(dpm)2 (13a) during the reaction of that compound with H2S at 60°C in C6D6

3.34 The 31P{1H} NMR spectrum of Ru(SH)2(dpm)2 (15) in C6D6

3.35 31P{1H} NMR spectra acquired during the reaction of cct-Ru(SH)2(CO)2(PPh3)2 (14a) with PhSH at 25°C in C6D6

3.36 UV/vis. spectra acquired at 1 min intervals during the reaction of cct-Ru(SH)2(CO)2(PPh3)2 (14a) with PhSH at 25°C in THF

3.37 Time dependence of the concentrations of species detected by 31P{1H} NMR during the reaction of cct-Ru(SH)2(CO)2(PPh3)2 (14a) with PhSH at 25°C in C6D6

a) at 77 mM PhSH

b) at 690 mM PhSH

c) at 1700 mM PhSH

d) at 2900 mM PhSH

e) at 810 mM PhSH and 470 mM PPh3

3.38 The log plot of the concentration of cct-Ru(SH)2(CO)2(PPh3)2 (14a) during its reaction with thiophenol in C6D6 at 25°C

3.39 The dependence on [PhSH] of the observed initial rate constant for the loss of cct-Ru(SH)2(CO)2(PPh3)2 (14a) during the reaction with PhSH at several
concentrations of added PPh₃

3.40 Phosphine dependence of the inverse of the observed initial rate constant for the loss of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a) during the reaction with PhSH at several [PhSH]

3.41 Thiol dependence of the calculated rate constant $k_B$ for the second step of the reaction of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ with thiophenol at 25°C in C$_6$D$_6$

3.42 $^1$H NMR spectrum (hydride region) of the products of the reaction of Ru(CO)$_2$(dpm)(PPh$_3$)$_2$ with ethanethiol

3.43 $^{31}$P($^1$H) NMR spectrum of the products of the reaction of Ru(CO)$_2$(dpm)(PPh$_3$)$_2$ with ethanethiol

4.1 The logarithmic dependence of the concentration of Ru(CO)$_2$(PPh$_3$)$_3$ (2, [2]₀ = 7.5 mM) during its reaction with $p$-tolyl disulphide in C$_6$D$_6$ at 18°C with or without a free-radical trap

4.2 The UV/visible absorption spectrum of a solution of Ru(CO)$_2$(PPh$_3$)$_3$ and $p$-tolyl disulphide in THF at 26°C

4.3 The dependence on [2] of the initial rate of the reaction Ru(CO)$_2$(PPh$_3$)$_3$ (2) with $p$-tolyl disulphide in THF at 26°C

4.4 a) The dependence on [RSSR] of the initial rate of the reaction of Ru(CO)$_2$(PPh$_3$)$_3$ (2) with $p$-tolyl disulphide in THF at 26°C

b) Plot of 1/(initial rate) against 1/[RSSR] for the same reaction

4.5 $^1$H NMR spectrum of cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (9b) in C$_6$D$_6$

4.6 FT-IR spectrum of cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ in HCB

4.7 a) The structure of cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b)

b) A stereoscopic view of the same structure

4.8 The structure of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$
5.1 a) $^1$H NMR spectrum of $\text{cct-RuCl(SEt)(CO)}_2\text{(PPh}_3)_2$
   
   b) Expanded region of the $^1$H NMR spectrum of a sample of $\text{cct-Ru(SEt)}_2\text{(CO)}_2\text{(PPh}_3)_2$ containing 20% $\text{cct-RuCl(SEt)(CO)}_2\text{(PPh}_3)_2$

5.2 a) The FT-IR spectrum of $\text{cct-RuCl(SEt)(CO)}_2\text{(PPh}_3)_2$ in Nujol mull
   
   b) Carbonyl region of the FT-IR spectrum of a sample of $\text{cct-Ru(SEt)}_2\text{(CO)}_2\text{(PPh}_3)_2$ containing 20% of $\text{cct-RuCl(SEt)(CO)}_2\text{(PPh}_3)_2$ in a Nujol mull

5.3 The FAB-Mass spectrum of $\text{cct-RuCl(SEt)(CO)}_2\text{(PPh}_3)_2$ in a $p$-nitrobenzyl alcohol matrix

5.4 The $^1$H NMR spectrum of a C$_6$D$_6$ solution of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$ at 20°C

5.5 The $^1$H COSY NMR plot for a C$_6$D$_6$ solution of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$

5.6 The methylene region of $^1$H NMR spectra of a C$_6$D$_6$ solution of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$

5.7 Simulated $^1$H NMR spectra of a) the CH$_{2a}$ protons, and b) the CH$_{2b}$ protons of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$

5.8 The FT-IR spectrum of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$ in Nujol

5.9 The FAB-Mass spectrum of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$ in a $p$-nitrobenzyl alcohol matrix

5.10 The structure of one half of a molecule of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$

5.11 The structure of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$

5.12 Stereoscopic view of the structure of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$

5.13 a) $^{13}$C solid state (CP/MAS) NMR spectrum of $[(\text{CO})_2\text{(PPh}_3)\text{Ru(SCH}_2\text{CH}_3)_3\text{Na(THF)}_2]$
b) $^{13}$C solid state (CP/MAS) NQS NMR spectrum of $[(CO)_{2}(PPh_{3})Ru(SCH_{2}CH_{3})_{3}Na(THF)]_{2}$

5.14 $^{13}$C{$^{1}$H} NMR spectrum of $[Ru(CO)_{2}(PPh_{3})Ru(SEt)_{3}Na(THF)]_{2}$ in C$_{6}$D$_{6}$ at 20°C

5.15 $^{13}$C APT NMR spectrum of $[Ru(CO)_{2}(PPh_{3})Ru(SEt)_{3}Na(THF)]_{2}$ in C$_{6}$D$_{6}$ at 20°C

5.16 The Heteronuclear Correlation ($^{13}$C/$^{1}$H) NMR plot for $[Ru(CO)_{2}(PPh_{3})Ru(\mu SEt)_{2}(\mu SEt)Na(THF)]_{2}$ in C$_{6}$D$_{6}$

5.17 The $^{1}$H $[Ru(CO)_{2}(PPh_{3})Ru(\mu SEt)_{2}(\mu SEt)Na(THF)]_{2}$ in toluene-d$_{8}$ at -78°C

6.1 $^{31}$P{$^{1}$H} NMR spectra acquired during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in C$_{6}$D$_{6}$ at 45°C

6.2 $^{1}$H NMR spectra acquired during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in C$_{6}$D$_{6}$ at 45°C

6.3 Time dependence of the concentrations of observed complexes during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in C$_{6}$D$_{6}$ at 45°C

6.4 Log plot of [9e] during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in C$_{6}$D$_{6}$ at 45°C

6.5 The dependence of $d[12e]/dt$ on [22e] during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in C$_{6}$D$_{6}$ at 45°C

6.6 Time dependence of the concentration of observed complexes during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in the presence of PPh$_{3}$ in C$_{6}$D$_{6}$ at 45°C

6.7 Time dependence of Q$_{1}$ and Q$_{2}$ during the reaction of cct-RuH(SCH$_{2}$Ph)(CO)$_{2}$(PPh$_{3}$)$_{2}$ (9e) with P(C$_{6}$H$_{4}$pCH$_{3}$)$_{3}$ in the presence of PPh$_{3}$ in C$_{6}$D$_{6}$ at 45°C
6.8 UV/vis. spectra acquired every 900 s during the reaction of cct-RuH(SEt)(CO)2(PPh3)2 and CO in THF at 26°C

6.9 Log plot of absorbance versus time for the reaction of cct-RuH(SEt)(CO)2(PPh3)2 (9d) and CO in THF at 26.5°C

6.10 Eyring plot for the reactions of cct-RuH(SR)(CO)2(PPh3)2 with CO in THF

6.11 1H NMR spectrum acquired 30 min after the start of the reaction of cct-RuH(SC6H5)(CO)2(PPh3)2 (9j) with excess HBF4/H2O in C6D6 at room temperature

6.12 The time dependence of the intensity of the 1H NMR signals due to cct-RuH(SH)(CO)2(PPh3)2 in 4% v/v CD3OD/C6D6 at 19°C

6.13 The log plot of the intensity of the 1H NMR signals due to cct-RuH(SH)(CO)2(PPh3)2 in 4% v/v CD3OD/C6D6 at 19°C

6.14 UV/vis. absorbance spectra of a THF solution of cct-Ru(SC6H4pCH3)2(CO)2(PPh3)2 at 25°C being irradiated at 430 nm

6.15 FAB Mass spectrum of the solid residue from a THF solution of cct-Ru(SC6H4pCH3)2(CO)2(PPh3)2 irradiated for 90 min under a Hanovia lamp

6.16 a) Observed isotopic pattern for the fragment m/z = 1149±4
   b) The predicted isotopic patterns for four possible formulations for the fragment

6.17 31P{1H} NMR spectra acquired during the reaction of cct-Ru(SH)2(CO)2(PPh3)2 (14a) with P(C6H4pCH3)3 in C6D6 at 25°C

6.18 1H NMR spectra acquired during the reaction of cct-Ru(SH)2(CO)2(PPh3)2 (14a) with P(C6H4pCH3)3 in C6D6 at 25°C

6.19 The time dependence of the concentrations of the observed complexes during the reaction of cct-Ru(SH)2(CO)2(PPh3)2 (14a) with P(C6H4pCH3)3 in C6D6 at 25°C

6.20 1H NMR spectrum of a C6D6 solution of the product from the reaction
of a THF solution of $cct$-$\text{Ru}(\text{SC}_6\text{H}_4\text{pCH}_3)_2(\text{CO})_2(\text{PPh}_3)_2$ with $\text{H}_2$

6.21 $^{31}\text{P}^{(1}\text{H})$ NMR spectrum of $\text{C}_6\text{D}_6$ solution of the product from the reaction of a THF solution of $cct$-$\text{Ru}(\text{SC}_6\text{H}_4\text{pCH}_3)_2(\text{CO})_2(\text{PPh}_3)_2$ with $\text{H}_2$

6.22 The time dependence of the intensity of the $^1\text{H}$ NMR signals due to $cct$-$\text{Ru}(\text{SH})_2(\text{CO})_2(\text{PPh}_3)_2$ in 4% v/v CD$_3$OD/C$_6$D$_6$ at 25°C
LIST OF ABBREVIATIONS

A = absorbance
A∞ = absorbance after infinite reaction time
alkyl/polym. = polymerization unit
APT = attached proton test (13C NMR pulse sequence)
AT = acquisition time during an FT-NMR pulse sequence
atm. = atmosphere(s)
atm. dist. = atmospheric pressure distillation tower (Fig. 1.3)
Beq = isotropic equivalent thermal parameters
B, Biso = isotropic thermal parameters
BDH = British Drug Houses Chemicals Ltd.
bipy = 2,2'-bipyridyl
br. = broad
Bu = butyl
BuS4 = 1,2-bis((3,5-di-tert-butyl-2-mercapto-phenyl)thio)ethanato(2-)
Bz = benzyl (CH2C6H5)
c = cis
C = a constant
calcd. = calculated
ccc = cis, cis, cis
cct = cis, cis, trans
CDE = cyclododecene
CDT = 1,5,9-cyclodecatriene
COD = 1,5-cyclooctadiene
COSY = Homonuclear Correlated Spectroscopy (FT-NMR experiment)
COT = 1,3,5-cyclooctatriene
Cp = cyclopentadienyl
CP/MAS = cross-polarization/magic angle spinning (13C solid state NMR technique)
ctc = cis, trans, cis
δ = bending mode (IR) or chemical shift (NMR)
d = doublet (NMR) or bond distance
D = deuterium
D1, D2 = delay times in an FT-NMR pulse sequence
DBU = 1,8-diazabicyclo-[5,4,0]-undec-7-ene
DEA = diethanolamine
deC4 = unit for the separation of C-4 hydrocarbons
def = deformation
dippp = 1,3-bis(diisopropylphenylphosphino)propane
dma = N,N-dimethylacetamide
dmdppe = 1-dimethylphosphino-2-diphenylphosphinoethane
dmpe = 1,2-bis(dimethylphosphino)ethane
dms = dimethylsulphoxide
dpm = bis(diphenylphosphino)methane
dppe = 1,2-bis(diphenylphosphino)ethane
dq = doublet of quartets
dt = doublet of triplets
ε = molar extinction coefficient
Elem. Anal. = elemental analysis
est. = estimated
Et = ethyl
F(000) = electrons per unit cell
FAB/MS = fast-atom bombardment mass spectroscopy
FT = Fourier transform
GC = gas chromatograph(y)
gof = goodness of fit indicator
h = hour
$\Delta H^\ddagger$ = enthalpy of activation
$H_b$ = bridging hydrogen atom
HCB = hexachloro-1,3-butadiene
HDS = hydrodesulphurization
HETCOR = heteronuclear correlation (FT-NMR experiment)
Ht = terminal hydride ligand
H2TPP = tetraphenylporphyrin
I = intensity
IR = infra-red (spectroscopy)
IUPAC = International Union of Pure and Applied Chemistry
J = coupling constant (NMR)
Keq = equilibrium constant
KMS = Kezdy-Mangelsdorf-Swinbourne method
$k_{obs}$ = observed pseudo-first order rate constant
$l$ = path length (spectroscopy)
L = ligand (usually PPh3 in this work)
$\mu$ = absorption coefficient
$m$ - = meta-
M = metal, or unit of molarity
MCB = Matheson, Coleman and Bell
$m/z$ = mass to charge ratio
Me  =  methyl
Merox  =  mercaptan oxidation process
min  =  minutes
mol  =  moles or molecular
MSD  =  Merck, Sharp and Dohme
multi.  =  multiplet
n  =  order of the rate dependence on free ligand concentration
NMR  =  nuclear magnetic resonance
nOe  =  nuclear Overhauser effect
o-  =  ortho-
p-  =  para-
P1, P2  =  duration of pulses in an FT-NMR pulse sequence
Ph  =  phenyl
PPh3  =  triphenylphosphine
ppm  =  parts per million
ppth  =  parts per thousand
Py  =  -2-C5H4N
q  =  quartet
Q  =  quotient (defined in Section 6.1.1)
qn  =  quintet
ρ  =  density
R  =  alkyl or aryl group, or rate of change of absorbance (dA/dt)
R, RW  =  agreement factors (defined on page 283)
rearr.  =  rearrangement
RNA  =  ribonucleic acid
s  =  singlet
ΔS‡  =  entropy of activation
\( \theta \) = Bragg angle
\( t \) = \textit{trans}
\( t \) = triplet
\( T \) = constant delay time or temperature
\( T_1 \) = longitudinal relaxation time
\( \text{THF} \) = tetrahydrofuran
\( \text{THT} \) = tetrahydrothiophene
\( \text{TMS} \) = tetramethylsilane
\( \text{tol} \) = \( p \)-tolyl (-C₆H₄PCH₃)
\( \text{ttt} \) = \textit{trans, trans, trans}
\( \text{UV/vis.} \) = ultra-violet or visible absorption (spectroscopy)
\( V \) = volume (of the unit cell)
\( v/v \) = concentration by volume
\( \text{vac. dist.} \) = vacuum distillation tower (Fig. 1.3)
\( v \) = frequency or stretching mode (IR)
\( v_D/v_H \) = isotopic shift
\( w_{0.5} \) = peak width at half-height
\( \text{wt.} \) = weight
\( Z \) = formulas per unit cell
NUMERICAL KEY TO THE RUTHENIUM COMPLEXES

<table>
<thead>
<tr>
<th></th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ccr-RuCl₂(CO)₂(PPh₃)₂</td>
</tr>
<tr>
<td>2</td>
<td>Ru(CO)₂(PPh₃)₃</td>
</tr>
<tr>
<td>3</td>
<td>ccr-RuH₂(CO)₂(PPh₃)₂</td>
</tr>
<tr>
<td>4</td>
<td>ccr-RuH(Cl)(CO)₂(PPh₃)₂</td>
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<tr>
<td>5</td>
<td>cis-RuCl₂(dpm)₂</td>
</tr>
<tr>
<td>6</td>
<td>trans-RuCl₂(dpm)₂</td>
</tr>
<tr>
<td>7</td>
<td>cis- or trans-RuH₂(dpm)₂</td>
</tr>
<tr>
<td>8</td>
<td>trans-RuH(BH₄)(dpm)₂</td>
</tr>
<tr>
<td>9</td>
<td>ccr-RuH(ER)(CO)₂(PPh₃)₂</td>
</tr>
<tr>
<td>10</td>
<td>Ru(CO)₃(PPh₃)₂</td>
</tr>
<tr>
<td>11</td>
<td>ccr-RuH(ER)(CO)₂(PPh₂Py)₂</td>
</tr>
<tr>
<td>12</td>
<td>ccr-RuH(ER)(CO)₂{P(C₆H₄pCH₃)}₃₂a</td>
</tr>
<tr>
<td>13</td>
<td>cis- or trans-RuH(ER)(dpm)₂</td>
</tr>
<tr>
<td></td>
<td>a R = H (trans only)</td>
</tr>
<tr>
<td></td>
<td>b C₆H₅</td>
</tr>
<tr>
<td></td>
<td>c CH₂C₆H₅</td>
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<td>ccr-Ru(SR)₂(CO)₂(PPh₃)₂</td>
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<tr>
<td>15</td>
<td>cis- or trans-Ru(SH)₂(dpm)₂</td>
</tr>
<tr>
<td>16</td>
<td>Ru(CO)₂(PPh₃)(dpm)</td>
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<td>17</td>
<td>isomer of RuH(SCH₂CH₃)(CO)(PPh₃)(dpm)</td>
</tr>
<tr>
<td>18</td>
<td>isomer of RuH(SCH₂CH₃)(CO)(PPh₃)(dpm)</td>
</tr>
<tr>
<td>19</td>
<td>ccr-RuS₂(CO)₂(PPh₃)₂</td>
</tr>
<tr>
<td>20</td>
<td>ccr-RuCl(SCH₂CH₃)(CO)₂(PPh₃)₂</td>
</tr>
<tr>
<td>21</td>
<td>[Ru(CO)₂(PPh₃)(SEt)₃Na(THF)]₂</td>
</tr>
<tr>
<td>22</td>
<td>ccr-RuH(SR)(CO)₂(PPh₃)(P{C₆H₄pCH₃})₃a</td>
</tr>
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</table>
23  \( cct-Ru(SR)_{2}(CO)_{2}(PPh_{3})(P(C_{6}H_{4}pCH_{3})_{3}) \)\(^{a}\)
24  \( cct-Ru(SR)_{2}(CO)_{2}(P(C_{6}H_{4}pCH_{3})_{3})_{2} \)\(^{a}\)

\(^{a}\) Complexes 2, 11, 12, 14, and 22 through 24 are further identified by one of the following letters, which indicate the thiolate or selenolate group (ER). In the case of complexes 14 with two different thiolate ligands, two such initials are shown in the abbreviation.

- a  \( SH \)  f  \( SC_{6}H_{4}oCH_{3} \)
- b  \( SC_{6}H_{4}pCH_{3} \)  g  \( SC_{6}H_{4}mCH_{3} \)
- c  \( SCH_{3} \)  h  \( SeC_{6}H_{5} \)
- d  \( SCH_{2}CH_{3} \)  i  \( SC_{6}H_{5} \)
- e  \( SCH_{2}C_{6}H_{5} \)  j  \( SC_{6}F_{5} \)
ACKNOWLEDGEMENTS

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1. INTRODUCTION

The mechanism of the hydrodesulphurization (HDS) of sulphur-containing organics in fuel remains a mystery, even after decades of research. Even the kinetics of the reaction, outside of the adsorption and desorption steps, are not understood. Analogies to the reactions of homogeneous complexes can lead to greater understanding of heterogeneous catalysts. Such analogies are central to a mechanism proposed recently\(^1\) for thiophene HDS. Although such research has emphasized thiophenes because of their resistance to desulphurization, three decades of related research into the coordination chemistry of thiols, thioethers, disulphides, and other sulphur compounds have identified many modes of coordination in, and reactions of, their complexes. The kinetics of the formation and subsequent reactions of such complexes have been largely ignored. It is the purpose of the research described in this thesis to assist in this regard.

Two ruthenium complexes, RuH\(_2\)(CO)\(_2\)(PPh\(_3\))\(_2\) and Ru(CO)\(_2\)(PPh\(_3\))\(_3\), were chosen because of the high HDS activity of ruthenium sulphide (Fig. 1.6), and because of the ease by which the two complexes and their reaction products could be identified by IR and NMR spectroscopies. The reactions of these and related complexes with thiols, disulphides, thioethers, thiophenes and sulphur itself were to be observed and monitored kinetically if possible. In addition, the products and their properties and reactivities were further subjects for study. Finally, the effect of ligand choice on reactivity and rate was to be examined.

This first chapter reviews the applications, natural occurrence, and nomenclature of sulphur compounds, the industrial use of HDS, some theories on the mechanism of the reaction, and the coordination chemistry of simple sulphur-containing compounds.
1.1 SULPHUR

1.1.1 History and Applications

Sulphur (Fig. 1.1) can be both beneficial and harmful, according to popular belief. Sulphurous hot springs have long been used as healing baths. This, along with the natural fumigating action of sulphurous vapours, led to myths about sulphur's medicinal properties. Pliny the Elder, in his "Natural History" (c. 77 A.D.), reported the use of sulphur for medicine, fumigation, and religious ceremonies. However, the production of sulphur from the gases of volcanoes and fumaroles naturally suggested an association with hell and the centre of the earth. Apollonius of Tyana (AD 17-97) believed that "volcanoes are caused by a mixture of bitumen and sulphur in the earth, which smokes by its own nature." The connection of volcanoes, "brimstone" (probably sulphur), and hell is a common theme in the Bible (Gen. 19:24, Rev. 14:9-11; 20:10; 21:8). The presence of sulphur within the earth, according to the alchemical sulphur-mercury theory of metals, was essential for the natural production of gold.

Although our understanding of sulphur and its compounds has increased, the element still retains its two-sided nature. Much of the recent research into sulphur chemistry has been aimed at sulphur removal, rather than the practical applications of its compounds. Large amounts of sulphur are removed from natural gas, petroleum, and coal-based fuels, not for the price the sulphur will fetch, but to prevent catalyst fouling, pipe corrosion, and environmental damage.

The production of sulphur as waste from fuel processing has the result of keeping down the price of sulphur, and consequently the price of sulphuric acid. In fact, 80% of sulphur is converted to sulphuric acid, which is used as a reagent in the production of phosphate fertilizers, synthetic fibres (Rayon, Nylon 6), white pigments, and steel pickling. U.S. production of sulphuric acid in 1988 (86 x 10^9 lb) was larger than for any other chemical. Other sulphur chemicals used industrially are hydrogen sulphites and sulphates (pulping processes), sulphites (tanning, sugar refining, etc.), sodium...
Fig. 1.1 The Spirit of Sulphur?
thiosulphate (photography), sulphur dioxide and carbon disulphide (solvents), sulphur hexafluoride (transformer oil), xanthates (fungicides), thiokols (plastics), and several compounds used in the treatment of rubber.

1.1.2 Natural Occurrence

Sulphur occurs as the native element, as well as in organic and inorganic compounds. Sulphur is mined or extracted by the Frasch process as the native element at a number of sites, such as Sicily and Louisiana. It is also "recovered as a byproduct in smelting sulfide ores, from sour natural gas, and from pyrite." The United States, with its reserves of elemental sulphur, relies on the Frasch process. Canada, on the other hand, obtains 85% of its sulphur from the desulphurization of natural gas.

The sulphur-containing minerals, other than sulphur itself, are sulphides (e.g. pyrite FeS2), sulpharsenides (e.g. cobaltite (Co,Fe)AsS), sulphosalts (e.g. tetrahedrite Cu12Sb4S13) and sulphates (e.g. gypsum CaSO4). Sulphur-containing organics, hydrogen sulphide, and even elemental sulphur are found in petroleum. The sources of these compounds are the sulphur compounds in the original biological matter, and the biogenic reduction of sulphate minerals to hydrogen sulphide, followed by reactions with components of petroleum. The type of functional group and the concentration of the sulphur compound depend on the fraction of petroleum studied. "Sulfur in the lower-boiling straight-run distillates is mainly in the form of mercaptans, sulfides, and disulfides, whereas thermally-cracked distillates contain the more refractory thiophene type, in addition to the thiophenols that occur in catalytically cracked distillates." A thorough study by the U. S. Bureau of Mines described the relationship between sulphur content (weight percent) and boiling point of the fuel fraction (Fig. 1.2), and identified 200 individual sulphur compounds contained in
Fig. 1.2 The dependence of sulphur content of three crude oils on the fraction distilled.

Table 1.1 Estimated Concentrations of Selected Sulphur Compounds Identified in Wasson, Texas, crude oil.

<table>
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<tr>
<th>Name</th>
<th>b.p. (°C)</th>
<th>ppm by wt.</th>
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<tbody>
<tr>
<td>methanethiol</td>
<td>5.9</td>
<td>24.0</td>
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<tr>
<td>ethanethiol</td>
<td>35.0</td>
<td>53.0</td>
</tr>
<tr>
<td>2-thiopropane</td>
<td>37.4</td>
<td>8.8</td>
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<td>2-propanethiol</td>
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<td>2-thiabutane</td>
<td>66.7</td>
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<td>2-butanethiol</td>
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<td>2-pentanethiol</td>
<td>112.4</td>
<td>14</td>
</tr>
<tr>
<td>2,3-dithiapentane</td>
<td>133. (est.)</td>
<td>-</td>
</tr>
<tr>
<td>2-methylthiacyclopentane</td>
<td>133.2</td>
<td>23</td>
</tr>
<tr>
<td>2-hexanethiol</td>
<td>138.9</td>
<td>28</td>
</tr>
<tr>
<td>trans-2,5-dimethylthia-cyclopentane</td>
<td>142.0</td>
<td>25</td>
</tr>
<tr>
<td>cis-2,5-dimethylthiacyclopentane</td>
<td>142.3</td>
<td>24</td>
</tr>
<tr>
<td>2-methylthiacyclohexane</td>
<td>153.0</td>
<td>29</td>
</tr>
<tr>
<td>cyclohexanethiol</td>
<td>158.7</td>
<td>12</td>
</tr>
<tr>
<td>2-methylbenzo[b]thiophene</td>
<td>243. (est.)</td>
<td>24.8</td>
</tr>
<tr>
<td>3-methylbenzo[b]thiophene</td>
<td>246. (est.)</td>
<td>9.5</td>
</tr>
<tr>
<td>2,4-dimethylbenzo[b]thiophene</td>
<td>-</td>
<td>9.4</td>
</tr>
<tr>
<td>2,5- and/or 2,7-dimethylbenzo-[b]thiophene</td>
<td></td>
<td>10.1</td>
</tr>
</tbody>
</table>

a) Ref. 8
b) Tentative identification only.
four crude oils (Table 1.1). Although thiophene itself is low boiling, heterocyclic compounds such as thiophene are usually more common in the heavier fractions of oil because of their ability to form hydrogen bonds.

Coal contains up to 10 wt. % sulphur, consisting of sulphate sulphur (sulphates of iron, calcium, and others, less than 0.1 wt. %), pyritic sulphur (pyrite and marcasite, up to 8.0 wt. %), and organic sulphur (thiols, sulphides, and thiophenes, up to 6.0 wt. %). The first two classes of sulphur compounds can be extracted by washing and gravity separation. Of the organic sulphur in bituminous coal, thiols make up 10-30%, sulphites 5-27%, and thiophenes 40-70%. These compounds, especially the thiophenes, are difficult to remove. Conventional coal-cleaning processes, such as leaching, have had only mediocre success. The only effective technique is conversion to coal-derived liquids, followed by hydrodesulphurization (Section 1.2.2).

A wide variety of sulphur-containing chemicals is found in biology. Sulphur minerals are oxidized by weathering to sulphates, which are required by most plants and some micro-organisms. Plants convert these sulphates to the amino acids L-cystine, L-cysteine, and L-methionine, which are required, with the vitamins thiamine and biotin, by the higher animals. These organic sulphur compounds are "largely degraded to hydrogen sulfide as a result of microbial action on plants and animals after their death." The classes of sulphur-containing compounds, a few examples, and the materials in which they have been found are the following:

a) Thiols: 3-methyl-1-butanol (skunk), ergothioneine (cereal grains), glutathione (widespread), transfer RNA (bacteria), a variety of enzymes, and the amino acids L-cysteine and homocysteine.

b) Disulphides: the amino acids cystine and homocystine, lipoic acid (widespread), thiamine disulfide, and several antibiotics.
c) Sulphides: pheromones, the amino acid methionine, vitamins thiamine and biotin, the penicillin and cephalosporin classes of antibiotics,\textsuperscript{17} and many of the odoriferous volatiles in foods, such as kahweofuran (coffee).

d) Thiophenes: more than 150 thiophene derivatives isolated from Compositae and fungi.\textsuperscript{18}

e) Thioesters: the thioesters of the two thiols Coenzyme A and acyl carrier protein "are involved in the functioning of oxidoreductases, transferases, hydrolases, ligases, lyases, and isomerases."\textsuperscript{17}

f) Coordination Compounds: The sulphur-containing ligands found in metalloproteins are S\textsuperscript{2-} and the residues of the amino acids cysteine and methionine. Methionine-coordinated metal ions can be found in some cytochromes c (heme Fe atoms)\textsuperscript{19} and in blue copper proteins such as azurin and plastocyanin.\textsuperscript{20} Cysteine-bound metal ions are found in metallothioneins (Cd),\textsuperscript{21} liver alcohol dehydrogenase (Zn),\textsuperscript{22} rubredoxin (Fe),\textsuperscript{23} azurin and plastocyanin (Cu),\textsuperscript{20} and zinc fingers such as those in the yeast protein ADR1.\textsuperscript{24} Ferredoxins contain sulphide-bridged iron atoms bound to cysteine or other ligands.\textsuperscript{25-7} The structure of the FeMo cofactor of nitrogenase is not known, but estimates of the stoichiometry of its thiolate-bound core are in the range 1Mo, 6-8Fe, 6-9S.\textsuperscript{25,28-9}

1.1.3 Nomenclature of Sulphur Compounds

The nomenclature of sulphur chemistry was invented by the devil. If one omits for the moment the difference between "sulphur" (British) and "sulfur" (American), and ascribes the thiol vs. mercaptan problem to the vagaries of a nomenclature system built around historical labels, one is still faced with a bewildering array of systematic and trivial names. An extreme example is the word "sulphide", which means a binary
metal/sulphur compound to a geochemist, a thioether complex to a coordination chemist, an $S^{2-}$ ion to an inorganic chemist, a thiol to some biochemists, and either a thioether or a thiolate salt to an organic chemist. IUPAC confusingly allows its use for thioethers, thiolate salts and $S^{2-}$ ligands. Table 1.2 presents a summary of the terms used to refer to compounds or ligands which contain only sulphur, carbon, hydrogen, and/or metal atoms. In the following work, the terms thiol, thioether, thiolate anion, and disulphide are used to refer to the organic species RSH, RSR, RS⁻, and RSSR. The term sulphide is reserved for complexes containing the ligand $S^{2-}$. The "ph" spelling is used, except in direct quotes from sources that use the other convention.

1.2 THE EXTRACTION OF SULPHUR FROM FOSSIL FUELS

1.2.1 Reasons for Sulphur Extraction

The deleterious effects of high-sulphur-content fossil fuels are catalyst fouling, corrosion of pipes and reactor vessels, undesirable properties of the fuel products, and air pollution during processing or after combustion. As the world reserves of low-sulphur fuels are consumed and the demands of environmental legislation and the public become more stringent, the use of desulphurization will increase.

1.2.1.1 Catalyst Fouling

Noble metal catalysts in the catalytic reformer, some hydrocracking units, and the butadiene hydrogenator section of the alkylation unit of the refinery are poisoned by sulphur-containing compounds. It is the poisoning of the reformer catalyst which is the economic incentive for hydrodesulphurization.
<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
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<td>30</td>
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<td>RSH</td>
<td>alkyl hydrosulfide</td>
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<td>32, 30</td>
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<td>dialkyl sulfane</td>
<td>outdated</td>
<td>30</td>
</tr>
<tr>
<td>RSSR</td>
<td>dialkyl thioether</td>
<td>prefix</td>
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</tr>
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<td>30</td>
</tr>
<tr>
<td>RSSR</td>
<td>thio-</td>
<td>trivial</td>
<td>30</td>
</tr>
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<td>30</td>
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<td>RSSR</td>
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<td>30</td>
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<td>dialkyldisulfane</td>
<td>1</td>
<td>30</td>
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<td>dithiodi-</td>
<td>prefix, 3</td>
<td>30</td>
</tr>
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<tr>
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<td>alkylsulfanyl</td>
<td>free radical</td>
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<td>thio</td>
<td>ligand</td>
<td>31</td>
</tr>
<tr>
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<td>disulfido-</td>
<td>ligand</td>
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<td>hydrogensulfide</td>
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</tr>
<tr>
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<td>mercapto-</td>
<td>ligand</td>
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<td>RS-</td>
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<td>anion</td>
<td>30</td>
</tr>
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<td>alkylthio-</td>
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<tr>
<td>RS-</td>
<td>alkanethiolato-</td>
<td>ligand</td>
<td>31</td>
</tr>
</tbody>
</table>

Notes: 1. S-S chain is straight, not branched.
2. S atom bridges two carbons already in a ring.
3. Identical R groups.
4. Compounds of the formula RS(CH₂)nSR’ have been referred to as disulphides.130
5. Radicofunctional nomenclature.
6. For use when an S atom replaces a CH₂ group in the parent formula.
1.2.1.2 Corrosion

Corrosion in the refinery due to sulphur compounds occurs at high temperatures or pressures. Regions where these conditions exist, such as pipe still heaters, fractionators, and reactors, are prone to iron oxide and iron sulphide scale formation. At low temperatures, acid attack by HCl, H2S, or CO2 in condensates is the principal cause of corrosion.34

1.2.1.3 Undesirable Properties of Fuel Products

Fuel products high in hydrogen sulphide, thiols, and volatile sulphides have distinctly unpleasant odours. This problem is rectified by either extraction of the sulphur, or conversion of the thiols to the non-volatile disulphides, which are often allowed to remain in the fuel product.9 The stability of fuel products is compromised if H2S, disulphides, or polysulphides are present. The last two species "actively promote the formation of sludges."35 Sulphur compounds are removed from kerosenes to decrease smoke formation.36 The effectiveness of alkyl-lead anti-knock agents is inhibited by thiols and disulphides.37 However, since the use of alkyl-lead compounds is diminishing, this inhibition is no longer a justification for desulphurization.

1.2.1.4 Air Pollution

The bulk of anthropogenic emissions of sulphur gases in the U.S. are of sulphur dioxide.38 Although industrial emissions of hydrogen sulphide are in sufficient quantities to cause concern, they represent only 1% of the total anthropogenic sulphur emissions in Canada.39 The gaseous products of fossil fuel combustion contain sulphur dioxide and sulphur trioxide in ratios of between 40:1 and 80:1.14 Fuel combustion in
stationary sources, such as heating systems in buildings, and power generating stations, is responsible for greater emissions than combustion by mobile sources such as transportation vehicles (Table 1.3). In the United States, where coal combustion plays a greater role in power generation, the stationary source emissions are significantly greater than in Canada.

Stack gases of fluid catalytic crackers are a major source of sulphur oxides. These emissions can be reduced by scrubbing of the gases, or hydrotreating of the cracker feedstock.41

Once emitted, $\text{SO}_2$ is oxidized in the atmosphere to $\text{SO}_3$ in a reaction catalyzed by metallic oxide particulates. Sulphur trioxide reacts with water or particulates to form sulphuric acid or sulphates, respectively. Both products cause reduced visibility, corrosion of materials, and acid rain. The observed useful life of galvanized sheet steel at 65% humidity and 13 $\text{g/m}^3$ $\text{SO}_2$ (rural setting) is 30-35 years. At 1040 $\text{g/m}^3$ $\text{SO}_2$ (heavily industrial setting), the useful life is reduced to 3-5 years.42 The effects of sulphur oxides on the environment are more difficult to measure, but the serious consequences of large scale damage are sufficient to keep the subject under intense scientific and political scrutiny.

1.2.2 Sulphur Extraction from Petroleum

The removal of organic sulphur from petroleum is accomplished by amine treatment, caustic treatment, molecular sieve adsorption, or catalytic hydrotreating.43 The last mentioned process is the most effective at removing sulphur and therefore is used to treat feedstocks of the catalytic reformer, and refinery product streams which need to be particularly low in sulphur. The placement of desulphurization units within a simplified refinery flow-plan is shown in Fig. 1.3. Hydrotreating (Fig. 1.4) involves passing the feed over catalysts of nickel, cobalt or molybdenum oxides on alumina, under high
Table 1.3 Canadian Nationwide Emissions of Sulphur Oxides, in 1980\textsuperscript{a}

<table>
<thead>
<tr>
<th>Source</th>
<th>Emissions (x 10\textsuperscript{6} kg SO\textsubscript{2})</th>
<th>Percent of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMBUSTION IN VEHICLES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>marine</td>
<td>60</td>
<td>1.4</td>
</tr>
<tr>
<td>diesel</td>
<td>39</td>
<td>0.9</td>
</tr>
<tr>
<td>gasoline</td>
<td>19</td>
<td>0.5</td>
</tr>
<tr>
<td>railroad</td>
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<td>0.1</td>
</tr>
<tr>
<td>aircraft</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>subtotal</td>
<td>123</td>
<td>2.9</td>
</tr>
<tr>
<td>STATIONARY SOURCES</td>
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<td></td>
</tr>
<tr>
<td>power generation by utilities</td>
<td>696</td>
<td>16.5</td>
</tr>
<tr>
<td>residential, commercial and industrial</td>
<td>556</td>
<td>13.2</td>
</tr>
<tr>
<td>fuel wood</td>
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<td>0.1</td>
</tr>
<tr>
<td>subtotal</td>
<td>1,255</td>
<td>29.8</td>
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<td>INDUSTRIAL PROCESSES</td>
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<td></td>
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<td>Cu, Ni production</td>
<td>1,723</td>
<td>40.9</td>
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<tr>
<td>natural gas processing</td>
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<td>8.3</td>
</tr>
<tr>
<td>Fe production</td>
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<td>5.2</td>
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<tr>
<td>other metals</td>
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<td>4.0</td>
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<tr>
<td>tar sands operations</td>
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<td>3.2</td>
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<tr>
<td>pulping</td>
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</tr>
<tr>
<td>TOTAL</td>
<td>4,218</td>
<td>100.0</td>
</tr>
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</table>

\textsuperscript{a} Adapted from reference 39b.
Fig. 1.3 An overview of a petroleum refinery, emphasizing the placement of desulphurization units. Abbreviations are defined in the list of abbreviations.
Fig. 1.4 Flow plan for a naphtha hydrotreater.45
pressures of hydrogen. If the temperature is kept below 300°C, only the thiols are converted to H₂S, and the process is called hydrosweetening. Naphtha (catalytic reformer feedstock) hydrotreating usually occurs at catalyst bed temperatures of up to 370°C. At these temperatures, the following reactions take place:

a) Hydrodesulphurization (HDS)

\[ \text{C}_x\text{H}_y\text{S} + 2\text{H}_2 \rightarrow \text{C}_x\text{H}_{y+2} + \text{H}_2\text{S} \]

b) Hydrodenitrogenation (HDN)

c) Hydrodeoxygenation (HDO)

d) Hydrogenation of olefins and some aromatics

e) Hydrocracking

\[ \text{RCH}_2\text{CH}_2\text{R'} + \text{H}_2 \rightarrow \text{RCH}_3 + \text{R'}\text{CH}_3 \]

After conversion, the products are separated; hydrogen is recycled; and H₂S is converted to sulphur in a Claus plant.

The HDS catalysts are usually MoO₃, with CoO as a promoter, deposited from an ammonia solution onto a high surface area alumina support. The oxides are converted to sulphides by presulphiding the catalyst with H₂/H₂S mixtures. Heavy metals in the feed poison the HDS catalyst, but this is preferable to poisoning of the expensive reformer catalyst.

The sulphides of Ru, Os, Rh, and Ir are far more efficient HDS catalysts than those of either Co or Mo, possibly because of the intermediate heats of formation of the noble metal sulphides (Fig. 1.5). However, the success of catalysts containing both Co and Mo, and the cost of the noble metal catalysts, prohibit their use industrially.

The mechanism of the hydrodesulphurization reaction is not known. Thiophene is the model substrate of choice, because it is the parent molecule of the least easily desulphurized class of molecules. The hydrocarbon products of the reaction of thiophene with 1 atm of hydrogen, over cobalt molybdate on alumina at 288°C, are butadiene (2%),
Fig. 1.5 The dependence of the HDS activity of the transition metal sulphides on their heat of formation (DBT = dibenzothiophene). Mixtures of metal sulphides are shown as filled squares at the average of the heats of formation of the individual sulphides. The commercial catalyst is shown as a hollow circle.
1-butene (48%), cis-2-butene (20%), trans-2-butene (24%), and butane (6%). Central to the debate over the mechanism are the mode of coordination of thiophene to the surface and the nature of the first step in the reaction pathway.

Studies of thiophene adsorption onto clean or sulphided surfaces of various metals found examples of S-bound perpendicular, S-bound tilted, and \( \eta^5 \)-bound thiophenes. IR studies on molybdenum sulphide catalysts showed evidence for thiophenes coordinated by one \( \eta^2 \) or \( \eta^3 \) or two \( \eta^4 \) or \( \eta^5 \) double bonds. Perpendicular binding through the S atom is preferred in molybdenum sulphide anion vacancies, according to quantum chemical extended Hückel theory studies. Coordination complex analogues for four of these binding modes have been reported (Fig. 1.6). It is likely that the mode of binding on surfaces varies depending on the adsorbed species. One study of thiophenes and thianthrenes adsorbed on commercial CoMo/Al2O3 catalysts at normal operating conditions divided the molecules into those concentrating their electron density at the sulphur, and those having their electron density delocalized over an extensive \( \pi \) system. The former group would bind by the sulphur atom. The latter group, especially if steric hindrance existed around the sulphur, would bind in the manner of a \( \pi \) complex. This is consistent with observations in coordination chemistry: benzothiophene and dibenzothiophene, which fall in the latter group, bind to metal atoms by the benzene, not thiopene, ring.

Angelici used parallels with coordination chemistry to argue in favour of \( \eta^5 \) coordinated thiophenes in HDS. He argued that a) \( \eta^5 \) coordination is stronger and more activating than the \( \eta^1 \) coordination, and that b) product distributions of exchange reactions of D2 with thiophene bound to HDS catalyst surfaces are very similar to those of exchange reactions of CD3OD with Ru(Cp)(\( \eta^5 \)-thiophene)+.

After adsorption, what is the first step in the HDS of thiophene; desulphurization to butadiene followed by hydrogenation, or hydrogenation to di- or tetrahydrothiophene followed by desulphurization? Studies by Desikan and Amberg suggest the former,
a) $\eta^1$-coordination\textsuperscript{57,58}

\[
\begin{align*}
\text{Fe} & \quad \text{S} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ru} & \quad \text{PPh}_3 \quad \text{S} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

b) $\eta^2$-coordination\textsuperscript{59}

\[
\begin{align*}
\text{(NH}_3\text{)}_5\text{Os} & \quad \text{S} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

c) $\eta^4$-coordination\textsuperscript{60,61}

\[
\begin{align*}
\text{Ir} & \quad \text{S} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

d) $\eta^5$-coordination\textsuperscript{62}

\[
\begin{align*}
\text{Ru} & \quad \text{S} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

Fig. 1.6 Transition metal complexes exhibiting different modes of thiophene coordination.
because the HDS of tetrahydrothiophene gives a different product distribution than the HDS of thiophene. However, results with benzo thiophene and the presence of tetrahydrothiophene in thiophene HDS effluent suggest that both pathways are being followed simultaneously.

It is likely that two kinds of sites exist. One type, responsible for desulphurization, is poisoned by H₂S, thiophene, pyridine and NH₃. The other, weakly electrophilic site, responsible for hydrogenation, is poisoned only by NH₃ or alkali.

The Lipsch-Schuit mechanism proposes η¹-coordination of the thiophene, followed by H atom donation from an OH or SH group to the α carbon, causing C-S bond cleavage. This would be repeated, liberating butadiene. The sulphur atom would then be removed from the surface by hydrogenation (Fig. 1.7). This mechanism has been criticized for its use of S-bound thiophene species, and because the hydrogenation of the sulphide on the surface would be rate limiting.

Kolboe proposed intramolecular β-elimination of H₂S from thiophene, which would produce adsorbed diacetylene. This is supported by IR detection of an acetylene on the surface of the catalyst, but would require unstable benzyne species if it were the pathway of reaction of benzo thiophenes.

Mechanisms involving η²- or η⁵-coordination of the thiophene have since been proposed. Angelici has developed a mechanism (Fig. 1.8) based on observed reactions of thiophene coordination complexes, including the donation by hydride complexes of H⁻ to bound thiophene complexes (reaction 1.3), the protonation of the allyl sulphide intermediate (reaction 1.4), and the elimination of butadiene from Fe(CO)₄(2,5-dihydrothiophene) (reaction 1.5).
Fig. 1.7 The Lipsch-Schult mechanism for thiophene HDS.66
Fig. 1.8 The Angelici mechanism for thiophene HDS.1
The mechanism assumes that hydride species would be available on the surface of the catalyst "as a result of dissociative adsorption of $H_2$."\textsuperscript{1} The mechanism does not satisfy the concerns of Gellman \textit{et al.}\textsuperscript{69}, about the slow rate of hydrogenation of sulphide species on the surface.

More recently, Wang and Angelici\textsuperscript{55} have used analogies from coordination chemistry to study the more difficult problem of the mechanism of the HDS of dibenzothiophene.

\subsection*{1.3 REACTIONS OF SULPHUR-CONTAINING ORGANICS WITH TRANSITION METAL COMPLEXES}

The reactions which occur on the surface of the HDS catalyst involve thiols, sulphides and disulphides. Their reactivity is affected by their coordination to the surface. These reactivity changes are most easily studied in the chemistry of the analogous homogeneous systems.

The coordination of sulphur compounds to transition metal centres is usually, but not always, followed by S-H, S-S or S-C bond cleavage. Despite the fact that, of the three groups, the S-H bonds have the greatest bond dissociation energies (83-91 kcal/mol),\textsuperscript{74}
they are the most easily cleaved because of their ionic character. Thiols are acidic in aqueous solution, with $pK_a$'s of 6.6, 7.0 and 10.7 for aryl thiols, hydrogen sulphide and alkyl thiols, respectively (Table 3.8). The S-S bonds of di- and poly-sulphides are also easily cleaved, having a bond strength of 66 kcal/mol (for HSSH). Sulphur-carbon bonds (61-77 kcal/mol), on the other hand, are rarely cleaved. Coordinated thioethers ($M$-$SR_2$) are more common than organometallic thiolato complexes ($M(R)(SR)$) that result from oxidative addition of thioethers to metal centres. The following sections describe reactions with transition metal complexes in which S-H, S-S or S-C bonds have been cleaved.

1.3.1 Reactions Involving S-H Bond Cleavage

Oxidative addition of thiols has been known since the early 1960's, for example, with Vaska's compound.

\[
\text{Ph}_3\text{P} - \text{Ir} - \text{PPh}_3 + \text{RSH} \rightarrow \text{Ph}_3\text{P} - \text{Ir} - \text{PPh}_3
\]

(refs. 76-80)

Similar reactions are:

\[
\text{Pt(PPh}_3)_n + \text{H}_2\text{S} \rightarrow \text{Pt(PPh}_3)_2(\text{SH}_2) \rightarrow \text{Pt(PPh}_3)_2\text{H(SH)}
\]

n=2 or 3 (refs. 81-2)

\[
\text{trans-Mo(dppe)}_2(\text{N}_2)_2 + \text{RSH} \rightarrow \text{Mo(dppe)}_2(\text{H})(\text{SR}) + 2\text{N}_2
\]

dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (refs. 83-5)

\[
\text{Ru(CO)}_2(\text{PPh}_3)_3 + \text{RSH} \rightarrow \text{cct-RuH(SR)(CO)}_2(\text{PPh}_3)_2 + \text{PPh}_3
\]

R = H, Et, C$_6$H$_4$pCH$_3$ (ref. 86)
Reaction 1.9 will be more fully described in Sections 3.1 and 3.2 of this work.

Examples of $\text{H}_2\text{S}$ or thiol coordination without cleavage of the S-H bond, such as that in equation 1.7, are rare, although that type of structure is proposed to be the intermediate in all such reactions. A few observed compounds of this type are $\text{Fe}(\text{RSH})(\text{CO})_4$, $[\text{Ru}((\text{NH}_3)_5(\text{HSEt}))^2]_2^+$, $[\text{PhCH}_2\text{SH}]\text{Ru}(\mu\text{O}_2\text{CCH}_3)_4\text{Rh}(\text{HSCH}_2\text{Ph})$, $[\text{CpRu}((\text{PPh}_3)_2(\text{H}_2\text{S}))]^+$, and possibly $\text{Fe}(\text{TPP})(\text{PhSH})(\text{SPh})$ ($\text{H}_2\text{TPP}=\text{tetraphenylporphyrin}$).

Oxidative addition of thiols is often followed by dimerization, because thiolate ligands have a tendency to adopt bridging positions.

$$2\text{MCl}((\text{PPh}_3)_3 + 2\text{RSH} \rightarrow [\text{M}(\text{Cl})(\text{PPh}_3)]_2(\mu\text{SR})_2 + 2\text{PPh}_3$$  \hspace{1cm} 1.10

$\text{M}=\text{Rh}$ or $\text{Ir}$ (refs. 93-4)

$$2\text{RuH}_2\text{P}_4 + 4\text{H}_2\text{S} \rightarrow \text{P}_3\text{Ru}(\mu\text{SH})_3\text{Ru}(\text{SH})\text{P}_2 + 3\text{P} + 4\text{H}_2$$  \hspace{1cm} 1.11

$\text{P}=\text{PPhMe}_2$ (ref. 95)

$$2\text{Fe}(\text{CO})_4\text{L} + 2\text{RSH} \rightarrow (\text{CO})_3\text{Fe}(\mu\text{SR})_2\text{Fe}(\text{CO})_3 + 2\text{CO} + \text{H}_2 + 2\text{L}$$  \hspace{1cm} 1.12

$\text{L}=\text{CO}$ or $\text{H}_2$ (refs. 96-7)

The hydrido-thiolato products of the oxidative addition may react with excess thiol in a second step.

$$\text{RuH}(\text{SH})(\text{CO})_2((\text{PPh}_3)_2 + \text{H}_2\text{S} \rightarrow \text{Ru}(\text{SH})_2(\text{CO})_2((\text{PPh}_3)_2 + \text{H}_2$$  \hspace{1cm} 1.13

(ref. 86)

$$\text{MoH}(\text{SR})(\text{dppe})_2 + \text{RSH} \rightarrow \text{Mo}(\text{SR})_2(\text{dppe})_2 + \text{H}_2$$  \hspace{1cm} 1.14

(refs. 83-5)

This type of reaction can be inhibited by the use of bulky thiols, or the use of exactly one equivalent of thiol in the initial reaction. This problem of subsequent reaction, along
with the tendencies of these complexes either to dimerize or eliminate thiol, restricts the number of well-characterised hydrido thiolato complexes.

The kinetics of the oxidative addition reaction are rarely studied. The reaction of trans-Mo(dppe)2(N2)2 with n-propyl or phenyl thiol (reaction 1.8 followed by reaction 1.14) was monitored by UV. The rate had a first-order dependence on the concentration of the complex, and zero to first-order dependence on the thiol concentration. The proposed mechanism (Scheme 1.1) included two unobserved species [MoH(SR)(dppe)2] and [MoH2(SR)2(dppe)2], modelled after the known complexes [MoH(tpbt)(dppe)2] (tpbt = 2,4,6-iPr3C6H2S-) and [MoH2Cl2(dppe)2].

