Aspects of the Transition-Metal
Coordination Chemistry of Phenylphosphine

by

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Abstract

This thesis describes the synthesis and reactions of phosphido complexes of both the early and late transition-metals.

The thermal reaction of dodecacarbonyltriruthenium with phenylphosphine (and its cyclohexyl analogue) was investigated and new trinuclear clusters with combinations of terminal phosphine, bridging phosphido and μ₃-phosphinidene ligands were isolated. These have been characterised by n.m.r. methods and the single-crystal structures of \([\text{Ru}_3(\mu-H)_2(\mu_3-PPh)(PPhH_2)(CO)_8]\) and \([\text{Ru}_3(\mu-H)(\mu_3-PPhH_3)(CO)_9]\) have been deduced. The pyrolysis of \([\text{Ru}_4(\mu-H_2)(\mu_3-PPh)_2(\mu_3-PPh)(CO)_9]\) was investigated and was found to yield new hexanuclear clusters of which the fluxional trigonal prismatic structures \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_3-PPh)(CO)_{12}]\) and \([\text{Ru}_4(\mu_3-PPh_2)(\mu_3-PPh)(CO)_{12}]\) have been crystallographically determined. Their metal frameworks were found to have interesting features and are compared with the known structure \([\text{Ru}_4(\mu_3-PPh_2)(\mu_3-PPh)(CO)_{12}]\).

We have synthesised the terminal phosphine complexes \([\text{IrCl}_2(PMe_2Ph)_3(PHR'R'')][\text{ClO}_4]\) (\(R' = R'' = H, R = H R'' = Ph, R' = R'' = Ph\)) and these were found to deprotonate readily in the presence of base to afford the corresponding neutral phosphido complexes. Reactions of these phosphido complexes with both organic and metallic electrophiles was investigated and the crystal structure of \([\text{IrCl}_2(PMe_2Ph)_3(PHR'R'')(\text{Ph})_2]\)Au][\text{ClO}_4]\ was determined. Investigating the origin of the broad n.m.r. spectrum of \([\text{IrCl}_2(PMe_2Ph)_3][\text{ClO}_4]\) (formed from the reaction of the phosphido complex \([\text{IrCl}_2(PMe_2Ph)_3(PPhMe)]\) with MeI