Addition of thiols across a metal-metal bond produces a bridging thiolate and either a bridging hydride,

\[
\text{Ru}_3(\text{CO})_{12} + \text{EtSH} \rightarrow (\text{CO})_3\text{Ru} \begin{array}{c} \text{S} \\ \text{Et} \end{array} \text{Ru}(\text{CO})_3 + 2 \text{CO} \quad (\text{refs. 98-9})
\]

or a terminal hydride,

\[
\begin{array}{c}
\text{H} \\
\text{P} \\
\text{P} \\
\text{CO} \\
\text{MeSH} \\
\text{P} \\
\text{P} \\
\text{H} \\
\text{Me} \\
\text{P} \\
\text{P} \\
\text{H} \\
\text{CO}
\end{array}
\]

\[
\text{PP} = \text{dpm (ref. 100)}
\]

or no hydride ligand.

\[
\text{PhSH} \rightarrow [\text{Cp}^*\text{RuCl}_2]_2 \rightarrow [\text{Cp}^*\text{Ru}(\mu\text{SPh})_3\text{RuCp}^*]\text{Cl} + (3\text{HCl})
\]

\[
\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5 \quad (\text{ref. 101})
\]
Scheme 1.1 The proposed mechanism for the reaction of trans-Mo(dppe)$_2$(N$_2$)$_2$ with thiols (adapted from ref. 84).
Similarly, one or both of the S-H bonds in \( \text{H}_2\text{S} \) may be cleaved, and one or both of the hydrogens eliminated.

\[
\begin{align*}
\text{X-Pd-Pd-X} + \text{H}_2\text{S} & \rightarrow \text{X-Pd-S-Pd-X} + \text{H}_2 \\
\text{X} &= \text{Cl, Br; } \text{P-P} = \text{dpm (refs. 102-5)}
\end{align*}
\]

During the conversion of \( \text{H}_2\text{S} \) to elemental sulphur, the production of hydrogen gas in a process based on this type of chemistry would be preferable to the production of water as found in modern Claus plants.

1.3.2 Reactions Involving S-S Bond Cleavage

Oxidative addition of disulphides involves cleavage of S-S bonds, forming two terminal thiolate ligands,

\[
\text{M(Ph}_3\text{)}_2(\text{N}_3)_2 + \text{RSSR} \rightarrow \text{M(SR)}_2(\text{Ph}_3)_2 + 3\text{N}_2
\]

\( \text{R} = \text{Me, Bu or Ph; M} = \text{Pd or Pt (ref. 95)} \)
or forming a thiolate-bridged structure.

$$3\text{Fe(CO)}_5 + 3\text{PhSSPh} \rightarrow (\text{CO})_3\text{Fe(μSPh)}_3\text{Fe(μSPh)}_3\text{Fe(CO)}_3$$ 1.21

(refs. 107-9)

The intermediate in disulphide oxidative addition reactions may be a disulphide coordinated by one or two sulphur atoms to the metal. This is usually not observed; but such compounds have been isolated.

$$[\text{CpFe(CO)}_2(\text{THF})]\text{BF}_4 + \text{PhSSPh} \rightarrow [\text{CpFe(SPh)}_2(\text{THF})] \text{BF}_4 + \text{THF}$$ 1.22

(refs. 110-2)

Reactions of disulphides with metal hydrides produce a thiolate complex and one equivalent of liberated thiol.

$$[\text{FeH(CO)}_5]^+ + \text{RSSR} \rightarrow [\text{Fe(SR)(CO)}_4]^+ + \text{RSH}$$ 1.23

(ref. 113)

$$\text{RuH}_2(\text{PPh}_3)_4 + \text{MeSSMe} \rightarrow \text{RuH(SMe)(PPh}_3) + (\text{PPh}_3? + \text{MeSH}?)$$ 1.24

(ref. 114)

Addition of disulphides across metal-metal bonds leads to thiolate-bridged structures, either directly or through a monomeric thiolate complex.

$$\text{Cl}_2\text{W=WCl}_2 + \text{PhSSPh} \rightarrow \text{Cl}_2\text{W=WCl}_2$$ 1.25

$$\text{P=P = dpm (ref. 115)}$$
\[
[Ru(CO)2Cp]2 + RSSR \rightarrow Ru(SR)(Cp)(CO)2 + [Ru(Cp)(CO)(\mu SR)]_2
\]
\[R = \text{Ph, Me or CH}_2\text{Ph (ref. 116)}\]

\[
M_2(CO)_{10} + RSSR \rightarrow 2M(SR)(CO)5 \rightarrow M_2(CO)_{8}(\mu SR)_2
\]
\[R = \text{Me, n-Bu, sec-Bu, t-Bu, Ph; } M=\text{Re, Mn (ref. 117)}\]

The first steps in reaction 1.27 were photolytic cleavage of the dimer to form \( M(CO)_{5}^- \), followed by RS group transfer from RSSR. *Pseudo*-first-order kinetics showed that the rate decreased with the bulk of the alkyl group of the disulphide, although diphenyl disulphide reacted more quickly than the dialkyl disulphide due to either its weaker S-S bond or "the electron accepting capability of the phenyl group" which would favourably affect the rate of the donation of an electron from \( M(CO)_{5}^- \) to the disulphide.¹¹⁷

The reactions of elemental sulphur with transition metal complexes also involve S-S bond cleavage. Sulphur has been widely used as an S atom donor, along with ethylene and propylene sulphides, and alkyl trisulphides. The products are mononuclear,

\[
M(CO)_{2}(PPh)_{3} + \frac{3}{8}S_8 \rightarrow M(CO)_{2}(PPh)_{2}S_2 + (SPPh_3?)
\]
\[M = \text{Os, Ru (ref. 118)}\]

dinuclear,

\[
2\text{CpRuP}_{2}\text{Cl} + \frac{1}{4}S_8 + 2\text{Ag}^+ \rightarrow [\text{CpP}_{2}\text{Ru}(\mu S)_2\text{RuCpP}_{2}]^{2+} + 2\text{AgCl}
\]
\[P = \text{PPh}_3; \text{Cp}=\text{C}_5\text{H}_5 \text{ or C}_5\text{H}_4\text{Me (refs. 119 and 120)}\]
or polynuclear inorganic sulphides.

\[
\text{Pt(PPh}_3\text{)\textsubscript{2,3}} + S\textsubscript{8} \rightarrow [\text{PtS(PPh}_3\text{)\textsubscript{2}}\text{]}\textsubscript{n}
\]  \hspace{1cm} (ref. 82)

The resulting sulphur bridge in dinuclear complexes can be unsupported and of several atoms.

\[
[RuCp(CO)\textsubscript{2}]\textsubscript{2} + \frac{5}{8}S\textsubscript{8} \rightarrow [RuCp(CO)\textsubscript{2}(\mu S\textsubscript{5})]
\]  \hspace{1cm} (ref. 121)

Metal hydrides react with sulphur to yield mercapto complexes, some of which react further to give inorganic sulphido complexes.

\[
[Cp^*\textsubscript{2}Zr(H(\mu H))]\textsubscript{2} + S\textsubscript{8} \rightarrow Cp^*\textsubscript{2}Zr(SH)\textsubscript{2} \rightarrow Cp^*\textsubscript{2}ZrS\textsubscript{5}
\]  \hspace{1cm} (Cp* = \eta^5-C\textsubscript{5}H\textsubscript{4}Bu (ref. 122-3)

\[
\text{RuH}_2\text{(PPh}_3\text{)}_4 + \frac{1}{4}S\textsubscript{8} \rightarrow \text{RuH(SH)(PPh}_3\text{)}_3 + \text{SPPh}_3
\]  \hspace{1cm} (ref. 18)

\[
\text{Pt(SH)_2(PPh}_3\text{)}_2 + \frac{3}{8}S\textsubscript{8} \rightarrow \text{PtS}_4\text{(PPh}_3\text{)}_2 + \text{H}_2\text{S}
\]  \hspace{1cm} (ref. 124)

There are even reports of the sequential insertion of sulphur into the M-C bonds of metal alkyl complexes.

\[
\text{Cp(NO)WR}_2 + \frac{1}{4}S\textsubscript{8} \rightarrow \text{Cp(NO)W(SR)_2}
\]  \hspace{1cm} (R=CH\textsubscript{2}SiMe\textsubscript{3} (refs. 125-6))
1.3.3 Reactions Involving S-C Bond Cleavage

The Pd\(_2\)X\(_2\) (dpm)\(_2\) dimers which extracted sulphur from hydrogen sulphide (reaction 1.18) failed to extract sulphur from thiols or sulphides\(^{103}\) because of the greater resistance to cleavage of S-C bonds compared to S-H and S-S bonds. The same reason can be given for the stability of metal thioether complexes relative to their thiol or disulphide cousins. Examples of stable ruthenium thioether complexes include [Ru(NH\(_3\))\(_5\)L]\(^{2+}\) (L=Me\(_2\)S, tetrahydrothiophene (THT), thiophene)\(^{88,127}\), cis- and trans-[Ru(bipy)\(_2\)L\(_2\)]\(^{2+}\) (bipy=2,2'-bipyridyl, L=MeSPh, phenothiazine, 1,4-dithiane)\(^{128}\), [CpRu(PPh\(_3\))\(_2\)L]\(^+\) (L=THT, ethylene sulphide)\(^{129}\), mer-[RuCl\(_3\)L\(_3\)] (L=Me\(_2\)S, Et\(_2\)S, PhSMe, THT, etc.)\(^{130-2}\) and [RuCl\(_3\)(Et\(_2\)S)\(_2\)]\(^-\)\(^{131}\). In addition, a large number of transition metal crown thioether complexes have been reported\(^{133}\).

Stoichiometric sulphur extraction from thiols and thioethers is known (see also Jang et al.)\(^{134}\).

\[ \begin{align*}
\text{P}P = \text{dpm (ref. 135)} \\
\text{Ta}_2\text{Cl}_6(\text{SMe}_2)_3 \xrightarrow{4 \text{ atm } \text{H}_2, \text{dipp}} \frac{\text{Na/Hg}}{\text{P}} \xrightarrow{4 \text{ atm } \text{H}_2, \text{dipp}} \text{Ta} - \text{H} - \text{Ta} + \text{CH}_3\text{CH}_3 \\
\text{P}P = \text{iPr}_2\text{P(CH}_2)_3\text{PPr}_2 \text{ (dipp) (ref. 136)}
\end{align*} \]
A reaction similar to 1.37, but involving sulphur atom abstraction from PhSSPh has been reported. Oxidative addition reactions of thioethers involving cleavage of only one S-C bond (especially an allyl-S bond) are far more common than reactions involving cleavage of 2 S-C bonds.

\[
\text{CH}_2=\text{CHCH}_2\text{SAr} + \text{RhH(PPh}_3)_4 \rightarrow \frac{1}{2}[\text{Rh(PPh}_3)_2(\mu\text{SAr})_2] + 2\text{PPh}_3 + \text{CH}_2=\text{CHCH}_3
\]

Ar = Ph, PhMe etc. (ref. 137)  \hspace{1cm} 1.38

\[
\text{CH}_2=\text{CHCH}_2\text{SPh} + 2\text{PdL}_2 \rightarrow L\text{-Pd-Pd-L} + 2\text{L}
\]

L = P(C_6H_{11})_3 (refs. 138-40)  \hspace{1cm} 1.39

\[
2\text{Fe(CO)}_5 + 2\text{RSR} \rightarrow (\text{CO})_3\text{Fe(µSR)}_2\text{Fe(CO)}_3 + 4\text{CO} + \text{R-R}
\]

R = Me, Et, cyclopentyl, Ph (ref. 96)  \hspace{1cm} 1.40

\[
\text{"NiL}_2" + \text{ArSAr} \rightarrow \text{trans-Ni(µSAr)(µAr)L}_2
\]

(in-situ)  \hspace{1cm} 1.41

L=PEt_3 or P(nBu)_3 (refs. 141-2)

Strained-ring thioethers such as ethylene and propylene sulphides are a special case. Although coordinated ethylene sulphide exists in the complex

\[
[\text{CpRu(PPh}_3)_2(\text{SC}_2\text{H}_4)]^+, \text{ it more typically donates the sulphur atom, liberating ethylene.}
\]

\[
\text{FeH}_2(\text{CO})_4 + \text{S} \rightarrow [\text{Fe(µSH)}_2(\text{CO})_4] \rightarrow \text{Fe}_2\text{S}_2(\text{CO})_6 + \text{Fe}_3\text{S}_2(\text{CO})_9
\]

(ref. 143)  \hspace{1cm} 1.42

Thiophenes are another special case. A few of their transition metal complexes have been mentioned (section 1.2.2). Examples of reactions in which one or both of the S-C bonds of a thiophene group have been cleaved by reaction with transition metal complexes are shown below.
\[ 2\text{Ni(bipy)(COD)} + \begin{array}{c} \text{Ni(bipy)} \downarrow \text{NiS} \\ \text{Ni(bipy)}_2 + \end{array} \]

(ref. 144)

\[ 2\text{Fe(CO)}_5 + \begin{array}{c} \text{Fe(CO)}_3 \\ \text{( + "S" + 4CO) } \end{array} \]

(ref. 145)

\[ \text{Fe}_3(\text{CO})_{12} + \begin{array}{c} \text{Fe(CO)}_3 \text{Fe(CO)}_5 \\ \text{Fe(CO)}_3 \end{array} \]

(ref. 146)
2. GENERAL EXPERIMENTAL PROCEDURES

The materials, the general techniques common to most of the experiments, and the syntheses of the non-sulphur-containing ruthenium complexes, are described in this chapter. Details of individual experiments can be found in the last section of each subsequent chapter.

2.1 MATERIALS

All of the ruthenium complexes were synthesized from RuCl₃.3H₂O, supplied by Johnson Matthey. Thiophene, benzyl trisulphide, benzene selenol, triphenyl phosphine sulphide, and the thiols, sulphides, and disulphides were supplied by Aldrich. Diphenyl sulphide was purified before use by mixing 1:1 with acetone, adding a concentrated acetone solution of KMnO₄ until it stayed purple, filtering and fractionally distilling under vacuum. Elemental analysis and NMR spectroscopy showed the thioether to be pure. Other chemicals used were benzophenone (BDH), dpm (Aldrich), fluoboric acid (MCB), sodium borohydride (BDH), sodium tetraphenylboron (Fisher), tetrafluoroboric acid diethyl ether complex (Aldrich), triphenyl phosphine (BDH), tris-p-tolyl phosphine (Strem) and sodium methylate (Fisher). Sodium ethyl and p-tolyl thioclates were synthesized by the reaction of the thiol with an excess of sodium in undistilled diethyl ether under N₂. After 1 h, unreacted sodium was removed with tweezers and the white suspension filtered. The salt was dried under vacuum overnight and stored under N₂ or Ar. Na/Hg amalgam was prepared by dissolving Na slivers into Hg under Ar until the solution solidified. Then extra Hg was added until the solution could be easily stirred. Tetra-n-butyl ammonium tetrafluoroborate was synthesised by Mr. A. Pacheco of this research lab, from the reaction of tetra-n-butyl ammonium hydroxide with tetrafluoroboric acid, followed by recrystallization (twice) from ethyl acetate and n-pentane.

The solvents, analytical or glass distilled grade, were dried by refluxing for several days over drying agents under N₂, and distilling from the drying agent immediately before use.
Tetrahydrofuran or "THF" (supplied by BDH), toluene (Omnisolve), benzene (BDH), diethyl ether (BDH), and hexanes (BDH) were dried over sodium and benzophenone. Pentane was dried over phosphorus pentoxide. Acetone was dried over K₂CO₃. Methanol (BDH, glass distilled) was dried over magnesium turnings treated with iodine. N,N-dimethylacetamide (BDH) to be used in the synthesis of RuH(Cl)(CO)₂(PPh₃)₂ was not distilled, but only degassed by repeated freeze/thaw cycles under hydrogen. C₆D₆, CD₂Cl₂, CD₃OD, D₂O, C₆D₅CD₃, (CD₃)₂CO, and THF-d₈ were supplied by Cambridge or MSD Isotopes. All of these, except CD₃OD and D₂O, were received as ampoules, and transferred to storage vessels and thence to the NMR sample tubes under an inert gas (N₂ or Ar). CD₃OD and D₂O were received in bottles and were not stored under anaerobic conditions.

Gases (N₂, Ar, H₂, O₂, CO, H₂S, HCl, and MeSH) were used as received from Matheson.

The thiols and thiolate salts are extremely smelly, and all of the sulphur-containing organics are extremely toxic. Hydrogen sulphide and methanethiol must be handled with particular care because of the fatal consequences of accidental exposure to these gases. Selenium-containing compounds such as benzene selenol are even more toxic than their sulphur-containing analogues.

2.2 EQUIPMENT AND TECHNIQUES

2.2.1 Reaction Conditions

Except where noted, synthetic scale reactions were performed in THF at room temperature and under one atmosphere of an inert gas (either N₂ or Ar), using standard Schlenk tube techniques. NMR scale *in situ* experiments were performed in the following manner. Into a wide-mouth Schlenk tube was placed a 5 mm glass NMR tube containing a known weight of the solid reagents, or the unknown to be characterized. After evacuation of the Schlenk tube, the gas was admitted. The cap to the Schlenk tube was removed, with the gas flow sufficiently high to
prevent the entry of air. The solvent, usually C₆D₆, was pipetted into the NMR tube, which was sealed with a septum flushed with an inert gas. The liquid reagent was then injected through the septum to start the reaction.

2.2.2 Spectroscopy and Chromatography

All NMR spectra were acquired at 19°C and using a Varian XL-300 at 300 MHz (1H) or 121 MHz (31P nuclei) unless otherwise stated. Other NMR spectrometers used were a Bruker AC-200, a Bruker WH-400 for special experiments requiring greater field strength, and a Bruker AMX-500 for 31P-decoupled 1H spectra. Solid state 13C NMR spectra were acquired using a Bruker MSL-400 operated by Dr. L. Randall; the spectrometer contained zirconium spinners and a standard MAS probe tuned to 100.6 MHz. The solid state spectra were obtained with adamantane as external reference, and reported with respect to TMS. Solution NMR chemical shifts were measured with respect to TMS in C₆D₆ for 1H and 13C, triphenyl phosphine in C₆D₆ for 31P, and BF3:(C₂H₅)₂O in 1:1 C₆D₆:(C₂H₅)₂O for 11B nuclei, all as external references. The 31P chemical shifts, however, are reported here with respect to 85% H₃PO₄ aqueous solution which shows a resonance, in the XL-300 at room temperature (20°C), at 6.05 or 5.46 ppm downfield of PPh₃ in C₆D₆ or CD₂Cl₂, respectively. The deuterium lock signal was the solvent itself. All of the 31P and 13C spectra were 1H broad-band decoupled. The chemical shift of triphenylphosphine in C₆D₆ with respect to aqueous 85% H₃PO₄ was determined by acquiring the 31P spectrum of a 10 mm NMR tube containing the former solution, with a 5 mm NMR tube containing the latter solution held inside it by plastic O-rings. The chemical shift of PPh₃ has been reported previously.¹⁴⁷

UV/vis spectra were measured taken in specially designed 1 cm or 1 mm quartz or glass cells (Fig. 2.1) sealed under the desired gas. The spectrometer, a Perkin Elmer 552A, contained an electronically temperature controlled cell holder accurate to ±0.2°C.
Fig. 2.1 Anaerobic UV/vis. cell.
Infrared spectra of Nujol or hexachloro-1,3-butadiene mulls, or THF, toluene, or CH$_2$Cl$_2$ solutions were taken in a Nicolet 5DX FTIR internally calibrated with a He/Ne laser.

Fast Atom Bombardment Mass Spectra (FAB-MS) were acquired by Ms. C. Beaulieu of this department, using an AEI MS 9 mass spectrometer with a 6 kV ion source, a 7-8 kV, 1 mA xenon gun, and a 10 s/decade scan rate. The samples were contained in a p-nitrobenzyl alcohol matrix. The theoretical isotope patterns were predicted using the simulation program PEEKS-1982.

The experimental conditions of the X-ray crystallography experiments will be described in the sections which detail their results.

The conductivity of solutions was measured with a Yellow Springs Instrument Co. 3403 Cell (with a cell constant of 1 cm$^{-1}$) and a Serfass Conductivity Bridge Model RCM 15B1.

Organic products were separated in a Hewlett Packard HP 5890A gas chromatograph with a 15 m OV101 column at 30°C with helium carrier gas, a split/splitless injector, and a flame ionization detector. The injection volume of liquids was 0.1 µL. Hydrogen gas was detected qualitatively with a 10 ft molecular sieve column and a thermal conductivity detector.

Quantitative measurement of gas production was achieved using a constant pressure gas-uptake apparatus, described in section 2.2.3.

Microanalyses were performed by Mr. P. Borda of this department.

2.2.3 Kinetic Measurements

The reaction rates were monitored by one or more of three methods; UV/vis. spectroscopy, NMR spectroscopy, and gas-uptake measurements. Times were recorded from an electronic stopwatch during the NMR experiments, and from a Lab-Chron 1400 timer during uptake and UV/vis. experiments.

The constant pressure gas-uptake apparatus (Fig. 2.2) has been briefly described in the literature$^{149,150}$. This equipment can be used to measure the rate of gas-uptake or evolution at
Fig. 2.2 Constant pressure gas uptake apparatus. The following parts are labelled:
A reaction flask, B hook, C stopcock, D stopcock, E fine valve, F two-way valve to a gas cylinder, G agitating motor and mechanism, H temperature-controlled oil bath, J n-dibutyl phthalate manometer, K mercury manometer.
constant gas pressure. A solution of the required concentration of reagent (thiol or phosphine) was placed in reaction flask A, and a glass bucket containing the ruthenium complex was suspended from a hook inserted through sidearm B. A ground glass joint sealed the hook to the flask while allowing the hook to be rotated to drop the bucket. The flask was attached to coiled glass tubing, which in turn was attached via valve C to valve D. With the needle valve E closed, the solution was degassed three times by freezing, evacuating, and adding 400 torr of the desired gas (usually N\textsubscript{2} or Ar) through valve F. Then the coils and valve C (closed) were reattached to valve D, and the reaction flask was clamped to a shaker mechanism G and immersed in the oil bath H at the reaction temperature (±0.05°C). After 20 min of temperature equilibration, the section of the system between C and F was evacuated and filled to 400 torr. Then valve C was opened, the system set to the final reaction pressure, the bucket dropped, and the timer and shaker started. As gas evolved, the height of the liquid (n-dibutyl phthalate) in the left column of manometer J decreased. Gas was withdrawn slowly through needle valve E to restore the balance in manometer J. The resulting dip in the mercury manometer K was measured by a Precision Tool Vernier Microscope Type 2158. Both manometers were suspended in a water bath at 25°C. Calibration permitted the conversion of mercury height measurements to millimoles of gas produced.

The monitoring of reaction kinetics by FT-NMR spectroscopy requires the assumption that the areas under the peaks in the spectra are proportional to the concentrations of the respective nuclei. This is true only if

1) all of the peaks to be compared are due to protons with identical T\textsubscript{1} values (and identical nOe effects for 31P NMR), or
2) the time between pulses is greater than five times the longest T\textsubscript{1} value of the relevant nuclei.\textsuperscript{151-2}

The time between pulses was 1.364 s and 0.750 s for the \textsuperscript{1}H and 31P\{\textsuperscript{1}H\} NMR experiments respectively. Because the T\textsubscript{1} values of most of the nuclei involved were greater than 1/5\textsuperscript{th} of these times, condition 2 was not satisfied for most of the experiments described herein. The
error involved is small, however, if the $T_1$ values of the reactants and products are almost identical. This occurs in a series of related complexes if the varying group does not significantly affect the magnetic environment around the nucleus being measured. For example, it was shown that the ratios of concentrations in mixtures of complexes of the type $cct$-$RuH(SR)(CO)2(PPh3)2$ can be accurately measured by $31P\{1H\}$ or $1H$ NMR. Thus, a known C$_6$D$_6$ solution of $cct$-$RuH(SCH3)(CO)2(PPh3)2$ and $cct$-$RuH(SC6H4-p$-$CH3)(CO)2(PPh3)2$ containing 55% of the latter, was analyzed by comparing the intensities of the hydride triplets, the methyl singlets, and the $31P\{1H\}$ singlets. The results (58%, 57% and 60%, respectively), show that the accuracy is sufficient for kinetic experiments. The error is greater when comparing complexes with greater differences in structure, or when comparing complexes and free ligands. In particular, free triphenylphosphine in solution has a very large $T_1$ value of 26 s.153

2.2.4 Data Handling for Kinetic Experiments

Many of the reactions in coordination chemistry are of the type

$$M + L \rightarrow P$$

where M, L, and P are a metal complex, a reagent, and a product, respectively. If the reaction rate is first order with respect to [M] and $n$th order with respect to [L],

$$-\frac{d[M]}{dt} = k[M][L]^n$$

Eqn. 2.1

and if $[L] > 10 [M]$ (pseudo-first order conditions), then the rate law can be simplified.

$$-\frac{d[M]}{dt} = k_{obs}[M]$$

where $k_{obs} = k[L]^n$

Eqn. 2.2

The integrated rate law can be expressed in terms of [M],
\[ ln[M]_t = ln[M]_0 - k_{obs} t \]  
Eqn. 2.3

or in terms of a measurable quantity A (hereafter referred to as absorbance) such as IR or UV/vis. absorbance, if one assumes that L does not absorb, \( A_\infty \) is the final absorbance, \( [M]_\infty \) is zero (the reaction goes to completion), and \( C_m \) and \( C_p \) are proportionality constants for the absorbances of M and P (i.e. for UV/vis., \( C = \varepsilon \cdot l \), where \( \varepsilon \) is the extinction coefficient and \( l \) is the path length).

\[
A_t = C_m[M]_t + C_p[P]_t \\
A_t - A_\infty = C_m[M]_t + C_p[P]_t - C_m[M]_\infty - C_p[P]_\infty \\
= C_m[M]_t + C_p([M]_0 - [M]_t) - C_p[M]_0 \\
= (C_m - C_p)[M]_t \\
A_0 - A_\infty = (C_m - C_p)[M]_0
\]

Inserting these expressions into the integrated rate law (Eqn. 2.3), one obtains the final expression.

\[ ln(A_t - A_\infty) = ln(A_0 - A_\infty) - k_{obs} t \]  
Eqn. 2.4

A plot of \( ln(A_t-A_\infty) \) or \( ln[M]_t \) versus time is referred to as a pseudo-first order log plot, and is linear if the reaction is pseudo-first order. The slope of the line is equal to \( -k_{obs} \).

There are at least six methods for the calculation of \( k_{obs} \). The first three use the pseudo-first order plot, but differ in the way that \( A_\infty \) is determined. The error involved in the determination of \( A_\infty \) is the weakest point of these methods. These three methods are:

1. Waiting for five or more half lives, and directly measuring \( A_\infty \).
2. Calculating \( A_\infty \) from \( [M]_0 \) and the \( C_p \) of an independently synthesized and characterized sample of the product,
3. Optimizing the straightness (correlation coefficient) of the pseudo-first order log plot by varying the value of \( A_\infty \). The value of \( A_\infty \) which gives the straightest line should be similar to that determined by methods 1 or 2.
The other three methods calculate \( k_{\text{obs}} \) directly, and thereby avoid the problem of error in \( A_\infty \). These methods are based on two series of absorbance readings at times \( t_1, t_2, \text{etc.} \), and at times \( t_1 + T, t_2 + T, \text{etc.} \), where \( T \) is a constant delay time. Applying equation 2.4, one obtains

\[
(A_\infty - A_t) = (A_\infty - A_0)e^{-k_{\text{obs}}t} \quad \text{Eqn. 2.5}
\]

and

\[
(A_\infty - A_{t+T}) = (A_\infty - A_0)e^{-k_{\text{obs}}(t+T)} \quad \text{Eqn. 2.6}
\]

Subtracting these equations, one obtains\textsuperscript{154}

\[
(A_{t+T} - A_t) = (A_\infty - A_0)(1 - e^{-k_{\text{obs}}T})e^{-k_{\text{obs}}t}
\]

\[
\ln(A_{t+T} - A_t) = \ln((A_\infty - A_0)(1 - e^{-k_{\text{obs}}T})) - k_{\text{obs}}t \quad \text{Eqn. 2.7}
\]

The application of these methods, however, can place undue weight on the less accurate late data points. Ordinary or weighted least squares linear regression can lead to a bias.\textsuperscript{155} The type of linear regression which should be used is therefore a concern, as is the choice of \( T \).\textsuperscript{155} These methods for calculating \( k_{\text{obs}} \) are:

4. The Guggenheim method,\textsuperscript{154,156} in which a plot of \( \ln(A_{t+T} - A_t) \) versus time has a slope of \( -k_{\text{obs}} \) (Eqn. 2.7),

5. The Kezdy-Mangelsdorf-Swinbourne (KMS) method,\textsuperscript{154-5,157-9} in which a plot of \( A_t \) versus \( A_{t+T} \) has a slope of \( e^{k_{\text{obs}}T} \),

\[
A_t = A_\infty(1 - e^{k_{\text{obs}}T}) + A_{t+T}e^{k_{\text{obs}}T} \quad \text{Eqn. 2.8}
\]

and

6. The R/R method,\textsuperscript{160} in which \( k_{\text{obs}} \) is determined from the average value of \( R_t/R_{t+T} \). The rates are determined from the tangents to the plot of the time dependence of \( [M] \).

\[
R_t/R_{t+T} = e^{k_{\text{obs}}T} \quad \text{Eqn. 2.9}
\]

where
R_t = (dA/dt)_t = (A_O - A_\infty)(-k)e^{-k_{obs} \cdot t} \quad \text{Eqn. 2.10}

Equation 2.8 is obtained by dividing equation 2.5 by equation 2.6, and rearranging. Equation 2.10 can be derived from equation 2.4 by rearranging to equation 2.11 and then taking the derivative.  

\[ A_t = (A_O - A_\infty)e^{-k_{obs} \cdot t} + A_\infty \quad \text{Eqn. 2.11} \]

In order to compare these six methods, \( k_{obs} \) was calculated using each method, from the UV/vis. absorbance data for the reaction of \( cct-RuH_2(CO)_2(PPh_3)_2 \) (1.0 mM) with ethanethiol (94.5 mM) at 26°C in THF to give \( cct-RuH(SEt)(CO)_2(PPh_3)_2 \) (see section 3.3 and Fig. 3.10). The values of \( k_{obs} \), obtained from the absorbance data at 400 nm taken up to 3400 s after the reaction started, and using a delay time (T) of 1600 s, are 7.01, 7.63, 6.73, 6.61, 6.58, and 6.50 x 10^-4 s^-1 calculated by methods 1 through 6, respectively. The first two methods are the least accurate because they rely heavily on the accuracy of a single point, \( A_\infty \). The differences (3 %) between the other four are considered to be of the same order as the experimental error. Method 3 was used to calculate the \( A_\infty \) and \( k_{obs} \) values reported in this thesis.

Rate constants from multiple experiments are quoted with 90 % confidence limits, calculated with the use of t-factors.

Plots of \( k_{obs} \) versus [M] are linear and horizontal for all reactions pseudo-first order in [M]. Plots of \( k_{obs} \) versus [L] should be linear and horizontal (n=0), linear through the origin (n=1), or curved (0<n<1 or n>1).
2.3 SYNTHESES OF THE PRECURSOR COMPLEXES

Throughout the equations in section 2.3, the abbreviation "L" will be used for triphenylphosphine.

2.3.1 cct-RuCl₂(CO)₂(PPh₃)₂

The cct isomer of this complex (1) has been synthesized through a variety of routes:¹⁶¹-²

\begin{align*}
\text{MeOH} & \quad \text{CO} \\
\text{RuCl}_3 + 6L & \rightarrow \text{RuCl}_2L_n \rightarrow \text{RuCl}_2(CO)_{2L_2} \quad 2.1 \\
\text{reflux} & \\
n = 3, 4 \quad (\text{refs. 163-4}) \\
\text{RuCl}_3 + L + \text{CDT} + \text{H}_2 + \text{CO} & \rightarrow \text{RuCl}_2(CO)_{2L_2} + \text{CDE} \quad 2.2 \\
\text{CDT} = 1,5,9\text{-cyclododecatriene, CDE = cyclododecene} \quad (\text{ref. 165})
\end{align*}

\begin{align*}
\text{1. MeOH} & \quad 2L \quad \text{2L} \\
\text{RuCl}_3 + \text{CO} & \rightarrow \text{Ru(THF)(CO)₃Cl}_2 \rightarrow \text{RuCl}_2(CO)_{2L_2} \quad 2.3 \\
\text{2. THF} & \\
(\text{ref. 166}) & \\
\text{L} & \\
\text{Ru}_3(CO)_9L_3 + \text{Cl}_2 & \rightarrow [\text{RuCl}_2(CO)_{2L}]_2 \rightarrow \text{RuCl}_2(CO)_{2L_2} \quad 2.4 \\
(\text{ref. 167}) &
\end{align*}

Other methods give other isomers of the complex, often the yellow \textit{mt} isomer¹⁶¹ which can be converted by heating in solution¹⁶⁸-⁹ or in the solid state¹⁷⁰ to the white cct isomer.

Although the \textit{cis} positions of the carbonyls are evident from the two stretching bands in the IR spectrum, it requires \textsuperscript{13}C NMR to prove the cct geometry. The substituted, \textit{o-} and \textit{m-} carbons of the phenyl groups appear in that spectrum as triplets,¹⁶⁵ a phenomenon characteristic of complexes with \textit{trans} triphenylphosphine ligands.¹⁷¹ No X-ray crystallographic structure has been reported of this complex.
The method used in this work, based upon reaction 2.1, was used previously in this laboratory. The complex RuCl₃·xH₂O (3 g, 10 mmol) was dissolved in reagent methanol (400 mL) under air, and the solution refluxed for 15 min. To the cooled solution was added triphenylphosphine (20 g, 76 mmol), and the mixture was refluxed for 1 h; the resulting dark brown suspension was filtered and washed with methanol (150 mL). The RuCl₂(PPh₃)₃ thus isolated was dissolved in CH₂Cl₂ (300 mL) under N₂. The flask was flushed with CO and the solution stirred overnight. The resulting yellow solution was concentrated by vacuum distillation of half of the solvent. A pale yellow precipitate appeared. Methanol (40 mL) was added to encourage the precipitation. The white product was collected by filtration and dried over 24 h under vacuum. The yield was 6 g, or 80%. IR (Nujol) 2057, 1994 cm⁻¹ ν(CO); IR (CH₂Cl₂) 2059, 1996 cm⁻¹ ν(CO); ³¹P{¹H} NMR (C₆D₆) δ 15.65 ppm (s). The IR frequencies are within the range of reported values.

2.3.2 Ru(CO)₂(PPh₃)₃

The direct reaction of phosphines with Ru(CO)₅ does not proceed past the disubstituted product. Other methods are used for the synthesis of Ru(CO)₂(PPh₃)₃ (2).

\[
\begin{align*}
\text{MeCN} & \quad \text{MeO}^- \\
\text{RuHCl(CO)L₂} + \text{MeCN} & \quad [\text{RuH(CO)(MeCN)₂L₂}]^+ \quad \rightarrow \quad \text{Ru(CO)₂L₃} + \text{MeOH} + \text{MeCN}
\end{align*}
\]

(ref. 173)

\[
\begin{align*}
\text{Ru(CO)₃L₂} + \text{ArN₂}^+ & \quad \rightarrow \quad [\text{Ru(N₂Ar)(CO)₂P₂}]^+ \\
& \quad \rightarrow \quad \text{Ru(CO)₂L₃}
\end{align*}
\]

(ref. 174)

\[
\begin{align*}
\text{RuHCl(CO)₂L₂} + \text{L} + \text{DBU} & \quad \rightarrow \quad \text{Ru(CO)₂L₃} + \text{DBU·HCl}
\end{align*}
\]

DBU = 1,8-diazabicyclo-[5,4,0]-undec-7-ene (ref. 175)
Another method\textsuperscript{176} used Ru(PPh\textsubscript{3})\textsubscript{4}(MeCN)\textsubscript{2} generated by the electrochemical reduction of RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4} in acetonitrile.

\[
\text{RuCl}_2L_4 + 2\text{MeCN} \xrightarrow{2e^-} \text{RuL}_4(\text{MeCN})_2 \xrightarrow{-2\text{Cl}^-} \text{Ru(CO)2L}_3 
\]

A method which appears obvious in hindsight is the reaction of ccr-RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (Section 2.3.3) with PPh\textsubscript{3}

\[
\text{RuH}_2(\text{CO})_2L_2 + L \rightarrow \text{Ru(CO)2L}_3 + \text{H}_2 
\]

which has not yet been reported, although the reverse reaction was observed as long ago as 1972.\textsuperscript{173} The details and kinetics of reaction 2.9 are described in Section 3.3.

The method used in the present work was only reported fairly recently.

\[
\text{Na/Hg} \quad \text{RuCl}_2(\text{CO})_2L_2 + L + 2\text{Na} \rightarrow \text{Ru(CO)2L}_3 + 2\text{NaCl} \quad \text{(ref. 172)} 
\]

Samples of ccr-RuCl\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (2 g, 2.6 mmol) and PPh\textsubscript{3} (1.4 g, 5.2 mmol) were dissolved in distilled and dried THF (400 mL) under an inert gas. Sodium/mercury amalgam (15 to 20 mL) was added, and the mixture stirred for 2 to 3 days. The suspension was allowed to settle, and the supernatant solution was transferred to a separate flask and filtered through diatomaceous earth. The orange filtrate was reduced in volume to 100 mL by vacuum distillation. Addition of hexanes (140 mL) induced the formation of a deep yellow precipitate, which was collected by filtration and dried under vacuum overnight. The yields were 60 to 80\%.

Elem. Anal. Calcd. for RuP\textsubscript{3}O\textsubscript{2}C\textsubscript{56}H\textsubscript{45}: C, 71.3; H, 4.8. Found: C, 71.0; H, 4.8. IR (Nujol) 1902 cm\textsuperscript{-1} \nu(CO); \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}) \delta 49.26 ppm (s); UV/vis. (THF) \lambda_{\text{max}} 345 nm (\textepsilon=17,000 M\textsuperscript{-1} cm\textsuperscript{-1}). The \nu(CO) stretch falls within the range of reported values for this complex.\textsuperscript{173-4,177}

The geometry of this 5-coordinate complex is believed to be trigonal bipyramidal. The single carbonyl stretching band in the IR spectrum indicates \textit{trans} and therefore axial carbonyls. The
single peak in the $^{31}$P{¹H} NMR spectrum indicates equivalent and therefore equatorial phosphines.

2.3.3 cct-RuH₂(CO)₂(PPh₃)₂

Although in the present work cct-RuH₂(CO)₂(PPh₃)₂ (3) was prepared from Ru(CO)₂(PPh₃)₃ (2), as indicated in equation 2.11,

\[
\text{Ru(CO)₂L₃} + \text{H₂} \xrightarrow{\text{(ref. 173,177)}} \text{RuH₂(CO)₂L₂} + \text{L}
\]

complex 3 was known¹⁷⁸ (equation 2.12) well before 2 was first synthesized.¹⁷³

\[
\text{Ru(CO)₃L₂} + \text{H₂} \xrightarrow{120 \text{ atm} \ 130°C \ (\text{ref. 178})} \text{RuH₂(CO)₂L₂} + \text{CO}
\]

\[
\text{Ru₃(CO)₁₂} + \text{Na/NH₃} \xrightarrow{\text{H₃PO₄}} \text{RuH₂(CO)₄} \xrightarrow{\text{L}} \text{RuH₂(CO)₂L₂}
\]

\[
[\text{Ru(N₂Ar)(CO)₂L₂}]\text{BF₄} \xrightarrow{\text{NaBH₄ \ ethanol \ (ref. 174)}} \text{RuH₂(CO)₂L₂}
\]

Ru(CO)₂(PPh₃)₃ (1.2 g, 1.2 mmol) was dissolved in THF (50 mL) under H₂ (1 atm) and stirred for 30 min. The yellow colour faded, but reintensified when the volume of the solvent was reduced by vacuum distillation. Hydrogen was reintroduced. After the yellow colour had faded again, hexanes (40 mL) were added to induce precipitation. The suspension was filtered and the white product dried in a vacuum at room temperature for several days; yield 95%. Elem. Anal. Calcd. for C₃₈H₃₂O₂P₂Ru: C, 66.8; H, 4.7. Found: C, 67.1; 4.8. IR (Nujol) 2012, 1977 cm⁻¹ v(CO); 1880, 1825 cm⁻¹ v(Ru-H); IR (CH₂Cl₂) 2017, 1977 cm⁻¹ v(CO); IR (THF) 2019, 1981 cm⁻¹ v(CO); $^{31}$P{¹H} NMR (C₆D₆) δ 56.29 ppm (s). $^{1}$H NMR (C₆D₆) δ -6.34 (t, 2H,
J_{PH}=23.4 \text{ Hz, Ru-H}, 7.05 \text{ (multi, 18H, } m-, p-\text{Ph), 7.90 ppm (multi, 12H, } o-\text{Ph). The UV/vis. absorbance was negligible between 625 and 350 nm, rising steeply at lower wavelengths. The IR frequencies, hydride chemical shift, and the } 2J_{PH} \text{ value are close to the reported values.}^{174}

The white product has two carbonyl stretching bands in the IR spectrum, indicating cis carbonyls (C_{2v} symmetry). The complex contains magnetically equivalent hydride ligands and magnetically equivalent phosphorus atoms, as indicated by the high field triplet in the ^1H NMR spectrum. Therefore two structures are possible; cct and tcc. L'Epplattenier and Calderazzo^{178} favoured the former, but presented no evidence. Because the ^1H NMR signal of the } o-\text{phenyl protons is separated from that of the } m- \text{ and } p-\text{phenyl signals by greater than 0.5 ppm, a phenomenon associated with trans phosphines}^{180}, \text{ then the observed isomer is believed to be cct-RuH}_2(CO)_2(PPh_3)_2.

2.3.4 cct-RuH(Cl)(CO)_2(PPh_3)_2

The complex RuH(Cl)(CO)_2(PPh_3)_2 (4) has been synthesised from RuHCl(CO)(PPh_3)_3 and, in the method used here, from RuCl_2(PPh_3)_3.

\[
\text{RuHCl(CO)L}_3 + \text{CO} \rightarrow \text{RuHCl(CO)_2L}_2 + \text{L}
\]  
\text{(Ref. 175)}

\[
\text{RuCl}_2\text{L}_3 + \text{H}_2 \rightarrow \text{RuHClL}_3 \stackrel{1:1 \text{H}_2/\text{CO}}{\rightarrow} \text{RuHCl(CO)_2L}_2 + \text{RuCl}_2(\text{CO})_2\text{L}_2
\]  
\text{(dma = N,N-dimethylacetamide, ref. 164, 181)}

RuCl_2(PPh_3)_3 (0.40 g, 0.42 mol) was dissolved in 10 mL of degassed dma under H_2 (1 atm), giving a red-brown solution. After 30 min, the hydrogen atmosphere was replaced with CO (1 atm). The solution turned yellow within 5 min. After another 30 min, the solvent volume was reduced by vacuum distillation, and methanol (20 mL) added. The resulting white precipitate was filtered and dried under vacuum. The yield was 40%. ^{31}P\{^1H\} \text{ NMR (C}_6\text{D}_6) \delta 38.43 \text{ ppm}
(s). $^1$H NMR (CD$_2$CD$_2$) $\delta$ -3.86 ppm (t, $J_{PH} = 19.2$ Hz, Ru-H), 7.04 (multi, $m$- and $p$-phenyl), 7.99 (multi, o-phenyl). The NMR data match those reported by Dekleva$^{182}$ for $cct$-RuH(Cl)(CO)$_2$(PPh$_3$)$_2$, synthesized from RuH(Cl)(PPh$_3$)$_3$ in CH$_2$Cl$_2$ under CO.

The wide difference in chemical shifts between the $m$-$p$- and the o-phenyl signals indicates the presence of trans phosphine ligands; the structure is therefore $cct$. Joshi and James$^{183}$ reached the same conclusion based on the $^{13}$C NMR spectrum of a sample of 4 formed by hydrogenolysis of a norbornenolyl derivative.

In the $^1$H NMR spectrum of 4, the ratio of the peak areas of the hydride versus the phenyl proton signals is 1:21, although 1:30 is the theoretical value. The difference is caused by the longer T$_1$ values of the phenyl protons, which do not allow for complete relaxation between pulses. The same effect is observed in an analytically pure sample of the similar complex $cct$-RuH(SEt)(CO)$_2$(PPh$_3$)$_2$ (Chapter 3), for which the hydride:phenyl peak area ratio is also 1:21 under the same NMR conditions.

As noted, the second step of the synthesis involved exposure of the solution to CO and not the 1:1 H$_2$/CO mixture recommended earlier.$^{164}$ The use of CO alone is reported$^{164}$ to give $tcc$-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$. However, in our hands, the pure CO treatment reproducibly gave pure $cct$-RuHCl(CO)$_2$(PPh$_3$)$_2$; the reason for the differing results is not known.

### 2.3.5 cis- and trans-RuCl$_2$(dpm)$_2$

The cis (5) and trans (6) isomers of the complex RuCl$_2$(dpm)$_2$ can be differentiated by $^1$H and $^{31}$P($^1$H) NMR spectroscopy. The ratio of isomers depends on the synthetic method. Those reported to produce the trans isomer are:

$$\text{ethanol}$$  
$$\text{RuCl}_3 + 2\text{dpm} \xrightarrow{\text{reflux}} \text{RuCl}_2(\text{dpm})_2$$  
$^{2.17}$

(ref. 184)
1. ethanol, reflux

\[
\text{RuCl}_3 + \text{CO} \xrightarrow{\text{reflux}} \text{RuCl}_2(\text{dpm})_2
\]

2. C\text{C}_\text{H}_\text{H}_\text{H}, reflux, dpm

\[
\text{RuCl}_2\text{L}_\text{3} + 2\text{dpm} \rightarrow \text{RuCl}_2(\text{dpm})_2 + 3\text{L}_\text{3}
\]

The reactions reported to form the cis isomer are:

\[
\text{RuCl}_3 + \text{L}' \xrightarrow{\text{dpm}} \text{L}'\text{Ru} (\mu\text{Cl})_3\text{RuL}'_3 \xrightarrow{\text{L}' = \text{PEt}_2\text{Ph}} \text{RuCl}_2(\text{dpm})_2
\]

\[
\text{RuCl}_2(\text{dmso})_4 + 2\text{dpm} \xrightarrow{\text{toluene}} \text{RuCl}_2(\text{dpm})_2 + 4\text{dmso}
\]

Although no X-ray crystal structure of either isomer has been reported, that of the related complex trans-RuCl\text{L}_\text{2}(\text{Ph}_2\text{PCH}_2\text{AsPh}_2)_2 has been described by Balch et al.\textsuperscript{188}

A sample of 5 was kindly donated by Dr. C.-L. Lee, who had prepared it by the method of Chaudret et al.\textsuperscript{187}a; A solution of RuCl\text{L}_3\text{H}_\text{2O} (2 g, 8 mmol) in dmso (30 mL) was refluxed for 30 min, during which time it turned yellow/orange. After reduction of the volume to 10 mL, and addition of a large excess of acetone, a yellow precipitate of cis-RuCl\text{L}_2(dmso)_4 formed. This was collected by filtration and dried under vacuum. A refluxing 100 mL toluene solution of this product (1 g, 2 mmol) and dpm (1.6 g, 4.2 mmol) turned bright yellow over 2 h. The solution was then allowed to cool, and diethyl ether (100 mL) was added. Filtration afforded a yellow product. \textsuperscript{31}P{\textsuperscript{1H}} NMR (C\text{C}_\text{D}_6) -0.44 ppm (t), -26.72 ppm (t). Similar \textsuperscript{31}P{\textsuperscript{1H}} NMR shifts and coupling constant have been reported.\textsuperscript{187}

A mixture of 5 and 6 was also synthesized and donated by Dr. C.-L. Lee; RuCl\text{L}_3\text{H}_\text{2O} (3 g, 10 mmol) in methanol (250 mL) was refluxed for 2 h, with hydrogen gas bubbling through the solvent. The resulting solution was transferred into a boiling mixture of methanol, dpm (9.2 g,
24 mmol), and 37% aqueous formaldehyde (7 mL). Refluxing was continued for another hour, after which the solution was cooled to room temperature and filtered. The yellow compound was reprecipitated twice from CH2Cl2/petroleum ether. 31P{1H} (CD2Cl2) δ -0.35 (t, Jpp=35.9 Hz, 5), -8.03 (s, 6J), -26.38 ppm (t, Jpp=35.9 Hz, 5). The integration showed that 70% of the mixture was the trans isomer 6. The 31P{1H} NMR chemical shift of 6 in CH2Cl2 is -6.9 ppm,186 relative to P(OMe)3 at 141 ppm downfield of 85% H3PO4.

2.3.6 RuH2(dpm)2

Difficulties encountered in the synthesis of RuH2(dpm)2 (7) have no doubt restricted its use in experimental chemistry. The complex cannot be formed by the reactions of dpm with RuH2(PPh3)4, or LiAlH4 with RuCl2(dpm)2 (5 or 6), which instead form RuH2(dpm)(PPh3)2187 and RuHCl(dpm)2,189 respectively. The reaction of NaBH4 with 5 produced mostly RuH(η1BH4)(dpm)2 with some Ru(η1BH4)2(dpm)2 (Section 2.3.7). The only successful method to date requires the preparation of the air-sensitive compound Ru(COD)(COT) (COD=1,5-cyclooctadiene, COT=1,3,5-cyclooctatriene).

\[
\text{COD} \xrightarrow{\text{RuCl}_3} \text{Ru(COD)(COT)} \xrightarrow{\text{dpm}} \text{Ru(COD)(dpm)2} \xrightarrow{\text{H}_2} \text{RuH}_2(\text{dpm})_2
\]

A 20 mL ethanol solution of COD (17 mL, 140 mmol) and RuCl3·3H2O (0.7 g, 2.7 mmol) was refluxed under argon for 20 min. Zn dust (6 g), activated by washing with water, 2% HCl, EtOH, and dry Et2O, was added. The resulting mixture was refluxed for 45 min, filtered, and dried to a gelatinous residue by overnight evaporation under vacuum. The solubles from this residue were extracted by washing with pentane (100 mL), and passing the resulting solution through a 20 cm neutral alumina column (Brockmann Activity II 80-200 mesh). The volume of the yellow filtrate was reduced to 5 mL by vacuum transfer. The solution was cooled in a dry
ice/acetone bath overnight, resulting in the formation of yellow crystals.\textsuperscript{191} A 20 mL toluene solution of dpm (640 mg, 1.7 mmol) was added to the product. After overnight exposure to H$_2$, the solution was reduced in volume by vacuum transfer of most of the solvent, and hexanes (20 mL) were added to encourage the formation of the yellow precipitate, which was collected by filtration.\textsuperscript{191} The overall yield is typically low (10-40%), and attempts by Dr. C.-L. Lee to perform increased-scale syntheses resulted in lower, not higher yields.

**Characterization of cis- and trans-RuH$_2$(dpm)$_2$:** Elem. Anal. Calcd. for RuP$_4$C$_5$O$_4$H$_{46}$: C, 68.9; H, 5.3. Found: C, 68.9; H, 5.2.

$^1$H NMR (C$_6$D$_6$)\textsuperscript{191} $\delta$ -7.58 (dq, $^2$J$_{\text{transPH}}$ = 73 Hz, $^2$J$_{\text{cisPH}}$ = 18 Hz, RuH of cis-isomer), -4.80 (qn, $^2$J$_{\text{cisPH}}$ = 19 Hz, RuH of trans-isomer), 4.10 (multi, CH$_2$ of cis-isomer), 4.63 (multi, CH$_2$ of trans-isomer), 4.81 ppm (multi, CH$_2$ of cis-isomer).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$)\textsuperscript{191} $\delta$ 14.06 (t, $^2$J$_{\text{cisPP}}$ = 19.3 Hz, cis-isomer), 9.11 (s, trans-isomer), 0.57 ppm (t, $^2$J$_{\text{cisPP}}$ = 18.8 Hz).

Similar $^1$H NMR data has been reported.\textsuperscript{47} The product is always formed as a 1:4 mixture of the trans and cis isomers.\textsuperscript{187} Although this was the synthetic method used by G. Rastar and the present author to prepare samples for the present study, the reaction of NaBH$_4$ with S was investigated as a possible alternate route (Section 2.3.7).

### 2.3.7 An Attempted New Synthesis of RuH$_2$(dpm)$_2$: The Synthesis of trans-RuH(η$^1$BH$_4$)(dpm)$_2$

Hydrogen was bubbled through a suspension of cis-RuCl$_2$(dpm)$_2$ (0.5 g, 0.5 mmol) in benzene (30 mL) and methanol (50 mL) for 10 min. Fresh sodium borohydride (2 g, 50 mmol) was added in 3 portions over 5 min. Hydrogen was bubbled through the resulting mixture for 1 h, after which methanol (100 mL) was added. The white product isolated by filtration was washed with methanol (20 mL) and dried under vacuum at room temperature. The yield was 0.45 g. The spectroscopic analysis of the product is consistent with RuH(η$^1$BH$_4$)(dpm)$_2$ (8),
although the presence of some \( \text{Ru}(\eta^1\text{BH}_4)_2(\text{dpm})_2 \) is suggested by the FAB/MS data.

Reprecipitation from methanol/benzene resulted in partial conversion to RuH\(_2\)(dpm)\(_2\). As a result, the elemental analysis was of an unpurified sample.

\[
\text{RuCl}_2(\text{dpm})_2 + 2\text{NaBH}_4 \rightarrow \text{RuH(BH}_4)(\text{dpm})_2 + 2\text{NaCl} + "\text{BH}_3"
\]

2.23

Elem. Anal. calcd. for C\(_{50}\)H\(_{49}\)BP\(_4\)Ru: C, 67.8; H, 5.6. Found: C, 65.2; H, 5.5.

FT-IR (Nujol or HCB): \(2397\) cm\(^{-1}\) (\(v(\text{B-H})\), \(v_D/v_H = 0.755\)); \(2346\) (\(v(\text{B-H})\), 0.754); \(1788\) (\(v(\text{B-H}_b)\) or \(v(\text{Ru-H}_2)\), 0.732); \(1069\) cm\(^{-1}\) (\(8(\text{BH}_3)\), 0.723);

\(^1\)H NMR (C\(_6\)D\(_6\), 20\(^\circ\)C) \(\delta -10.60\) (qn, 1H, \(2J_{\text{PH}} = 19.5\) Hz, Ru-H), -1.05 (br, 4H, BH\(_4\) ), 4.53 (dt, 2H, \(2J_{\text{HAHB}} = 14\) Hz, \(2J_{\text{PH}} = 3\) Hz, CH\(_a\) (methylene)), 4.97 (dt, 2H, \(2J_{\text{HAHB}} = 14\) Hz, \(2J_{\text{PH}} = 4\) Hz, CH\(_b\) (methylene)), 6.88 (multi, 12H, \(m-/p\)-Ph), 7.07 (multi, 12H, \(m-/p\)-Ph), 7.46 (s, 8H, o-Ph), 7.71 ppm (s, 8H, o-Ph);

\(^1\)H NMR (C\(_6\)D\(_5\)CD\(_3\), -89\(^\circ\)C) \(\delta -10.5\) (br, RuH), -9.0 (br, Ru-H\(_b\)-B);

\(^1\)H NMR T\(_1\) values (C\(_6\)D\(_5\)CD\(_3\), 20\(^\circ\)C) 0.36 s (BH\(_4\) ), 0.56 s (RuH), (C\(_6\)D\(_5\)CD\(_3\), -58\(^\circ\)C) 0.26 s (BH\(_4\) ), 0.35 s (RuH);

\(^31\)P\((^1\)H) NMR (C\(_6\)D\(_6\), 20\(^\circ\)C) \(\delta 2.43\) ppm (s);

\(^{11}\)B NMR (C\(_6\)D\(_6\), 20\(^\circ\)C) \(\delta -2\) (br, major), 46 (br, minor), -46 ppm (br, minor);

FAB/MS (\(p\)-nitrobenzylalcohol) m/e 1036 (RuH(BH\(_4\))(dpm)\(_2\)-O\(_2\)NC\(_6\)H\(_4\)CH\(_2\)OH); 1008 (RuH(BH\(_4\))(dpm)\(_2\)-O\(_2\)NC\(_6\)H\(_4\)); 900 (Ru(BH\(_4\))(dpm)\(_2\)); 885 (RuH(BH\(_4\))(dpm)\(_2\)); 869 (Ru(dpm)\(_2\)); 501 (RuH(BH\(_4\))(dpm)); plus 20 other fragments (Table 2.1, Fig. 2.3).

The \(^1\)H NMR spectrum of the product (Fig. 2.4) resembles that of trans-\([\text{RuH}(\eta^2\text{H}_2)(\text{dppe})_2]\text{BF}_4\),\(^{192}\) which has a broad peak at -4.6 ppm (H\(_2\)) and a quintet at -10.0 ppm (\(J_{\text{PH}} = 16\) Hz) in acetone-d\(_6\). However, the T\(_1\) measurements and the microanalysis, which showed the virtual absence of chlorine, eliminate the possibility of the product being trans-\([\text{RuH}(\eta^2\text{H}_2)(\text{dpm})_2]\text{Cl}\). Further, the THF and the benzene solutions of the product do not conduct at room temperature.
Table 2.1 Fragments detected in the FAB/mass spectrum of Ru(H)(BH₄)(dpm)₂

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<th>Observed m/z</th>
<th>Expected m/z</th>
<th>Fragment Allocation</th>
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<td>1038</td>
<td>Ru(H)(BH₄)(dpm)₂ + O₂NC₆H₄CH₂OH</td>
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<tr>
<td>1008</td>
<td>1007</td>
<td>Ru(H)(BH₄)(dpm)₂ + O₂NC₆H₄</td>
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<td>900</td>
<td>Ru(BH₄)₂(dpm)₂</td>
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<td>885</td>
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<td>869</td>
<td>Ru(dpm)₂</td>
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<tr>
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<td>792</td>
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Table 2.2 ¹H NMR DATA FOR trans-RuH(X)(dpm)₂

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<th>Hₜ</th>
<th>JPHₐ</th>
<th>JPHₖ</th>
<th>JPHₜ</th>
<th>JPHₘ</th>
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<th>ref.</th>
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<td>n.a.</td>
<td>18.9</td>
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<td>C₆D₆</td>
<td>c</td>
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<td>-</td>
<td>-</td>
<td>CD₃OD</td>
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a  n.a. = not applicable
Hₐ, Hₖ = methylene protons
Hₜ = terminal hydride
Coupling constants and chemical shift in Hz and ppm, respectively
b Section 2.3.6 of this work
c Section 3.4 of this work
d Section 2.3.7 of this work
Fig. 2.3 FAB mass spectrum of RuH(BH₄)(dpm)₂ in p-nitrobenzyl alcohol.
Fig. 2.4 1H NMR spectrum of RuH(BH4)(dpm)₂ under H₂ at 20°C, 300 MHz

a) full spectrum (solvent = C₆D₆)
b) phenyl region (C₆D₆)
c) methylene region (C₆D₅CD₃)
The methylene region of the $^1$H NMR spectrum contains an ABX$_2$ pattern, consistent with a trans-Ru(X)(Y)(dpm)$_2$ structure, and the coupling constants and chemical shifts are comparable to those in similar complexes (Table 2.2). In the phenyl region, two multiplets are observed for the o-phenyl protons, and two for the m- and p-phenyl protons, compared to only one of each type for $\mathfrak{a}$. The complexes of the formula trans-RuX$_2$(dpm)$_2$ are of D$_{4h}$ symmetry, and have equivalent phenyl groups. In contrast, trans-RuX(Y)(dpm)$_2$ complexes (C$_{4v}$) such as $\mathfrak{b}$ have phenyl groups in two different environments; four in the hemisphere of the X, and four in the hemisphere of the Y ligand.

The linewidth of the broad peak in the $^1$H NMR spectrum increases as the temperature decreases, while the terminal hydride remains at -10.5 ppm, although the quintet pattern is not resolved at lower temperatures (Fig. 2.5). At -79°C, the broad peak is barely visible, and a new broad peak at -9.0 ppm appears. These changes are believed to result from the slowing down of the exchange between the BH$_1$ (terminal) hydrogens and the hydrogen(s) bridging the Ru and B atoms, the new peak being due to the bridging hydrogen. At -89°C the integral of that peak has increased to half that of the quintet at higher field. At even lower temperatures, where the peak would be better resolved, the area should be equal to that of the quintet, assuming v$^1$BH$_4$ coordination. The peak for the terminal borohydride hydrogen atoms, if it were close to that of B$_2$H$_6$ ($\delta = 4$ ppm),$^{193a,194}$ would be obscured by the solvent. The slowing of the exchange has been observed in only a few borohydride complexes.$^{193}$

The $^1$H NMR spectrum of a toluene-d$_8$ solution of the complex changed irreversibly at temperatures greater than 50°C; the principal product was $\mathfrak{z}$.

$$\text{RuH(BH}_4\text{)(dpm)}_2 \longrightarrow \text{RuH}_2\text{(dpm)}_2 + "\text{BH}_3"$$

The complex trans-RuD(BD$_4$)(dpm)$_2$ was synthesized from $\mathfrak{f}$ and NaBD$_4$ under H$_2$. The $^1$H NMR spectrum of this product indicates 88% deuteration at the hydride and borohydride positions. This suggests that H$_2$ played no role in the reaction, and indeed later experiments
Fig. 2.5 $^{1}$H NMR (300 MHz) spectra of RuH(BH$_4$)(dpm)$_2$ in C$_6$D$_5$CD$_3$ below ambient temperatures.
showed that \( N_2 \) was as effective in the synthesis. The pattern at 4.97 ppm due to one of the methylene protons has changed to a triplet at 4.93 ppm (\( J_{PH}=4.3 \) Hz). Including this triplet, the ratio of the multiplets at 4.9 and 4.5 ppm has changed from 1:1 in \( \text{RuH(BH}_4\text{(dpm)})_2 \) to 1:0.5 in \( \text{RuD(BD}_4\text{(dpm)})_2 \). Therefore monodeuteration at the methylene site has occurred, giving a complex of the ligand \( \text{Ph}_2\text{PCHDPPh}_2 \). The H-D coupling is not resolved.

The \( ^{11}\text{B} \) NMR spectra of \( \delta \) or the borodeuteride contain a very broad singlet (\( w_{0.5}=3000 \) Hz) at -2 ppm, and two equally broad minor peaks which are present in varying intensities of up to 25% in different samples. None of the peaks have been positively identified, although the fact that three peaks were observed suggests that none of the samples are pure. No changes in the spectrum were observed down to -80°C or with broad band \( ^1\text{H} \) decoupling. Very few \( ^{11}\text{B} \) NMR spectra of transition metal borohydride complexes have been reported; for example, the spectrum of \( \text{IrH}_2(\text{n}_2\text{BH}_4)(\text{PBu}_t^2\text{Me})_2 \) consists of a singlet at 13.1 ppm (\( w_{0.5}=350 \) Hz) in \( \text{C}_6\text{D}_6 \).

The IR spectra of borohydride complexes are characteristic for the bonding mode of the \( \text{BH}_4^- \) ligand. Four structures have been considered.

\[
\text{M—H—B} \quad \text{M—H—B} \quad \text{M—H—B} \quad \text{M}^+\text{BH}_4^- \\
\text{I} \quad \text{II} \quad \text{III} \quad \text{IV}
\]

The IR spectrum of \( \delta \) and its deuteride (Fig. 2.6) are most consistent with structure I. Structures III and IV have \( \nu(\text{B-H}) \) bands at 2450-2600 and 2200-2300 cm\(^{-1}\), respectively, which are not observed in the spectrum of \( \delta \). Structure II requires a bridge stretching band at 1300-1500 cm\(^{-1}\), but no peak appears in this region of the spectrum of \( \delta \) which does not appear in that of \( \text{RuD(BD}_4\text{(dpm)})_2 \). However, Marks and Kolb\(^{195}\) predicted that for structure I two bands, \( \nu(\text{M-H}_b) \) and \( \nu(\text{B-H}_b) \), would be observed in the region of 1650-2150 cm\(^{-1}\). Based on this, the one band at 1788 cm\(^{-1}\) in the spectrum of \( \delta \) is more consistent with structure II. However, Holah \textit{et al.}\(^{196}\) took the absence of a band at 1900-2000 cm\(^{-1}\), as found here, to be indicative of structure I rather than II, and this suggests that structure I is the correct assignment. The IR results are
Fig. 2.6 FT-IR spectra of HCB mulls of a) RuH(BH$_4$)(dpm)$_2$ and b) RuD(BD$_4$)(dpm)$_2$ (88 % deuteration). The peaks due to HCB are marked with asterisks.
therefore somewhat ambiguous, but structure II, a 20 electron, seven-coordinate species, is considered unlikely. The monodentate borohydride complex FeH(BH3)(dmpe)2, which has been structurally characterized as type I, has IR bands (cm⁻¹) at 2340 (ν(B-Ht)), 2030 (ν(Fe-Hb), ν(B-Hb)), 1788 (ν(Fe-H2) and 1045 (BH3 def.).197

Ruthenium borohydride complexes which have been reported include RuH(BH4)(PR3)3
(PR3=PPh3,198-200 PPh2Me,201 PPhMe2,202 or PMe3203), RuH(η2BH4)(CO)(PR3)2
(PR3=PPh3,200 PPr3, PMe(tBu)2204), RuH(BH4)(CO)2(PCy3)2200, CpRu(BH4)(PR3)2
(Cp=C5H5 or C5Me5, R=Ph,205 Me, Et, Cy206), and Ru3(CO)9(H)(BH4)207.

Although RuH(BH4)(dpm)2 reacts with Lewis bases such as thiophene and amines to form RuH2(dpm)2, this route is not of higher yield or greater reliability than the preparation of the latter complex from Ru(COD)(COT).

Note added in proof: Bianchini et al.302 have very recently reported the synthesis of RuH(η1BH4)(PP3) from RuCl2(PP3) and NaBH4 (PP3 = P(CH2CH2PPh2)3). The variable temperature ¹H NMR spectra of the complex bear a strong resemblance to those of RuH(η1BH4)(dpm)2.
3. THE REACTIONS OF RUTHENIUM COMPLEXES WITH THIOLS

3.1 THE REACTION OF Ru(CO)2(PPh3)3 WITH H2S AND THIOLS

The Ru0 complex Ru(CO)2(PPh3)3 (2) reacts rapidly at room temperature with a variety of ligands, including H2, C2H4, PhCCPh, O2,173 and CO.177 A possible mechanism, based on the reported kinetics for the reactions with H2 and CO is:172

\[
\begin{align*}
\text{Ru(CO)2(PPh3)3} & \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{Ru(CO)2(PPh3)2} + \text{PPh3} \\
\text{Ru(CO)2(PPh3)2} + X & \overset{k_2}{\rightarrow} \text{RuX(CO)2(PPh3)2} \\
\end{align*}
\]

where \( X = \text{CO or H}_2 \) and

\[
\frac{-d[2]}{dt} = \frac{k_1 k_2 [2][X]}{k_{-1}[\text{PPh3}] + k_2[L]}
\]

The rate of reaction shows an inverse dependence on [PPh3]. In the absence of added PPh3, the rate is independent of [X], suggesting that under these conditions the second term in the denominator of the rate law is significantly greater than the first, and that the overall rate is determined by the rate of PPh3 loss for both the H2 and CO substitution reactions.172

The oxidative addition reaction of 2 with H2S, examined earlier in this laboratory,86

\[
\text{Ru(CO)2(PPh3)3} + \text{H}_2\text{S} \rightarrow \text{RuH(SH)(CO)2(PPh3)2} + \text{PPh3}
\]

is complete after 2 h at -35°C in THF. The product is isolated in 95% yield by addition of hexanes.86 This reaction and the corresponding reactions with thiols (briefly examined in an earlier report from this laboratory)86 and selenols
Ru(CO)$_2$(PPh$_3$)$_3$ + REH $\rightarrow$ RuH(ER)(CO)$_2$(PPh$_3$)$_2$ + PPh$_3$  \[ \text{2} \]

ER = a SH, b SC$_6$H$_4$CH$_3$, c SCH$_3$, d SCH$_2$CH$_3$, e SCH$_2$C$_6$H$_5$, f SC$_6$H$_4$OCH$_3$,
    g SC$_6$H$_4$mCH$_3$, h SeC$_6$H$_5$, i SC$_6$H$_5$, or j SC$_6$F$_5$

are complete within minutes at room temperature, and form a series of products with the formula RuH(ER)(CO)$_2$(PPh$_3$)$_2$ (9), the characterization of which is described in the following section.

Complex 2 failed to react with ethanol (85 mM) in THF. Alcohols are structurally similar to thiols, but are much less acidic ($pK_a$'s 3.5 to 5.5 units higher). We shall see in Section 3.5 that the more acidic thiols bind more strongly in these systems than the less acidic thiols.

### 3.2 THE CHARACTERIZATION OF RuH(ER)(CO)$_2$(PPh$_3$)$_2$

Analytically pure samples of several of the title complexes (9a, c-h) have been isolated. The carbon analyses of 9b and 9i were 1% low. In addition, 9j was isolated but not purified, and samples of RuH(SCH$_2$CH$_3$)(CO)$_2$(PPh$_2$Py)$_2$ (11d) (where Py=2-C$_5$H$_4$N) and RuH(SCH$_2$CH$_3$)(CO)$_2$(P(C$_6$H$_4$mCH$_3$)$_3$)$_2$ (12d) were prepared in situ in C$_6$D$_6$ in order to make comparisons with their NMR spectra.

The $^1$H NMR spectra of 9 (Figs. 3.1 and 3.2, and Table 3.1) contain a high field triplet due to the hydride ligand, split by two equivalent phosphines. The coupling constant $^2$J$_{PH}$ is within the range 19.5 to 20.5 Hz in C$_6$D$_6$, comparable to those of other complexes with phosphines cis to hydride ligands, such as mer-RuH$_2$(CO)(PPh$_3$)$_3$ (cis $^2$J$_{PH}$=16, 29, 30 Hz, trans $^2$J$_{PH}$=74 Hz),208
Fig. 3.1 1H NMR spectrum of cct-RuH(SEt)(CO)₂ (PPh₃)₂ in C₆D₆ at 20°C and 300 MHz.
Fig. 3.2 $^1$H NMR spectrum of $cct$-RuH(SCH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ (9e) in C$_6$D$_6$ at 20°C and 300 MHz.
Table 3.1 $^{31}$P($^1$H) and $^1$H NMR Data for cct-RuH(ER)(CO)$_2$(PPh$_3$)$_2$ Complexes in C$_6$D$_6$ at 20°C and 300 MHz.

<table>
<thead>
<tr>
<th>9</th>
<th>ER</th>
<th>31P $^a$</th>
<th>Ru-H $^b$</th>
<th>2J$_{PH}$</th>
<th>CH$_3$</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>SH</td>
<td>42.01</td>
<td>-4.79</td>
<td>20.1</td>
<td>-</td>
<td>-3.00 (t, 3J$<em>{PH}$=4.9, 3J$</em>{HH}$=3, SH)</td>
</tr>
<tr>
<td>9c</td>
<td>SCH$_3$</td>
<td>37.14</td>
<td>-4.68</td>
<td>20.5</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>9d</td>
<td>SCH$_2$CH$_3$</td>
<td>37.25</td>
<td>-4.67</td>
<td>20.4</td>
<td>0.77</td>
<td>1.28 (q, 3J$_{HH}$=7.4, CH$_2$)</td>
</tr>
<tr>
<td>9e</td>
<td>SCH$_2$C$_6$H$_5$</td>
<td>37.09</td>
<td>-4.63</td>
<td>20.3</td>
<td>-</td>
<td>2.53 (s, CH$_2$)</td>
</tr>
<tr>
<td>9f</td>
<td>SCH$_2$C$_6$H$_5$</td>
<td>37.26</td>
<td>-4.32</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9g</td>
<td>SCH$_6$H$_5$</td>
<td>38.45</td>
<td>-4.31</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9h</td>
<td>SCH$_6$F$_5$</td>
<td>37.43</td>
<td>-4.33</td>
<td>19.5</td>
<td>2.04</td>
<td>-</td>
</tr>
<tr>
<td>9i</td>
<td>SCH$_6$H$_4$PCH$_3$</td>
<td>37.39</td>
<td>-4.36</td>
<td>19.5</td>
<td>1.93</td>
<td>-</td>
</tr>
<tr>
<td>9j</td>
<td>SCH$_6$H$_4$OCH$_3$</td>
<td>36.55</td>
<td>-4.23</td>
<td>19.5</td>
<td>2.19</td>
<td>-</td>
</tr>
<tr>
<td>9k</td>
<td>SCH$_6$H$_4$mCH$_3$</td>
<td>37.45</td>
<td>-4.23</td>
<td>19.5</td>
<td>2.19</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ singlet.

$^b$ triplet, except for that of 9a, which is a doublet of triplets (3J$_{HH}$ = 3 Hz).

Table 3.2 FT-IR Data for cct-RuH(ER)(CO)$_2$(PPh$_3$)$_2$ Complexes in Nujol, HCB, or CH$_2$Cl$_2$ at room temperature.$^a$

<table>
<thead>
<tr>
<th>9</th>
<th>ER</th>
<th>Nujol $v$(CO)</th>
<th>HCB $v$(CO)</th>
<th>CH$_2$Cl$_2$$^b$ $v$(CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>SH</td>
<td>2029, 1984</td>
<td>1901</td>
<td>2035, 1979</td>
</tr>
<tr>
<td>9c</td>
<td>SCH$_3$</td>
<td>2021, 1970</td>
<td>1899</td>
<td>2029, 1971</td>
</tr>
<tr>
<td>9d</td>
<td>SCH$_2$CH$_3$</td>
<td>2025, 1964</td>
<td>1925</td>
<td>2029, 1971</td>
</tr>
<tr>
<td>9e</td>
<td>SCH$_2$C$_6$H$_5$</td>
<td>2019, 1981</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>9f</td>
<td>SCH$_6$H$_5$</td>
<td>2030, 1981</td>
<td>1920</td>
<td>b</td>
</tr>
<tr>
<td>9g</td>
<td>SCH$_6$H$_4$PCH$_3$</td>
<td>2021, 1987</td>
<td>1900</td>
<td>2021, 1987, 1900</td>
</tr>
<tr>
<td>9h</td>
<td>SCH$_6$H$_4$mCH$_3$</td>
<td>2026, 1983</td>
<td>1906</td>
<td>2035, 1975</td>
</tr>
<tr>
<td>9i</td>
<td>SCH$_6$H$_4$OCH$_3$</td>
<td>2025, 1991</td>
<td>1900</td>
<td>2035, 1977</td>
</tr>
<tr>
<td>9j</td>
<td>SCH$_6$H$_5$</td>
<td>2027, 1978</td>
<td>1919</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All frequencies in units of cm$^{-1}$.

$^b$ $v$(RuH) not detected.
The IR spectra of $\mathcal{Q}$ in Nujol mull (Fig. 3.3) include two carbonyl stretch bands of unequal intensity, one in the range 2019 to 2030 and the other in the range 1964 to 1991 cm$^{-1}$, and a single $\nu$(Ru-H) stretch at 1899 to 1925 cm$^{-1}$; the exact frequencies are listed in Table 3.2. In CH$_2$Cl$_2$ solution, the $\nu$(CO) bands appear at 2035 and 1979 (ER=SH) or 2029 and 1971 cm$^{-1}$ (ER=SC$_2$H$_5$), and the $\nu$(Ru-H) band is not detected. The presence of two carbonyl bands in the IR spectra indicates that the carbonyls have cis positions in both solid state and in solution.

There are two possibilities for the structure of $\mathcal{Q}$ in solution, given that the phosphine ligands are equivalent and cis to the hydride ligand, and the carbonyl ligands are mutually cis:

![Structures](image)

The relative positions of the phosphines were determined by $^1$H and $^{13}$C($^1$H) NMR spectroscopy. If the two PPh$_3$ ligands are trans, the $^{13}$C($^1$H) NMR signal of the phosphorus-bound carbons should be a triplet, and the chemical shift difference between the $o$- and the $m$-/p-phenyl signals in the $^1$H NMR spectrum should be greater than 0.5 ppm. Conversely, if the two PPh$_3$ ligands are cis, then the $^{13}$C NMR signal should be a doublet, while the $^1$H NMR
Fig. 3.3  

a) The FT-IR spectrum of \( \text{cct-RuH(SMe)(CO)2(PPh3)2} \) (9c) in HCB. The peaks due to HCB are marked with asterisks. 

b) The carbonyl region of the corresponding spectrum of \( \text{cct-RuH(SPh)(CO)2(PPh3)2} \) (9f).
chemical shift difference should be less than 0.5 ppm. $^{180}$ The $^{13}$C spectrum (Fig. 3.4) of RuH(SC$_2$H$_5$)(CO)$_2$(PPh$_3$)$_2$ in CD$_2$Cl$_2$ shows triplets at 135.6 (t, $|J_{CP}+J_{CP'}|=23.3$, P-C), 134.6 (t, $|J_{CP}+J_{CP'}|=5.9$, o-Ph), 128.2 (t, $|J_{CP}+J_{CP'}|=4.4$, m-Ph), and 130.1 ppm (s, p-Ph). The $^1$H NMR chemical shift difference between the o- and m-/p-phenyl signals of complexes 9a-j in C$_6$D$_6$ is 0.9 ppm. These observations show that the phosphine ligands are trans, and therefore that 9 exists as the cct isomer in solution.

The solid state structure of 9b was investigated by X-ray crystallography, and was shown to be the cct isomer (Figs. 3.5 and 3.6 and Tables 3.3 and 3.4). $^{209}$ No other monomeric ruthenium hydrido thiolato complex has been crystallographically characterized, although the structure of a triruthenium complex has been reported. $^{98}$ Some deviations from the octahedral geometry at the metal are due to the four ligands cis to the hydride ligand crowding the hydride. The P-Ru-P bond angle is 172.6°, and the C(1)-Ru-S bond angle is 167.2°.

The Ru-S bond length (2.458 Å) is similar to that for the thiolate ligand (2.453 Å) trans to a carbonyl in the complex Ru(pyS)$_2$(CO)$_2$(PPh$_3$)$_2$ (pyS=o-SC$_5$H$_4$N). $^{210,211}$ Shorter RuII-S bonds (2.406 to 2.429 Å) exist in thiolate ligands trans to weaker π acceptors than CO, such as phosphine or thiolate groups, $^{210-12}$ although an apparent exception is (PhMe$_2$P)$_3$Ru(µSH)$_3$Ru(PMe$_2$Ph)$_2$(SH) with a terminal Ru-S (trans to a bridging SH ligand) bond length of 2.44 Å. $^{213}$ The MII-S-C bond angle is large (113.6°) in 9b, as it is in other complexes with thiolates trans to carbonyls, such as Fe(SPh)$_2$(CO)$_2$(dppe) (112.4 to 114.9°). $^{214}$ Smaller angles (107.7 to 109.6°) are found in complexes with thiolates trans to phosphine or thiolate ligands. $^{210-2,214}$

The length (1.875 Å) of the Ru-C bond trans to the thiolate ligand in 9b is slightly shorter than that found in Ru(pyS)$_2$(CO)$_2$(PPh$_3$) (1.895 Å), $^{211}$ possibly because of the intramolecular interactions which exist in the pyridyl complex. The Ru-C bond trans to hydride is 1.945 Å in 9b, (cf. 1.970 Å in [RuH(H$_2$O)(CO)$_2$(PPh$_3$)$_2$]$^+$), $^{215}$ longer than that trans to the thiolate because of the strong trans influence of hydride ligands. $^{216}$ The aquo complex shows
Fig. 3.4 $^{13}$C($^1$H) NMR spectrum of cct-RuH(SEt)(CO)$_2$(PPh$_3$)$_2$ (9d) in CD$_2$Cl$_2$ at 200°C and 75 MHz, as provided by Dr. C.-L. Lee. Inset shows an expansion of the phenyl region.
Fig. 3.5 X-ray crystallographic structure of cct-RuH(SC₆H₄p-CH₃)(CO)₂(PPh₃)₂ (9b).

Fig. 3.6 Stereo-view of the structure of cct-RuH(SC₆H₄p-CH₃)(CO)₂(PPh₃)₂ (9b). Hydrogen atoms (other than hydride) omitted for clarity.
Table 3.3 Selected bond lengths (Å) with estimated standard deviations in parentheses, for RuH(S\(_{\text{C6H4pCH3}}\))(CO)\(_2\)(PPh\(_3\))\(_2\) (26).

<table>
<thead>
<tr>
<th>atom</th>
<th>atom</th>
<th>distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>H(1)</td>
<td>1.58 (3)</td>
</tr>
<tr>
<td>Ru</td>
<td>C(1)</td>
<td>1.875 (3)</td>
</tr>
<tr>
<td>Ru</td>
<td>C(2)</td>
<td>1.945 (3)</td>
</tr>
<tr>
<td>Ru</td>
<td>P(1)</td>
<td>2.361 (1)</td>
</tr>
<tr>
<td>Ru</td>
<td>P(2)</td>
<td>2.381 (1)</td>
</tr>
<tr>
<td>Ru</td>
<td>S</td>
<td>2.458 (1)</td>
</tr>
<tr>
<td>S</td>
<td>C(39)</td>
<td>1.769 (3)</td>
</tr>
<tr>
<td>P(1)</td>
<td>C(3)</td>
<td>1.828 (3)</td>
</tr>
</tbody>
</table>

Table 3.4 Selected bond angles (°) with estimated standard deviations in parentheses, for RuH(S\(_{\text{C6H4pCH3}}\))(CO)\(_2\)(PPh\(_3\))\(_2\) (26).

<table>
<thead>
<tr>
<th>atom</th>
<th>atom</th>
<th>atom</th>
<th>angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>Ru</td>
<td>C(1)</td>
<td>81 (1)</td>
</tr>
<tr>
<td>H(1)</td>
<td>Ru</td>
<td>C(2)</td>
<td>92.80 (9)</td>
</tr>
<tr>
<td>H(1)</td>
<td>Ru</td>
<td>P(1)</td>
<td>91.59 (9)</td>
</tr>
<tr>
<td>H(1)</td>
<td>Ru</td>
<td>S</td>
<td>96.7 (1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>Ru</td>
<td>C(2)</td>
<td>93.79 (8)</td>
</tr>
<tr>
<td>C(2)</td>
<td>Ru</td>
<td>S</td>
<td>96.7 (1)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Ru</td>
<td>P(2)</td>
<td>172.63 (3)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Ru</td>
<td>S</td>
<td>84.04 (4)</td>
</tr>
<tr>
<td>P(2)</td>
<td>Ru</td>
<td>S</td>
<td>90.39 (4)</td>
</tr>
<tr>
<td>C(39)</td>
<td>S</td>
<td>Ru</td>
<td>113.6 (1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>P(1)</td>
<td>C(9)</td>
<td>105.4 (1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>P(1)</td>
<td>C(15)</td>
<td>102.3 (1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>P(1)</td>
<td>Ru</td>
<td>117.53 (9)</td>
</tr>
<tr>
<td>C(9)</td>
<td>P(1)</td>
<td>C(15)</td>
<td>101.1 (1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>P(1)</td>
<td>Ru</td>
<td>111.35 (8)</td>
</tr>
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<td>P(1)</td>
<td>Ru</td>
<td>117.30 (8)</td>
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<tr>
<td>C(21)</td>
<td>P(2)</td>
<td>C(33)</td>
<td>103.3 (1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>P(2)</td>
<td>C(27)</td>
<td>104.4 (1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>P(2)</td>
<td>Ru</td>
<td>115.49 (8)</td>
</tr>
<tr>
<td>C(33)</td>
<td>P(2)</td>
<td>C(27)</td>
<td>101.2 (1)</td>
</tr>
<tr>
<td>C(33)</td>
<td>P(2)</td>
<td>Ru</td>
<td>113.98 (8)</td>
</tr>
<tr>
<td>C(27)</td>
<td>P(2)</td>
<td>Ru</td>
<td>116.71 (9)</td>
</tr>
<tr>
<td>O(1)</td>
<td>C(1)</td>
<td>Ru</td>
<td>174.3 (3)</td>
</tr>
<tr>
<td>O(2)</td>
<td>C(2)</td>
<td>Ru</td>
<td>173.4 (3)</td>
</tr>
</tbody>
</table>

Table 3.5 \(\text{^31P}(1H)\) and \(1H\) NMR Data for RuH(SEt)(CO)\(_2\)L\(_2\).

<table>
<thead>
<tr>
<th>L</th>
<th>(\delta)</th>
<th>(\delta)</th>
<th>(\delta)</th>
<th>(2J_{\text{PH}})</th>
<th>(\text{CH}_2)</th>
<th>(\text{CH}_3)</th>
<th>(3J_{\text{HH}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phol3 (12)</td>
<td>35.17</td>
<td>-4.52</td>
<td>20.2</td>
<td>1.46</td>
<td>0.86</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>PPh3 (9d)</td>
<td>37.25</td>
<td>-4.67</td>
<td>20.4</td>
<td>1.28</td>
<td>0.77</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>PPh2Py (11)</td>
<td>39.76</td>
<td>-4.06</td>
<td>20.7</td>
<td>0.97</td>
<td>0.79</td>
<td>7.2</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Ph=C\(_{\text{C6H5}}\) tol=C\(_{\text{C6H4pCH3}}\) Py=-2-C\(_{\text{C5H5N}}\)
inequivalent Ru-P bond lengths that result from crystal packing effects.\textsuperscript{215} The Ru-P bond lengths in 9b are essentially equivalent, and match closely those in related complexes.\textsuperscript{215,217}

The Ru-H bond length in 9b is slightly shorter (1.58 Å) than those found in [RuH(H\textsubscript{2}O)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}]\textsuperscript{+} (1.7 Å).\textsuperscript{215} RuH(Cl)(PPh\textsubscript{3})\textsubscript{3} (1.7 Å),\textsuperscript{218}\textsuperscript{a} and trans-RuH(Cl)(diop)\textsubscript{2} (1.65 Å)\textsuperscript{218b} (diop = 4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane).

The effects of changes in the ER group on the NMR spectra of these complexes correlate with differences in electron-withdrawing ability and steric bulk. The chemical shift (δ) of the hydride ligand (Table 3.1) decreases as the thiolate ligand is changed in the order:

<table>
<thead>
<tr>
<th>ER</th>
<th>Chemical Shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC\textsubscript{6}H\textsubscript{4}OH\textsubscript{3}CH\textsubscript{3}</td>
<td>-4.23</td>
</tr>
<tr>
<td>SAryl</td>
<td>-4.33±0.03</td>
</tr>
<tr>
<td>SAlkyl</td>
<td>-4.65±0.03</td>
</tr>
<tr>
<td>SeC\textsubscript{6}H\textsubscript{5}</td>
<td>-4.75</td>
</tr>
<tr>
<td>SH</td>
<td>-4.79</td>
</tr>
</tbody>
</table>

This order is consistent with an electronic effect, and is almost the same as that observed for the acidic protons of the free thiols themselves in the same solvent, C\textsubscript{6}D\textsubscript{6}.

<table>
<thead>
<tr>
<th>ER</th>
<th>Chemical Shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArylSH</td>
<td>3.1±0.1</td>
</tr>
<tr>
<td>CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}OH\textsubscript{3}SH</td>
<td>2.92</td>
</tr>
<tr>
<td>AlkylSH</td>
<td>1.2±0.2</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}SeH</td>
<td>1.19</td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The coupling constant \(2J_{PH}\) (Table 3.1) is less variable than the chemical shift, having values of 19.5 (SAryl), 19.8 (SePh), 20.1 (SH) and 20.4 ± 0.1 Hz (SAlkyl). The chemical shift and the coupling constant provide a reliable indication of the nature of the R group in complexes of the formula RuH(SR)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}.

The chemical shift of the \(31P(\text{\textsuperscript{1}H})\) NMR singlet varies in a different order, with the ER = SH and SC\textsubscript{6}H\textsubscript{4}OH\textsubscript{3}CH\textsubscript{3} positions completely reversed compared to the previous sequence,

<table>
<thead>
<tr>
<th>ER</th>
<th>Chemical Shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH</td>
<td>42.01</td>
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<tr>
<td>SC\textsubscript{6}F\textsubscript{5}</td>
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</tr>
<tr>
<td>SAryl</td>
<td>37.35±0.9</td>
</tr>
<tr>
<td>SAlkyl</td>
<td>37.14±0.11</td>
</tr>
<tr>
<td>SeC\textsubscript{6}H\textsubscript{5}</td>
<td>36.98</td>
</tr>
<tr>
<td>SC\textsubscript{6}H\textsubscript{4}OH\textsubscript{3}CH\textsubscript{3}</td>
<td>36.55</td>
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</tbody>
</table>

presumably because of the steric effect of these ER groups on the Ru-P distance. The \(31P\) chemical shift of ccr-RuX(Y)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} complexes depends strongly and inversely on the Ru-P bond length, which in turn depends on the bulk of the X and Y ligands (Fig 3.7). This
Fig. 3.7 Relationship between the $^{31}$P NMR chemical shift and the Ru-P bond length of thiolato-phosphine ruthenium complexes (■). The line is that fitted by Dekleva$^{182}$ to data for triarylphtophine ruthenium complexes (○).

Fig. 3.8 The UV/vis. spectra of cct-RuH(ER)(CO)$_2$(PPh$_3$)$_2$ (9) in THF at room temperature, where ER = SC$_6$H$_4$pCH$_3$ (9b), SCH$_3$ (9c), or SeC$_6$H$_5$ (9h). The spectra of Ru(CO)$_2$(PPh$_3$)$_3$ (2) and RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) are included for comparison.
correlation was reported for a series of ruthenium hydrido, chloro, and/or acetato phosphine complexes. The bond lengths and chemical shifts of the four thiolato complexes 9h, 14a, 14b (Section 4.2), and 21 (Section 5.3) fit the reported correlation well. As has been observed for RuH(Cl)(CO)2(PPh3)2 with the dichloro- and dihydrido- analogues (1 and 3), the 31p chemical shift of RuH(SR)(CO)2(PPh3)2 (42.01 for 2a) is within a few ppm of the average (38.35) of the chemical shifts of Ru(SR)2(CO)2(PPh3)2 (20.40 for R=H, Section 4.2) and RuH2(CO)2(PPh3)2 (56.29 ppm).

The effect of changes in the phosphine ligand of RuH(SCH2CH3)(CO)2(PR3)2 on the 1H NMR spectra is summarized in Table 3.5. The three complexes 9d, 11, and 12 have similar spectra, presumably because PPh113, PPh2Py, and P(C6H4pCH3)3 are similar in nature.

There is no apparent trend in ν(Ru-H) in the IR spectra in Nujol. The symmetric ν(CO) band is randomly scattered within a narrow 11 cm\(^{-1}\) range, while the asymmetric ν(CO) band varies over a wider 27 cm\(^{-1}\) range, in the following order for RuH(X)(CO)2(PPh3)2 in Nujol (the range of ν(CO) values observed for CH2Cl2 solutions of 9 is much narrower):

\[
X = \text{SPhoMe} > \text{SPhpMe} > \text{SH} \equiv \text{SPhmMe} > \text{SPh} \equiv \text{SCH2Ph} = \text{Br}^{164} > \text{SePh} > \text{H} > \text{SMe} >> \text{SEt}
\]

The π backbonding from Ru to the CO π* antibonding orbitals, which lowers the ν(CO), is seen to be stronger in alkyl vs. aryl thiolato complexes; the difference is attributed to the π-acceptor ability of the aromatic rings.

The UV/visible spectra of these complexes (Fig 3.8) contain a strong absorbance near 400 nm, which is most probably due to a thiolate ligand-to-metal charge transfer. The extinction coefficient and \( \lambda_{\text{max}} \) are somewhat higher in the spectra of the aryl vs. alkyl thiolate complexes. The \( \lambda_{\text{max}} \) is particularly high in the selenolate complex.
The small and unpredictable effect of changes in the R group on the charge transfer bands of thiolato complexes has been observed previously in studies of trans-Tc(SR)2(dmpe)2n+ (n=0,1)220a and MoL4n- (L=dithio acid or 1,1-dithiolate ligand, n=2,3,4).220b

Reported complexes similar in structure to 9 include the following Ir79 and Os221 complexes.

where E = S, Se; R = H, C3H7, C4H9, C6H5

3.3 THE REACTION OF RuH2(CO)2(PPh3)2 WITH H2S AND THIOLS

As was shown in the previous report from these laboratories,86 the dihydride complex cct-RuH2(CO)2(PPh3)2 (3) reacts with H2S or thiols at room temperature, giving complete conversion to RuH(SR)(CO)2(PPh3)2 (2, R = H, alkyl or aryl) within 2 h.

\[
\text{RuH2(CO)2(PPh3)2} + \text{RSH} \rightarrow \text{RuH(SR)(CO)2(PPh3)2} + \text{H2} \quad 3.4
\]

The H2 produced in this reaction was qualitatively detected by gas chromatography and quantitatively measured in a gas-uptake experiment. After 50 min at 30°C, the gas production due to reaction 3.4 had slowed to a value of 1.2 equivalents/Ru.
Fig. 3.9 ¹H NMR spectra acquired during the reaction of cct-RuH₂(CO)$_2$(PPh₃)$_2$ (3, 10 mM) with H₂S (1 atm.) in C₆D₆.

a) after 2 to 9 minutes at 25°C
b) after 34 to 39 minutes at 25°C
c) after raising the temperature to 50°C.
The reaction of 3 with excess H$_2$S was monitored by $^1$H NMR spectroscopy (Fig. 3.9). The pseudo-first order log plot is linear for 3 half-lives, and the observed rate constant (at 25.0°C in C$_6$D$_6$) is 5.7 x 10$^{-4}$ s$^{-1}$.

The rate of the reaction with ethanethiol in THF was monitored by the change in absorption at 400 nm in the visible spectrum (Fig. 3.10). Because the spectra of 3 and 9 do not cross (Fig. 3.8), no isosbestic points are observed. If the reaction occurs under pseudo-first order conditions (large excess of EtSH), the log plot (Fig. 3.11) is linear for 4 half-lives. Shaking the vessel between absorbance measurements has no effect on the rate. Over the range 0.36 to 2.86 mM 3 at 95 mM EtSH and 26°C, the rate constant is invariant (Fig. 3.12), which shows that the rate is first order with respect to [3].

The observed rate constant does not vary with changes in the thiol concentration. At 1 mM 3 the observed rate constant is essentially unchanged (Fig. 3.13) even though the thiol concentration was changed from 45 to 190 mM. The rate of reaction is therefore independent of [EtSH]. The value of the rate constant at 26°C is 6.7(±0.2) x 10$^{-4}$ s$^{-1}$ (average of 11 results).

Corresponding results were obtained in the reaction with p-thiocresol. The reaction is again pseudo-first order (Fig. 3.14), with the average rate constant slightly lower, at 6.2 (±0.4) x 10$^{-4}$ s$^{-1}$ (average of 11 results). Again, the observed rate constant is independent of the concentration of 3 (Fig. 3.15) over the range of 0.045 to 0.96 mM 3 at 95 mM thiocresol, and independent of [CH$_3$PC$_6$H$_4$SH] (Fig. 3.16) over the range 9.5 to 110 mM at 0.93 mM 3. The rate law for both systems is therefore

$$\frac{-d[3]}{dt} = k[3]$$

which implies that the first and rate determining step of the mechanism is loss of H$_2$.

$$\begin{align*}
\text{RuH}_2(CO)_2(PPh)_2 & \xrightarrow{k_1, -H_2} \text{Ru}(CO)_2(PPh)_2 \xrightarrow{k_2, RSH} \text{RuH}(SR)(CO)_2(PPh)_2 \\
\text{RuH}_2(CO)_2(PPh)_2 & \xrightarrow{k_1, H_2} \text{Ru}(CO)_2(PPh)_2 \xrightarrow{k_2, -RSH} \text{RuH}(SR)(CO)_2(PPh)_2
\end{align*}$$
Fig. 3.10 Plot of absorbance at 400 nm versus time during the reaction of cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3, 1.0 mM) with ethanethiol (95 mM) in THF at 26°C.

Fig. 3.11 Logarithmic plot of absorbance at 400 nm vs. time for the reaction of cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3, 1.0 mM) with ethanethiol (95 mM) in THF at 26°C.
Fig. 3.12 Dependence of the pseudo-first order rate constant on the concentration of cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) for the reaction with ethanethiol (95 mM) in THF at 26°C. Bars indicate estimated error (8 %) on individual measurements of $k$.

Fig. 3.13 Dependence of the pseudo-first order rate constant on the thiol concentration for the reaction of cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3, 1.0 mM) with ethanethiol in THF at 26°C. Bars indicate estimated error (8 %) on individual measurements of $k$. 
Fig. 3.14 Logarithmic plot of absorbance at 400 nm vs. time for the reaction of $ccl-RuH_2(CO)_2(PPh_3)_2$ (3, 1.0 mM) and p-thiocresol (91 mM) in THF at 26°C.
Fig. 3.15 Dependence of the pseudo-first order rate constant on the concentration of \( \text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3) for the reaction with \( p \)-thiocresol (92 mM) in THF at 26\(^\circ\)C. Bars indicate estimated error (8 \%) on individual measurements of \( k \).

Fig. 3.16 Dependence of the pseudo-first order rate constant on thiol concentration for the reaction of \( \text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3, 0.93 mM) with \( p \)-thiocresol in THF at 26\(^\circ\)C. Bars indicate estimated error (8 \%) on individual measurements of \( k \).
The unobserved intermediate \( \text{"Ru(CO)2(PPh3)2"} \) has been previously invoked to explain the mechanism of the reaction of \( \text{Ru(CO)2(PPh3)3} \) with a variety of ligands.\(^{173}\)

The full rate law for this mechanism is:

\[
\frac{-d[3]}{dt} = \frac{k_2[RSH][k_1[3] + k_2[9]] - k_2[9]}{k_1[H_2] + k_2[RSH]}
\]

If one assumes that \( k_1[H_2] \) is much less than \( k_2[RSH] \) when RSH is present in excess, then this rate law simplifies to

\[
\frac{-d[3]}{dt} = k_1[3]
\]

consistent with the observed data.

The rate of the reaction with 95 mM EtSH is unchanged if one substitutes the argon atmosphere with \( H_2 \) (1 atm). This allows us to put a lower limit on the ratio of \( k_2/k_1 \). The concentration of \( H_2 \) in benzene can be calculated from published data\(^{222}\) to be 14.4 mM under these conditions. If \( k_2[RSH] \gg k_1[H_2] \), then \( k_2/k_1 \gg 0.15 \). However, under 24 atm of \( H_2 \), the reaction is reversed, in that the dihydride can be formed from 9 in the absence of free thiol (Chapter 6).

The temperature dependence of the rate (Fig 3.17) allows the calculation of \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) values (Table 3.6), which do not differ significantly between the reactions with ethanethiol and \( p \)-thiocresol. The essentially zero \( \Delta S^\ddagger \) value is consistent with an activated complex similar in structure to \( \text{Ru(n}_2\text{H}_2)(\text{CO})_2(\text{PPh3})_2 \). A small but positive \( \Delta S \) is expected for the change from a "static metal dihydride" to a rotor-like \( n_2\text{-H}_2 \) complex.\(^{223}\) The \( \Delta H^\ddagger \) values (90 kJ mol\(^{-1}\)) for the reactions of 3 are approximately what one would predict for the cleavage of two Ru-H bonds (about 250 kJ mol\(^{-1}\) each)\(^{224}\) and the formation of an \( H_2 \) molecule (\( H-H \) bond = 436 kJ mol\(^{-1}\)).\(^{225}\) This again is consistent with an activated complex similar in structure to \( \text{Ru(n}_2\text{H}_2)(\text{CO})_2(\text{PPh3})_2 \), assuming that the decrease in the \( H-H \) bond energy of the latter,
Fig. 3.17 Eyring Plot for the Reactions of \textit{cct-}RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (3) with several reagents (Table 3.6).

Table 3.6 Kinetic Data for the Reactions of RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (3) with Various Reagents in C\textsubscript{6}D\textsubscript{6} at 26\textdegree C.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reagent</th>
<th>(k (s^{-1})) (\times 10^{-4})</th>
<th>(\Delta H^\ddagger) (\text{kJ mol}^{-1})</th>
<th>(\Delta S^\ddagger) (\text{J K}^{-1} \text{mol}^{-1})</th>
<th>(\Delta G^\ddagger) (\text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}pSH</td>
<td>6.2(±0.6) (\times 10^{-4})</td>
<td>96 (±8)</td>
<td>10 (±30)</td>
<td>92 (±17)</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}SH</td>
<td>6.7(±0.4) (\times 10^{-4})</td>
<td>84 (±8)</td>
<td>-30 (±30)</td>
<td>92 (±17)</td>
</tr>
<tr>
<td>CO</td>
<td>6.5(±0.2) (\times 10^{-4})</td>
<td>92 (±8)</td>
<td>-20 (±30)</td>
<td>96 (±17)</td>
</tr>
<tr>
<td>PPh\textsubscript{3}</td>
<td>6.4(±0.7) (\times 10^{-4})</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The units for the activation parameters are \(\text{kJ mol}^{-1}\) for \(\Delta H^\ddagger\) and \(\Delta G^\ddagger\), and \(\text{J K}^{-1} \text{mol}^{-1}\) for \(\Delta S^\ddagger\).
compared to free $H_2$, is exactly matched by the Ru-$H_2$ bond energy. Chinn and Heinekey\textsuperscript{222} reported that for the isomerization of trans-[RuH$_2$(Cp)(dmdppe)]$^+$ to [Ru($n^2$H$_2$)(Cp)(dmdppe)]$^+$ (dmdppe = Me$_2$PCH$_2$CH$_2$PPh$_2$),

\[
\begin{align*}
\text{Me}_2P & \quad \text{Ru} \quad \text{Me}_2P \\
\text{H} & \quad \text{H} \quad \text{PPh}_2
\end{align*}
\]

the thermochemical data are $\Delta S = 19\pm1$ J mol$^{-1}$ K$^{-1}$ and $\Delta H = 3.9\pm0.3$ kJ mol$^{-1}$. The activation parameters ($\Delta S^\ddagger = -7.8$ eu or $-33$ J mol$^{-1}$ K$^{-1}$ and $\Delta H^\ddagger = 17.6$ kcal mol$^{-1}$ or 73.7 kJ mol$^{-1}$) were also reported in Fig. 1 of their article, but were mislabelled as being for the reverse reaction. The $\Delta H^\ddagger$ value is similar to that observed in the present system, suggesting that the activated complex in the present system has a structure intermediate between the cis-dihydride and the molecular hydrogen complexes.

The reactions of cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ with non-protonating reagents provide useful comparisons (Table 3.6). The reaction with CO,

\[
\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{CO} \rightarrow \text{Ru}(\text{CO})_3(\text{PPh}_3)_2 + \text{H}_2
\]

monitored by the change in absorbance at 350 nm, is pseudo-first order (Fig. 3.18) with an observed rate constant independent of [3]. The rate constant (at 41°C and 1 atm of CO) is $4.1(\pm0.4) \times 10^{-3}$ s$^{-1}$ (average of 2 results) at 1 mM of the complex, and $4.0 \times 10^{-3}$ s$^{-1}$ (single result) at 0.25 mM. At 0.09 atm of CO and 1 mM 3, the rate decreases by only 5%. The rate constant was measured at several temperatures (Fig. 3.17), and corrected to 26°C, is $6.1 \times 10^{-4}$ s$^{-1}$.

Measurement of the kinetics of the reaction with PPh$_3$

\[
\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{PPh}_3 \rightarrow \text{Ru}(\text{CO})_2(\text{PPh}_3)_3 + \text{H}_2
\]
Fig. 3.18 Logarithmic plot of absorbance at 350 nm vs. time for the reaction of \( \textit{cct-} \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3, \( 1.1 \times 10^{-3} \) M) with CO (1 atm) in THF at 26°C.

Fig. 3.19 Logarithmic plot of absorbance at 400 nm vs. time for the reaction of \( \textit{cct-} \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3, \( 6 \times 10^{-4} \) M) and PPh₃ (0.38 M) in THF at 26°C.
presented some technical difficulties. When monitored by UV/visible spectroscopy under N₂ at 26°C and 400 nm, the reaction did not go to completion unless the cell was stirred or shaken between absorbance measurements. Monitoring the reaction by measuring the gas production in the "gas-uptake" apparatus was tried, because the apparatus allows for shaking. The amount of gas produced (1.0 equivalents/Ru) and the 31P{¹H} NMR spectra showed the reaction to be complete after 3 days. However, the pseudo-first order log plots of gas evolution were not linear. These problems probably resulted from the back reaction, which is rapid at this temperature under 1 atm of H₂ (in the absence of added phosphine), and may be significant under the conditions used for reaction 3.6 if the diffusion of the H₂ product into the gas phase is slow. If this is the case, and if the rate law is similar to that for thiols, then k₋₁[H₂] is of the same magnitude as k₂[PPh₃] after the generation of some H₂, and therefore k₋₁ must be one to two orders of magnitude larger than k₂ (assuming [H₂] = 1/2 [3]₀ = 0.5 mM, [PPh₃] = 60 mM). Therefore, the rate of the reaction of the intermediate, Ru(CO)₂(PPh₃)₂, with EtSH is one or more magnitudes faster than the reaction of the same intermediate with PPh₃.

Under conditions designed to guarantee that k₋₁[H₂] is much less than k₂[PPh₃], namely [PPh₃]/[3] greater than 130 and vigorous shaking between absorbance measurements to ensure H₂ removal, the pseudo-first order log plot is linear for 3 half-lives (Fig. 3.19). At 0.33 mM of the dihydride, and 50 mM PPh₃, the rate constant is 6.4 (±0.7) x 10⁻⁴ s⁻¹ (average of 3 experiments), and at 375 mM PPh₃, the rate constant was 6.5 x 10⁻⁴ s⁻¹ (single experiment). Therefore, the observed rate law and suggested mechanism for the reactions with CO and PPh₃ correspond to those for the thiol reactions. As predicted by the mechanism, the observed pseudo-first order rate constant k is independent of the concentration or nature of the added reagent, and corresponds to k₁.

Of the three products of these reactions, only one, Ru(CO)₂(PPh₃)₃, can be converted back into 3 by the application of 1 atm of H₂ to its solution (in the absence of free phosphine). The other two, RuH(SR)(CO)₂(PPh₃)₂ (Section 6.1.4) and Ru(CO)₃(PPh₃)₂, require
elevated pressures for conversion back to 3.

RuH2(CO)2(PPh3)2 failed to react with methanol (247 mM) in THF within 1 h.

3.4 THE REACTION OF RuH2(dpm)2 WITH H2S AND THIOLS

The mixture of cis- and trans-RuH2(dpm)2 (7) reacts too quickly with H2S (reaction 3.7, R=H) at room temperature to monitor the course of the reaction accurately by NMR spectroscopy. 191

\[
\text{RuH2(dpm)2 + RSH} \rightarrow \text{RuH(SR)(dpm)2 + H2} \quad \text{3.7}
\]

\[dpm = \text{Ph2PCH2PPh2}\]
\[R = \begin{array}{c}
\text{a} \text{H, b C6H5, c CH2C6H5}
\end{array}\]

The product of the reaction with H2S is exclusively trans-RuH(SH)(dpm)2 (Fig. 3.20).

Reaction 3.7 (R = Ph, CH2Ph) produces 1:5 mixtures of cis- and trans-RuH(SR)(dpm)2. These complexes are easily identified by their characteristic \(1H\) and \(31P\{1H\}\) NMR spectra (Figs. 3.21 through 3.23, and Table 3.7). The hydride region of the \(1H\) NMR spectrum contains quintets for the trans-complexes and \(AX2YZ\) (doublet of doublet of triplet) patterns for the cis complexes. The \(2J_{\text{transPH}}\) couplings are 90 to 100 Hz, while the \(2J_{\text{cisPH}}\) coupling constants are 16 to 23 Hz, typical values for such constants. 208 The \(31P\{1H\}\) NMR spectrum (Fig. 3.23) contains a strong singlet for the major product, trans-13, and four weak multiplets for cis-13, corresponding to the four different phosphine atoms in the molecule. The following assignments for cis-RuH(SPh)(dpm)2 in toluene-d8 are consistent with the NMR spectra, but have not been confirmed by decoupling experiments. The \(2J_{\text{cisPP}}\) values are assumed to be negative, following a generalization suggested by Baker and Field 226 that this is usually the case (an opposing view has been expressed by Bookham et al.). 227
The reaction with thiophenol (Fig. 3.24) is an order of magnitude faster at 25°C than that with α-toluenethiol (Fig. 3.25). There is too much scatter in the data to conclude that the rate of loss of cis-RuH2(dpm)2 is pseudo-first order. However, it is clear that the rate depended strongly on the thiol concentration (Fig. 3.25).

A mechanism consistent with a dependence on the nature and concentration of thiol is the following, in which the cis- and trans-RuH2(dpm)2 reactants are treated as one species.

\[
RSH \xrightleftharpoons{K_1} RS^- + H^+
\]

\[
\begin{align*}
RuH_2(dpm)_2 + H^+ & \xrightarrow{k_2} [RuH(H_2)(dpm)_2]^+ \\
& \xrightarrow{k_3 -H_2} [RuH(dpm)_2]^+ \\
& \xrightarrow{SR^- \text{ fast}} RuH(SR)(dpm)_2
\end{align*}
\]

Assuming a steady state condition for the unobserved molecular hydrogen species [RuH(n^2H_2)(dpm)_2]^+, and assuming that \(K_1\) is small, the rate law for this mechanism is:

\[
d\left[13\right] = \frac{k_2 k_3 K_1^{1/2} [RSH]^{1/2}}{k_2 + k_3}
\]

However, the mechanism is incomplete because of the question of the nature of the equilibrium between cis- and trans-RuH2(dpm)2 at room temperature. According to Chaudret et
After 8 min

(trans-13a (RuH))

(cis-7 (RuH))

trans-13a (RuSH)

10 min

20 min

Fig. 3.20 a) $^1$H NMR spectra (hydride region) for the reaction of cis- and trans-RuH$_2$(dpm)$_2$ (11 mM) with H$_2$S in C$_6$D$_6$ at 25°C and 300 MHz.\textsuperscript{191}
Fig. 3.20 b) $^1$H NMR spectra (methylene region) for the reaction of cis- and trans-RuH$_2$(dpm)$_2$ (11 mM) with H$_2$S in C$_6$D$_6$ at 25°C and 300 MHz.\textsuperscript{191}
Fig. 3.21 $^1$H NMR spectra (hydride region) for the reaction of RuH$_2$(dpm)$_2$ (4.1 mM) with PhCH$_2$SH (280 mM) in C$_6$D$_6$ at 25.0°C.
Fig. 3.22 ¹H NMR spectrum (300 MHz) of a sample of RuH(SPh)(dpm)₂ prepared in situ from RuH₂(dpm)₂ and thiophenol in C₆D₆, with expanded views of the hydride region and part of the methylene region.
Fig. 3.23 a) $^{31}$P$^1$H NMR spectrum (expanded vertical scale) of a sample of RuH(SPh)(dpm)$_2$ (13b) prepared in situ from RuH$_2$(dpm)$_2$ and thiophenol in toluene-d$_8$.

b) Simulated spectrum for cis-13b.
Table 3.7 NMR Data for Ru(X)(Y)(dpm)₂ Complexes in C₆D₆ solution.ᵃ

a) *trans* isomers

<table>
<thead>
<tr>
<th>XY</th>
<th>31P</th>
<th>Ru-Hᵇ</th>
<th>2JₚH</th>
<th>PCH₂P</th>
<th>SH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)₂</td>
<td>9.11</td>
<td>-4.80</td>
<td>18.9</td>
<td>4.63</td>
<td></td>
</tr>
<tr>
<td>H(SH)ᵈ</td>
<td>0.39</td>
<td>-9.46</td>
<td>19</td>
<td>4.56, 5.23</td>
<td>-3.55 (br)</td>
</tr>
<tr>
<td>H(SPh)ᵉ</td>
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<td>-10.86</td>
<td>19.9</td>
<td>4.27, 4.78</td>
<td></td>
</tr>
<tr>
<td>H(SBz)ᵈ</td>
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<td>-10.16</td>
<td>20.0</td>
<td>4.44, 5.19</td>
<td></td>
</tr>
<tr>
<td>(SH)₂</td>
<td>-7.05</td>
<td>-</td>
<td>-</td>
<td>5.10</td>
<td>-3.73 (1.3JₚH=5.7)</td>
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</table>

b) *cis* isomers

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<th>XY</th>
<th>31P</th>
<th>2JₚPP</th>
<th>Ru-Hᶠ</th>
<th>2JₚH</th>
<th>PCH₂P</th>
<th>SH</th>
</tr>
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<tr>
<td>(H)₂</td>
<td>14.06</td>
<td>28.4</td>
<td>-7.53</td>
<td>72.7, 18.3</td>
<td>4.10, 4.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.57</td>
<td>29.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(SPh)ᵈ</td>
<td>v.i.</td>
<td>v.i.</td>
<td>-6.29</td>
<td>92, 24, 16</td>
<td>n.r.</td>
<td>-</td>
</tr>
<tr>
<td>H(SBz)ᵈ</td>
<td>n.r.</td>
<td>n.r.</td>
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<td>101</td>
<td>n.r.</td>
<td>-</td>
</tr>
<tr>
<td>(SH)₂</td>
<td>-5.93</td>
<td>28.5</td>
<td>-</td>
<td></td>
<td>4.62, 5.10</td>
<td>-1.92</td>
</tr>
<tr>
<td></td>
<td>-22.65</td>
<td>26.5</td>
<td></td>
<td></td>
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</tbody>
</table>

ᵃ Bz=CH₂C₆H₅, n.r.=not resolved, v.i.=vide infra (the ³¹P{¹H} NMR spectrum of *cis*-RuH(SPh)(dpm)₂ is described in Section 3.4).
ᵇ quintets.
ᶜ The NMR spectra of RuH₂(dpm)₂ have been reported previously.¹⁸⁷
ᵈ prepared *in situ*.
ᵉ prepared *in situ* in toluene-d₈.
ᶠ ddtt.
al., the cis:trans ratio of a prepared sample in solution is constant over a wide range of temperatures, which suggests that the isomerization reaction is very slow or nonexistent. However, they concluded that there was a temperature-independent equilibrium between the isomers because the reactions with HBF4/H2O and CH2Cl2 gave only the trans isomers of the products [RuH(H2O)(dpm)2]+ and RuH(Cl)(dpm)2, respectively. In general, complexes of the type MH2(PR3)4 and MH2L2 (L=chelating diphosphine) are stereochemically non-rigid. Although the trans-MH2L2 complexes can be generated in situ, via deprotonation of the molecular H2 species,

\[
\text{trans } [\text{MH}(n^2\text{H}_2)\text{L}_2]^+ \rightarrow \text{trans } \text{MH}_2\text{L}_2 + \text{H}^+ \\
M = \text{Ru, Fe}, \quad L = \text{dppe}
\]

the subsequent isomerization to the cis complexes is rapid at room temperature. It is therefore believed that cis- and trans-7 are in equilibrium at room temperature, and one or both of them react with the proton from the thiol to form [RuH(n^2H2)(dpm)2]+.

During the reaction with thiol, the ratio of cis:trans 7 does not change over time, even as the concentrations of each decline. This ratio is 6.7 (±1): 1 (average of 11 measurements), somewhat higher than the ratio observed in the absence of thiol. This could be caused by a situation wherein the reaction of trans-7 with H+ is faster than both the reaction of cis-7 with H+ and the isomerization of cis-7 to trans-7.

The ratio of the isomers of the product is constant during the reaction (Fig. 3.24) and up to 4 h after reaction 3.7 was complete. The two isomers of RuH(SR)(dpm)2 are possibly being formed independently by parallel reactions, or as a single isomer, the other isomer being produced by a rapid equilibrium between the isomers. The latter possibility is less likely, because other than the dihydrides, most six-coordinate compounds are non-fluxional.

The proposed mechanism has to take into account the possible equilibrium between the isomers of the dihydride 7. Scheme 3.1 shows the suggested mechanism.

After a study of the related reaction,
Fig. 3.24 Time dependence of concentrations during the reaction of RuH₂(dpm)₂ (4.6 mM) with thiophenol (70 mM) in C₆D₆ at 25°C. Dashed line shows an extrapolation to the concentration of cis-7 in a solution of 7 in C₆D₆.

Fig. 3.25 Time dependence of the concentration of cis-RuH₂(dpm)₂ (cis-7) in the reaction with thiols in C₆D₆ at 25°C and [7]₀ = 4.2 mM.
FeH₂(dmpe)₂ + RSH → FeH(SR)(dmpe)₂ + H₂

\[ \text{dmpe}=(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P(\text{CH}_3)}_2 \]

Boyd et al.\textsuperscript{230} proposed a mechanism analogous to that in Scheme 3.1 because they observed the intermediate \textit{trans}-[FeH(\text{n}_2\text{H}_2)(\text{dmpe})₂]⁺ during the reactions with thiols\textsuperscript{230} and alcohols,\textsuperscript{231} and because the hydride ligands of FeH₂(dmpe)₂ exchanged with added D₂ in the presence of alkanethiols.

\[ \text{FeH}_2(\text{dmpe})_2 + \text{REH} \rightleftharpoons \text{[FeH(n}_2\text{H}_2)(\text{dmpe})_2]' + \text{RE}^- \]

\( E = \text{O, S (ref. 230)} \)

In the present ruthenium system, [RuH(\text{n}_2\text{H}_2)(\text{dpm})₂]⁺ is not detected, although a minor intermediate is observed, which reaches a maximum concentration (in the reaction with thiophenol) of 12% after 0.5 half-lives (Figs. 3.22 and 3.24). This unknown species appears in lower concentrations in the reaction with \( \alpha \)-toluenethiol, but not at all in the reaction with H₂S. The species also appears in the \(^1\text{H}\) spectrum of a mixture of RuH₂(dpm)₂ and \( p \)-toluenesulphonic acid (Fig. 3.26). It is seen in each case as a quintet (\( \delta = 9.6 \text{ ppm}, \text{ } ^2\text{J}_{\text{PH}} = 19.3 \text{ Hz in toluene-d8} \) in the hydride region of the \( ^1\text{H}\) NMR spectrum, indicative of a complex of the type \textit{trans}-RuH(X)(dpm)₂. The unknown is not \textit{trans}-[RuH(H₂O)(dpm)₂]⁺, because this complex resonates at a higher field.\textsuperscript{187} There was no peak in the \( ^1\text{H}\) NMR spectrum consistent with a molecular hydrogen ligand, even at lower temperatures, suggesting that the unknown is not \textit{trans}-[RuH(\text{n}_2\text{H}_2)(\text{dpm})₂]⁺. An inversion-recovery experiment was designed which produces a spectrum with positive peaks for all of the protons which have \( T_1 \) relaxation times less than 60 ms. Most molecular hydrogen complexes have \( T_1 \)'s of less than 100 ms at high field strengths, unless exchange is occurring with a terminal hydride ligand,\textsuperscript{232-3} and indeed such ruthenium complexes have particularly low \( T_1 \) values.\textsuperscript{232,234} No positive peak was observed within the range \( \delta +10 \) to \( -10 \) ppm, when a spectrum was acquired with this pulse sequence during a reaction of RuH₂(dpm)₂ with PhSH. Thus, there is no direct evidence for the presence of [RuH(\text{n}_2\text{H}_2)(\text{dpm})₂]⁺. It is possible, however, that the \( n^2\text{H}_2 \) peak is not observed.
Scheme 3.1 Proposed mechanism for the reaction of RuH$_2$(dpm)$_2$ with thiols, based on that proposed by Boyd et al.$^{229}$
Fig. 3.26 The $^1$H NMR spectrum (hydride region) acquired during the reaction of RuH$_2$(dpm)$_2$ (7.9 mM) with $p$-toluenesulphonic acid (200 mM). The products have not been identified.
because it is broad, or that the unknown complex is \([\text{RuH(dpm)}_2]^+\), in analogy to the intermediate proposed by Boyd \textit{et al.}\textsuperscript{230}

The difference in the mechanisms for the reactions of \(\text{RuH}_2(\text{dpm})_2\) (7) and \(\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2\) (3) with thiols is believed to result from the more basic hydride ligands of the former complex. Thus, the hydride ligands of both \textit{cis}- and \textit{trans}-7 exchange with 4% CD\(_3\)OD in C\(_6\)D\(_6\) in 10 min at room temperature, while the intensity of the hydride signals in the \(1\text{H} \) NMR spectrum of 3 under the same conditions does not decrease significantly even after 2 h. The exchange reaction of 7 with CD\(_3\)OD probably proceeds by an equilibrium analogous to reaction 3.11. The acidity of \(\text{n}^2\text{H}_2\) complexes is decreased by increased electron density at the metal centre.\textsuperscript{229,235} Such complexes containing electron-withdrawing ancillary ligands, such as \([\text{Ru}(\text{n}^5\text{C}_5(\text{CH}_3)_5)(\text{n}^2\text{H}_2)(\text{CO})_2]^+ (\text{pK}_a = -5)\textsuperscript{236}\) are much more acidic than complexes containing electron-donating ligands such as \([\text{Ru}(\text{n}^5\text{C}_5\text{H}_5)(\text{n}^2\text{H}_2)(\text{dpm})]^+ (\text{pK}_a = 7.1).\textsuperscript{235}\) Complex 3 is probably insufficiently basic to be protonated by a thiol.

Why is the \textit{trans} isomer of \(\text{RuH(X)(dpm)}_2\) observed exclusively (X=SH and BH\(_4\) in this work, H\(_2\)O\textsuperscript{+187} and Cl\textsuperscript{187}), or predominantly (X=SPh and SBz), but \(\text{RuH}_2(\text{dpm})_2\) is predominantly \textit{cis}? This tendency of \(\text{RuH(X)(dpm)}_2\) to exist solely or predominantly as a \textit{trans} complex has been noted previously.\textsuperscript{237} Of the complexes of this type, it is likely that only \(\text{RuH}_2(\text{dpm})_2\) is fluxional in solution at room temperature, although the process is slow on the NMR time-scale. Its geometry therefore depends on thermodynamic factors such as steric interactions between PPh\(_2\) groups (favouring \textit{trans}), and the \textit{trans}-influence of the hydride ligands (favouring \textit{cis} geometry). Obviously, the latter effect is stronger; of the 12 dihydrido phosphine ruthenium complexes studied by Meakin \textit{et al.},\textsuperscript{228} nine are exclusively \textit{cis} in solution, and the other three are predominantly \textit{cis}. The remaining \(\text{RuX(Y)(dpm)}_2\) complexes, with the possible exception of \(\text{RuH(BH}_4)(\text{dpm})_2\), are probably geometrically rigid. The factors which determine the observed geometry are therefore kinetic rather than thermodynamic, and depend on the mechanism of the formation reaction. The preponderance of \textit{trans} products is
Scheme 3.2 A partial mechanism for the formation of RuX(Y)(dpm)₂ complexes.

consistent with mechanisms involving 5-coordinate square-pyramidal [RuX(dpm)₂]+ intermediates. Of the two possible geometries for such intermediates, that with 4 rather than 3 equatorial phosphines is sterically favoured. The trans product is therefore expected to be the major product (Scheme 3.2), unless Y or X is large. If X is large, then the other intermediate will be favoured, and a cis product obtained. If Y is large, then the reaction yielding the trans-product will be slower than the reaction yielding the cis-product.

3.5 THE THIOL EXCHANGE REACTIONS OF cct-RuH(SR)(CO)₂(PPh₃)₂

The title complexes (9) exchange with added thiols.

\[ \text{RuH(SR)(CO)₂(PPh₃)₂ + R'SH} \iff \text{RuH(SR')(CO)₂(PPh₃)₂ + RSH} \]
For example, the reaction of \textit{ccr-RuH(Se)(CO)}_2(PPh_3)_2 (9d) with thiophenol generates \textit{ccr-RuH(SPh)(CO)}_2(PPh_3)_2 (9i) and free ethanethiol; both products are detected by \textit{1H} NMR spectroscopy (Fig. 3.27).

The reaction of \textit{ccr-RuH_2(CO)}_2(PPh_3)_2 (3) with a mixture of 5 equivalents each of ethanethiol and thiophenol initially produces a mixture of 9i and 9d, but the final product is almost exclusively 9i. The reactions of 3 with various binary mixtures of thiols were monitored by \textit{1H} and/or \textit{31P{1H}} NMR spectroscopy in C_6D_6 at 50°C (Fig. 3.28) to determine the equilibrium constants for reaction 3.12. The observed equilibrium constants (±10%) are 2.2 (R/R' = C_6H_4pCH_3/C_6H_5), 71 (CH_2CH_3/C_6H_5), and 8.4 (CH_2CH_3/CH_2C_6H_5). To confirm that equilibrium had been reached, the equilibrium between 9i and 9d (R/R' = CH_2CH_3/C_6H_5) was approached from the "other side" by adding EtSH to a solution of 9i. After one hour, no further reaction was detected. Although equilibrium may not have been reached in this experiment, the K_{obs} value calculated from the results (83) serves as an upper limit for K_{eq}.

Comparisons of the thermodynamic stability of complexes of the formula \textit{ccr-RuH(SR)(CO)}_2(PPh_3)_2 (9) can be more easily made if the equilibrium constants are recalculated as K_{eq} values for reaction 3.12 where R = Et.

\[
K_{eq} = \frac{\text{[RuH(SR')(CO)}_2(PPh_3)_2][EtSH]}{\text{[RuH(Se)(CO)}_2(PPh_3)_2][R' SH]}
\]

These K_{eq} values decrease in the following order:

R' = C_6H_5 > C_6H_4pCH_3 > CH_2C_6H_5 > CH_2CH_3

K_{eq} = 71, 32, 8.4, 1

It is clear that the thermodynamic stability of 9 depends on the nature of the thiolate group, the aryl thiolato complexes being more stable than the alkyl thiolato complexes. This order of stability is similar to the order of acidity of the free thiols in aqueous solution,

C_6H_5SH \cong CH_3C_6H_4pSH > C_6H_5CH_2SH > CH_3CH_2SH
after 12-16 min

62-66 min

187-192 min

Fig. 3.27 1H NMR spectra acquired during the reaction of cct-RuH(SET)(CO)_2(PPh_3)_2 (8 mM) with thiophenol (1500 mM) in C_6D_6 at 22°C.
Fig. 3.28 Time dependence of concentrations during the reaction of ccf-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (9.9 mM) with PhSH (1.6 M) and EtSH (2.5 M) in C$_6$D$_6$ at 36° C.

Table 3.8 Published $p$K$_a$ Values for Selected Thiols in Aqueous Solution.

<table>
<thead>
<tr>
<th>Thiol</th>
<th>$p$K$_a$</th>
<th>$T$(°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td>7.0</td>
<td>25</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>25</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td>7.04</td>
<td>18</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>7.06</td>
<td>25</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>7.24</td>
<td>25</td>
<td>242</td>
</tr>
<tr>
<td>CH$_3$SH</td>
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<td>25</td>
<td>243</td>
</tr>
<tr>
<td>CH$_3$CH$_2$SH</td>
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<td>25</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>10.50</td>
<td>20</td>
<td>244</td>
</tr>
<tr>
<td></td>
<td>10.60</td>
<td>25</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>10.61</td>
<td>25</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td>25</td>
<td>239</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHSH</td>
<td>10.86</td>
<td>25</td>
<td>243</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_2$SH</td>
<td>9.4</td>
<td>25</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td>10.7</td>
<td>25</td>
<td>243</td>
</tr>
<tr>
<td>C$_6$H$_5$SH</td>
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<td>25</td>
<td>245</td>
</tr>
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<td></td>
<td>6.5</td>
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<td>25</td>
<td>243</td>
</tr>
<tr>
<td>CH$_3$C$_6$H$_4$mSH</td>
<td>6.58</td>
<td>25</td>
<td>243</td>
</tr>
<tr>
<td>CH$_3$C$_6$H$_4$pSH</td>
<td>6.52</td>
<td>25</td>
<td>243</td>
</tr>
<tr>
<td>C$_6$F$_5$SH</td>
<td>2.68</td>
<td>25</td>
<td>245</td>
</tr>
</tbody>
</table>

* not available.
although the published values of the $pK_a$'s of thiols show some variation; the value for thiophenol in particular varies widely (Table 3.8). The most stable complexes in the series 9 are those with the least basic thiolate ligands. The reason for this trend is not known. The same type of relationship between the acidity of a free thiol and its tendency to replace a thiolate ligand was observed by Que et al.,247 during studies of the thiol exchange reactions of an iron tetramer.

$$[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} + n\text{R'SH} \rightleftharpoons [\text{Fe}_4\text{S}_4(\text{SR})_{4-n}(\text{SR}')_n]^{2-} + n\text{RSH} \quad 3.13$$

(refs. 247-8)

They noted that acidity is not the only factor involved. For example, sulphur ligands such as ethanethiolate bind much more strongly than oxygen ligands such as $p$-cresolate, despite the fact that the two reagents are equally basic.

The pseudo-first order rate constant for the forward step of the reaction of 9d with thiophenol (reaction 3.12, R=Et, R'=Ph) in C$_6$D$_6$ at 22(±1)°C is essentially independent of [9d]. The rate constant is $1.9 \times 10^{-4}$ s$^{-1}$ at 1.8 mM 9d (single result) and $2.0(±0.2) \times 10^{-4}$ s$^{-1}$ at 9 mM (average of 4 results). The pseudo-first order log plot of [9d] is linear for 3 half-lives (Fig. 3.29). The rate is also independent of the thiophenol concentration (Fig. 3.30) over the range 0.12 M to 3.4 M.

$$-\frac{d[9d]}{dt} = k[9d]$$

The rate constants and rate law are identical for the reactions of 9 with R'SH (reaction 3.12), with CO (Section 6.1.2), and with P(C$_6$H$_4$pCH$_3$)$_3$ (Section 6.1.1). The mechanisms for all three of these reactions are thought to begin with elimination of PPh$_3$, followed by coordination of R'SH, CO, or P(C$_6$H$_4$pCH$_3$)$_3$, respectively. If this is the case, then the mechanism for reaction 3.12 may be that in Scheme 3.3. The expected rate law, assuming that the back reactions with rate constants $k$-2 and $k$-3 are negligible, and reaction step $k$4 is rapid, is
Fig. 3.29 Logarithmic plot of the concentration of 9d versus time during the reaction of 
cct-RuH(SEt)(CO)2(PPh3)2 (9d, 8.5 mM) and PhSH (1.5 M) in C6D6 at 22°C.

Fig. 3.30 Dependence of the pseudo-first order rate constant on [PhSH] for the 
reaction with cct-RuH(SEt)(CO)2(PPh3)2 (9 mM) in C6D6 at 22°C. Bars indicate 
estimated error (10 %) on individual measurements of k.
Scheme 3.3 The proposed mechanism for the reaction of RuH(SR)(CO)\(_2\)(PPh\(_3\))\(_2\) (9) with R'SH.
rate = \frac{k_1 k_2 [9] [R'SH]}{k_1 [PPh_3] + k_2 [R'SH]}

or, if \( k_1 [PPh_3] \ll k_2 [R'SH] \),

rate = k_1 [9]

as observed. If PPh_3 were added in sufficiently high concentrations, then a decrease in the rate would be observed. In fact, only a small decrease in the rate constant (2.1 x 10^{-3}, 1.7 x 10^{-3}, and 1.8 x 10^{-3} s^{-1} \pm 10\% at [PPh_3]=0, 260, and 660 mM, respectively) is observed for the reaction of 9c (R=Me, [9c]_0=6 mM) with PhSH (80 mM) in C_6D_6, monitored by NMR spectroscopy at 40°C. This result suggests that \( k_1 \ll k_2 \).

The thiol proton in the proposed intermediate [RuH(SR)(RSH)(CO)_2(PPh_3)] may be equally bonded to the two sulphur atoms, in the same way as the sodium atom in the complex [Ru(CO)_2(PPh_3)(\mu SEt)_2(\mu 3SEt)Na(THF)]_2 (Section 5.2) is shared by three sulphurs on the same ruthenium centre. Similar sharing of a proton by a thiolate and a chloride ligand on the same metal centre is observed in the complex Ru(HCl)(buS_4)(PPh_3) (buS_4^{2-} = 1,2-bis((3,5-di-tert-butyl-2-mercapto-phenyl)thio)ethanato(2-)).\textsuperscript{249} The structure of this complex is shown in Section 7.2.

3.6 THE SLOWER REACTION OF RuH(SR)(CO)_2(PPh_3)_2 WITH H_2S AND THIOLS

The reactions of free R'SH with RuH(SR)(CO)_2(PPh_3)_2 (9) result in substitution, by R'S\(^-\), of either the thiolate ligand (reaction 3.12), or the hydride ligand (reaction 3.14). The latter reaction, which is significantly slower, forms a bis-thiolato complex (14, Section 4.2).

\[
\text{RuH(SR)(CO)_2(PPh_3)_2 + RSH} \rightarrow \text{Ru(SR)2(CO)_2(PPh_3)_2 + H}_2
\]

The new complex 14 can therefore be prepared in one "pot," via 9, from the reaction of Ru(CO)_2(PPh_3)_3 (2) or RuH_2(CO)_2(PPh_3)_2 (3) with thiols. For example, 2 reacts with excess
Ill PhSH in THF at room temperature to produce RuH(SPh)(CO)₂(PPh₃)₂ within 5 min (100% conversion, reaction 3.3), and Ru(SPh)₂(CO)₂(PPh₃)₂ after 3 days (46%, reaction 3.14).

Because of the extremely slow rate of reaction 3.14 and the further reaction of 14 (R=H) under conditions of heat or light (Chapter 6), reaction 3.14 was not successfully monitored kinetically or used as the synthetic route to 14 (except for R=H). As Chapter 4 describes, the reaction of disulphides with Ru(CO)₂(PPPh₃)₃ is the preparative route of choice for 14 (R=aryl). The characterization of 14 is therefore described in that chapter.

The reaction of 3 with acetic acid:

$$\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 + 2\text{HOAc} \rightleftharpoons \text{Ru(OAc)}_2(\text{CO})_2(\text{PPh}_3)_2 + 2\text{H}_2$$

(3.15)

probably proceeds via RuH(OAc)(CO)₂(PPh₃)₂, if the chemistry is analogous to that observed with thiols. However, there was no mention, in the report, of any attempt to detect or isolate the acetato(hydrido)-intermediate, which has since been observed in the present work (Chapter 2).

Reaction 3.14 (R=H) was followed by NMR spectroscopy at 60°C (Fig. 3.31). The starting material, RuH(SH)(CO)₂(PPh₃)₂ (9a), is easily generated in-situ by the reaction of 3 with excess H₂S at 60°C for 3 min. The 9a thus generated reacts with H₂S more slowly. After 40 min (almost 2 half-lives), free PPh₃ is observed, indicating some decomposition or side-reaction is occurring. Up to this point, the reaction has a half-life of approximately 1400 s, assuming pseudo-first order behaviour. For comparison, reaction 3.4 (which forms 9 from RuH₂(CO)₂(PPh₃)₂ and H₂S or RSH) has a half-life of 24 s at this temperature in THF (calculated by extrapolation of data acquired between 26 and 46°C).

Although these preliminary data do not include the dependence of the rate on [H₂S], it is possible to speculate on the mechanism of reaction 3.14. Reductive elimination of thiol from RuH(SR)(CO)₂(PPh₃)₂ cannot be the first step, as this would subsequently lead to the reformation of the starting material (i.e. no reaction would occur). The first steps of three possible mechanisms are protonation of the hydride (Scheme 3.4), elimination of PPh₃ (Scheme 3.5), or (less likely) elimination of CO.
Fig. 3.31 $^1$H NMR spectra acquired during the reaction of \textit{ccl}-RuH(SH)(CO)$_2$(PPh)$_3$)$_2$ (9a) with H$_2$S in C$_6$D$_6$ at 60°C.
Scheme 3.4 A mechanism for the reaction of $\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2$ (2) with RSH, in which the first step is protonation of the hydride.

\[
\begin{align*}
\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2 & \xrightarrow{k_1, \text{H}^+} \text{RuH}^+(\text{SR})(\text{CO})_2(\text{PPh}_3)_2 \\
& \xrightarrow{k_2, \text{H}_2} \text{Ru}(\text{SR})(\text{CO})_2(\text{PPh}_3)_2
\end{align*}
\]

Scheme 3.5 A possible mechanism for the reaction of $\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2$ (2) with RSH, in which the first step is dissociation of $\text{PPh}_3$ from the complex.
The first of these mechanisms involves the formation of a molecular hydrogen complex, 
\[ \text{[Ru}\left(\text{n}^2\text{H}_2\right)\text{(SR)}(\text{CO})_2(\text{PPh}_3)_2]^+ \]. Two types of experiments to detect this complex or the chloro analogue were performed.

a) The reactions of acids such as alcohols,\(^{251}\) HBF\(_4/\text{Et}_2\text{O},^{192,236}\) and H\(_2\text{C(SO}_2\text{CF}_3)_2\)\(^{252}\) have been used to protonate hydrides to form molecular hydrogen complexes. Attempts at the protonation of RuH(S\(_2\text{H}_4\text{p-CH}_3\))(\text{CO})_2(\text{PPh}_3)_2 by HBF\(_4/\text{Et}_2\text{O}, \text{HBF}_4/\text{H}_2\text{O}\) or HCl(aqueous) failed to produce evidence of a molecular hydrogen complex (Section 6.1.5).

b) Metathesis reactions of transition metal chloro-complexes with NaBPh\(_4\) under H\(_2\) gas have also been used to generate molecular hydrogen complexes.\(^{253}\) A mixture of RuCl\(_2\)(\text{CO})_2(\text{PPh}_3)_2 and NaBPh\(_4\) in acetone under H\(_2\) was passed through diatomaceous earth after reacting at room temperature for 90 min, and a white solid was precipitated by removal of some of the solvent under vacuum. The \(31\text{P}^1\text{H}\) NMR spectrum shows that the only phosphorus-containing compound in the recovered solid was RuCl\(_2\)(\text{CO})_2(\text{PPh}_3)_2.

The failure to produce a \(n^2\text{H}_2\) complex may result from the insufficient basicity of the hydride ligand of 9. As described in Section 3.4, the presence of carbonyl ligands greatly decreases the basicity of hydrido-complexes. The intermediate \(n^2\text{H}_2\) complex shown in Scheme 3.4 is therefore unlikely.

The mechanisms which involve initial loss of CO or PPh\(_3\) do not require a \(n^2\text{H}_2\) complex as an intermediate. Because the phosphine ligands of 9 are known to be labile (Section 6.1.1), the latter mechanism (Scheme 3.5) is considered more likely. It involves the same initial steps and the same intermediate, [RuH(SR)(RSH)(\text{CO})_2(PPh_3)], which were proposed for the reaction of 9 with R'SH (reaction 3.12, Scheme 3.3). The intermediate therefore represents the branching point of the two reactions. If thiol is eliminated (which is statistically favoured), then the product will be 9; if H\(_2\) is eliminated, then the product will be Ru(SR)_2(\text{CO})_2(PPh_3)_2 (14).
3.7 THE REACTION OF RuH(SH)(dpm)\(_2\) WITH H\(_2\)S

The title complex (13) probably undergoes thiol exchange reactions in a manner similar to reaction 3.12, although experiments to confirm this were not performed. The title complex also reacts with H\(_2\)S and presumably other thiols to produce a *bis*-thiolate complex (15, cf. reaction 3.14).

\[
\text{RuH(SH)(dpm)\(_2\) + H\(_2\)S} \rightarrow \text{Ru(SH)\(_2\)(dpm)\(_2\) + H\(_2\)}
\]

(3.16)

The reaction of *trans*-RuH(SH)(dpm)\(_2\) (13a) with H\(_2\)S was monitored by NMR spectroscopy (Fig. 3.32). A C\(_6\)D\(_6\) solution of RuH\(_2\)(dpm)\(_2\) (7.4 mM) under H\(_2\)S (1 atm) reacts within 3 min at 60°C to form 13a, which reacts more slowly (T\(_{1/2}\) = 20 min) to form a 1:1.8 mixture of *cis-* and *trans-*15. The H\(_2\) produced in the reaction was detected by \(^1\)H NMR spectroscopy. The rate of disappearance of the hydride signal of 13a is pseudo-first order, with a log plot linear over more than 3 half-lives (Fig. 3.33). The rate dependence on [H\(_2\)S] was not determined.

The \(^1\)H NMR spectrum of 15 in C\(_6\)D\(_6\) (Fig. 3.32) contains two signals at -1.92 and -3.74 ppm for the *cis* and *trans* isomers, respectively. The former signal is a complicated multiplet, but the latter is a simple quintet (\(3J_{PH}=5.6\) Hz) due to the *cis* coupling of the SH group of *trans-*15 to four equivalent phosphorus atoms. The methylene signal of the *trans* complex appears at 5.10 ppm, while the *cis* complex has two methylene multiplets: one at 4.62 and the other under the peak at 5.10 ppm.

The \(^{31}\)P{\(^1\)H} NMR spectrum of the *cis/trans* mixture (Fig. 3.34) contains a singlet (*trans-*15) at -7.05 ppm, and two triplets (*cis-*15) at -5.93 (\(2J_{PP}=28.5\) Hz) and -22.65 ppm (\(2J_{PP}=26.5\) Hz).

As previously mentioned, six-coordinate complexes are generally not fluxional. Although iron(II) and ruthenium(II) phosphine dihydrides have been found to be exceptions,\(^{228}\) there is no reason to suppose that 15 is fluxional. In fact, the observation of a different *cis:* *trans* ratio (2:1) in the filtrate from reaction 3.16\(^{254}\) shows that the isomerization reactions between the isomers of 15 are slow at room temperature.
after 3 - 10 min

trans-15a (RuSH)

trans-13a (RuSH)

cis-15a (RuSH)

11 - 19 min

98 - 120 min

Fig. 3.32 a) 1H NMR spectra (hydride region) acquired during the reaction of RuH(SH)(dpm)_2 (13a, 7.4 mM) with H_2S in C_6D_6 at 60.0°C.
Fig. 3.32 b) $^1$H NMR spectra (methylene region) acquired during the reaction of RuH(SH)(dpm)$_2$ (13a, 7.4 mM) with H$_2$S in C$_6$D$_6$ at 60.0°C.
Fig. 3.33 Logarithmic plot of concentration of trans-RuH(SH)(dpm)$_2$ (13a) during the reaction of that compound (7.4 mM) with H$_2$S (1 atm) at 60.0°C in C$_6$D$_6$.

Fig. 3.34 The $^{31}$P($^1$H) NMR spectrum of Ru(SH)$_2$(dpm)$_2$ (15) in C$_6$D$_6$ (δ with reference to PPh$_3$ in C$_6$D$_6$).
The reaction of \textit{trans}-RuH(BH_4)(dpm)_2 (Section 2.3.7, 0.4 g) with H_2S (1 atm) in THF (30 mL) over 5 days at room temperature\textsuperscript{254} produces a similar mixture of \textit{cis}- and \textit{trans}-L\textsubscript{15} (\textit{cis}: \textit{trans} = 1:2, yield = 80%).

\[
\text{RuH(BH}_4\text{)(dpm)}_2 + 2\text{H}_2\text{S} \rightarrow \text{Ru(SH)}_2\text{(dpm)}_2 + 2\text{H}_2 + \text{"BH}_3\text{"}
\]

3.8 THE THIOL EXCHANGE REACTIONS OF \textit{cct}-Ru(SR)_2(CO)_2(PPh_3)_2

The title compound (14) reacts with added thiols to exchange the thiolate groups, in a reaction reminiscent of that with \textit{ccr}-RuH(SR)(CO)_2(PPh_3)_2 (reaction 3.12).

\[
\text{Ru(SR)}_2\text{(CO)}_2\text{L}_2 + n\text{R'SH} \rightleftharpoons \text{Ru(SR)}_2\text{-n(SR')}_n\text{(CO)}_2\text{L}_2 + n\text{RSH}
\]

For example, the reaction of \textit{ccr}-Ru(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})(CO\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2} (14b, 6 mM) in C\textsubscript{6}D\textsubscript{6} with H\textsubscript{2}S (1 atm) at room temperature is complete within 5 min, giving pure \textit{ccr}-Ru(SH\textsubscript{2})(CO\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2} (14a). However, the reaction of 14b (6 mM) with excess EtSH at room temperature produces equilibrium mixtures of the 14b, \textit{ccr}-Ru(SCH\textsubscript{2}CH\textsubscript{3})(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})(CO\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2} (14bd), and \textit{ccr}-Ru(SCH\textsubscript{2}CH\textsubscript{3})(CO\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2} (14d) within 20 min, after which the ratio is unchanging (monitored for a further 50 min). The 14b:14bd:14d ratio is 24:52:24 or 10:45:45 after the addition of 260 or 960 mM EtSH, respectively. The \textit{p}-thiocresol produced in the reaction is clearly detected in the \textsuperscript{1}H NMR spectrum. From three experiments of this type, rough estimates of the two equilibrium constants were calculated.

\[
K_1 = \frac{[\text{Ru(SEt)(Stol)(CO)}_2(PPh_3)_2] [\text{tolSH}]}{[\text{Ru(Stol)}_2(CO)_2(PPh_3)_2] [\text{EtSH}]}
\]

\[
K_2 = \frac{[\text{Ru(SEt)}_2(CO)_2(PPh_3)_2] [\text{tolSH}]}{[\text{Ru(SEt)(Stol)(CO)}_2(PPh_3)_2] [\text{EtSH}]}
\]

where Et = CH\textsubscript{2}CH\textsubscript{3} and tol = C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3}
At 20°C, these constants were $4 \times 10^{-2}$ and $1 \times 10^{-2}$ (±25%), respectively.

The Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ complex (14a, 5.7 mM) reacts with p-thiocresol (220 mM) in C$_6$D$_6$ (1 mL) at 210°C to produce Ru(SH)(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (14ab) (56% conversion) and Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b) (10%) after 140 min. The reaction of 14a with thiophenol is similar (Fig. 3.35 and 3.37). However, with 1500 equivalents of ethanethiol, no reaction is observed even after several hours. This is probably a result of the greater binding strength of the more acidic thiols such as H$_2$S and the aryl thiols (Section 3.5). The mixed products of the reactions of 14a with thiols are detected by $^{31}$P{H} and H NMR spectroscopy (Fig. 3.35 and Table 4.1 on page 159).

The reaction of 14a (0.70 mM) with thiophenol (2.0 mM) can also be followed by UV (Fig. 3.36). Isosbestic points are observed for the first 10 min at 367 nm ($\varepsilon = 2100$) and 386 nm ($\varepsilon = 1830$), because only Ru(SPh)$_2$(CO)$_2$(PPh$_3$)$_2$ (14i) is produced in the first 10 to 20 min, with no trace (NMR evidence) of Ru(SH)(SPh)(CO)$_2$(PPh$_3$)$_2$ (14ai). The rate constant at 25°C is $2.3 \times 10^{-3}$ s$^{-1}$, significantly higher than the result in C$_6$D$_6$ (4.2 x 10$^{-4}$ s$^{-1}$, see below).

The rate of the same reaction of 14a with PhSH was also monitored by $^{31}$P{H} NMR spectroscopy at 25.0°C. At low [PhSH], the monosubstituted product (14ai) is produced more quickly and in greater amounts than the disubstituted product (14i, Fig. 3.37a). The reaction does not proceed to completion presumably because an equilibrium is attained. Since H$_2$S is very soluble in benzene$^{255}$, a significant amount of the H$_2$S produced in the reaction must remain in solution. At high [PhSH], the rate of loss of 14a is pseudo-first order (Fig. 3.37c,d). The log plot (Fig. 3.38) is linear for 2.5 half-lives, with a pseudo-first order rate constant of $4.0 \times 10^{-4}$ s$^{-1}$. Because first order behaviour is not observed over the full range of thiol concentrations tested, the initial rate method was adopted for the kinetic study. The rate constant was calculated from the initial rate of loss of 14a as determined from the $^{31}$P{H} NMR spectra. This rate constant is independent of [PhSH] (77 to 1700 mM), although it decreases slightly at very high concentrations of thiol (Fig. 3.39). The average value is $4.2 \ (±0.3) \times 10^{-4}$ s$^{-1}$ (average of 5 results). If extra PPh$_3$ is added, the rate decreases and becomes dependent on [PhSH] (Fig.
Fig. 3.35  $^{31}P\{^1H\}$ NMR spectra acquired during the reaction of $ecl$-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a, 9.4 mM) with PhSH (700 mM) at 25°C in C$_6$D$_6$. Chemical shift shown with respect to PPh$_3$ in C$_6$D$_6$. 
Fig. 3.36 UV/vis. spectra acquired at 1 min intervals during the reaction of cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14g, 0.70 mM) with PhSH (2.0 M) at 25°C in THF.
Fig. 3.37 Time dependence of the concentrations of species detected by $^{31}$P($^1$H) NMR during the reaction of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a, 6 mM) with PhSH at 25°C in C$_6$D$_6$.

a) at 77 mM PhSH

b) at 690 mM PhSH
c) at 1700 mM PhSH

d) at 2900 mM PhSH
e) at 810 mM PhSH and 470 mM PPh₃

Fig. 3.38 The log plot of the concentration of cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a) during its reaction (5.3 mM Ru) with thiophenol (1.7 M) in C₆D₆ at 25°C.
Fig. 3.39 The dependence on [PhSH] of the observed initial rate constant for the loss of \( \text{cct-Ru(SH)}_2(\text{CO})_2(\text{PPh}_3)_2 \) (14a) during the reaction with PhSH at several concentrations of added PPh3. Bars indicate estimated error (10 %) on individual measurements of \( k \).

Fig. 3.40 Phosphine dependence of the inverse of the observed initial rate constant for the loss of \( \text{cct-Ru(SH)}_2(\text{CO})_2(\text{PPh}_3)_2 \) (14a, 6 mM) during the reaction with PhSH at several [PhSH]. The lines are drawn from a fixed point at [PPh3]=0 mM based on data from experiments with no added phosphine.
Scheme 3.6 The proposed mechanism for the first step of the reaction of Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a) with PhSH.
A mechanism consistent with these observations is shown in Scheme 3.6. The proton in the intermediate complex Ru(SH)$_2$(PhSH)(CO)$_2$(PPh$_3$) probably is shared by all three thiolate groups, rather than being simply attached to one of them. This kind of intermediate was discussed in Section 3.5. The rate law predicted by the mechanism in Scheme 3.6, assuming that $k_2$ is negligible, is:

$$-d[14a]/dt = \frac{k_1k_2[PhSH][14a]}{k_1[PPh_3] + k_2[PhSH]}$$

Under pseudo-first order conditions, [PhSH] is essentially constant during the reaction. PPh$_3$ is neither produced nor consumed in the reaction and [PPh$_3$] is therefore constant. Thus the observed initial rate constant $k_{obs}$ is given by

$$k_{obs} = \frac{k_1k_2[PhSH]}{k_1[PPh_3] + k_2[PhSH]}$$

or

$$\frac{1}{k_{obs}} = \frac{k_1k_2[PhSH]}{k_1k_2[PhSH]} + \frac{1}{k_1}$$

A plot of $1/k_{obs}$ against [PPh$_3$] should be a straight line with a slope inversely proportional to [PhSH]. Although there is considerable scatter in the data, this is perhaps the case (Fig. 3.40). The slope of the line drawn through the data for 67 mM PhSH is 14000, giving a value for $k_1/k_2$ of 0.4. The slope for 770 mM PhSH is 1800, giving a value for $k_1/k_2$ of 0.6. The average value is 0.5.

During the reaction of 14a with low [PhSH], 14ai is produced at a higher initial rate than 14i. It was initially supposed that 14ai may be an intermediate in the formation of 14i. The reaction equations would therefore be the following.

$$\text{Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ + PhSH} \rightarrow \text{Ru(SH)(SPh)(CO)$_2$(PPh$_3$)$_2$ + H}_2\text{S}$$

$$14a \quad k_A \quad 14ai$$
Ru(SH)(SPh)(CO)₂(PPh₃)₂ + PhSH → Ru(SPh)(CO)₂(PPh₃)₂ + H₂S

However, at high [PhSH] (Fig. 3.37c,d), 14i is observed first, and the appearance of 14ai is considerably delayed. The rate constant for the second step was calculated, assuming that a) the first substitution reaction is first order with respect to [14a] and independent of [PhSH], b) the second substitution reaction is first order with respect to [14ai] and nth order with respect to [PhSH], and c) n and [PhSH] are constant with respect to time. The rate equations, based on these assumptions, are:

\[-d[14a]\] = \[k_A[14a]\]  \[\frac{d[14i]}{dt} = k_B'[14ai][PhSH]^n = k_B[14ai]\]

where \(k_B = k_B'[PhSH]^n\).

The integrated rate laws for this type of system are known. 256

\[
\begin{align*}
14a \rightarrow 14ai \rightarrow 14i \\
[k_A]_t &= \exp(-k_At) \\
[k_A]_0 &= \exp(-k_A t) \\
[k_B - k_A] &= \exp(-k_B t) \\
[k_A]_0 &= 1 + \frac{k_B \exp(-k_A t) - k_A \exp(-k_B t)}{k_A - k_B}
\end{align*}
\]

The value of \(k_A\) is already known \((k_A = k_1 = 4.2 \times 10^{-4} \text{ s}^{-1})\). For each experiment, the plots of the observed and predicted concentrations of Ru(SH)₂(CO)₂(PPh₃)₂ (14a), Ru(SH)(SPh)(CO)₂(PPh₃)₂ (14ai), and Ru(SPh)(CO)₂(PPh₃)₂ (14i) were compared for several values of \(k_B\). The best value for \(k_B\) was taken to be that which produced the best fit of the predicted concentration curve (calculated using the above equations) to the observed curve in the
Fig. 3.41 Thiol dependence of the calculated rate constant $k_B$ for the second step of the reaction of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ with thiophenol at 25°C in C$_6$D$_6$. Solid line assumes a first-order dependence at all [PhSH]. Dashed line shows an incorrect interpretation of the rate dependency.
initial rate region (the first two data points, Fig. 3.37). It is tempting to interpret the plot of the [PhSH] dependence of the $k_B$ values (Fig. 3.41) as showing $n$ to be 0 at low thiol concentrations, and 1 at high thiol concentrations. The error on each point, although difficult to estimate, is probably too large for this interpretation, and the sloping line for a supposed first-order dependence on [PhSH] (dotted line in Fig. 3.41) should extrapolate back to the origin, which it fails to do. It is clear, however, that the value of $k_B$ depends on [PhSH]. This indicates that either

i) the reaction of $14ai$ with PhSH is dependent on [PhSH], and is sufficiently fast at high [PhSH] that $14ai$ is not observed, or

ii) $14ai$ is not an intermediate in the formation of $14i$ under these conditions.

The first possibility is counter-intuitive, because one would expect that the mechanism of the reaction of $14ai$ with PhSH would correspond to that of $14a$ with PhSH. A mechanism consistent with the second possibility and with the mechanism proposed for the loss of $14a$ (Scheme 3.6) is shown in Scheme 3.7. According to this mechanism, the unobserved five-coordinate complex [Ru(SH)(SPh)(CO)2(PPh3)] is an intermediate for which PPh3 and PhSH compete to form $14ai$ (directly) and $14i$ (via other intermediates), respectively. This accounts for the observation that high [PhSH] favours early formation of $14i$ (Figs. 3.37b,c,d), while added PPh3 increases the initial rate of formation of $14ai$ at the expense of $14i$ (Fig. 3.37e).

With this mechanism, we can now interpret the observed dependence of $k_B$ on [PhSH] (Fig. 3.41). At very low [PhSH], $k_B$ should be independent of [PhSH], because in this region, the pathway via $14ai$ is predominant. The value of $k_B$ in this range should therefore equal that of $k_4$. As mentioned earlier, the flattened region at low [PhSH] in Fig. 3.41 is believed to result from scatter in the data, although it is interesting that the lowest observed value of $k_B$ (4 x 10^{-4} s^{-1}) is very close to the value of $k_1$ (3.8 x 10^{-4} s^{-1}). Because $14a$ and $14ai$ are so similar, the values of $k_4$ and $k_1$ are expected to be similar. At higher [PhSH], the other pathway should be predominant. That is, $14i$ is formed without $14ai$ having been an intermediate. The value of $k_B$/[PhSH] in this region (3 x 10^{-3} M^{-1} s^{-1}) is presumably that of $k_5$. 
Scheme 3.7 The proposed mechanism for the reaction of Ru(SH)$_2$(CO)$_2$(PPh)$_3$$_2$ (14a) with PhSH.

14a

14ai

14i
As we have seen, if one assumes that \( k_2 \) is negligible, then one can calculate that \( k_1/k_2 \) is approximately 0.5. This leads one to speculate about the value of \( k_4/k_5 \). Both ratios are concerned with competing reactions of PPh\(_3\) and PhSH for a five-coordinate intermediate. If \( k_4/k_5 \) were also approximately 0.5, or even if \( k_4 \) and \( k_5 \) were of the same magnitude, then under the conditions of excess added thiol and no added phosphine, \( k_5[\text{PhSH}] \) would be far greater than \( k_4[\text{PPh}_3] \), and therefore no \( 14\text{ai} \) would have been observed in the initial rate region. That the initial rate of production of \( 14\text{ai} \) is significant at 77 mM PhSH (Fig. 3.37a) suggests that \( k_4/k_5 \) is much larger than \( k_1/k_2 \) or that \( k_5 \) is larger than \( k_2 \). It is difficult to explain why \( k_4/k_5 \) should be larger than \( k_1/k_2 \), but it is clear why \( k_5 \) should be larger than \( k_2 \). For statistical and steric reasons, the thiol which is ejected from Ru(SPh)(SH)(PhSH)(CO)\(_2\)(PPh\(_3\)) is more likely to be PhSH (\( k_5 \)) than H\(_2\)S (\( k_6 \)). The corresponding complex Ru(SH)\(_2\)(PhSH)(CO)\(_2\)(PPh\(_3\)) is more likely, for statistical reasons, to eliminate H\(_2\)S (\( k_3 \)) than PhSH (\( k_2 \)). Also, the steric crowding which might encourage elimination of PhSH from Ru(SPh)(SH)(PhSH)(CO)\(_2\)(PPh\(_3\)) is weaker in Ru(SH)\(_2\)(PhSH)(CO)\(_2\)(PPh\(_3\)). These arguments suggest that \( k_5 \) should be larger than \( k_2 \).

Why does \( \text{cco-Ru(SC}_6\text{H}_4\text{pCH}_3)\text{2(CO)}_2(\text{PPh}_3)_2 \) \( (14\text{b}) \) react more quickly with thiols than does \( \text{cco-Ru(SH)}_2(\text{CO})_2(\text{PPh}_3)_2 \) \( (14\text{a}) \)? The rate determining step in Scheme 3.5 and 3.6 is dissociation of PPh\(_3\) from the complex. It is possible that the bulky thiolate groups in \( 14\text{b} \) labilize the phosphine. This is supported by the observation (Section 6.2.2) that the phosphine-exchange reaction of \( 14\text{b} \) with P(C\(_6\)H\(_4\)pCH\(_3\))\(_3\) proceeds more quickly than that of \( 14\text{a} \).

### 3.9 THE REACTIONS OF OTHER CARBONYL(PHOSPHINE)RUTHENIUM(0) COMPLEXES WITH H\(_2\)S AND THIOLS

The bisphosphine tricarbonyl complex Ru(CO)\(_3\)(PPh\(_3\))\(_2\), \( (10) \), is much less reactive than Ru(CO)\(_2\)(PPh\(_3\))\(_3\) \( (2) \). After 3 h in refluxing THF under H\(_2\)S, only 6% of a sample of \( 10 \) had
been converted to \( cct\)-RuH(SH)(CO)\(_2\)(PPh\(_3\))\(_2\), of which half had reacted further (reaction 3.14) to produce \( cct\)-Ru(SH)\(_2\)(CO)\(_2\)(PPh\(_3\))\(_2\). \( ^{254} \)

\[
\text{Ru}(\text{CO})\(_3\)(\text{PPh}\(_3\))\(_2\) + \text{H}_2\text{S} \rightarrow \text{RuH}(\text{SH})(\text{CO})\(_2\)(\text{PPh}\(_3\))\(_2\) + \text{CO} \tag{3.19}
\]

The only related reactions which have been reported previously are the reaction of \( \text{Ru}(\text{CO})\(_3\)(\text{PPh}\(_3\))\(_2\) \) with pyridine-2-thiol, producing \( \text{Ru}(\text{pyS})\(_2\)(\text{CO})\(_2\)(\text{PPh}\(_3\))\(_2\), \(^{211} \) and reaction 3.20:

\[
\text{M}(\text{CO})\(_3\)(\text{PPh}\(_3\))\(_2\) + 2\text{HX} \rightarrow \text{MX}_2(\text{CO})\(_2\)(\text{PPh}\(_3\))\(_2\) + \text{CO} + \text{H}_2 \tag{3.20}
\]

\( \text{M=Os, } X=\text{Cl, Br, I (ref. 257a)} \)
\( \text{M=Ru, } X=\text{Cl, Br (ref. 257b), OCOR (ref. 257b,c,d)} \)

A mechanism proposed\(^{257a} \) for this reaction (Scheme 3.8) was supported by the isolation of complexes of the formula \( [\text{OsX}(\text{CO})\(_3\)(\text{PPh}\(_3\))\(_2\)]X \) (\( X=\text{Br, I, I}_3 \))\(^{257a} \) and \( \text{OsH(Cl)(CO)}\(_2\)(\text{PPh}\(_3\))\(_2\).\(^{257e} \) The mechanism of reaction 3.19 may parallel that in Scheme 3.8.

Scheme 3.8 A mechanism proposed by Collman and Roper\(^{257a} \) for the reaction of \( \text{Os(CO)}\(_3\)(\text{PPh}\(_3\))\(_2\) \) with \( \text{HX} \) (\( X=\text{Cl, Br, I} \)).
Samples of the complex Ru(CO)$_2$(PPh$_3$)(dpm) (16), kindly supplied by Dr. C.-L. Lee, react with thiols to form mixtures of thiolate complexes (Figs. 3.42 and 3.43). The major product has not been identified. Three identified minor products of the reaction with ethanethiol in THF are \textit{ccr}-RuH(SCH$_2$CH$_3$)(CO)$_2$(PPh$_3$)$_2$ (2d) and two isomers of RuH(SCH$_2$CH$_3$)(CO)(PPh$_3$)(dpm), one (17) containing a $2J_{\text{transPH}}$ coupling, and the other (18) containing only $2J_{\text{cisPH}}$ couplings. These three products are detected in the hydride region of the $^1$H NMR spectrum. The integrals of the hydride signals are in a ratio 9d:17:18 of 120:2.3:1. The peaks due to 16 and 9d comprise 28% and 13% of the $^{31}$P($^1$H) NMR signal, respectively. It is not clear which peaks in the $^{31}$P($^1$H) NMR spectrum correspond to 17 and 18. Possible structures for these isomers are shown below.

\[
\begin{align*}
\text{17} & \quad \text{18} \\
\begin{array}{c}
\text{Ph}_2\text{P} & \text{Ru} & \text{PPh}_2 \\
\text{PPh}_3 & \text{H} & \text{SEt} \\
\text{Ph}_3\text{P} & \text{CO} & \\
\end{array} & \begin{array}{c}
\text{Ph}_2\text{P} & \text{Ru} & \text{PPh}_2 \\
\text{OC} & \text{SEt} & \\
\text{PPh}_3 & \\
\end{array}
\end{align*}
\]

The detection of 17, 18, and 2d shows that loss of a carbonyl ligand and exchange of the phosphine ligands are significant reactions. The existence of three labile ligands on the starting complex 16 make this system too complicated to be amenable to a full study of its reactivity and kinetics.

Results obtained in the reaction of 16 with H$_2$ are summarized in the experimental section at the end of this chapter. The products of the reaction include trace amounts of \textit{ccr}-RuH$_2$(CO)$_2$(PPh$_3$)$_2$, and several unidentified species.
Fig. 3.42 $^1$H NMR spectrum (hydride region) of the products of the reaction of Ru(CO)$_2$(dpm)(PPh$_3$) with ethanethiol.
Fig. 3.43  $^{31}$P($^1$H) NMR spectrum of the products of the reaction of Ru(CO)$_2$(dpm)(PPh$_3$) with ethanethiol. The signals due to unreacted starting material are indicated with asterisks.
3.10 EXPERIMENTAL DETAILS

The reaction of Ru(CO)\(_2\)(PPh\(_3\))\(_3\) with hydrogen sulphide, thiols and selenols over several hours: Complex Ru(CO)\(_2\)(PPh\(_3\))\(_3\) (2) (400 mg, 0.4 mmol) in THF (50 mL) was reacted with a) gaseous H\(_2\)S (1 atm) at -35° C for 2 h, \(^8\)b) under gaseous MeSH (1 atm) at room temperature for 3 h, c) with excess (e.g. 8 equivalents) dissolved thiol at room temperature for 3 h, or d) with one equivalent of phenyl selenol for 1.5 h at room temperature. The product was precipitated by reduction of the solvent volume by vacuum distillation followed by addition of 100 mL hexanes, producing 40-95% yields of a) a pale tan powder, or b,c,d) a yellow powder, which analyzed for RuH(ER)(CO)\(_2\)(PPh\(_3\))\(_2\) (9). The same products can be similarly prepared from the reactions of cct-RuH\(_2\)(CO)\(_2\)(PPh\(_3\))\(_2\) with H\(_2\)S or thiols. Elem. Anal.:

9a (ER=SH) Calcd. for C\(_{38}\)H\(_{32}\)O\(_2\)P\(_2\)RuS: C, 63.8; H, 4.5; S, 4.5. Found: C, 63.8; H, 4.7; S, 4.6.

9b (ER=SC\(_6\)H\(_4\)pCH\(_3\)) Calcd. for C\(_{45}\)H\(_{38}\)O\(_2\)P\(_2\)RuS: C, 67.1; H, 4.8; S, 4.0. Found: C, 66.1; H, 4.8; S, 4.3

9c (ER=SCH\(_3\)) Calcd. for C\(_{39}\)H\(_{34}\)O\(_2\)P\(_2\)RuS: C, 64.2; H, 4.7; S, 4.4. Found: C, 63.9; H, 4.8; S, 4.4.

9d (ER=SCH\(_2\)CH\(_3\)) Calcd. for C\(_{40}\)H\(_{36}\)O\(_2\)P\(_2\)RuS: C, 64.6; H, 4.9; S, 4.3. Found: C, 64.8; H, 5.1; S, 4.5.

9e (ER=SCH\(_2\)C\(_6\)H\(_5\)) Calcd. for C\(_{45}\)H\(_{38}\)O\(_2\)P\(_2\)RuS: C, 67.1; H, 4.8; S, 4.0. Found: C, 67.0; H, 4.9; S, 4.3.

9f (ER=SC\(_6\)H\(_4\)oCH\(_3\)) Calcd. for C\(_{45}\)H\(_{38}\)O\(_2\)P\(_2\)RuS: C, 67.1; H, 4.8; S, 4.0. Found: C, 66.7; H, 4.8; S, 4.3.

9g (ER=SC\(_6\)H\(_4\)mCH\(_3\)) Calcd. for C\(_{45}\)H\(_{38}\)O\(_2\)P\(_2\)RuS: C, 67.1; H, 4.8; S, 4.0. Found: C, 66.7; H, 4.3; S, 3.5.

9h (ER=SeC\(_6\)H\(_5\)) Calcd. for C\(_{44}\)H\(_{36}\)O\(_2\)P\(_2\)RuSe: C, 63.0; H, 4.3. Found: C, 63.3; H, 4.6.

The NMR and IR spectra of these complexes are described and shown in Section 3.2 and summarized in Tables 3.1, 3.2, and 3.5. A sample of 9f (ER=C6F5) was obtained, as confirmed by NMR spectroscopy, but an elemental analysis was not performed. The cct-RuD(SC6H5)(CO)2(PPh3)2 complex was synthesized from 2 and PhSD. Samples of cct-RuH(SCH2CH3)(CO)2(PR3)2 (PR3=PPh2Py, or P(C6H4pCH3)3) were prepared in a similar manner from the corresponding tris-phosphine complexes, Ru(CO)2(PPh2Py)3 and Ru(CO)2(P(C6H4pCH3))3. The latter precursor was supplied by Dr. C.-L. Lee. The former precursor, Ru(CO)2(PPh2Py)3 was prepared by Mr. M. Prystay, from [RuCl2(CO)3]2 and PPh2Py, followed by sodium amalgam reduction of the resulting cct-RuCl2(CO)2(PPh2Py)2.

The non-reaction of Ru(CO)2(PPh3)3 with ethanol: Ru(CO)2(PPh3)3 (12 mg, 13 µmol) and ethanol (50 µL, 0.9 mmol) failed to react within 2 days in 10 mL THF at room temperature. The solvents were removed by vacuum distillation, and the unreacted solid, redissolved in C6D6, was identified by 31P{1H} NMR spectroscopy.

The X-ray crystallographic analysis of cct-RuH(SC6H4pCH3)(CO)2(PPh3)2:
Crystals of 9b suitable for X-ray crystallography were prepared by diffusion of hexanes into a saturated solution of the complex in THF, under Ar. The crystallographic data were acquired and analysed by Dr. S. J. Rettig of this department.

The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 31.1-35.6°. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, were essentially constant. The data were processed and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for four reflections).
The structure analysis was initiated in the centrosymmetric space group $P\bar{1}$, the choice being confirmed by the subsequent successful solution and refinement of the structure. The structure was solved by conventional heavy atom methods, the coordinates of the Ru, P, and S atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions ($d_{C-H} = 0.98 \, \text{Å}, B_{H} = 1.2 \, B_{\text{bonded atom}}$), except for the metal hydride which was refined with an isotropic thermal parameter. Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography.\textsuperscript{259b} Final atomic coordinates and equivalent isotropic thermal parameters $[B_{eq} = 4/3 \Sigma_{ij} b_{ij}(a_{i}a_{j})]$, bond lengths, and bond angles appear in Appendix 2, and Tables 3.3 and 3.4, respectively. Other crystallographic data for this structure and the other structures described in this work are presented in Appendix 1,\textsuperscript{209}

The reaction of $\text{ccf-RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ (3) with thiols: The preparation of 9 from 3 was carried out in the same manner as described for the synthesis from 2 (see above), except that reaction times of 3 to 4 h were required.

To confirm the production of $H_2$ from the reaction, $p$-thiocresol (50 mg, 0.2 mmol) was added to a 1 mL saturated solution of 3 in THF in an NMR tube. After 2 h, and again after 25 h, 0.2 mL samples of the vapour phase were injected onto a molecular sieve column. A strong $H_2$ peak was observed each time.

The amount of $H_2$ produced was determined by following the reaction between 3 (35 μmol) and PhSH (290 μmol) in a constant pressure uptake apparatus at 30°C. After 50 min, the gas evolution measured had levelled off and corresponded to 40 μmoles of gas.

The reaction of 3 with $H_2S$ was also monitored by $^1H$ NMR spectroscopy. A sample of 3 (4.17 mg, 10.3 mM) was dissolved in $C_6D_6$ (0.6 mL) under Ar in an NMR tube and
the Ar atmosphere was promptly replaced by flushing H₂S through syringe needles inserted into the septum seal of the NMR tube. The sample tube was inserted into the NMR probe, which was maintained at 25.0°C. Successive spectra were acquired at a rate of one every 6 min, with every third being of the ³¹P rather than ᵃH region of the NMR spectrum, in order to confirm that no products other than 9a were forming. The concentrations of 3 and 9a were calculated from the metal hydride signals in the ᵃH NMR spectra.

The reaction of cct-RuH₂(CO)₂(PPh₃)₂ (3) with CO: The reaction of 3 (0.25 to 1.1 mM) with CO (1 atm) in THF was monitored at 350 nm, where the product Ru(CO)₃(PPh₃)₂ (10, ε=930 M⁻¹ cm⁻¹) absorbs more strongly than 3 (ε=70 M⁻¹ cm⁻¹). The results at 41°C are described on page 86. Reactions at 25°C under N₂ with sufficient CO injected through a septum to give a CO partial pressure of 0.09 atm had virtually the same first order rate constant (5.4 x 10⁻⁴ s⁻¹) as reactions under a full atmosphere of CO (5.6 x 10⁻⁴ s⁻¹). The ³¹P NMR chemical shift of the product (55.1 ppm) was identical to that reported by Dekleva, after correction for the different reference (all of the ³¹P NMR chemical shifts in Dekleva’s work are exactly 1.5 ppm downfield of those observed in the present study, presumably because of a difference in the reference point).

The reaction of cct-RuH₂(CO)₂(PPh₃)₂ (3) with PPh₃: The reaction of 3 (0.34 mM) with PPh₃ (47 to 380 mM) in THF was monitored at 25°C and 400 nm, where the product 2 (ε=6000 M⁻¹ cm⁻¹) absorbs much more strongly than 3 (ε=40 M⁻¹ cm⁻¹). The plots of ln(A∞-A) versus time are linear for experiments with ratios of [PPh₃]:[3] of 130 or greater. To insure proper mixing, particularly for the H₂ co-product, the cell was quickly inverted four times between each measurement, or approximately every 25 seconds. Pseudo-first order kinetics were also observed if Ar was bubbled through the cell between measurements. The identity of the Ru product of the reaction,
Ru(CO)_2(PPh_3)_3 (2), was confirmed by comparing the ^31P{^1H} NMR spectrum of the product to that of a C_6D_6 solution of a known sample of 2 (Section 2.3.2).

The non-reaction of cct-RuH_2(CO)_2(PPh_3)_2 (3) with methanol:
MeOH (70 µl, mmol) and 2 (8 mg, 12 µmol) in THF (7 mL) failed to react within an hour. The solvents were removed by vacuum distillation, and the starting material was identified by its ^31P{^1H} and ^1H NMR spectra.

The reaction of cct-RuH_2(CO)_2(PPh_3)_2 (3) with acetic acid:
Acetic acid (50 µL, 870 µmol) and 3 (23 mg, 34 µmol) were mixed in THF (10 mL) for 24 h at room temperature, during which no colour appeared. The volatiles were then removed by evacuation. The ^1H and ^31P{^1H} NMR spectra of the residue redissolved in C_6D_6 showed signals for a major product consistent with cct-RuH(OAc)(CO)_2(PPh_3)_2. ^1H NMR (C_6D_6) δ -3.68 ppm (t, 1H, ^2J_{PH} = 19.0 Hz, Ru-H), 1.40 ppm (s, 3H, CH_3); ^31P{^1H} (C_6D_6) δ 45.24 ppm. These data match closely those found by Dekleva^[182] for cct-RuH(OCOPh)(CO)_2(PPh_3)_2 (^1H NMR (C_6D_6) δ -3.52 ppm (t, ^2J_{PH} = 20 Hz, Ru-H); ^31P{^1H} (C_6D_6) corrected δ 44.8 ppm). The acetate made in the present study was not purified or analysed, and contained 10% each (measured by ^31P NMR) of ccr-RuH_2(CO)_2(PPh_3)_2, Ru(CO)_3(PPh_3)_2, and an unknown (singlet at 44.63 ppm).

The reaction of cis- and trans-RuH_2(dpm)_2 (7) with thiols: A sample of 7 (6.0 mg, 6.9 µmol) was dissolved in C_6D_6 (0.5 mL) in an NMR tube under Ar, and the tube was capped with a septum. The gas phase of the NMR tube was then flushed with H_2S. The progress of the reaction was followed by NMR spectroscopy. The ^1H and ^31P{^1H} spectra after 45 min showed almost complete conversion to a new complex, believed to be trans-RuH(SH)(dpm)_2 (13a). ^1H NMR (C_6D_6) δ -9.46 (qn, ^2J_{PH} = 19 Hz, Ru-H),
-3.55 (br, Ru-SH), 4.54 (dt, \(2J_{HH} = 16\) Hz, \(2J_{PH} = 3\) Hz, CH\(_2\)), and 5.21 ppm (multi, CH\(_2\)); \(31^P\{^1H\} NMR (C_6D_6) \delta 0.40\) ppm (s).

The corresponding reaction of 7 with thiols was monitored by dissolving 7 (6.0 mg, 6.9 \(\mu\)mol) in C\(_6\)D\(_6\) or toluene-d\(_8\) (0.5 mL) in an NMR tube under Ar, and capping the tube with a septum. After an NMR spectrum of this sample had been acquired and the temperature of the probe had reached a steady 25\(^\circ\)C, PhSH (4 \(\mu\)L, 70 mM) or PhCH\(_2\)SH (5 to 60 \(\mu\)L, 70 to 850 mM) was injected through the septum. The progress of the reaction was followed by NMR spectroscopy. Three products were observed. Two of these, trans- and cis-RuH(SR)(dpm)\(_2\) (13) could be identified from their NMR spectra.

**trans-RuH(SPh)(dpm)\(_2\) (trans-13b):** \(^1H\) NMR (toluene-d\(_8\)) \(\delta -10.86\) (qn, \(1H\), \(2J_{PH} = 19.9\) Hz, Ru-H), 4.27 (dt, \(2H\), \(2J_{HH} = 13.8\) Hz, \(2J_{PH} = 3.3\), CH\(_2\)), and 4.78 (multi, \(2H\), CH\(_2\)); \(31^P\{^1H\} NMR \delta -2.06\) ppm (s).

**cis-RuH(SPh)(dpm)\(_2\) (cis-13b):** \(^1H\) NMR (toluene-d\(_8\)) \(\delta -6.29\) ppm (ddt, \(2J_{transPH} = 91.5\) Hz, \(2J_{cisPH} = 24.1, 16.3\) Hz, Ru-H). The \(31^P\{^1H\} NMR spectrum of the toluene-d\(_8\) solution of this product is described in Section 3.4 and shown in Fig. 3.23.

**trans-RuH(SCH\(_2\)Ph)(dpm)\(_2\) (trans-13c):** \(^1H\) NMR (C\(_6\)D\(_6\)) \(\delta -10.16\) (qn, \(2J_{PH} = 20.0\) Hz, Ru-H), 4.44 (dt, \(2J_{HH} = 13.5\) Hz, \(2J_{PH} = 3.2\), CH\(_2\)), and 5.19 (multi, CH\(_2\)); \(31^P\{^1H\} NMR \delta -1.68\) ppm (s).

**cis-RuH(SCH\(_2\)Ph)(dpm)\(_2\) (cis-13c):** \(^1H\) NMR (C\(_6\)D\(_6\)) \(\delta -7.17\) ppm (d of q, \(2J_{transPH} = 97\) Hz, \(2J_{cisPH} = 20\) Hz, Ru-H). The peaks for this complex were not resolved in the \(31^P\{^1H\} NMR spectrum of the toluene-d\(_8\) solution of the cis- and trans-13c mixture.

**Unknown minor product:** \(^1H\) NMR (C\(_6\)D\(_6\)) \(\delta -9.41\) ppm (qn, \(2J_{PH} = 19.4\) Hz, Ru-H); \(31^P\{^1H\} NMR (C_6D_6) \delta 0.20\) ppm (s). \(^1H\) NMR (toluene-d\(_8\)) \(\delta -9.66\) ppm (qn, \(2J_{PH} = 19.2\) Hz, Ru-H); \(31^P\{^1H\} NMR (toluene-d_8) \delta 0.15\) ppm (s). This unknown product, in the reaction with PhSH, reached a maximum of up to 12\% and thereafter declined. In the reaction with PhCH\(_2\)SH, the same product was observed, although at lower and more constant concentrations. The structure of this product remains unassigned.
An inversion-recovery NMR experiment with the following pulse sequence

\[
\begin{array}{c}
\text{P1} \\
\text{D1} \\
\text{D2} \\
\text{P2} \\
\text{AT}
\end{array}
\]

where

- \( \text{D1} = 1.00 \text{ s delay time} \)
- \( \text{D2} = 60 \text{ ms delay time} \)
- \( \text{P1} = 0.092 \text{ ms} = 180^\circ \text{ pulse} \)
- \( \text{P2} = 0.046 \text{ ms} = 90^\circ \text{ pulse} \)
- \( \text{AT} = 1.36 \text{ s acquisition time} \)

shows a positive peak for protons with \( T_1 \) values of less than 60 ms. During a reaction of \( \text{7} \) (2.3 mg, 4.5 mM) and PhSH (4 \( \mu \)L, 70 mM) in \( \text{C}_6\text{D}_6 \) (0.6 mL) at 20°C, spectra were acquired using this pulse sequence. Only negative peaks were observed.

The reaction of \textit{cis-} and \textit{trans-} \( \text{RuH}_2(\text{dpm})_2 \) (7) with \( p \)-toluenesulphonic acid:

Complex \text{7} (5.0 mg, 5.7 \( \mu \)mol) and \( p \)-toluenesulphonic acid (28 mg, 150 \( \mu \)mol) reacted in deuterated toluene (0.7 mL) at room temperature to form several products within a few minutes. A major product, a minor product, and unreacted \textit{cis-} and \textit{trans-} \( \text{RuH}_2(\text{dpm})_2 \) were evident in the \( ^1\text{H} \) and \( ^{31}\text{P} \{ ^1\text{H} \} \) NMR spectra. The major product was possibly \( \text{RuH}(\text{SO}_3\text{C}_6\text{H}_4\text{pCH}_3)(\text{dpm})_2 \). \( ^1\text{H} \) NMR (toluene-\( d_8 \)) \( \delta = -19.40 \text{ ppm (qn, } ^2\text{J}_{\text{PH}} = 19.7 \text{ Hz, Ru-H), 4.39 (multi, CH}_2 \text{), and 5.40 (multi, CH}_2 \text{); } ^{31}\text{P} \{ ^1\text{H} \} \) NMR (toluene-\( d_8 \)) \( \delta = -3.00 \text{ ppm (s). The minor product had the same NMR spectra as the unknown product observed in the reaction with thiols. } ^1\text{H} \) NMR (toluene-\( d_8 \)) \( \delta = -9.56 \text{ ppm (qn, } ^2\text{J}_{\text{PH}} = 19.2 \text{ Hz, Ru-H); } ^{31}\text{P} \{ ^1\text{H} \} \) NMR (toluene-\( d_8 \)) \( \delta = 0.20 \text{ ppm (s).} \)

The reactions of \textit{cis-} and \textit{trans-} \( \text{RuH}_2(\text{dpm})_2 \) (7) and \textit{cct-} \( \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3) with deuterated methanol: A \( \text{C}_6\text{D}_6 \) solution of each of \( \text{7} \) and \( \text{3} \) (4 mM) was prepared under Ar, and a \( ^1\text{H} \) NMR spectrum of the sample acquired while the probe temperature equilibrated to 25°C. Enough \( \text{CD}_3\text{OD} \) was then injected to make a 4% v/v \( \text{CD}_3\text{OD}/\text{C}_6\text{D}_6 \) mixture. The decay in intensity of the peaks in the \( ^1\text{H} \) NMR spectrum
was then observed with successive acquisitions using constant experimental parameters. The results are summarized in Section 3.4.

The reactions of cct-RuH2(CO)2(PPh3)2 (3) with binary mixtures of thiols:
Complex 3 (6.3 mg, 9.2 µmol), PhSH (4.7 µL, 9.2 µmol) and EtSH (3.4 µL, 9.2 µmol) were stirred in THF (7 mL) overnight at room temperature. The solvent was removed by evaporation under vacuum, and the residual solid redissolved in C6D6. 1H and 31P{1H} NMR spectra showed that the product was cct-RuH(SPh)(CO)2(PPh3)2 (9j).

This experiment was repeated ([3] = 10 mM, [EtSH] = 2.3 mM, [PhSH] = 1.62 mM) in an NMR tube to allow in situ monitoring of the reaction by 1H NMR spectroscopy at 35.5°C. Complex 3 was consumed, producing both 9j and cct-RuH(SEt)(CO)2(PPh3)2 (9d), the latter reaching a maximum of 32% and thereafter decreasing. After 50 min, no trace of 3 remained. After 100 min, the yield of 9j was 98%, the remainder being 9d.

Several such reactions were performed, with several different mixtures of thiols. The concentrations of thiols were chosen so as to produce a fairly even mixture of thiolate products, that is, the major product was not over 80% of the mixture.

The reaction of cct-RuH(SEt)(CO)2(PPh3)2 (9d) with thiophenol: Complex 9d (1.8 or 8.4 mM) and PhSH (0.12 to 3.4 M) were dissolved in C6D6 (0.7 mL) in an NMR tube. 1H NMR spectra were acquired every 8-20 min, for about 3 half-lives (190 min). Concentrations were calculated from the integration of the hydride signals. The observed rate constant, kobs, was determined from the plot of ln[9d] vs. time, which was linear (Fig. 3.29). One equivalent of free EtSH was detected by 1H NMR spectroscopy.

The reaction over 3 days of Ru(CO)2(PPh3)3 (2) with thiophenol: Complex 2 (86 mg, 91 µmol) and PhSH (190 µL, 1.3 mmol) were left for 3 days at room temperature in THF solution (10 mL). The solvent was then removed by vacuum distillation, and the orange
oily residue redissolved in C₆D₆. The $^{31}$P{¹H} NMR spectrum shows that the product mixture contained (other than free PPh₃): cct-RuH(SPh)(CO)₂(PPh₃)₂ (9i, 37.26 ppm, 40% of $^{31}$P signal), cct-Ru(SPh)₂(CO)₂(PPh₃)₂ (14i, 10.73 ppm, 55%), and an unknown (23.88 ppm, 5%). None of the starting complex (2) remained.

The same experiment, but with 300 mg of complex 2 and 0.5 mL PhSH, resulted in 90% conversion (based on $^{31}$P NMR signal integration) to 14i.²⁵⁴ A similar experiment with m-thiocresol (0.3 mL, 2.5 mmol) gave only 55% conversion to the bis-thiolato complex 14g, the other product being the mono-thiolato derivative 9g. No signal for 2 was detected in the $^{31}$P{¹H} NMR spectrum.²⁵⁴

The overnight reaction of Ru(CO)₂(PPh₃)₃ with H₂S: Ru(CO)₂(PPh₃)₃ (400 mg, 0.42 mmol) under H₂S (1 atm) in THF (20 mL), was stirred overnight at room temperature. The volume of solvent was reduced to 10 mL by vacuum transfer, and hexanes (150 mL) were added to induce precipitation. The isolated product had a $^{31}$P{¹H} NMR spectrum identical to that of a sample of cct-Ru(SH)₂(CO)₂(PPh₃)₂ synthesised from cct-RuH₂(CO)₂(PPh₃)₂ and H₂S (see below).²⁵⁴

The overnight reaction of cct-RuH₂(CO)₂(PPh₃)₂ (3) with H₂S: Complex 3 (400 mg, 0.6 mmol) in THF (30 mL) was exposed to H₂S overnight at room temperature. The solution was then reduced in volume by vacuum transfer; a solid, precipitated by addition of hexanes (150 mL), was filtered off and collected as a yellow powder (76% yield).²⁵⁴ The identity of the product, cct-Ru(SH)₂(CO)₂(PPh₃)₂, was determined from the NMR spectra, the analysis, and the X-ray crystal structure (Section 4.2). Elem. Anal. Calcd. for C₃₈H₃₂O₂P₂RuS₂: C, 61.0 H, 4.3 S, 8.6. Found: C, 60.4 H, 4.5 S, 8.7. ¹H NMR (C₆D₆) δ -1.93 ppm (t, $^3$J_H= 6.8, Ru-SH), 6.95 (multi, m-/p-Ph), 8.15 (multi, o-Ph); $^{31}$P{¹H} NMR (C₆D₆) δ 20.45 ppm (s). For more complete details of the characterization, refer to Section 4.2.
Kinetic monitoring of the reaction of cct-RuH(SH)(CO)2(PPh3)2 (9a) with H2S: Complex 9a was generated \textit{in situ} from the reaction of 3 with H2S at 60°C. The concentrations of 9a and the final product cct-Ru(SH)2(CO)2(PPh3)2 (14a) were calculated from their respective SH peak integrals. The experiment was stopped at the stage when PPh3 was detected in the 31P{1H} NMR spectrum, which occurred after 40-50 min at 60°C.

The non-reaction of cct-RuCl2(CO)2(PPh3)2 (1) with NaBPh4: Complex 1 (0.109 g, 145 μmol) and NaBPh4 (50 mg, 146 μmol) were mixed in acetone (25 mL, distilled, freeze-thaw degassed three times under H2) under H2 (1 atm) at room temperature. After 90 min, the suspension was filtered through diatomaceous earth. The volume of the clear and colourless filtrate was reduced to 5 mL by vacuum distillation. The white precipitate thus formed was filtered and redissolved in C6D6. The 31P{1H} NMR spectrum showed that this material was unreacted cct-RuCl2(CO)2(PPh3)2.

The reaction of trans-RuH(SH)(dpm)2 (13a) with H2S: Complex 13a was generated \textit{in situ} by dissolving trans- and cis- RuH2(dpm)2 (Z, 4.3 mg, 7.4 mM) in C6D6 (0.5 mL) in an NMR tube under Ar, capping the tube with a septum, and flushing the gas phase of the NMR tube with H2S. The tube was then placed into the NMR probe, which was maintained at 60°C. Successive spectra were acquired at a rate of one every 10 min, with every fourth being of the 31P rather than 1H region of the NMR spectrum. The 1H NMR spectrum after 100 min showed almost complete conversion to a 1:1.8 mixture of cis- and trans-Ru(SH)2(dpm)2 (cis- and trans-15).

\textit{trans-Ru(SH)2(dpm)2 (trans-15): 1H NMR (C6D6) δ -3.73 ppm (t, 3J_{PH} = 5.7 Hz, SH), 5.10 ppm (unresolved multi, CH2); 31P{1H} NMR (C6D6) δ -7.05 ppm (s).}
cis-Ru(SH)_2(dpm)_2 (cis-15): ^1H NMR (C_6D_6) δ -1.92 ppm (s, SH), 4.62 ppm (unresolved multi, CH_2), 5.10 ppm (unresolved multi, CH_2); ^31P{^1H} NMR (C_6D_6) δ -5.93 ppm (t, 2J_Pp = 28.5 Hz), -22.65 ppm (t, 2J_Pp = 28.4 Hz).

Cis- and trans-15 were isolated\textsuperscript{254} from the reaction of 7 (300 mg, 0.34 mmol) with H_2S (saturated solution) in THF (30 mL) after 24 h at room temperature. The yellow precipitate thus formed was collected by filtration. Elem. Anal.: Calcd. for C_{50}H_{46}P_{4}RuS_{2}: C, 64.2; H, 5.0. Found: C, 63.6; H, 5.0. The precipitate contained only 5% of the trans isomer, while the solid precipitated from the filtrate contained 33% of the trans isomer.

The reaction of trans-RuH(BH_4)(dpm)_2 with H_2S, using similar methods, produced a 1:2 mixture of cis- and trans-15\textsuperscript{254}

The reaction of cct-Ru(SC_6H_4pCH_3)_2(CO)_2(PPh_3)_2 (14b) with H_2S: Complex 14b (3 mg, 3.3 μmol) was dissolved in C_6D_6 (0.5 mL) and exposed to H_2S at room temperature. The complex had been converted entirely to cct-Ru(SH)_2(CO)_2(PPh_3)_2 by the time the first ^31P{^1H} NMR spectrum had been acquired, within 5 min after the start of the reaction.

The reaction of cct-Ru(SC_6H_4pCH_3)_2(CO)_2(PPh_3)_2 (14b) with ethanethiol: A saturated C_6D_6 solution of 14b was prepared in an NMR tube under Ar, the tube being capped with a septum. EtSH (24 μL, 0.32 mmol) was injected through the septum, and the tube was placed into the NMR probe at 20°C. Successive spectra were acquired at a rate of one every 6 min, with every third being of the ^1H rather than ^31P region of the NMR spectrum. The ^31P{^1H} NMR spectra after 26 min no longer changed. The solution contained 75% 14b and 25% cct-Ru(SC_2H_5)(SC_6H_4pCH_3)(CO)_2(PPh_3)_2 (14bd), based on the ^31P NMR integration. After 70 min, more EtSH (77 μL, 1.0 mmol) was added, which shifted the equilibrium. After 200 min, the product mixture was 11%
14b (δ 10.90 ppm), 44% 14bd (11.00 ppm), and 45% cct-Ru(SC$_2$H$_5$)$_2$(CO)$_2$(PPh$_3$)$_2$
(14d, 11.18 ppm).

This experiment was repeated three times, but with 6 mM of the starting complex and
three different concentrations of ethanethiol (260 to 1530 mM). Approximate $K_{eq}$ values
at 20°C (Section 3.8) were calculated from the $^1$H NMR spectra: $K_1 = 4(±1.4) \times 10^{-2}$, $K_2 = 1(±0.2) \times 10^{-2}$.

The reaction of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a) with thiols: p-Thiocresol (2.8 mg, 
0.223 M) and 14a (4.2 mg, 5.7 mM) were dissolved in C$_6$D$_6$ (1 mL) in an NMR tube
under Ar. Successive $^{31}$P{$^1$H} NMR spectra were acquired at 21°C, each taking 11 min.
By 2 h, the concentrations of the complexes had converged to 34% 14a, 56%
cct-Ru(SH)(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (14ab) and 10%
cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b).

A sample of 14a (4 mg, 7 mM) was dissolved in C$_6$D$_6$ (0.8 mL) in an NMR tube
under Ar, and PhSH (6 to 180 µL, 7.7 x 10$^{-2}$ M to 2.0 M) was injected, before the start of
monitoring by $^{31}$P{$^1$H} NMR spectroscopy at 21°C. The results of these experiments
are described in detail in Section 3.8.

Ethanethiol (0.25 mL, 3.3 mmol) and 14a (3 mg, 4.0 µmol) were dissolved in C$_6$D$_6$
and the reaction monitored in situ by $^{31}$P{$^1$H} NMR spectroscopy at room temperature.
By 20 min, no change had been observed in the spectra.

The reaction of Ru(CO)$_3$(PPh$_3$)$_2$ (10) with H$_2$S: The precursor complex 10 was
supplied by Dr. C.-L. Lee, who prepared it by the reaction of Ru(CO)$_2$(PPh$_3$)$_3$ with
CO.177 A refluxing THF (40 mL) solution of 10 (600 mg, 0.85 mmol), after being under
H$_2$S (1 atm) for 3 h, was evaporated to dryness, the reaction giving 5-10% conversion to
cct-RuH(SH)(CO)$_2$(PPh$_3$)$_2$ (9a) and 14a, as determined by $^{31}$P NMR spectroscopy, the
remainder being unreacted starting material.254
The reaction of Ru(CO)$_2$(dpm)(PPh$_3$)$_2$ (16) with thiols: The precursor complex, 16, was supplied by Dr. C.-L. Lee, who prepared it by the reaction of Ru(CO)$_2$(PPh$_3$)$_3$ with dpm (synthesis and characterization, including the crystallographically-determined structure of the 1,1-bis(diphenylphosphino)ethane (dpm-Me) analogue, to be published).

Ethanethiol (98 µL, 1.3 mmol) and 16 (16 mg, 19 µmol) were stirred in THF (5 mL) for 5 h at room temperature, after which the volatiles were removed by vacuum distillation. The hydride region of the $^1$H NMR spectrum of the residue in C$_6$D$_6$ contained three patterns at $\delta$ -4.65 (t, $^2$J$_{PH}$ = 19.8 Hz, RuH of 2d), -8.09 (ddd, $^2$J$_{transPH}$ = 107, $^2$J$_{cisPH}$ = 20.1, 13.8 Hz, RuH of 17), -8.55 ppm (ddd, $^2$J$_{cisPH}$ = 21.7, 20.1, 16.3 Hz, RuH of 18). The $^{31}$P($^1$H) NMR spectrum contained a large number of unidentified peaks, in addition to those for 16 and 9d. The relative intensities of the peaks mentioned above are described in Section 3.9.

Thiophenol (10 µL, 97 µmol) and 16 (7 mg, 9.0 µmol) were dissolved in C$_6$D$_6$. After 10 min, two singlets in the $^{31}$P($^1$H) NMR spectrum were observed, in addition to the peaks for the starting complex. The largest, at 15% of the integral, was of an unknown complex (at -9.67 ppm), while the smallest, barely detectable by $^{31}$P($^1$H) NMR spectroscopy, was cct-RuH(SPh)(CO)$_2$(PPh$_3$)$_2$ (9i, 37 ppm). The identity of this latter product was confirmed by the $^1$H NMR spectrum, which shows a triplet at -4.54 ppm ($^2$J$_{PH}$ = 19.8 Hz). No other hydride signal was observed.

The reaction of Ru(CO)$_2$(dpm)(PPh$_3$)$_2$ (16) with H$_2$: A sample of Ru(CO)$_2$(dpm)(PPh$_3$)$_2$ (7.4 mg, 9 µmol) was stirred in THF (5 mL) under H$_2$ for two days at room temperature. Hexanes were added to the light brown solution to induce precipitation of a product which was collected by filtration. The $^{31}$P($^1$H) NMR spectrum (C$_6$D$_6$) contained many peaks, all unidentified. The metal-hydride region of the $^1$H NMR spectrum contained four weak patterns, at $\delta$ -5.30 (m, unidentified), -6.33
(t, $^{2}J_{PH} = 23.3$ Hz, cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$), -8.43 (ddd, $^{2}J_{cisPH} = 22.1$, 14.1, and 4.0 Hz, unidentified), and -8.14 ppm (ddd, $^{2}J_{cisPH} = 21.8$, 13.6, and 4.1 Hz, unidentified).
4. REACTIONS OF CARBONYL (PHOSPHINE) RUTHENIUM COMPLEXES WITH DISULPHIDES, THIOETHERS, AND RELATED REAGENTS

4.1 THE REACTIONS OF Ru(CO)₂(PPh₃)₃ WITH DISULPHIDES

The reaction of 2 with p-tolyl disulphide (equation 4.1, R = C₆H₄pCH₃),

\[
\text{Ru(CO)₂(PPh₃)₃ + RSSR} \rightarrow \text{Ru(SR)₂(CO)₂(PPh₃)₂ + PPh₃}
\]

briefly mentioned in a previous publication from this laboratory, proceeds cleanly in THF, giving an isolable product, 14b (R=C₆H₄pCH₃). The same product is detected by \(^{31}\text{P}\{\text{H}\}\) NMR spectroscopy after the reactions of p-tolyl disulphide with cct-RuH(SEt)(CO)₂(PPh₃)₂ (9d, Section 4.4), and p-thiocresol with cct-RuH₂(CO)₂(PPh₃)₂ (3, Section 3.6).

Both 14b and the related complex cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a) have been fully characterized (Section 4.2). Other examples of cct-Ru(SR)₂(CO)₂(PPh₃)₂ complexes have been synthesized in this laboratory (Section 4.2) and other isomers have since been reported in the literature.260

The reaction of 2 (7.5 mM) with p-tolyl disulphide (210 mM) at 18°C in C₆D₆, monitored by \(^{31}\text{P}\{\text{H}\}\) NMR (Fig. 4.1), has a pseudo-first order rate constant of 1.2 x 10⁻³ s⁻¹ and a half-life of 560 s (9.4 min). In the presence of a large amount of 1,1-dicyclopentylene (2.1 M), a thyl-radical trap, the reaction rate is unchanged, suggesting that the reaction mechanism does not involve free radicals. After the reaction of 2 with p-tolyl disulphide in the presence of added phosphine, cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (9b) and Ph₃PO are observed in addition to 14b. This may be due to a side-reaction involving trace water.262

\[
\text{RSSR + Ph₃P + H₂O} \rightarrow 2\text{RSH} + \text{Ph₃PO}
\]
Fig. 4.1 The logarithmic dependence of the concentration of Ru(CO)$_2$(PPh$_3$)$_3$ (2, [2]$_0$=7.5 mM) versus time during its reaction with p-tolyl disulphide (210 mM) in C$_6$D$_6$ at 18°C with or without a thyl radical trap (1,1-dicyclopropylthylene).
The reaction of 2 with p-tolyl disulphide in THF, monitored by UV at 26°C, has an isosbestic point at 426 nm (Fig. 4.2), which decays because of a subsequent reaction which results in a UV spectrum having no maximum between 350 and 550 nm. This subsequent reaction, which is an order of magnitude slower than reaction 4.1, will be more fully described in Section 6.2.1. Because the subsequent reaction has an isosbestic at 395 nm, this wavelength was chosen for the collection of absorbance data for the measurement of the initial rate of reaction 4.1. This rate, calculated from the absorbances and the ε values of isolated samples of 2 and 14b, increases with [2], although the scatter in the data is greater than expected (Fig. 4.3). The dependence of the observed initial rate on [RSSR] is first order at low [RSSR] (< 4 mM), decreasing to zero order at high [RSSR] (Fig. 4.4a). This is qualitatively consistent with the following mechanism.

\[
\begin{align*}
\text{Ru(CO)}_2(\text{PPh}_3)_3 & \xrightleftharpoons[k_1]{k_-1} \text{Ru(CO)}_2(\text{PPh}_3)_2 \\
& \xrightleftharpoons[k_{2\text{RSSR}}]{k_-1} \text{Ru(SR)}_2(\text{CO})_2(\text{PPh}_3)_2 \\
\end{align*}
\]

\[
\frac{d[14]}{dt} = \frac{k_1 k_2 [2][\text{RSSR}]}{k_-1 [L] + k_2 [\text{RSSR}]}
\]

The observed initial rate constant at high [RSSR] (\(k_{\text{obs}} = 7 \times 10^{-3} \text{ s}^{-1}\)) should correspond to \(k_1\). The same constant can be calculated from the plot of the inverse of the rate equation (Fig. 4.4b). However, the value of \(k_1\) determined from the reaction of Ru(CO)$_2$(PPh$_3$)$_3$ with CO is \(4 \times 10^{-2} \text{ s}^{-1}\) (single experiment at 1.0 mM 2 and 1 atm CO in THF at 26°C). The reason for this discrepancy is not known. Reaction 4.1 is not sufficiently clean for accurate kinetic data. The proposed mechanism should therefore be considered as tentative.

The initial concentration of PPh$_3$ must be less than 0.05 mM because the concentration of PPh$_3$ in solutions of Ru(CO)$_2$(PPh$_3$)$_3$ is not detectable by $^{31}$P NMR. Thus, it is possible to place a lower limit of 80 on the value of \(k_-1/k_2\), although the exact value cannot be determined because the conventional method$^{172}$ requires addition of excess PPh$_3$, which causes a side reaction to occur. Values of \(k_-1/k_2\) have been determined for the corresponding mechanisms of the reactions of 2 with CO and H$_2$ (0.043 and 0.15, respectively, at 24°C in dma).$^{172}$ The
Fig. 4.2 The UV/visible absorption spectrum of a solution of Ru(CO)$_2$(PPh$_3$)$_3$ (0.60 mM) and p-tolyldisulphide (8.2 mM) in THF at 26°C a) after 70 s, b) 190 s, c) 320 s, d) 460 s, e) 620 s, f) 990 s, g) 1440 s, and thereafter every 600 s.
Fig. 4.3 The dependence on [2] of the initial rate of the reaction Ru(CO)$_2$(PPh$_3$)$_3$ (2) with $p$-tolyldisulphide (8 mM) in THF at 26°C.
Fig. 4.4  a) The dependence on [RSSR] of the initial rate of the reaction of Ru(CO)₂(PPh₃)₃ (2, 0.34 mM) with p-tolyl disulphide in THF at 26°C, showing the line which corresponds to the best-fit straight line in Fig. 4.4b.

b) Plot of 1/(initial rate) against 1/[RSSR] for the same reaction, including the best-fit straight line.
reaction of the unobserved intermediate Ru(CO)₂(PPh₃)₂ with p-tolyl disulphide is therefore three orders of magnitude slower than with CO or H₂, if one neglects the effect of solvent.

The reaction of 2 with ethyl disulphide is neither as fast nor as clean as that with p-tolyl disulphide, producing cct-RuH(SEt)(CO)₂(PPh₃)₂ (9c, 6 % by 3¹P NMR) and cct-Ru(SEt)₂(CO)₂(PPh₃)₂ (14c, 12 %) after 110 min at room temperature in C₆D₆. The rate of the k₂ step in the reaction with EtSSEt must be even slower than the rate with p-tolyl disulphide, as expected for the oxidative addition of a weaker Lewis acid.

4.2 THE CHARACTERIZATION OF cct-Ru(SR)₂(CO)₂(PPh₃)₂

The complex cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) was synthesized from Ru(CO)₂(PPh₃)₃ (2) and p-tolyl disulphide (Section 4.1), while cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a) was synthesized from 2 or cct-RuH₂(CO)₂(PPh₃)₂ (3) and H₂S (Sections 3.1 and 3.3). Both 14a and 14b have been fully characterized, and analyze correctly. The structures of both have been determined by X-ray crystallography. In addition, several other members of the series cct-Ru(SR)₂(CO)₂(PPh₃)₂ (Table 4.1) have been observed in situ by ¹H and 3¹P{¹H) NMR spectroscopy during the reactions of 14a or 14b with R'SH (reaction 3.18) or the reactions of cct-RuH₂(CO)₂(PPh₃)₂ (3) with binary mixtures of thiols in large excess (reaction 4.3, cf. sections 3.5, 3.6).

\[ \text{RuH}_2(CO)_2(PPh_3)_2 + (2-n)RSH + nR'SH \rightarrow \text{Ru(SR)}_{2-n}(SR')_n(CO)_2(PPh_3)_2 + 2H_2 \]

The 3¹P NMR chemical shift of 14 depends very little on the nature of the thiolate group, with the exceptions of complexes containing the -SH and -SC₆F₅ ligands, which have signals significantly further downfield (Table 4.1). The observed spectra show that the 3¹P chemical
Table 4.1 NMR Spectroscopic Data for Complexes of the Series cct-Ru(SR)(SR')(CO)2(PPh3)2a

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>R'</th>
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<th>31p  δ</th>
<th>1H NMRd</th>
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<td></td>
<td></td>
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<td>calc.c</td>
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<td>14a</td>
<td>H</td>
<td>H</td>
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<td>21.47</td>
<td>-1.93 (t, 3JPH=6.8, SH)</td>
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<tr>
<td>14ab</td>
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<td>C6H4pCH3</td>
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<td>16.07</td>
<td>-1.82 (t, 3JPH=7.3, SH)</td>
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<td>14j</td>
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<td>C6F5</td>
<td>18.30g</td>
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<td>C6H5</td>
<td>14.42g</td>
<td>14.46</td>
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<td>14d</td>
<td>CH2CH3</td>
<td>CH2CH3</td>
<td>11.25e</td>
<td>11.21</td>
<td>1.16 (t, 3JHH=7.4, CH3)</td>
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<td>1.97 (q, 3JHH=7.4, CH2)</td>
</tr>
<tr>
<td>14bd</td>
<td>CH2CH3</td>
<td>C6H4pCH3</td>
<td>11.00f</td>
<td>11.04</td>
<td>6.54 (d, 3JHH=8.1, o-Ph)</td>
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<td>C6H4pCH3</td>
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<td>6.86 (d, 3JHH=8.2, m-Ph)</td>
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<tr>
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<td>C6H5</td>
<td>10.69g</td>
<td>10.67</td>
<td>-</td>
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a C6D6 solutions at room temperature.
b observed chemical shift (ppm), with reference to 85 % H3PO4 in H2O.
c calculated from the empirical equation presented in Section 4.2.
d ppm, with reference to TMS in C6D6. Coupling constants are given in Hz. Data are for the protons of the thiolate ligands only.
e isolated sample.
f generated in situ via reaction 3.18.
g generated in situ via reaction 4.3.
shift (δ) of \textit{ccr-Ru(SR)(SR')}\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} in C\textsubscript{6}D\textsubscript{6} at room temperature is roughly predicted by the following simple additivity rule.

\[ \delta = 10.67 \text{ ppm} + X(R) + X(R') \]

where
\[
\begin{align*}
R &= \text{H} & \text{C}_6\text{F}_5 & \text{CH}_2\text{CH}_3 & \text{C}_6\text{H}_4\text{pCH}_3 & \text{C}_6\text{H}_5 \\
X &= 5.4 & 3.79 & 0.27 & 0.10 & 0.00 \text{ ppm}
\end{align*}
\]

The error is ±0.06 ppm except for the complexes containing the -SH ligand. The chemical shifts of \textit{14} in CD\textsubscript{2}Cl\textsubscript{2} are 21.91 (R=H), 11.43 (R=Ph), 11.39 (R=C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3}), and 11.77 ppm (R=C\textsubscript{6}H\textsubscript{4}mCH\textsubscript{3}), not significantly different from those in C\textsubscript{6}D\textsubscript{6}. The \textsuperscript{31}P chemical shifts in CDCl\textsubscript{3} of the \textit{ccr-Ru(SR)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}} complexes isolated by Catala et al.\textsuperscript{260b} were reported relative to P(OMe)\textsubscript{3}. After conversion to shifts relative to 85 \% H\textsubscript{3}PO\textsubscript{4} (assuming that the signal of P(OMe)\textsubscript{3} appears at 141 ppm\textsuperscript{263}), the reported shifts of these complexes are 22.8 (R=Me), 39.6 (tBu), 26.6 (C\textsubscript{6}F\textsubscript{4}H), and 29.4 ppm (C\textsubscript{6}F\textsubscript{5}, \textit{14j}). It is not known why the chemical shift reported by Catala et al. for \textit{14j} and that in the present study differ by more than 10 ppm. The spread of the chemical shifts are similar in the two studies. The difference between the chemical shifts of \textit{ccr-Ru(SR)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}} (R=Me and C\textsubscript{6}F\textsubscript{5}) in CDCl\textsubscript{3} is 6.6 ppm,\textsuperscript{260b} very similar to the difference (R=Et vs. C\textsubscript{6}F\textsubscript{5}) of 7.05 ppm in C\textsubscript{6}D\textsubscript{6} found in the present study.

The \textsuperscript{1}H NMR test described in Section 2.3.3, applied to the spectra of \textit{14a} and \textit{14b} (Fig. 4.5), proves that the PPh\textsubscript{3} ligands of those complexes are in \textit{trans} positions. The mercapto signals of \textit{14a} are triplets, 1.07 ppm downfield of the same signal in \textit{ccr-RuH(SH)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}} (9a). The methyl signal of \textit{14b} is at the same chemical shift (2.03 ppm) as its hydrido-thiolato analogue 9b.

The FT-IR spectra of \textit{14} (Fig. 4.6) contain two strong \textit{v}(CO) bands at 2046 and 1981 cm\textsuperscript{-1} (\textit{14a})\textsuperscript{126} or at 2028 and 1968 cm\textsuperscript{-1} (R=\textit{14b})\textsuperscript{254}, suggesting that both complexes contain \textit{cis}-carbonyls, and therefore that both are \textit{ccr} isomers in solution. The \textit{ccr} isomer is the most stable of the isomers of \textit{ccr-RuCl\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}}.\textsuperscript{169}
Fig. 4.5 $^1$H NMR spectrum of $cct$-Ru(SC$_6$H$_4$($\rho$-CH$_3$)$_2$)(CO)$_2$(PPh$_3$)$_2$ (9b), in C$_6$D$_6$, with an expanded view of the phenyl region.
Fig. 4.6 FT-IR spectrum of cct–Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ in HCB. The peaks due to HCB are indicated with asterisks.
The UV/vis spectrum of 14 contains a maximum at 371 (ε = 2460, 14a) or 430 nm (ε = 3040 M⁻¹ cm⁻¹, 14b), which causes the yellow colour. The absorption is probably caused by the same ligand-to-metal charge transfer which caused the similar band in the spectrum of cct-RuH(SR)(CO)₂(PPh₃)₂ (Section 3.2).

The solid state X-ray crystal structure of 14b (Fig. 4.7) was investigated by Dr. S. Rettig, and can be compared to the previously solved structure of a crystal of 14a (Fig. 4.8) synthesized in this lab. Both were shown to be of cct geometry. Bond lengths, bond angles, and other crystallographic data are listed in Tables 4.2 through 4.5 and Appendices 1 and 3. Related complexes for which X-ray crystal structures have been reported include ccc-Os(SC₆F₅)₂(CD)₂(PEt₂Ph)₂ and ccf-Ru(OCOPh)₂(CO)₂(PPh₃)₂.

The observed deviations from octahedral geometry around the Ru centre of 14b are due to the PPh₃ groups crowding the carbonyls in order to avoid the bulky thiolate ligands. The carbonyls therefore are slightly further apart (91.6°), and the thiolates closer together (83.05°) than expected for octahedral geometry. This effect is not observed in 14a (angles: C-Ru-C 89.1°, S-Ru-S 92.2°) because the mercapto ligands are considerably less bulky than the thiolates in 14b. The proximity of the S atoms in 14b (3.26 Å) but not 14a (3.56 Å) is probably caused by the bulky p-tolyl groups which point away from each other. The S atoms are not so close together as to indicate S-S attractive interactions, which have been reported for some cis-thiolate complexes. "S-S contacts are invariably shorter when the sulphur lone pairs (assuming approximate sp³ hybridizations) are oriented so as to allow overlap, resulting in an interaction which would normally be considered repulsive." Visual inspection of the structure of 14b shows that the thiolate ligands are oriented so as to allow almost no lone pair overlap. In both complexes, and in ccc-Fe(SPh)₂(CO)₂(dppe) (dppe = 1,2-bis{diphenylphosphino}ethane, S-S distance is 3.23 Å), the S-S interatomic distance is considerably longer than observed for S-S bonds such as in cct-Os(η²S₂Me)(CO)₂(PPh₃)₂ (2.022 Å).

The lengths of the Ru-S, Ru-C, and C-O bonds of 14a, 14b, and cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (9b, Section 3.2) are similar. The S-C bond lengths of
Fig. 4.7 a) The structure of cct-Ru(SC₅H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b), showing co-crystallised THF molecule, and b) a stereoscopic view of the same structure, with hydrogen atoms and the THF molecule omitted for clarity.
Fig. 4.8 The structure of Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$. Hydrogen atoms are omitted for clarity.
Table 4.2 Selected bond lengths (Å) with estimated standard deviations in parentheses, for \(cct\text{-Ru}(SC_6H_4pCH_3)_2(CO)_2(PPh_3)_2\) (14b).

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<td>Ru</td>
<td>C(2)</td>
<td>1.863 (8)</td>
<td>P(1)</td>
<td>C(9)</td>
<td>1.814 (8)</td>
</tr>
<tr>
<td>Ru</td>
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Table 4.3 Selected bond angles (°) with estimated standard deviations in parentheses, for \(cct\text{-Ru}(SC_6H_4pCH_3)_2(CO)_2(PPh_3)_2\) (14b).

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### Table 4.4 Selected bond lengths (Å) with estimated standard deviations in parentheses, for cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a).²⁶⁴

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### Table 4.5 Selected bond angles (°) with estimated standard deviations in parentheses, for cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a).²⁶⁴

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**14b** (1.778 and 1.788 Å) are slightly longer than that found in **9b** (1.769 Å), possibly because of the steric effect of the thiolate ligands in **14b**. The protons of the mercapto ligands of **14a** were located, although the errors in the bond lengths and angles are high.

The Ru-P bond lengths of the complexes increase with the increasing bulk of the ligands, in the following order:

\[
\text{RuH(SR)(CO)2(PPh3)2} < \text{Ru(SH)2(CO)2(PPh3)2} < \text{Ru(SR)2(CO)2(PPh3)2}
\]

As discussed in Section 3.2, an increase in Ru-P bond length has the effect of decreasing the \(^{31}\text{P}\) chemical shift (Fig. 3.7). The results here support the speculation (Section 3.2) that the changes in the \(^{31}\text{P}\) NMR chemical shift of **9** and **14** with changes in the thiolate group are due to steric effects.

### 4.3 THE REACTION OF *cct*-RuH\(_2\)(CO)\(_2\)(PPh\(_3\))\(_2\) (**3**) WITH DISULPHIDES

As mentioned in a communication from this laboratory,

\[
2\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{RSSR} \rightarrow 2\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2 + \text{H}_2
\]

rather than the *bis*-thiolato complex **14** that one might expect from a mechanism involving reductive elimination of H\(_2\) (cf. reaction 3.4) followed by oxidative addition of RSSR (cf. reaction 4.1). It was suggested by the authors of the report that the reaction involves two steps.

\[
\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{RSSR} \rightarrow \text{RuH(SR)(CO)}_2(\text{PPh}_3)_2 + \text{HSR}
\]
RuH₂(CO)₂(PPh₃)₂ + RSH \rightarrow RuH(SR)(CO)₂(PPh₃)₂ + H₂  

The evidence for this was the detection of RSH (0.02 mmol) after a 5 h reaction of a THF solution (40 mL) of the dihydride (0.41 mmol) and p-tolyl disulphide (0.41 mmol).

Although the suggested sequence of reactions is reasonable, it is not unequivocal that the detection of a small amount of thiol is evidence for reaction 4.5; the thiol could instead have been produced by reaction 4.6 (see below).

The reaction of 3 with an 18-fold excess of p-tolyl disulphide in C₆D₆ was monitored by NMR at 45°C. After 1 h, the conversion to 9b was 84%. If the reaction is monitored at room temperature, a small amount (less than 11%) of 14b is observed while the reaction to 9b proceeds. No p-thiocresol was detected in the ¹H NMR spectrum during this time, possibly because reaction 3.4 is faster than reaction 4.4; the concentration of thiol never reaches a level sufficient for detection. The production of the bis-thiolate complex 14b is evidence for reaction 4.6 (to be described in Section 4.4), although a small amount of this product could have been produced by reaction 4.7, for which no independent evidence exists.

RuH(SR)(CO)₂(PPh₃)₂ + RSSR \rightarrow Ru(SR)₂(CO)₂(PPh₃)₂ + RSH  

RuH₂(CO)₂(PPh₃)₂ + RSSR \rightarrow Ru(SR)₂(CO)₂(PPh₃)₂ + H₂

The rate of reaction 4.4, monitored by either NMR or UV/vis spectroscopy is neither reproducible nor pseudo-first order, not surprising considering that reactions 3.4, 4.5, 4.6 and possibly 4.7 are all occurring in the same solution. No isosbestic points are observed because the UV/vis spectra of 3 and 9b do not have cross-over points. The mechanism of reaction 4.4 was not determined.
4.4 THE REACTION OF $cct$-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ WITH DISULPHIDES

The reaction of $cct$-RuH(SMe)(CO)$_2$(PPh$_3$)$_2$ (9c) with $p$-tolyl disulphide in C$_6$D$_6$ was monitored by $^1$H and $^{31}$P{$_1$H} NMR at 45°C. The complex is cleanly converted to $cct$-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (9b). The reaction has a half-life of 8.3 min (at [9c]=17 mM, [RSSR]=250 mM), assuming pseudo-first order behaviour.

$$\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2 + \text{R'SSR'} \rightarrow \text{RuH(SR')}(\text{CO})_2(\text{PPh}_3)_2 + \text{RSSR'} \quad 4.8$$

The complex $cct$-RuH(SEt)(CO)$_2$(PPh$_3$)$_2$ (9d) reacts with $p$-tolyl disulphide in THF for two days at room temperature, resulting in complete conversion to $cct$-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b) and the photolysis products thereof (Section 6.2.1).

$$\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2 + \text{R'SSR'} \rightarrow \text{Ru(SR')}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{RSH} \quad 4.9$$

Reaction 4.8 is probably the first step in reaction 4.9.

4.5 THE REACTIONS OF CARBONYL (PHOSPHINE) RUTHENIUM COMPLEXES WITH STRAINED CYCLIC THIOETHERS

The strained cyclic thioethers ethylene and propylene sulphide, otherwise known as thiirane and methylthiirane, are commonly-used sulphur transfer agents and rarely coordinate.129 Propylene sulphide, for example, reacts overnight with $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3, reaction 4.10) or Ru(CO)$_2$(PPh$_3$)$_3$ (2, reaction 4.11), or for 3 days with $cct$-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a, reaction 4.12) at room temperature in THF to produce $cct$-RuS$_2$(CO)$_2$(PPh$_3$)$_2$ (19),254 a complex which has been reported previously$^{118a}$ (Section 4.7). The production of propene, H$_2$, and H$_2$S in these reactions has not been experimentally confirmed.
The production of SPhS in reaction 4.11 (identified by $^{31}$P{$^{1}$H} NMR spectroscopy) suggests the possibility of reaction 4.13, but propylene sulphide and PPh3 in C6D6 fail to react within 12 h at room temperature. Oxidation of the phosphine to the phosphine sulphide must therefore involve the ruthenium complex.

In the present work, reaction 4.10 (using a large excess of thioether) was monitored by $^{31}$P{$^{1}$H} NMR spectroscopy at 21°C, and initially two sulphur-containing complexes were observed, 19 (22 % of the $^{31}$P NMR signal after 10 min) and cct-RuH(SR)(CO)2(PPh3)2 (9, 10 %, R unknown). After 160 min, the signals due to these species had increased to 53 % and 29 %, respectively, while SPhS started to appear (12 % of the $^{31}$P NMR signal). After 7 days, the sole product detected in the $^{31}$P NMR spectrum was SPhS. The rate of loss of 3, as measured by $^{31}$P NMR spectroscopy, was not pseudo-first order. The initial rate constant was calculated from the concentrations of 3 and 9 (determined from the $^{31}$P NMR peak integration) assuming the initial rate is first order in [3]. The value of this rate constant (6.0 x 10^{-4} s^{-1} at 21°C) is similar to that of the reaction of 2 with thiols (Section 3.3), and is therefore consistent with a mechanism involving reductive elimination of H2 as the first and rate determining step. Similar
31P{1H} NMR experiments monitoring the reaction of 2 with propylene sulphide showed that reaction 4.11 is complete after 3 min at 25°C in C₆D₆.

4.6 THE NON-REACTIONS OF CARBONYL (PHOSPHINE) RUTHENIUM COMPLEXES WITH UNSTRAINED THIOETHERS

The two complexes Ru(CO)₂(PPh₃)₃ (2) and cct-RuH₂(CO)₂(PPh₃)₂ (3) fail to react with thioethers such as MeSMe, PhSPh, and dibenzothiophene.

\[
\text{Ru(CO)}_2\text{(PPh}_3\text{)}_3 + \text{RSR} \rightarrow \text{no reaction} \quad 4.14
\]

\[
\text{RuH}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 + \text{RSR} \rightarrow \text{no reaction} \quad 4.15
\]

A 35-fold excess of freshly distilled thiophene reacts with 3 at room temperature to produce cct-RuH(SR)(CO)₂(PPh₃)₂ (2% conversion, R=unknown alkyl group) after three days. This reaction is probably due to a trace (0.5ppth, calculated from the extent of conversion of 3 to 9) of thiol which was not removed by the distillation. At least four C₄-thiols have boiling points within 20°C of that of thiophene.

4.7 THE REACTIONS OF CARBONYL(PHOSPHINE)RUTHENIUM COMPLEXES WITH OTHER NEUTRAL SULPHUR-CONTAINING REAGENTS

The reaction of Ru(CO)₂(PPh₃)₃ (2) with elemental sulphur in benzene has been reported, although the fate of the extra phosphine ligand was not mentioned.¹¹⁸a

\[
\text{Ru(CO)}_2\text{(PPh}_3\text{)}_3 + \frac{3}{8}\text{S}_8 \rightarrow \text{RuS}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 + \text{(SPPh}_3\text{?)} \quad 4.16
\]
The same product complex (19) is observed, along with SPPh₃, after the reaction of sulphur with ccr-Ru(SH)₂(CO)₂(PPh₃)₂.²⁵⁴

Dibenzyl trisulphide has been used to oxidize bridging thiolate groups to sulphides.²⁶⁸ The trisulphide reacts with ccr-Ru(SC₆H₄p(CH₃)₂(CO)₂(PPh₃)₂ (14b) relatively quickly at room temperature, giving SPPh₃ and a host of minor products (<3 % each) after 40 min. The trisulphide reacts with 2 or 3 more slowly, producing SPPh₃, and two unknowns with ³¹P NMR singlets with chemical shifts (34.67 and 31.34 ppm in C₆D₆) different from those of any of the related complexes that have been previously isolated, such as ccr-Ru(SR)₂(CO)₂(PPh₃)₂ (R=H or CH₂Ph), ccr-RuH(SR)(CX)₂(PPh₃)₂, or ccr-RuS₂(CO)₂(PPh₃)₂. The desulphurization of trisulphides by triphenyl phosphine, giving disulphides and SPPh₃, has been reported.²⁶⁹

4.8 EXPERIMENTAL DETAILS

The reaction of Ru(CO)₂(PPh₃)₃ (2) with p-tolyl disulphide: Complex 2 (140 mg, 0.15 mmol) and the disulphide (91 mg, 0.36 mmol) were dissolved in THF (20 mL) in a Schlenk tube wrapped with foil in darkness at room temperature. The solution remained orange throughout the reaction. After 4.5 h, the volume of the solution was reduced to 5 mL by vacuum distillation, and hexanes (60 mL) were added to induce precipitation. The collected yellow solid was ccr-Ru(SC₆H₄p(CH₃)₂(CO)₂(PPh₃)₂ (14b, 85 % yield). Elem. Anal. Calcd. for C₅₂H₄₄O₂P₂RuS₂: C, 67.3; H, 4.8; S, 6.9. Found: C, 67.3; H, 4.7; S, 6.8. UV/vis max (0.25 mM in THF) 430 nm (ε 3000 M⁻¹ cm⁻¹); FT-IR (Nujol) 2028, 1968 cm⁻¹ (ν(C=O)); (HCB) : 2029, 1971 cm⁻¹; ¹H NMR (C₆D₆) δ 2.03 (s, 6H, CH₃), 6.54 (d, 4H, ₃JHH = 8.1 Hz, SC₆H₄), 6.86 (d, 4H, ₃JHH = 8.2 Hz, SC₆H₄), 6.99 (m, 18H, p-,m-PPh₃), 7.95 ppm (m, 12H, o-PPh₃); ¹³C{¹H} NMR (C₆D₆) 20.90 ppm (s, CH₃); ³¹P{¹H} NMR (C₆D₆) 10.95 ppm (s).

A crystal of 14b suitable for X-ray crystallography was prepared by diffusion of hexanes into a concentrated THF solution under Ar in darkness. The collection and analysis of the
crystallographic data were performed by Dr. S. J. Rettig of this department.209 The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 10.0-16.0^\circ$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, were essentially constant. The data were processed259a and corrected for Lorentz and polarization effects, and absorption (empirical, based on azimuthal scans for four reflections).209

The structure analysis was initiated in the centrosymmetric space group $P\bar{1}$, the choice being confirmed by the subsequent successful solution and refinement of the structure. The structure was solved by conventional heavy atom methods, the coordinates of the Ru, P, and S atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The asymmetric unit contains one tetrahydrofuran solvate molecule in addition to the complex molecule. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions ($d_{C-H} = 0.98\ \text{Å}$, $B_{H} = 1.2\ B_{\text{bonded}}$ atom). Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography.259b Final atomic coordinates and equivalent isotropic thermal parameters ($B_{eq} = 4/3\sum_{ij}b_{ij}(a_{i}a_{j})$), bond lengths, and bond angles209 appear in Appendix 3, and Tables 4.2 and 4.3 respectively. Other crystallographic data for this structure and the other structures described in this work are presented in Appendix 1.209

The reaction of Ru(CO)$_2$(PPh)$_3$3 (2) with ethyl disulphide: A sample of 2 (3.3 mg, 7.1 mM) was dissolved in C$_6$D$_6$ (0.46 mL) in an NMR tube at room temperature under Ar, and EtS$\text{Se}$Et (36 µL, 592 mM) was added to start the reaction. After 30 min, $cct$-RuH(SEt)(CO)$_2$(PPh)$_3$2 (9d, 4 % conversion), $cct$-Ru(SEt)$_2$(CO)$_2$(PPh)$_3$2 (14d, 6 %), and PPh$_3$ were detected by $^{31}$P($^1$H) NMR spectroscopy. After 110 minutes, these conversions had increased to 6 and 12 %, respectively.
Monitoring the reaction of Ru(CO)$_2$(PPh$_3$)$_3$ (2) with p-tolyl disulphide by $^{31}$P{$_1$H} NMR spectroscopy:

a) without added PPh$_3$: Complex 2 (4.2 mg, 7.5 mM) and p-tolyl disulphide (31.7 mg, 210 mM) were dissolved in C$_6$D$_6$ (0.46 mL) in an NMR tube at 18°C under Ar. After 30 min, ccr-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b, 91 % conversion) and PPh$_3$ were observed. After 60 min, the conversion had increased to 99 %. The pseudo-first order log plot was linear, with some scatter (Fig. 4.1); the rate constant was 1.2 x 10$^{-3}$ s$^{-1}$.

b) with added PPh$_3$: Complex 2 (2.7 mg, 4.1 mM), p-tolyl disulphide (15.7 mg, 91 mM), and PPh$_3$ (23.7 mg, 130 mM) were dissolved in C$_6$D$_6$ (0.70 mL) in an NMR tube at 26°C under Ar. After 30 min, ccr-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (9b, 6 % conversion), 14b (8 %), and OPPh$_3$ (5 % of the $^{31}$P NMR signal) were observed, in addition to the signals for the starting materials. After 30 min at 50°C, these conversions had increased to 41, 45, and 10 %, for 9b, 14b, and OPPh$_3$ respectively (the integration of the signal for OPPh$_3$ cannot be assumed to accurately represent the concentration of that species, because of its large T$_1$ value).

c) with added 1,1-dicyclopentylylene: Complex 2 (4.6 mg, 7.3 mM), and p-tolyl disulphide (31.8 mg, 200 mM) were dissolved in a mixture of C$_6$D$_6$ (0.49 mL) and 1,1-dicyclopentylylene (0.13 mL, 2.1 M) in an NMR tube at 18°C under Ar. After 5, 14, and 28 min, 14b (40, 67, and 87 % conversion) and PPh$_3$ were observed. The pseudo-first order log plot was linear (Fig. 4.1), with more scatter than observed without the free radical trap; the rate constant was 1.1 x 10$^{-3}$ s$^{-1}$.

The reaction of ccr-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with mixtures of thiols: Complex 3 (4.6 mg, 8.4 mM) and p-thiocresol (24.4 mg, 246 mM) were dissolved in C$_6$D$_6$ under Ar in an NMR tube, which was capped with a septum. Thiophenol (20 µL, 244 mM) was injected through the septum. After 400 min at 21°C, the products were ccr-RuH(SC$_6$H$_5$)(CO)$_2$(PPh$_3$)$_2$ ($^{31}$P{$_1$H} NMR δ 37.24 ppm, 46 %), ccr-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (37.42 ppm, 21 %), ccr-Ru(SC$_6$H$_5$)$_2$(CO)$_2$(PPh$_3$)$_2$ (10.69 ppm, 12 %), ccr-Ru(SC$_6$H$_5$)(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$
(10.78 ppm, 15 %), and cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (10.90 ppm, 6 %). Experiments
with other mixtures of thiols were performed in a similar manner.

The reaction of cct-RuH₂(CO)₂(PPh₃)₂ (3) with p-tolyl disulphide:

a) 21°C: Complex 3 (1.7 mg, 3.9 mM) and p-tolyl disulphide (20 mg, 130 mM) were dissolved
in C₆D₆ (0.63 mL) in an NMR tube under Ar. The reaction was monitored by ³¹P{¹H} NMR
spectroscopy, with the temperature of the sample being maintained at 21±1°C. After 40 min,
4 h, and 14 h, the species detected were 3 (55, 38, and 10 %),
cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (42, 57, and 74 %), and
cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (3, 5, and 11 %).

b) 45°C: Complex 3 (3.5 mg, 7.3 mM) and p-tolyl disulphide (23 mg, 130 mM) were dissolved
in C₆D₆ (0.69 mL) in an NMR tube under Ar. The reaction was monitored by ³¹P{¹H} NMR
spectroscopy, with the temperature of the sample being maintained at 45°C. After 30 min and
1 h, the species detected were 3 (33 and 16 %), and cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (67
and 84 %).

The reaction of cct-RuH(SR)(CO)₂(PPh₃)₂ with p-tolyl disulphide: a) over minutes: A
sample of cct-RuH(SMe)(CO)₂(PPh₃)₂ (9c, 8.0 mg, 17 mM) and p-tolyl disulphide (39 mg, 250
mM) were dissolved in C₆D₆ (0.65 mL) in an NMR tube under Ar. The reaction was monitored
by ¹H and ³¹P{¹H} NMR spectroscopy at 45°C. After 12 and 55 min, the species detected
were unreacted 9c (66 and 10 % of the hydride region of the ¹H NMR spectrum) and
cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (34 and 90 %). Only four spectra were acquired, not
enough to confirm that the rate of loss of 9c was first order. However, assuming pseudo-first
order behaviour, the observed rate constant was 1.4 x 10⁻³ s⁻¹, corresponding to a half-life of
8.3 min.

b) over days: A sample of cct-RuH(SEt)(CO)₂(PPh₃)₂ (14 mg, 19 μmol) and p-tolyl disulphide
(123 mg, 500 μmol) were dissolved in THF (10 mL) in a Schlenk tube under Ar. The yellow
solution turned to a more orange colour over 2 days at room temperature. The solvent was
removed by vacuum filtration, and the residue was redissolved in C6D6. The 31P{1H} NMR
spectrum revealed the presence of cct-Ru(SC6H4pCH3)2(CO)2(PPh3)2 (14b, 38 % of the
signal), PPh3 (15 %), and unknown species which generated nine signals (<7 % each), most of
which are also observed when solutions of cct-Ru(SC6H4pCH3)2(CO)2(PPh3)2 are irradiated
with 430 nm light (Section 6.2.1).

The reaction of cct-RuH2(CO)2(PPh3)2 (3) with propylene sulphide: A sample of 3 (3.6 mg,
12 mM) was dissolved in a mixture of CD2Cl2 (0.44 mL) and propylene sulphide (0.10 mL, 2.9
M) in an NMR tube under Ar. The reaction was monitored by 31P{1H} NMR at room
temperature (21°C). The species detected after 10 min, 38 min, 160 min, and 7 days were 3 (64,
39, 7, and 0 % of the signal), cct-RuS2(CO)2(PPh3)2 (22, 31, 53, and 0%), an unknown complex
with 31P and 1H NMR signals similar to those of cct-RuH(SR)(CO)2(PPh3)2 (10, 25, 29, and 0
%), and SPPPh3 (0, 4, 12, and 100 %). The chemical shifts of these four species were 56.19,
39.35, 38.36, and 42.86 ppm, respectively. The hydride region of the 1H NMR spectrum
contained triplets at -6.3 and -3.8 ppm, consistent with the presence of unreacted 3 and
cct-RuH(SR)(CO)2(PPh3)2. Similar results were obtained when C6D6 was used as the solvent.

The reaction of Ru(CO)2(PPh3)3 (2) with propylene sulphide: Propylene sulphide (50 µL,
1.1 M) was added to a solution of 2 (2.4 mg, 4.5 mM) in C6D6 (0.57 mL) at room temperature.
A 31P{1H} NMR spectrum acquired three minutes later detected three species; SPPPh3 (δ 41.97
ppm, 30 % of signal), cct-RuS2(CO)2(PPh3)2 (39.76 ppm, 30 %), and an unknown complex
(37.07 ppm, 40 %) with 31P and 1H NMR signals consistent with cct-RuH(SR)(CO)2(PPh3)2
(1H NMR δ -4.77 ppm, t, 2JPH = 20.4 Hz, R unknown but probably alkyl based on the 1H NMR
data).
The non-reaction of $cct$-Ru$_2$(CO)$_2$(PPh$_3$)$_2$ (3) with unstrained thioethers:

a) PhSPh: A sample of 3 (110 mg, 7.9 mM) was dissolved in a mixture of THF (20 mL) and PhSPh (0.6 mL, 180 mM) and the solution was stirred for 2 days under Ar at room temperature. The volume of the solvent was reduced to 10 mL by vacuum distillation and hexanes (30 mL) were added to the remainder to induce precipitation. The off-white solid collected by filtration was shown by $^{31}$P{H} NMR spectroscopy to be unreacted 3.

b) MeSMe: A sample of 3 (400 mg, 14.6 mM) was dissolved in a mixture of THF (40 mL) and MeSMe (0.5 mL, 170 mM) and the solution was stirred for a day at room temperature under N$_2$. The solvent was removed by vacuum distillation. $^{31}$P{H} NMR spectroscopy of the residue in C$_6$D$_6$ showed the presence of unreacted 3 and a small amount of $cct$-RuO$_2$(CO)$_2$(PPh$_3$)$_2$ (identified by comparison of the $^{31}$P NMR chemical shift to that reported by Dekleva).

c) thiophene: A sample of 3 (140 mg, 10 mM) was dissolved in a mixture of THF (20 mL) and thiophene (0.8 mL, 500 mM) and the solution was stirred for 3 days under Ar at room temperature. The volume of the solution was reduced to 5 mL by vacuum distillation and hexanes (20 mL) were added to the remainder to induce precipitation. The off-white solid collected by filtration was shown by $^{31}$P{H} NMR spectroscopy (C$_6$D$_6$) to be 3 (98 %) and $cct$-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ (9, 2 %, R unknown). The H NMR spectrum contained a weak triplet at -4.6 ppm (9), in addition to the triplet at -6.3 due to the dihydride (3).

d) dibenzothiophene: A sample of 3 (20 mg, 2.8 mM) and dibenzothiophene (154 mg, 84 mM) were dissolved in THF (10 mL) and the solution was left for four days under Ar at room temperature. The solvent was then removed by vacuum distillation, leaving a residue of 3 (identified by $^{31}$P{H} NMR spectroscopy).

The reactions of Ru(CO)$_2$(PPh$_3$)$_3$ and $cct$-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ with dibenzyl trisulphide:

Ru(CO)$_2$(PPh$_3$)$_3$ (150 mg, 7.9 mM) and dibenzyl trisulphide (286 mg, 51 mM) were dissolved in THF (20 mL) and the solution was stirred for 1 day. The volume of the solution was reduced
to 10 mL by vacuum distillation and hexanes (20 mL) were added to the remainder to induce precipitation of a yellow solid. This product was isolated by filtration and washed with hexanes (20 mL). The $^{31}\text{P}(^{1}\text{H})$ NMR spectrum ($\text{C}_6\text{D}_6$) of the product contained three peaks at 42.08 ppm (SPPh$_3$, 10 % of integral), 34.67 ppm (unknown, 20 %), and 31.34 ppm (unknown, 70 %). The filtrate was dried by vacuum distillation. The $^{31}\text{P}(^{1}\text{H})$ NMR spectrum ($\text{C}_6\text{D}_6$) of the residue contained the same three peaks but with different intensities (73, 25, and 2 %, respectively). The reaction of the trisulphide with $\text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ gave similar results.

The reaction of $\text{cct-Ru(SC}_6\text{H}_4\text{pCH}_3)_2(\text{CO})_2(\text{PPh}_3)_2$ (14b) with dibenzyl trisulphide: a sample of 14b (160 mg, 1.8 mM) and dibenzyl trisulphide (286 mg, 11.6 mM) were dissolved in THF (20 mL) under Ar in a darkened room. After 40 min, the solvent was removed by vacuum distillation. The $^{31}\text{P}(^{1}\text{H})$ NMR spectrum ($\text{C}_6\text{D}_6$) of the yellow residue redissolved in $\text{C}_6\text{D}_6$ showed that the major phosphorus-containing product was SPPh$_3$. Thirteen other signals were observed, although the integration of each of these peaks was less than 3 % of the total.
5 THE METATHESIS REACTIONS OF CHLORORUTHENIUM COMPLEXES WITH THIOLATE SALTS

5.1 INTRODUCTION

The metathesis reactions of transition metal chlorides with thiolate salts are common synthetic routes for the preparation of thiolate complexes. The driving force for the reaction is the precipitation of an insoluble salt (e.g. NaCl) or the formation of a volatile product (e.g. Me3SiCl). The following reactions illustrate the variety of thiolate salts that have been used.

\[
\text{CpRu(PPh}_3\text{)}_2\text{Cl} + \text{MSR} \rightarrow \text{CpRu(PPh}_3\text{)}_2\text{(SR)} + \text{MCl}
\]

- \(M = \text{Li; } R = \text{H, nPr, } i\text{Pr, C}_6\text{H}_4\text{PCH}_3\) (ref. 270)
- \(M = \text{Na; } R = \text{H}\) (refs. 90, 271)

\[
\text{CoX}_4^{2-} + 4\text{TiSR} \rightarrow \text{Co(SR)}_4^{2-} + 4\text{TiX}
\]

- \(X = \text{halide ion (ref. 272)}\)

\[
[\text{Cp}^*\text{RuCl}_2]_2 + 2\text{Me}_3\text{SiSR} \rightarrow [\text{Cp}^*\text{ClRu(µSR)}]_2 + 2\text{Me}_3\text{SiCl}
\]

- \(R = \text{Et, } i\text{Pr (ref. 101)}\)

\[
3\text{NbCl}_5 + 5 (\text{Al(SPh)}_3\text{-Et}_2\text{O}) \rightarrow 3\text{Nb(SPh)}_5 + 5 \text{AlCl}_3 + 3\text{Et}_2\text{O}
\]

- (refs. 265, 273)

Other commonly used reagents include the potassium, lead(H) and mercury(II) thiolate salts.265 An alternative method involves addition of a base and a thiol to the solution of the chloro-transition metal complex.

\[
\text{NEt}_3\text{RuCl}_2(\text{CO})_2\text{L}_2 + \text{pySH} \rightarrow \text{Ru(pyS)}_2(\text{CO})\text{L} + \text{Ru(pyS)}_2(\text{CO})_2\text{L} - \text{HNEt}_3\text{Cl}
\]

- \(\text{L} = \text{PPh}_3, \text{ref. 211}\)

Metathesis is also used in the following related reaction with alcohols.

\[
\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2 + \sigma\text{-C}_6\text{Cl}_4(\text{OH})_2 + 2\text{KOH} \rightarrow 5.6
\]

- \(\text{ccr-Ru(η}^2\text{O}_2\text{C}_6\text{Cl}_4)(\text{CO})_2(\text{PPh}_3)_2 + (2\text{KCl} + 2\text{H}_2\text{O})\)

- (ref. 274, 275)

Catala et al. have reported260,276 the metathesis reactions of several (chloro)-phosphine ruthenium complexes with thiolate salts. The thiolato (phosphine) products react with CO to
produce isomers of Ru(SR)₂(CO)₂(PPh₃)₂. Although the authors report results with several lead thiolates and four different phosphines, only the results with PPh₃ (L) and Pb(SC₆F₅)₂ are summarized below.

\[
Pb(SR)_2 + RuCl₃L₃ \rightarrow tcc-Ru(SR)_2(CO)L_2 \quad \text{acetone} \quad \text{(5.7)}
\]

\[
Pb(SR)_2 + RuCl₃L₃ \rightarrow Ru(SR)_3L_2 \quad \text{acetone} \quad \text{(5.8)}
\]

\[
Pb(SR)_2 + RuCl₃L₂(solv) \rightarrow cct-Ru(SR)_2(CO)L_2 \quad \text{Zn} \quad \text{solv} = \text{CH}_3\text{OH or CH}_3\text{NO}_2 \quad \text{(5.9)}
\]

\[
Pb(SR)_2 + RuCl₃L₃ \rightarrow ccc-Ru(SR)_2(CO)L_2 \quad \text{Zn} \quad \text{(5.10)}
\]

It is not clear in reference 276 whether reactions 5.7 and 5.8 occur under different conditions or whether both products are observed simultaneously. In addition, the same group²⁶⁰ᵇ report the metathesis reaction of tcc-RuCl₂(CO)₂(PPh₃)₂ to form the same isomer of the bis-thiolate complex.

\[
tcc-RuCl₂(CO)₂L₂ + Pb(SR)_2 \rightarrow tcc-Ru(SR)_2(CO)L₂ + PbCl₂ \quad \text{(5.11)}
\]

Metathesis reactions followed or preceded by carbonylation reactions are viable alternatives to the reactions of Ru(CO)₂(PPh₃)₃ with thiols or disulphides for the synthesis of cct-Ru(SAryl)₂(CO)₂(PPh₃)₂. For the alkyl analogues, metathesis reactions appear to be the only successful route.
5.2 THE REACTIONS OF \textit{ccr}-RuCl_2(CO)_2(PPh_3)_2 WITH SODIUM THIOLATES

The metathesis reaction of \textit{ccr}-RuCl_2(CO)_2(PPh_3)_2 (1) with sodium \textit{p}-thiocresolate proceeds cleanly in acetone, the pure product being identified by comparing its 1H and 31P\{1H\} NMR spectra with those of a sample prepared from Ru(CO)_2(PPh_3)_3 and \textit{p}-tolyl disulphide.

\[ \text{ccr-RuCl}_2(\text{CO})_2(\text{PPh}_3)_2 + 2\text{NaSR} \rightarrow \text{ccr-Ru(SR)}_2(\text{CO})_2(\text{PPh}_3)_2 + 2\text{NaCl} \]

The metathesis reaction of 1 with sodium ethanethiolate in acetone produces the desired complex, \textit{ccr}-Ru(SEt)_2(CO)_2(PPh_3)_2 (14d), but isolation and reprecipitation of this product were plagued by the formation of intractable oils. The same reaction in THF generates 14d and two new products \textit{ccr}-RuCl(SEt)(CO)_2(PPh_3)_2 (20) and [Ru(SEt)_3(CO)_2(PPh_3)Na(THF)]_2 (21) in varying ratios depending on the amount and freshness of thiolate used. If two equivalents are used, less than 10% conversion to 20 is observed. If a large excess of thiolate is used, the exclusive product is 21. At intermediate concentrations of thiolate, mixtures of 14d, 20, and 21 are observed. It is likely that reactions 5.14 through 5.16 occur consecutively.

\[ \text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{NaSEt} \rightarrow \text{RuCl(SEt)}(\text{CO})_2(\text{PPh}_3)_2 + \text{NaCl} \]

\[ \text{RuCl(SEt)}(\text{CO})_2(\text{PPh}_3)_2 + \text{NaSEt} \rightarrow \text{Ru(SEt)}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{NaCl} \]

\[ 2\text{Ru(SEt)}_2(\text{CO})_2(\text{PPh}_3)_2 + 2\text{NaSEt} + 2\text{THF} \rightarrow [\text{Ru(SEt)}_3(\text{CO})_2(\text{PPh}_3)\text{Na(THF)}]_2 + 2\text{PPh}_3 \]

The lability of the phosphine ligands of \textit{ccr}-Ru(SR)_2(CO)_2(PPh_3)_2 (14) has already been demonstrated (Section 3.8). Reaction 5.16 may simply proceed by elimination of PPh_3 followed by coordination of a third thiolate ligand. The full characterization of 21 is described in Section 5.3.

The two other products \textit{ccr}-RuCl(SEt)(CO)_2(PPh_3)_2 (20) and \textit{ccr}-Ru(SEt)_2(CO)_2(PPh_3)_2 (14d) have virtually identical solubility, and have not been successfully separated. However,
samples in which one or the other was predominant were obtained by reacting
RuCl₂(CO)₂(PPh₃)₂ (1) with different concentrations of thiolate.

A sample of ccr-RuCl(SEt)(CO)₂(PPh₃)₂ (20) containing only 2 % of 14d (estimated by
NMR spectroscopy) was characterized. The integration of the ¹H NMR spectrum (Fig. 5.1a)
shows that the ligands PPh₃ and SEt are present in a 2:1 ratio. The chemical shift difference
between the o- and the m-/p-phenyl signals is 1.2 ppm, clearly indicating trans phosphines. The
³¹P{¹H} NMR signal of 20 is a singlet at 14.54 ppm, intermediate in position between those of
ccr-RuCl₂(CO)₂(PPh₃)₂ (1, 15.66 ppm) and ccr-Ru(SEt)₂(CO)₂(PPh₃)₂ (14d, 11.27 ppm).
Two ν(CO) stretching bands in the infrared spectrum of 20 (Fig. 5.2a) indicate cis carbonyls.
Therefore, the geometry of the complex is the same as that of the starting material.

The FAB-Mass spectrum of 20 (Fig. 5.3 and Table 5.1) contains the molecular peak and several
identifiable fragments. The carbon analysis is low.

A sample of Ru(SEt)₂(CO)₂(PPh₃)₂ (14d) containing 20 % of 20 was characterized. The
integration of the ¹H NMR spectrum (Fig. 5.1b) shows that the ligands PPh₃ and SEt are present
in a 1:1 ratio. The chemical shift difference between the o- and the m-/p-phenyl signals is 1.2
ppm, indicating trans phosphines. The ³¹P{¹H} NMR signal of 14d (Table 5.2) is at
11.18 ppm, slightly higher than those of the bis-(aryl thiolato) derivatives such as 14b (Section
4.2). The same signal is observed after the reactions of Ru(CO)₂(PPh₃)₃ with excess ethanethiol
or ethyl disulphide, and the reaction of ccr-Ru(SC₆H₄pCH₃)₂(COX)₂(PPh₃)₂ (14b) with
ethanethiol (see Chapters 3 and 4). The infrared spectrum of the mixture of 14d and 20 contains
two ν(CO) bands due to 14d (Fig. 5.2b), indicating cis carbonyls. The structure is again cct.
Fig. 5.1  

a) $^1$H NMR spectrum (200 MHz, C$_6$D$_6$ solution) of cct-RuCl(SEt)(CO)$_2$(PPh$_3$)$_2$. The signals for THF are indicated by asterisks.

b) Expanded region of the $^1$H NMR spectrum (300 MHz, C$_6$D$_6$ solution) of a sample of cct-Ru(SEt)$_2$(CO)$_2$(PPh$_3$)$_2$ containing 20% of cct-RuCl(SEt)(CO)$_2$(PPh$_3$)$_2$. 
Fig. 5.2  

a) The FT-IR spectrum of \( \text{cct-RuCl(SEt)}(\text{CO})_2(\text{PPh}_3)_2 \) in a Nujol mull. The signals for Nujol are indicated by asterisks.

b) Carbonyl region of the FT-IR spectrum of a sample of \( \text{cct-Ru(SEt)}_2(\text{CO})_2(\text{PPh}_3)_2 \) containing 20% of \( \text{cct-RuCl(SEt)}(\text{CO})_2(\text{PPh}_3)_2 \), in a Nujol mull.
Fig. 5.3 The FAB-Mass spectrum of \textit{cct-RuCl(SEt)(CO)}_2(PPh_3)_2 in a \textit{p}-nitrobenzyl alcohol matrix. The peaks due to the matrix are indicated by asterisks.
Table 5.1 Fragments Detected in the FAB-Mass Spectrum of \( cct-RuCl(Se^t)(CO)_2(PPh_3)_2 \)

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</tr>
<tr>
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<td>M-CO</td>
</tr>
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</tr>
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* Fragment has a predicted m/z two units above that observed. All others have predicted values within one unit of those observed.

Table 5.2 NMR\(^a\) and IR\(^b\) Spectral Data for \( Ru(X)(Se^t)(CO)_2(PPh_3)_2 \).

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<tr>
<th>X</th>
<th>( ^{31}P ) NMR</th>
<th>( ^{1}H ) NMR</th>
<th>( ^{13}C ) NMR</th>
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<th>Asym. ( \nu(CO) )</th>
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<td>1964 cm(^{-1})</td>
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\( ^a \) \( C_6D_6 \) solutions at room temperature using a 300 MHz spectrometer.

\( ^b \) Nujol mulls.

\( ^c \) Section 3.2

\( ^d \) Section 3.8
The spectroscopic data for the series cct-Ru(X)(SEt)(CO)$_2$(PPh$_3$)$_2$ are summarized in Table 5.2. The $^1$H NMR shifts of the ethyl group in cct-RuH(SEt)(CO)$_2$(PPh$_3$)$_2$ are at significantly higher field than those in the other complexes because H$^-$ is not as electron withdrawing as Cl$^-$ or SR$^-$.

5.3 THE CHARACTERIZATION OF [Ru(SEt)$_3$(CO)$_2$(PPh$_3$)Na(THF)]$_2$

The $^{31}$P($^1$H) NMR signal of the title complex (21) is a singlet ($\omega_{1/2} = 8$ Hz at 18°C in toluene-d$_8$), which broadens at lower temperatures ($\omega_{1/2} = 29$ Hz at -58°C, 120 Hz at -78°C; all data at 121 MHz). In C$_6$D$_6$, the peak is asymmetric, which suggests the possibility of two peaks and therefore two environments for the P atoms in the complex.

The $^1$H NMR spectrum (Figs. 5.4 and 5.6a) is complicated, and can only be assigned with the help of a COSY experiment (Fig. 5.5) or selective homonuclear decoupling experiments (Fig. 5.6). The CH$_3$ region contains two triplets at 1.40 and 1.59 ppm (in C$_6$D$_6$) in a ratio of 2:1. There are therefore two different kinds of ethyl group, which will be referred to as (a) and (b) respectively. The CH$_3$ peak of Et(a) coincides with one of the two resonances of THF, which is present in the sample. The ratio of the ligands PPh$_3$ : THF : Et(a) : Et(b) is 1:1:2:1, based on the integration. The methylene region is quite complicated, due to overlapping signals, second order spectra, and inequivalence of geminal methylene protons. Irradiation of the CH$_3$ resonances simplifies the signals to two AB patterns. The two doublets for CH$_2$(a) evident in Fig. 5.6c are at 2.72 and 2.95 ppm. The $^2$J$_{HH}$ coupling constant in Et(a) is 9.0 Hz. The AB pattern for CH$_2$(b) is second order, so that only the two central peaks of the pattern are observed (Fig. 5.6b). A simple AB pattern consists of four lines, of which the outer two are short and of equal intensity, and the inner two are tall and of equal intensity. The ratio of the intensities of the outside peaks relative to those of the inside peaks can be calculated using the following formulae.277
Fig. 5.4 The $^1$H NMR spectrum (400 MHz) of a C$_6$D$_6$ solution of [(CO)$_2$(PPh$_3$)Ru(SCH$_2$CH$_3$)$_3$Na(THF)]$_2$ at 20°C.
Fig. 5.5 The $^1$H COSY NMR plot (400 MHz) for a C$_6$D$_6$ solution of [((CO)$_2$(PPh$_3$)Ru(SCH$_2$CH$_3$)$_3$Na(THF))]$_2$. 
Fig. 5.6 The methylene region of $^1$H NMR spectra of a C$_6$D$_6$ solution of [(CO)$_2$(PPh$_3$)Ru(SCH$_2$CH$_3$)$_3$Na(THF)]$_2$ at 400 MHz, with
a) no decoupling,
b) selective decoupling at 1.59 ppm (CH$_3$b), or
c) selective decoupling at 1.40 ppm (CH$_3$a and THF).
\[
\frac{I(A1)}{I(A2)} = \frac{D-J}{D+J}
\]

\[D = ((v_A - v_B)^2 + J^2)^{1/2}\]

\[v_{A2} = \frac{1}{2} (v_A + v_B - J + D)\]

\[v_{B1} = \frac{1}{2} (v_A + v_B + J - D)\]

Assuming that \(J\) is again 9 Hz, and taking 2.976 and 2.987 ppm as the positions of the two central peaks (\(v_{A2}\) and \(v_{B1}\)), then the relative intensities of the outside peaks compared to the inside peaks is calculated to be 16%; the outside peaks are therefore too small to be detected in the selective decoupling experiment or in the cross-sections of the COSY.

The methylene region of the \(^1H\) NMR spectrum (300 MHz) of \(21\) in \(C_6D_6\) was accurately simulated (Fig. 5.7) using the following data:

- CH\(_3\)(a): 1.41 ppm, t, \(\delta_{JHH} = 7.6\) Hz
- CH\(_3\)(b): 1.59 ppm, t, \(\delta_{JHH} = 7.3\) Hz
- CH\(_2\)(a): 2.708 ppm, d of q, \(\delta_{JHH} = 9.0\) Hz, \(\delta_{JHH} = 7.4\) Hz
  
  2.962 ppm, d of q, \(\delta_{JHH} = 9.0\) Hz, \(\delta_{JHH} = 7.4\) Hz
- CH\(_2\)(b): 2.953 ppm, d of q, \(\delta_{JHH} = 9.0\) Hz, \(\delta_{JHH} = 7.3\) Hz
  
  2.987 ppm, d of q, \(\delta_{JHH} = 9.0\) Hz, \(\delta_{JHH} = 7.4\) Hz

The peak positions in the simulated spectra match those in the observed spectrum within 0.005 ppm.

The infrared spectrum of \(21\) in Nujol (Fig. 5.8) contains two \(v(CO)\) bands at 2014 and 1952 cm\(^{-1}\), suggesting cis carbonyls. In solution, the equivalent thiolates must be those \textit{trans} to the carbonyls (assuming a \textit{fac} arrangement of thiolates), and are assigned to the Et(a) signals in the NMR spectra. The observations described to this point are consistent with any structure containing Ru(SEt)\(_3\)(CO)\(_2\)(PPh\(_3\)) units. The compound does not conduct in THF solution (up to 1 mM), whereas tetrabutylammonium iodide, a 1:1 electrolyte, has a conductivity of 1Mho at 0.2 mM in THF. The ruthenium could not have been oxidized to the paramagnetic trivalent state, because the peaks in the \(^1H\) NMR spectrum would have been broadened and shifted. Therefore the complex must contain one bound extraneous counter-ion per Ru atom. The elemental
Fig. 5.7 Simulated $^1$H NMR spectra (300 MHz) of a) the CH$_2$a protons, and b) the CH$_2$b protons of [(CO)$_2$(PPh$_3$)Ru(SCH$_2$CH$_3$)$_3$Na(THF)]$_2$. The peak positions match within 0.005 ppm of those in the observed spectrum (c) of the same complex in C$_6$D$_6$. The CH$_2$a and CH$_2$b protons are identified with the letters "A" and "B", respectively.
Fig. 5.8 The FT-IR spectrum of [(CO)$_2$(PPh$_3$)Ru($\mu$SEt)$_2$(($\mu$SEt)Na(THF))]$_2$ in Nujol. The peaks for Nujol are indicated by asterisks.
analysis and FAB-MS (Fig. 5.9 and Table 5.3) are consistent with, and the X-ray structure confirms, the formula \([(\text{PPh}_3)(\text{CO})_2\text{Ru}(\mu_2\text{SEt})_2(\mu_3\text{SEt})\text{Na}(\text{THF})])_2\) (21).

The FAB Mass Spectrum of 21 (Fig. 5.9) contains many peaks assignable to fragments of this molecule (Table 5.3). The peak corresponding to the highest m/e value is that of the dimer minus one THF moiety.

The X-ray structure of 21 is shown in figures 5.10 to 5.12. The bond lengths, angles, and other data are listed in tables 5.4, 5.5, and Appendix B, respectively. The structure contains a crystographically imposed centre of symmetry, and thus only one half of the atoms are labelled in Figures 5.11 and 5.12.

Each sodium atom is bound to three thiolate ligands of one \(\text{Ru(SEt)}_3(\text{CO})_2(\text{PPh}_3)\) fragment, one thiolate of the other fragment, and a THF molecule. The sodium atoms therefore have a coordination number of five, the sixth site being blocked by a phenyl group of the phosphine ligand. The coordination geometry at the Na is a distorted square pyramid. The \(\text{cis S-Na-S}\) angles are 71 or 72°, except those involving \(\text{S}^2\), because the sodium atom is shifted towards the empty site away from the centre of the square pyramid. The \(\text{cis S-Na-O}\) angles are all greater than 90° because the THF is leaning towards the empty sixth site. The Na-S bond lengths (Na1-S1, Na1-S3, and Na1*-S3) are 2.82 to 2.84 Å, comparable to the length of the same bond in NaSMe (2.8 Å).278 The Na1-S2 bond is slightly longer (3.0 Å) than the others, and can be classed as secondary bridging.92

There are three types of thiolates present; one (S1) \textit{trans} to the phosphine and doubly bridging, one (S3) \textit{trans} to a carbonyl and doubly bridging, and one (S2) \textit{trans} to a carbonyl and triply bridging. The Ru-S bond lengths for the thiolate ligands (SEt(a)) \textit{trans} to carbonyls (2.474, 2.467 Å) are virtually identical to those in the structures described in previous chapters. The Ru-S and the S-C bond lengths for the thiolate ligand (SEt(b)) \textit{trans} to the phosphine (2.434 and 1.746 Å, respectively) are somewhat shorter than in the SEt(a) ligands because of the \textit{trans} influence of the phosphine ligand. The Ru-S bond length of a similar thiolate ligand in Ru(pyS)_2(CO)_2(PPh_3) is comparable (2.42 Å).210 The S-C(sp^3) bond lengths of 21 are longer
Fig. 5.9 The FAB-Mass spectrum of [(CO)$_2$(PPh$_3$)Ru(μSEt)$_2$(μ$_3$SEt)Na(THF)]$_2$ in a $p$-nitrobenzyl alcohol matrix.
### Table 5.3 Fragments Detected in the FAB-Mass Spectrum of [(PPh₃)(CO)₂Ru(μ₂SEt)₂(μ₃SEt)Na(THF)]₂

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⁸ Indicated fragments have a predicted m/z value two or three units below those observed. All others have predicted values within one unit of those observed.
Fig. 5.10 The structure of one half of a molecule of \([\text{CO}_2(\text{PPh}_3)\text{Ru}(\mu\text{SEt})_2(\mu_3\text{SEt})\text{Na}(\text{THF})]_2\).
Fig. 5.11 The structure of [(CO)$_2$(PPh$_3$)Ru(μSEt)$_2$(μ$_3$SEt)Na(THF)]$_2$.

Hydrogen atoms omitted for clarity.
Fig. 5.12 Stereoscopic view of the structure of [(CO)₂(PPh₃)Ru(μSEt₂)(μ₃SEt)Na(THF)]₂. Hydrogen atoms omitted for clarity.
Table 5.4 Selected bond lengths (Å) with estimated standard deviations in parentheses for 21.209

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* denotes symmetry operation: 1-x, -y, -z.

Table 5.5 Selected bond angles (°) with estimated standard deviations in parentheses, for 21.209

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* denotes symmetry operation: 1-x, -y, -z.
than the S-C(sp²) bond lengths for the structures of ccr-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (9b) and ccr-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) described in Chapters 3 and 4.

The Ru-C and C-O bond lengths of 21 are comparable to those in carbonyls trans to thiolates in 9b, 14b, and 14a (Chapter 4). The Ru-P bond length is 2.375 Å, slightly shorter than that in the other complexes, probably because the trans influence of thiolates is weaker than that of phoshphines.

The CP/MAS (cross-polarized, magic angle spinning) solid-state ¹³C NMR spectrum of 21 (Fig. 5.13a) contains two strong peaks for the THF molecule (68.2 and 25.6 ppm), one of which partly obscures the methylene region. Two peaks are observed on either side of the THF peak, at 26.9 and 24.6 ppm. However, three peaks are expected, because there are three different ethyl groups in the solid state structure. It is possible that the third peak is obscured by the THF resonance. The methyl region clearly contains three signals, as expected. An NQS (Non-Quaternary Suppression) solid state ¹³C NMR experiment was performed to confirm the identification of the three high field peaks as methyl peaks (Fig. 5.13b). In such an experiment, strongly dipolar-coupled nuclei such as CH or CH₂ carbons are suppressed, while quaternary carbons and carbons in rapidly moving groups (e.g. CH₃ groups) are detected. The three high field peaks due to CH₃ groups are detected, in addition to the strong THF peak at 25.5 ppm. From the latter observation, one can conclude that the β carbons of the THF ligand are mobile, as suggested by the size of their thermal ellipsoids (Fig. 5.11). The THF ligand is therefore "wagging." The peaks were assigned by analogy to the solution ¹³C{¹H} NMR spectrum (see below).

The solution ¹³C{¹H} NMR spectrum of 21 (Fig. 5.14) was assigned with the help of an APT (Attached Proton Test) experiment (Fig. 5.15) and a HETCOR (¹³C/¹H NMR Heteronuclear Correlation) experiment (Fig. 5.16). The HETCOR plot allows direct correlation of the ¹³C{¹H} NMR signals with the assigned peaks of the ¹H NMR spectrum. The methylene region of the ¹³C{¹H} NMR spectrum again contains resonances due to the THF molecule, at 67.8 and 25.7 ppm. Also in the methylene region are a larger peak at 25.2 ppm and a smaller
Fig. 5.13  a) $^{13}$C solid state (CP/MAS) NMR spectrum of $[(\text{CO})_2(\text{PPh}_3)\text{Ru}(\mu_3\text{SEt})_2(\mu_3\text{SEt})\text{Na(THF)})_2]_2$.  
b) $^{13}$C solid state (CP/MAS) NQS NMR spectrum of $[(\text{CO})_2(\text{PPh}_3)\text{Ru}(\mu_3\text{SEt})_2(\mu_3\text{SEt})\text{Na(THF)})_2]_2$. 
Fig. 5.14 $^{13}$C($^1$H) NMR spectrum of [Ru(CO)$_2$(PPh$_3$)Ru(SEt)$_3$Na(THF)]$_2$ in C$_6$D$_6$ at 20°C and 75 MHz.
Fig. 5.15 $^{13}$C APT NMR spectrum of [Ru(CO)$_2$(PPh$_3$)$_2$Ru(SEt)$_3$Na(THF)]$_2$ in C$_6$D$_6$ at 20°C and 75 MHz.
Fig. 5.16 The Heteronuclear Correlation (13C/1H) NMR plot for 
[Ru(CO)2(PPh3)Ru(μSEt)2(μ3SEt)Na(THF)]_2 in C_6D_6 at 125 MHz. 
Points along the line defined by 13C δ = 23.5 ppm are believed to be artifacts.
peak at 26.6 ppm representing \( \text{CH}_2(a) \) and \( \text{CH}_2(b) \), respectively. The fact that only two such peaks are detected supports the conclusion from the \(^1\text{H} \) NMR spectral data that the two \( \text{Et}(a) \) groups are equivalent in solution on the NMR time-scale. The methyl region of the solution \(^{13}\text{C}\{^1\text{H}\} \) NMR spectrum contains a tall peak for the \( \text{CH}_3(a) \) groups, again confirming their equivalence. However, the small signal for the \( \text{CH}_3(b) \) groups appears split in the \(^{13}\text{C}\{^1\text{H}\} \) and APT spectra at 75 MHz, but not in the \(^{13}\text{C}\{^1\text{H}\} \) NMR spectrum at 125 MHz. The reason for this splitting is not known. The \(^1\text{H} \) NMR spectrum is unequivocal in demonstrating that there is only one type of \( \text{CH}_3(b) \) group in the solution. The \(^{13}\text{C}\{^1\text{H}\} \) NMR spectral assignments for the phenyl region are based on the assumption that the J\(_{PC}\) coupling constant decreases in the order P-bound, o-, m-, p-phenyl carbons.

The lack of conductivity in solution indicates that the sodium atoms do not dissociate from the complex. The solution NMR spectra of 21 do not reveal whether the complex exists as a dimer or monomer in solution. It is neither sufficiently stable for a determination of the molecular weight by the Signer method\(^{280}\) nor sufficiently soluble for a solvent freezing-point depression experiment. However, we know that the structure is not identical to that of the solid state because the \( \text{Et}(a) \) groups are equivalent in solution and not in the solid state.

For the two \( \text{Et}(a) \) groups attached to \( S_2 \) and \( S_3 \) to be chemically equivalent, as observed in the solution spectra, a mirror plane would have to exist between them. Because the positions of \( \text{Et}(b) \), THF and the Na atoms are not on this plane, these three groups must be in rapid motion across it to create such a mirror plane. In other words, the following motions must occur rapidly on the NMR time-scale.

1) Inversion at the chiral sulphur atom \( S_1 \) would bring \( \text{Et}(b) \) across the mirror plane. Inversion at \( S_2 \) or \( S_3 \) is not required, nor is it likely because it would bring the \( \text{Et}(a) \) groups into collision with the phenyl rings of the phosphine.

2) Rapid back-and-forth motion of Na\(^*\) between \( S_2 \) and \( S_3 \), and Na\(^1\) between \( S_2^* \) and \( S_3^* \). If the complex were a monomer in solution, then symmetry would only require that the Na\(^1\)-S\(^2\) and Na\(^1\)-S\(^3\) bonds be equivalent.
3) Rapid motion of the THF molecule between the sites \textit{trans} to \(S^2\) and \(S^3\). If the complex were a dimer in solution, this motion would not be possible without dissociation of the THF ligand because of hindrance from the phenyl rings. This motion would also have to occur simultaneously with motion 2, so that the site to which the THF is travelling would no longer be blocked by a phenyl group. Alternatively, the two THF ligands could be completely dissociated from the sodium atoms in solution. The \(^{1}H\) and \(^{13}C\{^{1}H\}\) NMR chemical shifts of the THF protons and carbons are not significantly different from those of THF alone in \(\text{C}_6\text{D}_6\). This is consistent with but not proof of THF dissociation.

The situation is made more complicated by the fact that the methylene protons of \(\text{CH}_2(b)\) (C\(^{19}\)) are not equivalent. If the mirror plane exists, then these protons should be equivalent. Therefore inversion at \(S^1\) (motion 1) is probably not occurring rapidly on the NMR time-scale. It is not clear whether or not motions 2 and 3 are occurring. However, it seems unlikely that the Et(a) protons could appear to be equivalent without at least motion 2 being rapid on the NMR time-scale.

Studies on the effect of the R group on the rate of the \textit{anti} to \textit{syn} isomerization of \([\text{Fe(CO)}_3(\mu\text{SR})]_2\) (equation 5.17)

\[
\begin{array}{c}
\text{anti} \\
\text{Fe} & \text{S} & \text{R} & \text{S} \\
\text{Fe} & & & \\
\text{syn} \\
\end{array}
\]

\[5.17\]

\((\text{Fe} = \text{Fe(CO)}_3, \text{ ref. 281-3})\)

have shown that bulkier and aromatic thiolates invert more quickly. The rate constant for the conversion of the \textit{anti} to the \textit{syn} isomer, in toluene solution at 35°C, range from \(1.1 \times 10^{-5}\) s\(^{-1}\) (R=Me)\(^{281}\) or \(2.4 \times 10^{-4}\) s\(^{-1}\) (R=Ph) to 0.6 s\(^{-1}\) (R=tBu)\(^{282}\) or higher\(^{283}\) for very bulky groups. The ethyl derivative undergoes this net inversion process only marginally faster than the methyl derivative.\(^{281}\) The mechanism is probably via Fe-S bond cleavage. Although the thiolates in
[(PPh₃)(CO)₂Ru(SEt)₃Na(THF)]₂ (21) and [Fe(CO)₃(μSEt)]₂ are not in identical environments, it seems reasonable that the inversion process in 21 is not rapid on the NMR time-scale.

The variable temperature ¹H NMR spectra of 21 shed little light on the problem of motion within the molecule. At temperatures greater than 60°C, changes in the appearance of the spectrum are rapid and irreversible. The signals due to THF (1.4 to 1.6 ppm) and an unknown complex presumably resulting from the decomposition of 21 (2.15 ppm) become more intense relative to the peaks of the dimer, which become amorphous. The ¹H NMR spectrum is not restored to its original appearance after the solution is cooled to 20°C, and only PPh₃ can be detected in the ³¹P{¹H} NMR spectrum. The ¹H NMR spectrum of a fresh sample at -78°C shows the peaks of 21 (but not those of THF or toluene-d⁷) to be greatly broadened (Fig. 5.17). This effect may result from a slowing of internal motions within the dimer. Spectra at even lower temperatures would be required to confirm this, although toluene-d₈ has too high a freezing point (-93°C) to be used in such experiments.

The only other compound containing [RuX₃(CO)₂(PPh₃)]⁻ fragments (X=halide or pseudo-halide), which has been mentioned in the literature, is [RuI₃(CO)₂(PPh₃)][PPh₃Me].

\[
\text{RuI}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{MeI} \rightarrow [\text{RuI}_3(\text{CO})_2(\text{PPh}_3)][\text{PPh}_3\text{Me}] \quad 5.18
\]

(ref. 284)

The related anions [RuX₃(CO)₃]⁻ (X=Cl, Br, I)²⁸⁵,²⁸⁶ and [RuCl₃(CO)(PPh₃)₂]⁻²⁸⁷ have also been reported.

The structure of 21 is unique in that the two Ru centres are connected to each other by a network of six bridging thiolate ligands and two sodium atoms; four thiolates (S₁, S₃, S₁*, and S₃*) bridge one Ru and one Na, while two thiolates (S₂ and S₂*) triply bridge one Ru and two Na atoms. Such triple bridging of thiolates between transition metal and alkali metal ions is unprecedented. The recently reported anionic species [Na{Ru(CO)₂(Se₄)₂}₂]³⁻ contains Se atoms (of Se₄²⁻ ligands) bridging Ru and Na atoms,²⁸⁸ while examples of alkyl thiolate ligands bridging three Ru atoms are known.²⁸⁹ More generally, there are few examples of transition
Fig. 5.17 The $^1$H NMR spectrum of [Ru(CO)$_2$(PPh$_3$)Ru($\mu$SEt)$_2$(\textmu_3SEt)Na(THF)]$_2$ in toluene-d$_8$ at -78°C
metal complexes containing alkali metal cations "trapped" via bridging thiolate ligands: (C₅Me₅)₂Lu(µS⁻Bu)₂Li(THF)₂,²⁹⁰⁻¹ [Li(dme)₄][U(edt)₄] (dme = 1,2-dimethoxyethane, edt = 1,2-ethylenedithiolate),²⁹² and (SC₆H₄pCH₃)₃Nb(µSC₆H₄pCH₃)₃Na(THF)₃.²⁹₃ There are many more examples of trapped alkali metal cations in alkoxide chemistry, particularly as by-products of metathesis reactions using alkoxide salts; these have been described in reviews of "double metal alkoxides" (complexes containing alkoxide ligands bridging two different metals).²⁹⁴ Double metal thiolates have not been reviewed. No previous Na/Ru double metal alkoxide or thiolate is known to us. Perhaps the mostly closely parallel alkoxide complex is Li₂Ti₂(OiPr)₁₀, the structure of which has recently been determined.²⁹⁵

Organic complexes containing alkali metal cations trapped by sulphur atoms are rare. Almost all of the reports covering crown thioether metal complexes deal exclusively with transition metals.²⁹⁶ No X-ray structure of a appears to have been reported. Comparisons between sodium crown-thioether complexes and 21, which represents an "inorganic crown thioether," will have to wait for the completion of the crystal structure of an example of a sodium crown-thioether complex. In the vast literature of the oxygen-containing crown ether ligands, there is, of course, an abundance of structures of sodium complexes.²⁹⁷⁻³⁰⁰
5.4 THE REACTIONS OF OTHER RUTHENIUM CHLORO COMPLEXES WITH SODIUM THIOLATES

The reaction of a RuCl₃/PPh₃ mixture with excess NaSEt under CO in refluxing MeOH produces a mixture of 10 to 20% each of cct-RuCl₂(CO)₂(PPh₃)₂ (1), cct-RuCl(SEt)(CO)₂(PPh₃)₂ (20), cct-Ru(SEt)₂(CO)₂(PPh₃)₂ (14d), and a product with the same ³¹P chemical shift as [(PPh₃)(CO)₂Ru(SEt)₃Na(THF)]₂, plus smaller amounts of several unidentified products. This experiment was attempted because of a report of the synthesis of cct-Ru(SC₆F₅)₂(CO)₂(PMePh₂)₂ directly from RuCl₃. With optimization of conditions, this method perhaps could provide a short-cut to the synthesis of these thiolato (carbonyl) phosphine complexes.

The complex cct-RuH(Cl)(CO)₂(PPh₃)₂ reacts with one equivalent of NaSC₆H₄pCH₃ in acetone to give 56% conversion to cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂.

\[
\text{RuH(Cl)(CO)₂(PPh₃)₂ + NaSR} \rightarrow \text{RuH(SR)(CO)₂(PPh₃)₂ + NaCl}
\]

If excess thiolate is used, 90% conversion to cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) is observed. The reactions of Ru(CO)₂(PPh₃)₃ and cct-RuH₂(CO)₂(PPh₃)₂ with thiols are the preferred synthetic routes to 9 because in these reactions the formation of the bis-thiolate product is easier to control.

A mixture of cis- and trans-RuCl₂(dpm)₂ (5 and 6) does not react with NaSEt. The role of the bulky phenyl rings of RuH(Cl)(dppe)₂ (dppe=Ph₂PCH₂CH₂PPh₂) has been cited to explain its non-reaction with LiAlH₄. However, cis-RuCl₂(dpm)₂ reacts easily with NaBH₄ (Chapter 2), possibly because the BH₄⁻ anion is considerably smaller than AlH₄⁻ and SEt⁻.
5.5 EXPERIMENTAL DETAILS

The reaction of \textit{cct-}RuCl_2(CO)_2(PPh_3)_2 (1) with NaSC_6H_4pCH_3: A white acetone (40 mL) suspension of 1 (140 mg, 0.18 mmol) and the thiolate salt (56 mg, 0.38 mmol) under CO (1 atm) turned yellow within one minute at room temperature. The suspension was filtered, after being stirred overnight. The solid was discarded and the volume of the yellow filtrate was reduced to 10 mL by vacuum distillation. MeOH (approx. 30 mL) was added to encourage precipitation. The solid product collected by filtration was pure \textit{cct-}Ru(SC_6H_4pCH_3)_2(CO)_2(PPh_3)_2 (14b), according to the $^{31}$P{$^1$H} and $^1$H NMR spectra, which are identical to those of a known sample of that complex prepared from Ru(CO)$_2$(PPh$_3$)$_3$ and the disulphide (Sections 4.1 and 4.2).

The reaction of \textit{cct-}RuCl_2(CO)_2(PPh_3)_2 (1) and NaSEt in acetone: A white acetone (20 mL) suspension of 1 (450 mg, 0.60 mmol) and the thiolate salt (120 mg, 1.4 mmol) under CO (1 atm) turned yellow within one minute at room temperature. The suspension was stirred overnight and then filtered through diatomaceous earth. The volume of the yellow filtrate was reduced to 5 mL by vacuum distillation. MeOH (30 mL) was added to encourage precipitation, and the vessel left for 2 h at 0°C. During this time, a yellow precipitate formed. The suspension was filtered. The collected solid product was a mixture of \textit{cct-}Ru(SC$_2$H$_5$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14d) and PPh$_3$ according to the $^{31}$P{$^1$H} NMR spectrum of the C$_6$D$_6$ solution of this product. All attempts at purifying this complex, or repeating the reaction, resulted in yellow or brown oils which contained the same product.

The reaction of \textit{cct-}RuCl_2(CO)$_2$(PPh$_3$)$_2$ (1) and NaSEt in THF: A yellow THF (100 mL) suspension of 1 (520 mg, 0.70 mmol) and the thiolate salt (1.4 g, 17 mmol) under Ar was stirred for 1 h at room temperature, filtered, and the solid discarded. The yellow filtrate was evaporated to dryness. The products from two such reactions were dissolved together in THF (10 mL). The volume of the solution was reduced to 3 mL by vacuum distillation, and hexanes (15 mL) were
added to induce precipitation. The suspension was filtered and the collected yellow solid was washed with 15 mL of cooled hexanes. The overall yield was 53%. The NMR spectra show the product to be pure \([(PPh_3)(CO)_2Ru(SEt)_3Na(THF))]_2 \((21)\). If only 2-3 equivalents of NaSEt were used, significant amounts of 1 remained after several hours. By using intermediate amounts of NaSEt and 15 min reaction times, mixtures of \(ccc-RuCl(SEt)(CO)_2(PPh_3)_2\) \((20)\) and \(ccc-Ru(SEt)_2(CX))_2(PPh_3)_2 \((14d)\) were obtained.

Characterization of \(ccc-RuCl(SEt)(CO)_2(PPh_3)_2\) \((20)\), containing 2% \(14d\) based on the 31P\{1H\} NMR spectrum:  

- Elem. Anal.: Calcd. for C₄₀H₃₅C₁₂O₂P₂RuS: C, 61.7; H, 4.5.  
  Found: C, 60.6; H, 4.6.  
- ¹H NMR (C₆D₆, 300 MHz) δ 1.13 (t, 3H, J_HH = 7.4 Hz, CH₃), 1.92 (q, 2H, J_HH = 7.3 Hz, CH₂), 7.0 (multi, 18H, m-/p-Ph), 8.25 ppm (multi, 12H, o-Ph); 31P\{1H\} NMR (C₆D₆, 121 MHz) δ 14.54 ppm (s); IR (Nujol) 2042, 1988 cm⁻¹ (v(CO)).

Characterization of \(ccc-Ru(SEt)_2(CO)_2(PPh_3)_2\) \((14d)\), containing 20% of \(20\) based on the 31P\{1H\} NMR spectrum, listing resonances due to the major component only:  

- ¹H NMR (C₆D₆, 300 MHz) δ 1.16 (t, 6H, J_HH = 7.4 Hz, CH₃), 1.97 (q, 4H, J_HH = 7.4 Hz, CH₂), 7.04 (multi, 18H, m-/p-Ph), 8.22 (multi, 12H, o-Ph); 31P\{1H\} NMR (C₆D₆, 121 MHz) δ 11.18 ppm (s); IR (Nujol) 2022, 1963 cm⁻¹ (v(CO)).

Characterization of \([(PPh_3)(CO)_2Ru(μ₂SEt)_2(μ₃SEt)Na(THF))]_2\) \((21)\):  

- Elem. Anal.: Calcd. for C₆₀H₇₆Na₂O₆P₂Ru₂S₆: C, 51.6; H, 5.5; S, 13.8.  
  Found: C, 51.7; H, 5.5; S, 14.1.  
- ¹H NMR (C₆D₆) δ 1.41 (t, 12H, J_HH = 7.6 Hz, CH₃(a)), 1.41 (multi, 8H, β-CH₂ of THF), 1.59 (t, 6H, J_HH = 7.3 Hz, CH₃(b)), 2.71 (d of q, 8H, 2J_HH = 9.0, 3J_HH = 7.3 Hz, CH₂(a)), 2.95 (d of q, 8H, 2J_HH = 9.0, 3J_HH = 7.3 Hz, CH₂(b)), 2.98 (d of q, 4H, 2J_HH = 9.0, 3J_HH = 7.5 Hz, CH₂(b)), 3.57 ppm (multi, 8H, α-CH₂ of THF), 7.06 (multi, 6H, p-Ph), 7.15 (t, 12H, 3J_HH = 7.0, m-Ph), 7.96 ppm (t, 12H, 3J_HH = 8.8 Hz, o-Ph); ¹³C\{1H\} NMR (C₆D₆, 75 MHz) δ 20.73 (CH₃(b)), 20.89 (CH₃(a)), 25.16 (CH₂(a)), 25.71 (β-C of THF), 26.62 (CH₂(b)), 67.85 (α-C of THF), 128.16 (p-Ph), 130.22 (m-Ph), 134.50 (d, JPC=9.4 Hz, o-Ph), 135.28 (d, JPC=41.9 Hz, P-C), 197.48 ppm (CO); 31P\{1H\} NMR
(C₆D₆, 121 MHz) δ 25.05 ppm (s); IR (Nujol) 2014, 1952 cm⁻¹ (ν(CO)). Solutions of 21 (up to 1 mM) in THF had no detectable conductance at room temperature under argon.

A crystal of [(PPh₃)(CO)₂Ru(μ₂SEt)₂(μ₃SEt)Na(THF)]₂ (21) suitable for X-ray crystallography was prepared by diffusion of hexanes into a concentrated THF solution under Ar in darkness. The structure analysis was performed by Dr. S. J. Rettig. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 20.0-26.5°. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, decayed uniformly by 12%. The data were processed and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections).

The structure analysis was initiated in the centrosymmetric space group P1̅, the choice being confirmed by the subsequent successful solution and refinement of the structure. The structure was solved by conventional heavy atom methods, the coordinates of the Ru, P, and S atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The complex has crystallographically imposed symmetry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (dC-H = 0.98 Å, B_H = 1.2 B_bonded atom). Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography. Final atomic coordinates and equivalent isotropic thermal parameters [B_eq = 4/3Σ_ij(b_ij(a_i * a_j))], bond lengths, and bond angles appear in Appendix 4, and Tables 5.4 and 5.5 respectively. Other crystallographic data for this structure and the other structures described in this work are presented in Appendix 1.

The reaction of RuCl₃ with PPh₃ and NaSEt: RuCl₃ (300 mg, 0.96 mmol) and PPh₃ (1.43 g, 5.4 mmol) were allowed to react in refluxing MeOH (30 mL) under N₂ for 15 min. During this time, the solution turned from brown to dark green. After the solution had cooled, NaSEt (155
mg, 1.8 mmol) was added, and CO introduced. The brown colour returned immediately, but again slowly changed to dark green. After 30 min, the volatiles were removed by vacuum distillation, leaving a yellow/brown unpurified product. The $^{31}$P{$^1$H} NMR spectrum (C$_6$D$_6$) shows that this product contained, in addition to PPh$_3$, cct-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ (1, 20 % of $^{31}$P NMR signal excluding that of free PPh$_3$), cct-RuCl(SEt)(CO)$_2$(PPh$_3$)$_2$ (20, 7 %), cct-Ru(SEt)$_2$(CO)$_2$(PPh$_3$)$_2$ (14d, 19 %), a product having the same chemical shift as [(PPh$_3$)(CO)$_2$Ru(SEt)$_3$Na(THF)]$_2$ (16 %), and several unknowns at lower concentrations. The reaction of cct-RuH(Cl)(CO)$_2$(PPh$_3$)$_2$ (4) and NaSC$_6$H$_4$pCH$_3$: Complex 1 (72 mg, 0.10 mol) and the thiolate salt (18 mg, 0.12 mmol) reacted very quickly in acetone (20 mL) at room temperature under Ar, the white solution turning yellow within minutes. After 2 h, the volatiles were removed by vacuum distillation, leaving a yellow powder. This un purified product was dried overnight, and then redissolved in C$_6$D$_6$. The $^{31}$P{$^1$H} NMR spectrum (121 MHz) shows that the product mixture contained unreacted 4 (20 % of $^{31}$P NMR signal), cct-RuH(SC$_6$H$_4$pCH$_3$)(CO)$_2$(PPh$_3$)$_2$ (9b, 60 %), cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b, 10 %), and small (<5 %) amounts of PPh$_3$, Ru(CO)$_2$(PPh$_3$)$_3$ (2), and Ru(CO)$_3$(PPh$_3$)$_2$ (10). The $^1$H NMR spectrum confirms the identification of the major product and the starting material.

The overnight reaction of 4 with three equivalents of NaSC$_6$H$_4$pCH$_3$ produced a mixture of 14b (90 %) and 9b (10 %).

The attempted reaction of trans-RuCl$_2$(dpm)$_2$ (6) with NaSEt: Complex 6 (140 mg, 0.15 mmol) failed to react with NaSEt (120 mg, 1.6 mmol) in acetone (25 mL) at room temperature. After one day, the suspension was washed through diatomaceous earth with THF (20 mL). The volume of the filtrate was reduced to 6 mL, and hexanes (20 mL) were added to induce precipitation. The collected yellow powder was unreacted starting material (identification by
$^{31}\text{P}(^{1}\text{H})\text{ NMR spectroscopy).}^{301}$ The same result was obtained from a similar experiment with NaSC$_6$H$_4$CH$_3$. 


6. THE REACTIONS OF THIOLATO RUTHENIUM(II) COMPLEXES WITH NON-SULPHUR-CONTAINING REAGENTS

Comparisons between the reactions described in this chapter and those of the preceding chapters allow for greater insight into the mechanisms of the reactions and the conditions under which Ru-S bonds may be broken. The latter information is required before a catalytic cycle for desulphurization can be designed.

6.1 THE REACTIONS OF cct-RuH(SR)(CO)2(PPh3)2 (9)

6.1.1 P(C6H4pCH3)3

The complex cct-RuH(SR)(CO)2(PPh3)2 (9) reacts with P(C6H4pCH3)3 to produce a complex (22) of a structure similar to that of 9 but containing inequivalent phosphines (1H and 31P{1H} NMR spectral evidence). This product reacts further to produce a third complex (12), again of a structure similar to 9, but containing equivalent phosphines. Based on the similarity of the NMR spectra of these complexes with those of the PPh3 analogues, it is believed that the structures are cct-RuH(SR)(CO)2(PPh3)(P(C6H4pCH3)3) (22) and cct-RuH(SR)(CO)2(P(C6H4pCH3)3)2 (12). The ethyl derivative of the latter (12d) has been independently synthesized via the reaction of Ru(CO)2(P(C6H4pCH3)3)3 with ethanethiol (Sections 3.1 and 3.2). The sequence of reactions between 9e and P(C6H4pCH3)3 is the following:

\[
\text{RuH(SR)(CO)2L}_2 + L' \rightarrow \text{RuH(SR)(CO)2LL'} + L  \quad 6.1
\]

\[
\text{RuH(SR)(CO)2LL'} + L' \rightarrow \text{RuH(SR)(CO)2L}_2' + L  \quad 6.2
\]
L = PPh₃, L' = P(C₆H₄pCH₃)₃, R = CH₂C₆H₅, C₆H₄pCH₃

The reaction of 9e (R = CH₂C₆H₅) with P(C₆H₄pCH₃)₃ (L') was followed by ³¹P{¹H) and ¹H NMR spectroscopy (Figs. 6.1 to 6.3) in C₆D₆ at 45°C under pseudo-first order conditions (large excess of L'). The rate of loss of 9e is pseudo-first order, the log plot being linear for at least 3 half-lives (Fig. 6.4) and has an observed rate constant of 1.1 (±0.1) x 10⁻³ s⁻¹ (average of 5 results, at [9e] = 11 mM). The rate constant for the corresponding reaction of cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (26) is 7.0 x 10⁻⁴ s⁻¹ (single experiment). The observed rate constant (for 9e) is independent of the concentration of L' (94 to 502 mM, at [9e] = 11 mM) or 9e (k₉obs = 1.2 x 10⁻³ s⁻¹ at [9e] = 2.65 mM and 130 mM L'). The rate law is simply:

\[-d[9e] \over dt = k₁[9e]\]

where \(k₁ = 1.1 \times 10⁻³\) s⁻¹.

It therefore seems likely that the first step of reaction 6.1 is the rate determining dissociation of the phosphine L (Scheme 6.1), although other less likely mechanisms are possible, such as initial reductive elimination of thiol. The rate law for the loss of 9e, assuming a steady state for RuH(SR)(CO)₂L (in Scheme 6.1), is the following:

\[-d[9e] \over dt = k₁[9e] - \frac{k₁[L][k₁[9e] + k₂[22]]}{k₂[L'] + k₁[L]}\]

That reaction 6.1 goes to completion implies that the rate of the k₂ reaction is negligible (i.e. \(k₂[22] << k₁[9e]\)), and thus if one assumes that \(k₁[L] << k₂[L']\) then the second term in the rate law is insignificant. This assumption appears to be valid during at least the first two half-lives if L' is present in large excess; this accounts for the observed pseudo-first order behaviour.

Reaction 6.2 must be significantly faster than reaction 6.1, because complex 22 never appears in large amounts (Fig. 6.3). The rate law for the proposed mechanism of reaction 6.2 (Scheme 6.1) is the following:
Fig. 6.1 $^{31}$P($^1$H) NMR spectra acquired during the reaction of cct-Ru(SCH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ (2e, 11 mM) with P(C$_6$H$_4$pCH$_3$)$_3$ (94 mM) in C$_6$D$_6$ at 45°C. Chemical shift scale is relative to PPh$_3$ in C$_6$D$_6$. 
Fig. 6.2 \(^1\)H NMR spectra (hydride region) acquired during the reaction of \(\text{cct-RuH(SCH}_2\text{Ph)(CO)}_2(\text{PPh}_3)_2\) (9e, 11 mM) with P(\(\text{C}_6\text{H}_4\text{CH}_3\))\(_3\) (94 mM) in \(\text{C}_6\text{D}_6\) at \(45^\circ\text{C}\).
Fig. 6.3 Time dependence of the concentrations of observed complexes during the reaction of cct-RuH(SCH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ (9e, 12 mM) with P(C$_6$H$_4$pCH$_3$)$_3$ (120 mM) in C$_6$D$_6$ at 45°C.

Fig. 6.4 Log plot of [9e] during the reaction of cct-RuH(SCH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ (9e, 12 mM) with P(C$_6$H$_4$pCH$_3$)$_3$ (120 mM) in C$_6$D$_6$ at 45°C.
Scheme 6.1 A proposed mechanism for the reaction of RuH(SR)(CO)$_2$(PPh$_3$)$_2$ with P(C$_6$H$_4$H$_2$CH$_3$)$_3$ (L=PPh$_3$, L'=P(C$_6$H$_4$H$_2$CH$_3$)$_3$).

\[
\begin{align*}
\text{RuH(SR)(CO)$_2$L}_2 & \xrightleftharpoons[k_{-1}, L]{k_1, -L} \text{RuH(SR)(CO)$_2$L} \\
2 & \\
\text{RuH(SR)(CO)$_2$L'$_2$} & \xrightleftharpoons[k_{-4}, L']{k_4, -L'} \text{RuH(SR)(CO)$_2$L'} \\
12
\end{align*}
\]
\[ \frac{d[12]}{dt} = \frac{k_4[L']}{k_4[L'] + k_3[L]} \{k_3[22] + k_4[12]\} - k_4[12] \]

This rate law simplifies if one assumes that \( k_4[L'] \gg k_3[L] \) in the presence of excess \( L' \).

\[ \frac{d[12]}{dt} = k_3[22] \]

The value of \( k_3 \) could then be determined by plotting \( \frac{d[12]}{dt} \) vs. [22]. The values of \( \frac{d[12]}{dt} \) are easily determined from the tangents to the plot of [12] against time (Fig. 6.3). The resulting plot should be a straight line of positive slope \( k_3 \), if the assumption of a negligible back reaction (\( k_3[L] \)) is correct. In fact, a decreasing trend is observed (Fig. 6.5), suggesting that the \( k_3[L] \) back reaction is significant. Because all back-reactions are negligible at the start of the reaction, an approximate value of \( k_3 \) can be obtained from the y-intercept of this plot. The value thus obtained (0.01 s\(^{-1}\)) shows that \( k_3 \) is an order of magnitude greater than \( k_1 \).

If PPh\(_3\) (\( L \), 100 mM) is added to the reaction of 9e (11 mM) with P(C\(_6\)H\(_4\)pCH\(_3\))\(_3\) (\( L' \), 110 mM) at 45°C in C\(_6\)D\(_6\), a mixture of three complexes, 9, 22, and 12 is obtained (Fig. 6.6). Because reaction 6.1 does not go to completion, the back reaction must be significant under these conditions. It is not surprising, therefore, that pseudo-first order behaviour is not observed. The fact that the initial rate is unchanged suggests that \( k_1/k_2 \ll 1 \).

\( p \)-Tolyl phosphine (\( L' \)), more basic than PPh\(_3\), may labilize the phosphine trans to it by increasing the electron density at the metal centre, thereby promoting formation of the activated complex en route from 22 to 12. The observation that \( k_3 \) is greater than \( k_1 \) suggests that reaction 6.2 may reach an equilibrium before reaction 6.1. This can be checked by plotting \( Q_1 \) and \( Q_2 \) against time for the experiment described above, in which both \( L \) and \( L' \) were present in excess, where:

\[ Q_1 = \frac{[22][L]}{[9][L']} \]
Fig. 6.5 The dependence of \( d[12e]/dt \) on \([22e]\) during the reaction of \( \text{cct-RuH(SCH}_2\text{Ph})(\text{CO})_2(\text{PPh}_3)_2 \) (9e, 12 mM) with \( \text{P(C}_6\text{H}_4\text{pCH}_3)_3 \) (120 mM) in \( \text{C}_6\text{D}_6 \) at 450°C.
Fig. 6.6 Time dependence of the concentrations of observed complexes during the reaction of \( \text{cct-RuH(SCH}_2\text{Ph})(\text{CO})_2(\text{PPh}_3)_2 \) (9e, 11 mM) with \( \text{P(C}_6\text{H}_4\text{pCH}_3)_3 \) (110 mM) in the presence of \( \text{PPh}_3 \) (100 mM) in \( \text{C}_6\text{D}_6 \) at 45°C.

Fig. 6.7 Time dependence of \( Q_1 \) and \( Q_2 \) (defined in Section 6.1.1) during the reaction of \( \text{RuH(SCH}_2\text{Ph})(\text{CO})_2(\text{PPh}_3)_2 \) (9e, 11 mM) with \( \text{P(C}_6\text{H}_4\text{pCH}_3)_3 \) (110 mM) in the presence of \( \text{PPh}_3 \) (100 mM) in \( \text{C}_6\text{D}_6 \) at 45°C.
Q_2 = \frac{[12[L]}{[22[L']}]

In fact, Q_1 varies over time (Fig. 6.7), while Q_2 settles quickly to a value of approximately 1.2. The equilibrium constants for reactions 6.1 and 6.2 are thus K_1=4 and K_2=1.2.

The rate of the exchange reaction of \textit{9} with thiols (Section 3.5)

\text{RuH(SR)(CO)}_2(PPh_3)_2 + R'SH \rightarrow \text{RuH(SR')(CO)}_2(PPh_3)_2 + RSH \quad 3.15

has the same simplified rate law and rate constant \((1.0 \times 10^{-3} \text{ s}^{-1} \text{ at } 45^\circ\text{C in C}_6\text{D}_6, R=\text{CH}_2\text{C}_6\text{H}_5, R'=\text{C}_6\text{H}_5)\) as reaction 6.1, suggesting that the rate determining steps of the two reactions are the same.

6.1.2 CO

The reactions of several complexes of the series \textit{cct-RuH(SR)(CO)}_2(PPh_3)_2 (\textit{9}) with CO (1 atm) to give Ru(CO)_3(PPh_3)_2

\text{RuH(SR)(CO)}_2(PPh_3)_2 + CO \rightarrow \text{Ru(CO)}_3(PPh_3)_2 + RSH \quad 6.3

in THF at several temperatures was monitored by UV/vis. spectroscopy (Fig. 6.8). Under \textit{pseudo}-first order conditions (1 atm CO) the \textit{pseudo}-first order log plot is linear for 3 half-lives (Fig. 6.9). The observed rate constant is independent of the pressure of CO (760 to 6 torr for R=Et, at 26°C), but is dependent on the choice of thiolate group. The rate law and rate constants (all at 55°C) are as follows.

\frac{-d[9]}{dt} = k[9]
Fig. 6.8 UV/vis. spectra acquired every 900 s during the reaction of *ccf*-RuH(SEt)(CO)$_2$(PPh$_3$)$_2$ (0.9 mM) and CO (1 atm) in THF at 26°C.
Fig. 6.9 Logarithmic plot of absorbance at 400 nm versus time for the reaction of \( \textit{cct-RuH(SEt)(CO)2(PPh3)2} \) (9e, 0.9 mM) and CO (1 atm) in THF at 26.5\(^\circ\)C.
R: CH₂CH₃ > CH₃ > CH₂Ph > C₆H₄pCH₃ > C₆H₅  
\[ k: \quad 1.2 \times 10^{-2} \quad 7.1 \times 10^{-3} \quad 2.2 \times 10^{-3} \quad 9.3 \times 10^{-4} \quad 5.5 \times 10^{-4} \text{ s}^{-1} \]

The temperature dependence of these rate constants has also been determined (Fig. 6.10). Because the rate law and rate constant of the reaction of 9d with CO (reaction 6.3, R=Et) extrapolated to 22°C (1.8 x 10^{-4} s^{-1}) are the same (within the experimental error) as those for the reaction of 9d with PhSH (reaction 3.12, Section 3.5) at the same temperature (1.9 x 10^{-4} s^{-1}), then the two reactions most likely proceed by analogous mechanisms. As explained in Sections 6.1.1 and 3.5, these mechanisms probably involve loss of a phosphine ligand as the first step. The subsequent steps of the mechanism of reaction 6.3 are co-ordination of CO and elimination of thiol, but the order in which they occur is not known. The path which leads to a 3-coordinate species (elimination of thiol before coordination of CO) seems less likely. The proposed mechanism is shown in Scheme 6.2.

Attempts to test the effect of a large excess of PPh₃ on the rate of reaction 6.3 were hindered by the occurrence of a side reaction of 9 with PPh₃ (Section 6.1.3).

The enthalpies of activation are 120±20 kJ/mol for 9b (R=C₆H₄pCH₃) and 100±10 kJ mol⁻¹ for 9d (R=C₂H₅), consistent with the suggestion (Section 6.1.1) that increased electron density at the metal centre increases the rate of reaction by stabilizing the activated complex \{RuH(SR)(CO)₂(PPh₃)\}⁺. Ethanethiolate, a more basic ligand than thiophenolate, would increase the electron density.

The large error inherent in the calculation of the entropy of activation (40±40 and 20±25 J mol⁻¹ K⁻¹ for 9b and 9d, respectively) precludes any conclusion about the possible effect of the nature of the thiolate group on ΔS⁺. However, it is clear that the entropy of activation is positive, as expected for a dissociative mechanism. The enthalpy term is mainly responsible for the difference in rates between the reactions of 8b (R=C₆H₄pCH₃) and 8d (CH₂CH₃) at this temperature.

It has now been established that reactions 6.1, 6.3, and 3.15 all proceed via the same rate determining step, suggested to be the initial dissociation of PPh₃ from the Ru centre. Further
Fig. 6.10 Eyring plot for the reactions of \( \text{cct-RuH(SR)(CO)}_2(\text{PPh}_3)_2 \) (9) with CO (1 atm) in THF, where R=\( \text{C}_6\text{H}_4\text{pCH}_3 \) (9b), \( \text{CH}_2\text{C}_6\text{H}_5 \) (9e), or \( \text{CH}_2\text{CH}_3 \) (9d).
Scheme 6.2 A proposed mechanism for the reaction of $\text{RuH(SR)(CO)}_2(\text{PPh}_3)_2$ with CO ($L = \text{PPh}_3$).

\[
\begin{align*}
\text{RuH(SR)(CO)}_2L_2 & \xrightleftharpoons[k_{1, L}]^{k_{1, -L}} \text{RuH(SR)(CO)}_2L \\
& \xrightleftharpoons[k_{2, L}]^{k_{2, -CO}} \text{RuH(SR)(CO)}_3L \\
& \xrightleftharpoons[k_{3, RSH}]^{k_{3, -RSH}} \text{Ru(HSR)(CO)}_3L \\
\text{Ru(CO)}_3L_2 & \xrightleftharpoons[k_{4, L}]^{k_{4, -L}} \text{Ru(CO)}_3L
\end{align*}
\]
evidence for this is the magnitude of the effect on the rate of reaction 6.1 when the phosphine
*trans* to the dissociating ligand has *p*-methyl substituents; the rate is increased ten-fold. This
strong an effect is consistent with a *trans* effect, rather than a *cis* effect. That is, if the rate
determining step were initial reductive elimination of thiol, then the effect of a change in the
phosphine in the *cis* position would not be as large as that observed. The evidence, therefore,
supports a rate determining step of PPh3 dissociation. However, *cct*-RuH(SC6H4pCH3)(CO)2(PPh3)2 reacts 1.7 times faster with CO than does *cct*-RuH(SC6H5)(CO)2(PPh3)2. If the rate-determining step were initial dissociation of PPh3, then
this would constitute a *cis*-effect. It is not possible to evaluate whether 1.7 is a reasonable value
because the magnitudes of the *cis*-effects of thiolate ligands on the rate of elimination of
phosphines have not been previously reported. If the first and rate-determining step is reductive
elimination of thiol, then a large rate difference is expected. The argument for initial phosphine
loss is considered stronger because the *trans*-effect of the phosphine is more pronounced, and
because the mechanisms of the reactions of 9 are expected to be analogous to those of 14. In the
latter system (Section 3.8 and 6.2.2), the evidence for initial phosphine loss includes kinetic
measurements of the inhibition by added PPh3 of the reaction of 14 with thiols.

Reaction 6.3 is the reverse of reaction 3.19 (Section 3.9), the kinetics and mechanism of
which are not known.

6.1.3 PPh3

A large excess of PPh3 in THF at room temperature converts *cct*-RuH(SEt)(CO)2(PPh3)2
(9d) to Ru(CO)2(PPh3)3 (2, 26 % conversion after 4 h, 100 % after 4 days).

\[
\text{RuH(SR)(CO)2(PPh3)2 + PPh3} \iff \text{Ru(CO)2(PPh3)3 + RSH} \quad 6.4
\]
The slow rate of this reaction shows that the rate determining step is not the same as that of reactions 6.1, 6.3, and 3.12. This result is not surprising because initial dissociation of a phosphine from the metal centre is an unlikely step in a reaction which has a net increase in the number of coordinated phosphines. The generation of thiol in this reaction was not confirmed. The reaction is the reverse of reaction 3.3 (section 3.1).

6.1.4 H₂

The complex cct-RuH(SMe)(CO)₂(PPh₃)₂ (9c), dissolved in THF and subjected to 60 atm of H₂ for 25 h at room temperature is largely converted to cct-RuH₂(CD)₂(PPh₃)₂ (3).

\[
\text{RuH(SR)(CO)₂(PPh₃)₂ + H₂} \rightleftharpoons \text{RuH₂(CO)₂(PPh₃)₂ + RSH} \quad \text{(6.5)}
\]

The generation of thiol in this reaction was not confirmed. The reverse reaction (reaction 3.4) proceeds even under 1 atm of H₂ (Section 3.3). Because reaction 3.4 is the reverse of reaction 6.5, the latter is believed to proceed via reductive elimination of thiol followed by oxidative addition of H₂.

6.1.5 Acids

The complex cct-RuH(SCH₂C₆H₅)(CO)₂(PPh₃)₂ (9e, 8.6 mol) was dissolved in a heterogeneous mixture of C₆D₆ (0.6 mL) and aqueous concentrated HCl (0.05 mL, 0.6 mmol). After 10 min at room temperature, 84 % conversion to cct-RuH(Cl)(CO)₂(PPh₃)₂ (4) was observed.

\[
\text{RuH(SR)(CO)₂(PPh₃)₂ + HCl} \rightarrow \text{RuH(Cl)(CO)₂(PPh₃)₂ + RSH} \quad \text{(6.6)}
\]
This reaction parallels reaction 3.12 (Section 3.5) in that HCl acts in the same manner as a thiol. As shown in Section 3.5, the most acidic thiols react preferentially, and thus the high reactivity of HCl seems reasonable. Reaction 6.6 is highly favourable, and the reverse reaction would require a very large excess of thiol (or in a more practical sense an excess of NaSR, cf. Section 5.4).

The products of the reaction of ccc-RuH(SC6H5)(CO)2(PPh3)2 (3.3 μmol) in C6D6 (0.6 mL) with HBF4/H2O (50 μL, 300 μmol) at room temperature have not been identified. However, the 1H (Fig. 6.11) and 31P(1H) NMR spectra are consistent with a major product of the formula ccc-RuH(X)(CO)2(PPh3)2 (where X is unknown). A broad peak at 1.5 ppm in the 1H NMR spectrum has the correct integral and chemical shift215 for the aquo ligand of ccc-[RuH(H2O)(CO)2(PPh3)2]+, suggesting that this is the major product. The same product is not observed when HBF4/Et2O is used as the protonating agent. Instead, a large number of unassigned peaks is observed in the 31P(1H) NMR spectrum.

6.1.6 CD3OD

The hydrido and mercapto hydrogen atoms of ccc-RuH(SH)(CO)2(PPh3)2 (9a) undergo deuterium exchange with 4% v/v CD3OD in C6D6 (Fig. 6.12).

\[
\text{D}^+ \quad \text{RuH(SH)(CO)2(PPh3)2} \rightleftharpoons \text{RuH(SD)(CO)2(PPh3)2 + RuD(SD)(CO)2(PPh3)2} \quad 6.7
\]

The first-order rate constants, at 19°C, are 4.1 x 10⁻⁵ and 2.9 x 10⁻⁴ s⁻¹, respectively (Fig. 6.13). Of the two hydrogens, the mercapto hydrogen exchanges more rapidly, suggesting that it is exchanging intermolecularly with the D⁺ ions in the solution, possibly with the following mechanism:
Fig. 6.11 $^1$H NMR spectrum acquired 30 min after the start of the reaction of cct-RuH(SC$_6$H$_5$)(CO)$_2$(PPh$_3$)$_2$ (9i, 5.6 mM) with excess HBF$_4$/H$_2$O (50 µL) in C$_6$D$_6$ at room temperature.
Fig. 6.12 The time dependence of the intensity (I) of the $^1$H NMR signals due to $cct$-RuH(SH)(CO)$_2$(PPh$_3$)$_2$ (4.4 mM) in 4% v/v CD$_3$OD/C$_6$D$_6$ at 190°C.

Fig. 6.13 The log plot of the intensity of the $^1$H NMR signals due to $cct$-RuH(SH)(CO)$_2$(PPh$_3$)$_2$ (4.4 mM) in 4% v/v CD$_3$OD/C$_6$D$_6$ at 190°C.
The mercapto hydrogens of \( \text{cct-Ru(SH)2(CO)2(PPh3)2} \) (14a) also exchange with 4% \( \text{CD3OD} \) in \( \text{CD2Cl2} \) (Section 6.2.4), showing that the exchange does not require a hydride cis to the mercapto group. The hydrido hydrogen of 9a is either exchanging intermolecularly or intramolecularly. The intermolecular exchange process is unlikely, because \( \text{cct-RuH2(CO)2(PPh3)2} \) shows no exchange in 4% \( \text{CD3OD} \) in \( \text{C6D6} \) even after 2 h (Section 3.4). The intramolecular exchange could take place in the following manner:

Osakada et al.\(^{304}\) have reported on the H/D exchange of the hydrido and mercapto hydrogens of \( \text{RuH(SH)(PPh3)3} \) with 4% \( \text{CD3OD} \) in \( \text{CD2Cl2} \). It appears from Figure 2 of their report that the rate of the exchange of the hydrido hydrogen is faster than that of the mercapto hydrogen. However, the authors of the report concluded the reverse, and therefore, that the mercapto hydrogen alone was exchanging with the \( \text{CD3OD} \), and the deuteration at the hydridic site was via intramolecular exchange. They cited the lack of H/D exchange of the complexes \( \text{RuH(SPh)(PPh3)3} \) and \( \text{RuH(Cl)(PPh3)3} \), and the observation of intramolecular exchange in \( \text{PtH(SH)(PPh3)2} \) by Ugo et al.\(^{82}\). The conclusions in the \( \text{RuH(SH)(PPh3)3} \) system are therefore analogous to those in the \( \text{cct-RuH(SH)(CO)2(PPh3)2} \) system.

The \( ^1\text{H NMR spectral data} \) (Fig. 6.12) also show a slight decrease in the intensity of the \( \alpha\)-phenyl proton signal, a phenomenon not observed with the \( \mu\)- and \( \pi\)-phenyl signals. The mechanism by which \( \alpha\)-hydrogen exchange could occur is not known for this system.
6.2 THE REACTIONS OF \textit{cct-}Ru(SR)₂(CO)₂(PPh₃)₂ (14)

All of the observations of the reactivity of these bis-thiolate complexes (14) toward H₂, thiols, and phosphines suggest that the reactivity of 14 and associated mechanisms are similar to those of the hydrido-thiolato complexes (9). The lability of the phosphines in 14 has already been noted (Sections 3.8 and 5.2). A major difference in reactivity between species of types 9 and 14 is the instability of solutions of 14 (but not 14a) in solution.

6.2.1 Light

Tetrahydrofuran solutions of \textit{cct-}Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) under Ar, when exposed to light at 430 nm in the UV/vis. spectrometer exhibit a changing spectrum with an isosbestic point at 395±2 nm (Fig. 6.14). Unfortunately, the products have not been identified unambiguously, with the exception of PPh₃. The presence of added water or O₂ (1 atm) had no effect on the spectral changes, including the isosbestic wavelength.

Two samples of 14b (4.4 mM in C₆D₆) in NMR tubes at room temperature were analyzed by ³¹P{¹H} NMR spectroscopy after 8 h of darkness for one sample and 8 h under a Hanovia UV lamp for the other. Both samples were exposed to room light immediately before and during the NMR spectrum acquisition. The amount of unreacted starting material remaining in the former "dark" sample (70 %) compared to the latter (2 %) shows that the reaction being observed is promoted by exposure to light.

In attempts to identify the products of this reaction, a FAB mass spectrum was acquired of the solid product obtained from one such reaction using a THF solution under a Hanovia lamp for 90 minutes (Fig. 6.15). The strong peak at m/z = 1149 (±5) must represent a fragment containing at least two Ru atoms, unless it is Ru(PPh₃)₄. The match between the observed and predicted isotopic patterns is poor for Ru(PPh₃)₄, but fair for two Ru₂ and one Ru₃ complexes (Fig. 6.16).
Fig. 6.14 UV/vis. absorbance spectra of a THF solution of cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (0.32 mM) at 25°C being irradiated at 430 nm (between spectral acquisitions), after a) 50, b) 300, c) 600, d) 1,200, e) 2,100, f) 3,300, g) 5,400, h) 8,000, i) 13,000 and j) 240,000 s.
Fig. 6.15 FAB Mass Spectrum of the solid residue from a THF solution of cci-Ru(SC_{6}H_{4}pCH_{3})_{2}(CO)_{2}(PPh_{3})_{2} irradiated for 90 min under a Hanovia lamp.
Fig. 6.16  a) Observed isotopic pattern for the fragment m/z = 1149±5, and b) the predicted isotopic patterns for four possible formulations for the fragment.
If the suggested fragmentation trees (shown in Scheme 6.3) are correct, then the most likely formula for the fragment at \( m/z = 1149 \) (Ru₂(SC₆H₄pCH₃)₃(CO)₂(PPh₃)₂) suggests that the unfragmented molecule could be Ru₂(SC₆H₄pCH₃)₄(CO)₃(PPh₃)₂ (\( m/z = 1300 \)).

If this were the case, however, then the suggested connections in Scheme 6.3 between the peak at 1300 and the peaks at 1562 and 1591 would have to be incorrect.

The suggested triply thiolate-bridged complex would have two singlet peaks in the \( ^{31}P\{^{1}H\} \) NMR spectrum and three \( \nu(CO) \) bands in the IR spectrum. The \( ^{31}P\{^{1}H\} \) NMR spectrum of the sample submitted for the FAB/mass spectroscopy contains several peaks, including two at 32.84 and 42.84 ppm of roughly equal intensity. The same two peaks were observed in the \( ^{31}P\{^{1}H\} \) NMR spectra of isolated product mixtures from many similar reactions. The IR spectrum contains three \( \nu(CO) \) bands at frequencies (2034, 1977, and 1941) different from those of \( ccc\text{-}Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ \) (2028, 1968 cm⁻¹). It is not certain whether the three \( \nu(CO) \) bands are due to the same complex which gives rise to the NMR and FAB/MS signals already discussed.

Precedents for the triply-bridged type of complex include \([(PMe₂Ph)₃Ru(μSMe)₃Ru(PMe₂Ph)₃]^{+}\) and \([(CO)₃Fe(μSMe)₃Fe(CO)₃]^{+}\) while several of the series L₃Ru(μCl)₃Ru(Cl)L₂ have been reported. In addition, \([(CO)₂(PPh₃)Ru(μSEt)₃Na(THF)]₂ \) (described in Section 5.3) has a similar structure and is formed via a similar \( ccc\text{-}Ru(SR)₂(CO)₂(PPh₃)₂ \) precursor (14d).

In summary, the products of the light-induced decomposition reaction of \( ccc\text{-}Ru(SR)₂(CO)₂(PPh₃)₂ \) cannot be identified with certainty, beyond the fact that at least one of them contains two or more Ru atoms. A possible formulation for one of the products is suggested.
Scheme 6.3 Suggested fragmentation trees for the FAB mass spectrum of the products from the light-induced decomposition of \( cct -Ru(SC_6H_4pCH_3)_2(CO)_2(PPh_3)_2 \) (14h).
6.2.2 P(C₆H₄pCH₃)₃

The complex cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a) reacts with P(C₆H₄pCH₃)₃ in C₆D₆ at 25°C to produce two previously unknown complexes of structures similar to 14a, the NMR data (Figs. 6.17 and 6.18) being consistent with the following reactions (L=PPh₃, L‘=P(C₆H₄pCH₃)₃, all complexes cct):

\[
\begin{align*}
\text{Ru(SH)₂(CO)₂L₂} & + \text{L'} \rightarrow \text{Ru(SH)₂(CO)₂LL'} + \text{L} & \text{6.8} \\
\text{Ru(SH)₂(CO)₂LL'} & + \text{L'} \rightarrow \text{Ru(SH)₂(CO)₂L'₂} + \text{L} & \text{6.9}
\end{align*}
\]

The rates of these sequential reactions were followed by ¹H NMR spectroscopy (Figs. 6.18 and 6.19). The observed concentrations match exactly those predicted for the system

\[
A \rightarrow B \rightarrow C
\]

for over 4 half-lives of the first reaction (with \(k_1 = 6 \times 10^{-4}\) and \(k_2 = 5 \times 10^{-4}\) s⁻¹ at 25°C). This shows that in contrast to the mechanism of the reaction of the phosphine with a hydrido-thiolato analogue described in Section 6.1.1 (reactions 6.1 and 6.2), the rates of the reverse reactions shown in equations 6.8 and 6.9 are negligible for at least four half-lives.

The complex cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) reacts much more quickly than 14a with L’, giving complete conversion to a new product of structure similar to 24a by the time the first NMR spectrum can be taken, 3 minutes after the start of the reaction. The new complex is presumably cct-Ru(SC₆H₄pCH₃)₂(CO)₂[P(C₆H₄pCH₃)₃]₂ (24b). The difference in rates suggests that the phosphines of 14b must be considerably more labile than those of 14a. This is consistent with the difference in rates of the reactions of 14a and 14b with thiols (Section 3.8).
Fig. 6.17 $^{31}$P{H} NMR spectra acquired during the reaction of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a, 8.3 mM) with P(C$_6$H$_4$pCH$_3$)$_3$ (230 mM) in C$_6$D$_6$ at 25°C. Chemical shift scale is relative to PPh$_3$ in C$_6$D$_6$. 
Fig. 6.18 ¹H NMR spectra acquired during the reaction of cct-Ru(SH)₂(CO)₂(PPh₃)₂ (14a, 8.3 mM) with P(C₆H₄pCH₃)₃ (230 mM) in C₆D₆ at 25°C.
Fig. 6.19 The time dependence of the concentrations of the observed complexes during the reaction of \textit{cct}-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a, 8.3 mM) with P(C$_6$H$_4$pCH$_3$)$_3$ (230 mM) in C$_6$D$_6$ at 25°C.
6.2.3 \( \text{H}_2 \)

A toluene solution of \( \text{cct-Ru(SC}_6\text{H}_4\text{pCH}_3)\text{2(CO)}_2\text{(PPh}_3\text{)}_2 \) (14b) was exposed to 24 atm of \( \text{H}_2 \) at room temperature for 100 min. The \( ^1\text{H} \) and \( ^3\text{P}\{^1\text{H}\} \) NMR spectra of the isolated product mixture in C\(_6\)D\(_6\) (Figs. 6.20 and 6.21) showed that the solution contained unreacted 14b (20 \% of the \( ^{31}\text{P} \) NMR signal), the major product \( \text{cct-RuH(SC}_6\text{H}_4\text{pCH}_3)\text{(CO)}_2\text{(PPh}_3\text{)}_2 \) (9b, 45 \%), \( \text{cct-RuH}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 \) (3, 1 \%), and several unknowns. The hydride region of the \( ^1\text{H} \) NMR spectrum contained, in addition to the expected peaks for 9b and 3, a triplet at -10.19 ppm (\( ^2\text{J}_{\text{PH}}=15.9 \) Hz) and a doublet of doublets at -6.40 ppm (\( ^2\text{J}_{\text{transPH}}=96.9, ^2\text{J}_{\text{cisPH}}=28.2 \) Hz). Complexes which could give rise to the latter pattern are \( \text{ccc-} \) or \( \text{cct-RuH(SR)(CO)}_2\text{(PPh}_3\text{)}_2 \). Neither of these isomers have been observed, although \( \text{ccc-Ru(SC}_6\text{F}_5)\text{2(CO)}_2\text{(PPh}_3\text{)}_2 \) is known.260b

\[
\text{Ru(SR)}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 + \text{H}_2 \rightarrow \\
\text{RuH(SR)(CO)}_2\text{(PPh}_3\text{)}_2 + \text{RuH}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 + \text{others} \quad 6.10
\]

Attempts to detect or isolate the organic products of the reaction were not made, except for the observation that the singlet (3.02 ppm) in the \( ^1\text{H} \) NMR spectrum which corresponds to the mercapto proton of \( \text{p-thiocresol} \) is very small indeed (Fig. 6.20), suggesting that the thiol is not the major organic product.

6.2.4 CD\(_3\)OD

The mercapto hydrogens of \( \text{cct-Ru(SH)}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 \) (14a) exchanged with 4\% CD\(_3\)OD in CD\(_2\)Cl\(_2\) (Fig. 6.22), probably by the same mechanism as that proposed for reaction 6.7.

\[
\text{Ru(SH)}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 + 2\text{CD}_3\text{OD} \rightarrow \text{Ru(SD)}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2 + 2\text{CD}_3\text{OH} \quad 6.11
\]
Fig. 6.20 a) $^1$H NMR spectrum of a C$_6$D$_6$ solution of the product from the reaction of a THF solution of $\text{cct-Ru(SC}_6\text{H}_4\text{pCH}_3\text{)}_2(\text{CO})_2(\text{PPh}_3)_2$ with H$_2$ (24 atm). b) Expanded view of the hydride region of the same spectrum.
Fig. 6.21  $^{31}$P{$^1$H} NMR spectrum of a C$_6$D$_6$ solution of the product from the reaction of a THF solution of cct-Ru(SC$_6$H$_4$CH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ with H$_2$ (24 atm). Chemical shift scale is shown relative to PPh$_3$ in C$_6$D$_6$. 
Fig. 6.22 The time dependence of the intensity (I) of the $^1$H NMR signals due to $\text{ccc-} \text{Ru}(\text{SH})_2(\text{CO})_2(\text{PPh}_3)_2$ (3.3 mM) in 4% v/v CD$_3$OD/C$_6$D$_6$ at 25°C.
Once again, a significant decrease in the intensity of the signal for the \( \sigma \)-phenyl proton was observed, although the mechanism by which such an exchange may occur is not known.

6.3 EXPERIMENTAL DETAILS

The reaction of \( \textit{cct-RuH(SR)(CO)}_2(\text{PPh}_3)_2 \) with \( \text{P(C}_6\text{H}_4\text{pCH}_3)_3 \):

The reagents were placed in an NMR tube within a wide-mouth Schlenk tube. The latter tube was evacuated and Ar introduced at 1 atm. \( \text{C}_6\text{D}_6 \) (0.6 mL) was added into the NMR tube, which was then sealed with a septum. The tube was inserted into the pre-warmed NMR probe (45°C), at which point the reaction was considered to have started. The change in reaction was monitored by \( ^1\text{H} \) NMR spectroscopy, with the assumption that the \( T_1 \)'s of the hydride ligands on the complexes observed were the same (Section 2.2.3). The products were not isolated, but were identified by comparison of their \( ^1\text{H} \) and \( ^{31}\text{P}(^1\text{H}) \) NMR spectra with those of the corresponding starting complex.

\( \textit{cct-RuH(SCH}_2\text{C}_6\text{H}_4)(\text{CO})_2(\text{P(C}_6\text{H}_4\text{pCH}_3)_3)_2 \): \( ^1\text{H} \) NMR (\( \text{C}_6\text{D}_6 \)) \( \delta \) -4.58 ppm (t, \( ^2\text{J}_{\text{PH}} = 20.3 \text{ Hz, RuH} \)); \( ^{31}\text{P}(^1\text{H}) \) NMR (\( \text{C}_6\text{D}_6 \)) \( \delta \) 36.49, 35.83 ppm (both single peaks, considered to be the centre two peaks of an AB pattern with the two outlying peaks unobserved, \( ^2\text{J}_{\text{PP}} \) unknown).

\( \textit{cct-RuH(SC}_6\text{H}_4\text{pCH}_3)(\text{CO})_2(\text{P(C}_6\text{H}_4\text{pCH}_3)_3)_2 \): \( ^1\text{H} \) NMR (\( \text{C}_6\text{D}_6 \)) \( \delta \) -4.53 ppm (t, \( ^2\text{J}_{\text{PH}} = 20.2 \text{ Hz, RuH} \)); \( ^{31}\text{P}(^1\text{H}) \) NMR (\( \text{C}_6\text{D}_6 \)) \( \delta \) 35.17 ppm (s).

\( \textit{cct-RuH(SC}_6\text{H}_4\text{pCH}_3)(\text{CO})_2(\text{P(C}_6\text{H}_4\text{pCH}_3)_3)_2 \): not detected

\( \textit{cct-RuH(SC}_6\text{H}_4\text{pCH}_3)(\text{CO})_2(\text{P(C}_6\text{H}_4\text{pCH}_3)_3)_2 \): \( ^1\text{H} \) NMR (\( \text{C}_6\text{D}_6 \)) \( \delta \) -4.22 ppm (t, \( ^2\text{J}_{\text{PH}} = 19.7 \text{ Hz, RuH} \)); \( ^{31}\text{P}(^1\text{H}) \) NMR (\( \text{C}_6\text{D}_6 \)) \( \delta \) 35.09 ppm (s).

The reaction of \( \textit{cct-RuH(SCH}_2\text{CH}_3)(\text{CO})_2(\text{PPh}_3)_2 \) (9d) with \( \text{PPh}_3 \): The complex (6.7 mg, 1.3 mM) and \( \text{PPh}_3 \) (270 mg, 150 mM) were dissolved in THF (7 mL). After 4 h at room
temperature, the solvent was removed by vacuum distillation, and the residue redissolved in C₆D₆. The ³¹P{¹H} NMR spectrum contained signals for Ru(CO)₂(PPh₃)₃ (2, 30 % of the ³¹P signal excluding the free PPh₃ or its oxide), the starting materials, and a small amount of OPPh₃. The conversion to 2 was calculated to be 26 %, using correction factors determined from the ³¹P{¹H} NMR spectrum of a known mixture of 2 and ccf-RuH(SR)(CO)₂(PPh₃)₂.

The ³¹P{¹H} NMR spectrum of the residue from a similar reaction ([9d] = 2.2 mM, [PPh₃] = 78 mM) of 4 days duration contained no signal for 9d. Conversion to 2 was therefore complete.

The reaction of cct-RuH(SCH₃)(CO)₂(PPh₃)₂ (9c) with H₂: A solution of 9c (8 mg, 2.3 mM) in THF (5 mL) was exposed to H₂ (60 atm) for 25 h in a glass-lined steel vessel. After depressurization, the solution was transferred by syringe into an Ar-filled Schlenk tube through a septum. The volatiles were removed by vacuum distillation, and the solid residue redissolved in C₆D₆. The ³¹P{¹H} NMR spectrum contained signals for ccf-RuH₂(CO)₂(PPh₃)₂ (δ 56.33 ppm, 86 % of the total signal), unreacted 9c (37.05 ppm, 5 %), Ru(CO)₂(PPh₃)₃ (49.25, 2 %), and ccr-RuO₂(CO)₂(PPh₃)₂ (33.93 ppm, 8 %).

The reaction of cct-RuH(SCH₂C₆H₅)(CO)₂(PPh₃)₂ (9e) with HCl: Complex 9e (6.9 mg, 8.6 mol) was dissolved in a heterogeneous mixture of C₆D₆ (0.6 mL) and aqueous concentrated HCl (0.05 mL, 0.6 mmol). The reaction was monitored by ³¹P{¹H} and ¹H NMR spectroscopies. After 10 min at room temperature, the ³¹P{¹H} NMR spectrum of the solution showed the presence of cct-RuH(Cl)(CO)₂(PPh₃)₂ (38.43 ppm, 84 % of the total signal), unreacted 9e (37.09 ppm, 5 %), and an unknown (38.76 ppm, 11 %). A ¹H NMR spectrum was acquired from 15 to 48 min after the start of the reaction. In addition to the triplet for cct-RuH(Cl)(CO)₂(PPh₃)₂ (δ -3.86 ppm, ²J₉₀ = 19.1 Hz, 76 % of the integral of the hydride region), two other triplets of unidentified species were observed, at δ -5.25 ppm (²J₉₀ = 16.7 Hz, 7 %) and -13.31 ppm (²J₉₀ = 15.4 ppm, 16 %). The triplet of the starting complex was not observed at this time.
The reaction of $\text{cct-RuH(Sc}_6\text{H}_5\text{(CO)}_2\text{(PPh}_3\text{)}_2$ (9i) with HBF$_4$:

A heterogeneous mixture of aqueous HBF$_4$ (50 μL, 48 wt. %, 300 μmol) and a 0.6 mL C$_6$D$_6$ solution of $\text{cct-RuH(Sc}_6\text{H}_5\text{(CO)}_2\text{(PPh}_3\text{)}_2$ (3.3 μmol) was prepared under argon at room temperature. The $^3$P{H} NMR spectrum acquired after 20 min showed singlets for unreacted 9i (37.19 ppm, 25 %) and an unidentified product (41.71 ppm, 75 %). The $^1$H NMR spectrum (Fig. 6.11) acquired after 30 min contained three triplets, for 9i (-4.33 ppm, $^2$J$_{PH}$ = 19.3 Hz, 27 %), the major product (-3.83 ppm, $^2$J$_{PH}$ = 18.3 Hz, 68 %), and a second unknown (-3.98 ppm, $^2$J$_{PH}$ = 17.6 Hz, 5 %). A broad peak at 1.5 ppm in the $^1$H NMR spectrum has the correct integral and chemical shift for the aquo ligand of $\text{cct-[RuH(H}_2\text{O)}(\text{CO)}_2\text{(PPh}_3\text{)}_2]^+$, suggesting that this could be the major product.

The reaction of $\text{cct-RuH(Sc}_6\text{H}_4\text{pCH}_3\text{(CO)}_2\text{(PPh}_3\text{)}_2$ (9b, 9.2 μmol) with HBF$_4$/Et$_2$O (0.2 mL, 1 mmol) in toluene-d$_8$ (0.6 mL) at 1°C was monitored by NMR spectroscopy. After 4 min, the $^3$P{H} NMR spectrum showed singlets at 38.6 ppm (unassigned, 63% of the integration), 37.8 ppm (9b, 15%) and 18.9 ppm (unassigned, 18%), in addition to a large number of very small unassigned peaks. After 30 min, the integrals of the three major peaks had changed to 26, 10, and 46%, respectively, while the size of the smaller peaks had increased. The hydride region of the $^1$H NMR spectrum contains an unassigned triplet at -5.1 ppm.

The reaction of $\text{cct-RuH(SH)}(\text{CO)}_2\text{(PPh}_3\text{)}_2$ with CD$_3$OD: Complex 9a (2.1 mg, 4.4 mM) was dissolved in C$_6$D$_6$ (0.66 mL) under Ar in a septum-sealed NMR tube. CD$_3$OD (26 μL) was injected to start the reaction. Successive $^1$H NMR spectra, acquired every 7-10 min, showed a decrease in the signals of the o-phenyl (7.91 ppm), mercapto (-3.01 ppm) and hydrido (-4.83 ppm) hydrogens. The temperature was maintained at 19°C. The results are further described in section 6.1.6.
The light-induced reaction of cct-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b): Complex 14b (18 mg, 0.32 mM) was dissolved in THF (6 mL) in a quartz cell under Ar. A UV/vis. spectrum (Fig. 6.14) was acquired after 50, 290, 610, 1200, 2100, 3300, 5400, 8000, 13,000, and 240,000 s, the absorbance at 430 nm being monitored continuously until 15,000 s, except during spectral acquisition (100 s per acquisition). The temperature was maintained at 25.5°C. The rate of change in absorbance decreased over time, but was not first- or second-order. An isosbestic point was observed at 393 nm. The spectrum acquired after 240,000 s showed a departure from the isosbestic. The solvent was removed from the sample by vacuum distillation, and the residue was redissolved in C$_6$D$_6$ for analysis by NMR. Five unassigned peaks were present, at 24.22, 24.23, 32.82, 32.87, and 42.88 ppm, each with approximately 20 % of the total integral. A similar experiment with only 4 h reaction time produced a $^{31}$P{$^1$H} NMR spectrum with peaks for unreacted 14b (60 %), PPh$_3$ (6 %), and unknowns at 23.60 (9 %), 24.16 (12 %, possibly OPPh$_3$), 34.31 (5 %), and 34.82 ppm (6 %).

A sample of ccf-Ru(SC$_6$H$_4$pCH$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$ (14b. 63 g, 4.5 mM) was dissolved in THF (15 mL) in a Pyrex Schlenk tube under Ar. The tube was held 15 cm from a Hanovia lamp for 90 min without cooling the sample solution, during which time the yellow/orange solution turned orange/red. The temperature of the solution did not increase significantly above room temperature. The volatiles were then removed by vacuum distillation, and some of the residue redissolved in C$_6$D$_6$. The $^{31}$P{$^1$H} NMR spectrum contained signals for unreacted 14b (30 %), PPh$_3$ (8 %), and unknowns at 13.90 (28 %), 24.18 (5 %), 32.84 (11 %), and 42.84 ppm (16 %). The FT-IR spectrum of the crushed residue in Nujol contained three v(CO) bands, at 2034, 1977, and 1941 cm$^{-1}$. The residue was submitted for FAB/MS.

The reaction of cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a) with P(C$_6$H$_4$pCH$_3$)$_3$: Complex 14a (2.8 mg, 8.3 mM) and P(C$_6$H$_4$pCH$_3$)$_3$ (31.8 mg, 230 mM) were placed in an NMR tube within a wide-mouth Schlenk tube. The latter tube was evacuated and Ar introduced. C$_6$D$_6$ (0.46 mL) was added to the NMR tube, which was then sealed with a septum and cooled
in liquid N\textsubscript{2}. After being transported to the NMR room, the tube was warmed to the melting point of benzene, and inserted into the pre-warmed NMR probe (25°C). At this point the reaction was considered to have started. The change in reaction was monitored by \textsuperscript{1}H NMR spectroscopy, with the assumption that the T\textsubscript{1}'s of the mercapto hydrogens on the three reactant and product complexes were the same (Section 2.2.3). The products were not isolated, but were identified by comparison of their \textsuperscript{1}H and \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectra with those of the starting complex \textsuperscript{14}a.

\textit{cc-t-Ru(SH)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})(P(C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{3}) \textsubscript{2} (23a):} \textsuperscript{1}H NMR (C\textsubscript{6}P\textsubscript{6}) \textit{8} -1.90 ppm (t, \textit{3}J_{PH} = 6.9 Hz, SH); \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}) \textit{8} 19.70, 19.87 ppm (both single peaks, considered to be the centre two peaks of an AB pattern with the two outlying peaks unobserved, \textit{2}J_{PP} unknown).

\textit{cc-t-Ru(SH)\textsubscript{2}(CO)\textsubscript{2}(P(C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{3}) \textsubscript{2} (24a):} \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}) \textit{8} -1.85 ppm (t, \textit{3}J_{PH} = 7.1 Hz, SH); \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}) \textit{8} 19.18 ppm (s).

The reaction of \textit{cc-t-Ru(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (14b) with P(C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{3}: The method described above was adopted for studying the title reaction. However, the reaction was complete by the time the first \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum was acquired (3 min). Only three peaks were observed; those of P(C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{3}, PPh\textsubscript{3} (-6.05 ppm), and the product (9.93 ppm). The last mentioned is 1 ppm upfield of the position of the starting material, and therefore probably results from the \textit{cc-t-Ru(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(P(C\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{3})\textsubscript{2} complex (24b).

The reaction of \textit{cc-t-Ru(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (14b) with H\textsubscript{2}: A toluene solution (50 mL) of \textit{14b} (42 mg, 0.90 mM) was exposed to H\textsubscript{2} (24 atm) at room temperature for 100 min in a glass-lined steel vessel. After depressurization, the solution was transferred by syringe into an Ar-filled Schlenk tube through a septum. After the volatiles were removed, the solid products were redissolved in C\textsubscript{6}D\textsubscript{6} and analyzed by \textsuperscript{1}H and \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectroscopies. The spectra indicated the presence of \textit{14b} (20 % of the \textsuperscript{31}P NMR signal), \textit{cc-t-RuH(SC\textsubscript{6}H\textsubscript{4}pCH\textsubscript{3})(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (9b, 45 %), cct-RuH\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (3, 1 %), and several
unknowns. The hydride region of the $^1$H NMR spectrum contained triplets at -4.33 (9b, $^2$J$_{PH}$=19.7, 71 %), -6.33 (3, $^2$J$_{PH}$=23.4, 4 %), and at -10.19 ppm (unknown, $^2$J$_{PH}$=15.9 Hz, 8 %) and a doublet of doublets at -6.40 ppm (unknown, $^2$J$_{transPH}$=96.9, $^2$J$_{cisPH}$=28.2 Hz, 17 %).

The reaction of $cct$-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a) with CD$_3$OD: Complex 14a (2.1 mg, 3.3 mM) was dissolved in C$_6$D$_6$ (0.85 mL) under Ar in a septum-sealed NMR tube. CD$_3$OD (34 µL) was injected to start the reaction. Successive $^1$H NMR spectra, acquired every 6 min, showed a rapid decrease in the intensity of the mercapto (-1.97 ppm) hydrogen signal, and a slower decrease in the intensity of the o-phenyl signal. The temperature was maintained at 25°C.
7. GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Potential Applications for the Complexes in Sulphur Chemistry

The dihydride complex \textit{ccr}-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ is not a likely catalyst for hydrodesulphurization (HDS) because none of its reactions with sulphur containing compounds, other than propylene sulphide, resulted in S-C bond cleavage. As discussed previously (Section 1.3), S-C bonds, especially those found in thiophenes, are more difficult to cleave than S-H and S-S bonds. The mechanism for such a S-C bond cleavage reaction with thioethers would almost certainly involve a thioether complex as an intermediate. In general, thioether transition metal complexes are unstable, usually with respect to dissociation of the thioether from the metal rather than decomposition via C-S bond cleavage.

The \textit{ccr}-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ complex is a potential catalyst for disulphide reduction (reaction 7.1) because reactions 4.4 and 6.5 together constitute a catalytic cycle for this reaction.

\begin{align*}
2\text{RuH}_2$(CO)$_2$(PPh$_3$)$_2$ + RSSR & \rightarrow 2\text{RuH}$(SR)$(CO)$_2$(PPh$_3$)$_2$ + H$_2$ \quad 4.4 \\
\text{RuH}$(SR)$(CO)$_2$(PPh$_3$)$_2$ + H$_2$ & \rightarrow \text{RuH}_2$(CO)$_2$(PPh$_3$)$_2$ + RSH \quad 6.5 \\
\text{Ru} \\
\text{RSSR} + H$_2$ & \rightarrow 2\text{RSH} \quad 7.1
\end{align*}

Problems which could be encountered include significant back reactions (reverse of reactions 4.4 and 6.5) under conditions of excess H$_2$ and thiol, and loss of the catalyst via production of \textit{ccr}-Ru(SR)$_2$(CO)$_2$(PPh$_3$)$_2$ (reactions 4.7 and 4.9) and its subsequent decomposition (Section 6.2.1).

Reduction of disulphides to thiols is practiced in organic chemistry as the last step in the synthesis of thiols, if the direct synthesis of the thiol gives lower yields or is less safe than synthesis via the disulphide. In addition, unstable thiols are often stored as the disulphide.309
Stoichiometric methods for the reduction of disulphides have been reviewed. The reduction of disulphides by o-methylbenzaldehyde and methanol is catalyzed by 3,3'-tetramethylene-bridged 4-methylthiazolium bromide. Thioredoxin and thioredoxin reductase together catalyse the reduction of disulphides in mammalian cells. The reverse reaction, oxidation of thiols to disulphides, is catalyzed by several transition metal complexes.

A potential non-catalytic application of the chemistry described in this thesis is the non-oxidative extraction of thiols from petroleum. Such a process would require two steps; extraction of the thiols by passing the oil fraction over a supported transition metal complex such as a derivative of ccf-RuH2(CO)2(PPh3)2, followed by regeneration of the same complex from the thiolate, ccr-RuH(SR)(CO)2(PPh3)2, by applying high pressures of hydrogen. Obviously, any complex containing either Ru or PPh3 would be too expensive for such an application. However, similar applications (both oxidative and non-oxidative) for unsupported iron carbonyls have been suggested, although cost remains a problem even in the iron system. Leaching of a supported transition metal catalyst, or incomplete separation of an unsupported catalyst, would also create problems of heavy-metal contamination of the fuel product.

7.2 Parallels to Surface Chemistry

The hydrido thiolato complex ccf-RuH(SR)(CO)2(PPh3)2 has parallels in the chemistry of thiols on transition metal surfaces. In most cases of thiol adsorption to such surfaces, cleavage of the S-H bond occurs and thiolato species are detected. The fate of the hydrogen atom is rarely reported. However, after H2S adsorption on a Ru(110) surface, mixtures of H2S, SH, S, and H species are detected, depending on the coverage. Examples of adsorption of thiols on the surface without S-H bond cleavage are reported to exist at low temperatures. The instability of S-bonded thiols is also recognized in transition metal solution chemistry. No such M-S(H)R species was directly observed in the present work.
A related type of complex, in which two or possibly three thiolate ligands share a proton, is proposed as an intermediate in the thiol exchange reactions of cct-RuH(SR)(CO)2(PPh3)2 and cct-Ru(SR)2(CO)2(PPh3)2 (reactions 3.12 and 3.18).

The type of bonding illustrated above may exist on the surface of HDS catalysts. The formation of such species on the surface would be associated with adsorption or liberation of 1/2 to 2/3 of the hydrogen from the adsorbed thiol. Isolated metal complexes with structures containing H⁺ or other cations trapped by thiolate groups are [Ru(CO)2(PPh3)(μSEt)2(μ3SEt)Na(THF)]2 (Section 5.2) and Ru(ClH)(buS4)(PPh3) (buS4²⁻ = 1,2-bis((3,5-di-tert-butyl-2-mercapto-phenyl)thio)ethanato)249 the latter being shown below.
7.3 Conclusions

One of the phosphine ligands of Ru(CO)$_2$(PPh$_3$)$_3$ (2) is quickly displaced by thiols and disulphides, producing species of the type cct-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ (9) and cct-Ru(SR)$_2$(CO)$_2$(PPh$_3$)$_2$ (14), respectively. The kinetics of the disulphide reaction are consistent with a two-step mechanism involving elimination of PPh$_3$ followed by oxidative addition of RSSR. Similar mechanisms have been proposed in earlier studies of the related reactions of 2 with CO and H$_2$. Complex 2 fails to react with unstrained thioethers.

Reactions of the related complex Ru(CO)$_2$(PPh$_3$)(dpm) (16, dpm = bis(diphenylphosphino)methane) are complicated by the lability of all of the three different ligands. Reactions of this complex with thiols produce mixtures of thiolate complexes. The two dihydrides cct-RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (3) and RuH$_2$(dpm)$_2$, as a cis/trans mixture (7), react with thiols to produce the hydrido-thiolato complexes cct-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ (9) and RuH(SR)(dpm)$_2$ (13), respectively. The mechanism appears to depend on the basicity of the hydride ligands; the more basic dihydride, 7, is probably protonated by the thiol, giving an unobserved molecular hydrogen intermediate. The reaction rate depends on the acidity and concentration of the thiol. The less basic dihydride, 3, reacts by slow reductive elimination of H$_2$ followed by rapid oxidative addition of thiol, the rate being independent of the nature or concentration of the thiol. The same rate constant, rate law, and activation parameters are found for the reaction of 3 with thiols, CO or PPh$_3$. The reaction of 3 with RSSR produces mostly 9, with small amounts of 14 that increase with time. The mechanism of the reaction with RSSR was not determined.

The hydrido-thiolato complexes cct-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ (9) are well characterized for a variety of R groups. The related complex cct-RuH(SePh)(CO)$_2$(PPh$_3$)$_2$ was also synthesized. The reactions of 9 with other thiols, P(C$_6$H$_4$CH$_3$)$_3$, CO, RSSR, HCl, PPh$_3$, and H$_2$, are also reported. The first three of these reactions share the same rate law and rate constant, the common rate determining step probably being initial loss of PPh$_3$. The rate constant depends
strongly on the choice of thiolate group, with the complexes containing the more basic thiolate
groups reacting faster. The entropy and enthalpy of activation for the reaction of 9b
(R=C₆H₄pCH₃) with CO are higher than those for the same reaction of 9d (R=CH₂CH₃),
although the error in the entropy values is large. The difference in enthalpy is mainly
responsible for the difference in rate. Some equilibrium constants for the exchange reactions of
9d (R=CH₂CH₃) with other thiols were determined, the Kₑq values increasing with the acidity
of the incoming thiol.

The reactions of cct-Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) are complicated by the extreme
lability of the phosphine ligands. The complex in solution is unstable in the presence of light,
exchanges phosphines rapidly with added P(C₆H₄pCH₃)₃, exchanges thiolate groups with added
thiols, and is converted by high pressures of H₂ to a mixture of 9b and 3.

The X-ray crystallographic structures of cct-RuH(SC₆H₄pCH₃)(CO)₂(PPh₃)₂ (9b) and cct-
Ru(SC₆H₄pCH₃)₂(CO)₂(PPh₃)₂ (14b) show that the Ru-P bond lengths in 14b are longer,
consistent with the higher lability of the phosphines of that complex. The phosphine ligands of
Ru(SH)₂(CO)₂(PPh₃)₂ (14a) on the other hand are less labile, and the Ru-P bond lengths
shorter, than in 14b. Complex 14a is stable in solution in the presence of light, and exchanges
phosphines more slowly with added P(C₆H₄pCH₃)₃.

The mercapto hydrogens of 9a (R=H) and 14a exchange with the acidic deuterons of added
CD₃OD. The hydridic and ortho-phenyl hydrogens exchange more slowly, presumably by
intramolecular processes.

Intermediates proposed for the mechanism of the thiol exchange reactions of 9 and 14 contain
two or three thiolate groups sharing a proton. A related complex, containing three thiolate
groups on a ruthenium centre sharing a sodium cation, was isolated and fully characterized. In
the solid state, this [Ru(CO)₂(PPh₃)(μSEt)₂(μ₃SEt)Na(THF)]₂ complex exists in dimeric form,
and is formed as a by-product from the synthesis of 14d (R=Et) from cct-RuCl₂(CO)₂(PPh₃)₂
and sodium ethanethiolate. In acetone, 9b and 14b can be formed cleanly from
ccf-RuHCl(CO)₂(PPh₃)₂ and cct-RuCl₂(CO)₂(PPh₃)₂, respectively, by reaction with ethanethiolate.

Complex 3 could be used as a catalyst for the reduction of disulphides by H₂, or as a recyclable reagent for the non-oxidative extraction of thiols from thiol-containing mixtures such as oil fractions. However, the cost of RuCl₃ and PPh₃ is too high to allow such direct applications. The chemistry described above will help instead to guide future researchers to related complexes with higher activity and lower costs, and systems that more closely parallel the processes occurring on the surfaces of industrial HDS catalysts.

7.4 Recommendations for Future Research

As has been suggested recently by another group,⁹⁰ the redox chemistry of cct-RuH(SH)(CO)₂(PPh₃)₂, cct-Ru(SH)₂(CO)₂(PPh₃)₂ and cct-RuS₂(CO)₂(PPh₃)₂ should be investigated. Initial experiments during the present research, but not otherwise reported here, show that high pressures of H₂ (24 atm) over CH₂Cl₂ solutions of cct-RuS₂(CO)₂(PPh₃)₂ for 2 h at room temperature do not cause formation of cct-RuH₂(CO)₂(PPh₃)₂ or cct-Ru(SH)₂(CO)₂(PPh₃)₂. However, such reactions may possibly be achieved in the presence of acid, because of the ease of electrophilic attack on the S²⁻ ligand.¹¹⁸,²²¹,³²¹-²

Research should focus on complexes which are capable of cleaving unstrained S-C bonds. The most likely candidates are bimetallic complexes containing at least one transition metal which bonds strongly with sulphur. One such complex, (CO)₃Mo(µH)₂(dpm)₂Ru(CO)₂⁻²³³ has some similarities to the complexes described in the present work. However, for closer parallels to industrial HDS catalysts, a Co/Mo bimetallic complex should be used. If the observations summarized in Figure 1.5 (p. 16)⁴⁷ can be extrapolated to solution chemistry, then a Co/Mo complex would have greater potential for HDS activity than a Ru/Mo complex.⁴⁷ Sulphido-
bridged Co/Mo clusters have been synthesised,\textsuperscript{324-6} but only from the reactions of Mo sulphide complexes with Co carbonyl complexes, rather than by the insertion of S into Co-Mo bonds.

The catalytic activity of \textit{cct-RuH2(CO)2(PPh3)2} for the reduction of disulphides to thiols under pressures of H\textsubscript{2} should be investigated.
8. REFERENCES


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(301) G. Rastar, P. G. Jessop, and B. R. James, unpublished results.


### APPENDIX 1: SUMMARY OF CRYSTALLOGRAPHIC DATA

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* Temperature 294 K, Rigaku AFC6S diffractometer, Mo $K_a$ radiation ($\lambda = 0.71069$ Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 x 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) - [S^2(C + iB) + (pF^2)^2]/Lp^2$ (S - scan rate, C - scan count, B - normalized background count, p - 0.035 for 1, 0.040 for 2, and 0.030 for 3), function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|)^2)/\Sigma w|F_o|^2)^{1/2}$, and gof = $[\Sigma(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for $R$, $R_w$, and gof are based on those reflections with $I \geq 3\sigma(I)$. 
Table A2.1 Final atomic coordinates (fractional) and B(eq).

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APPENDIX 3: ATOMIC COORDINATES FOR
cct-Ru(SC\textsubscript{5}H\textsubscript{4}pCH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (14b)

Table A3.1 Final atomic coordinates (fractional) and $B(\text{eq})$.

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Table A4.1 (cont.)

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### Table A4.2 Calculated hydrogen coordinates and $B_{iso}$.

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## APPENDIX 5: KINETIC DATA

Table A5.1 The reaction of \( \text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3) with \( p \)-thiocresol (reaction 3.4, page 77)

<table>
<thead>
<tr>
<th>[3] (mM)</th>
<th>[RSH] (mM)</th>
<th>T (°C)</th>
<th>( k_{\text{obs}} ) (s(^{-1}))</th>
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<tr>
<td>0.93</td>
<td>26</td>
<td>26</td>
<td>6.4 x 10(^{-4})</td>
</tr>
<tr>
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<td>26</td>
<td>6.7 x 10(^{-4})</td>
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<tr>
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<tr>
<td>0.045</td>
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<tr>
<td>0.073</td>
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<tr>
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<td>0.97</td>
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Table A5.2 The reaction of \( \text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3) with ethanethiol (reaction 3.4, page 77)

<table>
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<tr>
<td>1.0</td>
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<td>1.0</td>
<td>95</td>
<td>26</td>
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<td>7.3 x 10(^{-4})</td>
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<tr>
<td>1.0</td>
<td>95</td>
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<td>6.5 x 10(^{-4})</td>
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<tr>
<td>1.0</td>
<td>190</td>
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<td>1.1</td>
<td>95</td>
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<td>2.8 x 10(^{-3})</td>
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<td>47</td>
<td>5.7 x 10(^{-3})</td>
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<td>1.5</td>
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<td>47</td>
<td>6.0 x 10(^{-3})</td>
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Table A5.3  The reaction of \( \text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3) with carbon monoxide (reaction 3.5, page 86)

<table>
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<th>( k'_{\text{obs}} ) (s(^{-1}))</th>
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<tr>
<td>1.0</td>
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<td>( 5.7 \times 10^{-4} )</td>
</tr>
<tr>
<td>1.1</td>
<td>1</td>
<td>25</td>
<td>( 5.7 \times 10^{-4} )</td>
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<td>1.0</td>
<td>1</td>
<td>34</td>
<td>( 1.8 \times 10^{-3} )</td>
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<tr>
<td>1.0</td>
<td>1</td>
<td>41</td>
<td>( 4.1 \times 10^{-3} )</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>41</td>
<td>( 4.1 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.25</td>
<td>1</td>
<td>41</td>
<td>( 4.0 \times 10^{-3} )</td>
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<td>1.1</td>
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<td>51</td>
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Table A5.4  The reaction of \( \text{cct-RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) (3) with triphenyl phosphine (reaction 3.6, page 86)

<table>
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<th>( k_{\text{obs}} ) (s(^{-1}))</th>
</tr>
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<tr>
<td>0.31</td>
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<td>25</td>
<td>( 6.6 \times 10^{-4} )</td>
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<tr>
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<td>25</td>
<td>( 6.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.55</td>
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<td>25</td>
<td>( 6.5 \times 10^{-4} )</td>
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</table>

Table A5.5  The reaction of \( \text{cct-RuH(SCH}_2\text{CH}_3)(\text{CO})_2(\text{PPh}_3)_2 \) (9d) with thiophenol at 22°C (reaction 3.12, page 103)

<table>
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<tr>
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<td>9.7</td>
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<td>8.5</td>
<td>1500</td>
<td>( 1.9 \times 10^{-4} )</td>
</tr>
<tr>
<td>9.5</td>
<td>3400</td>
<td>( 2.0 \times 10^{-4} )</td>
</tr>
<tr>
<td>1.8</td>
<td>1300</td>
<td>( 1.9 \times 10^{-4} )</td>
</tr>
</tbody>
</table>
Table A5.6 The reaction of $cct$-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ (14a) with thiophenol at 25°C (reaction 3.18, page 119)

<table>
<thead>
<tr>
<th>[14a] (mM)</th>
<th>[PhSH] (mM)</th>
<th>[PPh$_3$] (mM)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>$k_P$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>69</td>
<td>0</td>
<td>4.7 x 10$^{-4}$</td>
<td>4 x 10$^{-4}$</td>
</tr>
<tr>
<td>7.8</td>
<td>77</td>
<td>0</td>
<td>4.2 x 10$^{-4}$</td>
<td>4 x 10$^{-4}$</td>
</tr>
<tr>
<td>6.2</td>
<td>330</td>
<td>0</td>
<td>4.0 x 10$^{-4}$</td>
<td>3 x 10$^{-4}$</td>
</tr>
<tr>
<td>5.1</td>
<td>690</td>
<td>0</td>
<td>4.4 x 10$^{-4}$</td>
<td>1 x 10$^{-3}$</td>
</tr>
<tr>
<td>9.4</td>
<td>700</td>
<td>0</td>
<td>3.8 x 10$^{-4}$</td>
<td>5 x 10$^{-4}$</td>
</tr>
<tr>
<td>5.3</td>
<td>1700</td>
<td>0</td>
<td>3.9 x 10$^{-4}$</td>
<td>5 x 10$^{-3}$</td>
</tr>
<tr>
<td>4.8</td>
<td>2800</td>
<td>0</td>
<td>3.4 x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>2900</td>
<td>0</td>
<td>3.2 x 10$^{-4}$</td>
<td>1 x 10$^{-2}$</td>
</tr>
<tr>
<td>5.7</td>
<td>770</td>
<td>23</td>
<td>3.1 x 10$^{-4}$</td>
<td>3 x 10$^{-3}$</td>
</tr>
<tr>
<td>5.4</td>
<td>750</td>
<td>240</td>
<td>3.6 x 10$^{-4}$</td>
<td>3 x 10$^{-3}$</td>
</tr>
<tr>
<td>6.5</td>
<td>66</td>
<td>220</td>
<td>2.5 x 10$^{-4}$</td>
<td>3 x 10$^{-4}$</td>
</tr>
<tr>
<td>6.2</td>
<td>66</td>
<td>325</td>
<td>1.3 x 10$^{-4}$</td>
<td>4 x 10$^{-4}$</td>
</tr>
<tr>
<td>6.3</td>
<td>64</td>
<td>460</td>
<td>1.1 x 10$^{-4}$</td>
<td>4 x 10$^{-4}$</td>
</tr>
<tr>
<td>6.1</td>
<td>67</td>
<td>490</td>
<td>1.1 x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>5.9</td>
<td>810</td>
<td>470</td>
<td>3.1 x 10$^{-4}$</td>
<td>2 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

Table A5.7 The reaction of Ru(CO)$_2$(PPh$_3$)$_3$ (2) with $p$-tolyl disulphide (RSSR) at 25°C (reaction 4.1, page 152)

<table>
<thead>
<tr>
<th>[2] (mM)</th>
<th>[RSSR] (mM)</th>
<th>initial rate (M s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>2.1</td>
<td>6.4 x 10$^{-7}$</td>
</tr>
<tr>
<td>0.31</td>
<td>2.1</td>
<td>6.1 x 10$^{-7}$</td>
</tr>
<tr>
<td>0.33</td>
<td>6.0</td>
<td>1.0 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.35</td>
<td>7.8</td>
<td>1.5 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.33</td>
<td>8.8</td>
<td>1.1 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.36</td>
<td>17</td>
<td>2.0 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.34</td>
<td>30.</td>
<td>2.1 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.35</td>
<td>51</td>
<td>2.0 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.083</td>
<td>8.0</td>
<td>1.3 x 10$^{-7}$</td>
</tr>
<tr>
<td>0.19</td>
<td>8.1</td>
<td>3.0 x 10$^{-7}$</td>
</tr>
<tr>
<td>0.72</td>
<td>7.9</td>
<td>2.3 x 10$^{-6}$</td>
</tr>
<tr>
<td>1.3</td>
<td>7.8</td>
<td>2.0 x 10$^{-6}$</td>
</tr>
<tr>
<td>1.3</td>
<td>7.9</td>
<td>2.5 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

Table A5.8 The reaction of $cct$-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ (9) with P(C$_6$H$_4$CH$_3$)$_3$ (L') at 45°C (reactions 6.1 and 6.2, page 218)

<table>
<thead>
<tr>
<th>R</th>
<th>[9] (mM)</th>
<th>[L'] (mM)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$Ph</td>
<td>2.7</td>
<td>130</td>
<td>1.2 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>11</td>
<td>94</td>
<td>1.0 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>12</td>
<td>120</td>
<td>1.1 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>10.</td>
<td>150</td>
<td>1.2 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>11</td>
<td>300</td>
<td>1.3 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>11</td>
<td>500</td>
<td>1.0 x 10$^{-3}$</td>
</tr>
<tr>
<td>-C$_6$H$_4$CH$_3$</td>
<td>12</td>
<td>260</td>
<td>7.0 x 10$^{-4}$</td>
</tr>
</tbody>
</table>
Table A5.9 The reaction of cct-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ (9) with 1 atm carbon monoxide (reaction 6.3, page 227)

<table>
<thead>
<tr>
<th>R</th>
<th>[9] (mM)</th>
<th>T (°C)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$</td>
<td>0.87</td>
<td>55</td>
<td>7.0 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>1.0</td>
<td>55</td>
<td>7.2 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$CH$_3$</td>
<td>0.88</td>
<td>26</td>
<td>3.2 x 10$^{-4}$</td>
</tr>
<tr>
<td>-CH$_2$CH$_3$</td>
<td>0.92</td>
<td>35</td>
<td>1.2 x 10$^{-3}$</td>
</tr>
<tr>
<td>-CH$_2$CH$_3$</td>
<td>0.89</td>
<td>55</td>
<td>1.2 x 10$^{-2}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>0.79</td>
<td>45</td>
<td>6.1 x 10$^{-4}$</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>0.74</td>
<td>55</td>
<td>2.2 x 10$^{-3}$</td>
</tr>
<tr>
<td>-C$_6$H$_5$</td>
<td>0.53</td>
<td>55</td>
<td>5.5 x 10$^{-4}$</td>
</tr>
<tr>
<td>-C$_6$H$_4$CH$_3$</td>
<td>0.86</td>
<td>45</td>
<td>2.3 x 10$^{-4}$</td>
</tr>
<tr>
<td>-C$_6$H$_4$CH$_3$</td>
<td>1.0</td>
<td>55</td>
<td>9.3 x 10$^{-4}$</td>
</tr>
<tr>
<td>-C$_6$H$_4$CH$_3$</td>
<td>1.0</td>
<td>60</td>
<td>1.6 x 10$^{-3}$</td>
</tr>
</tbody>
</table>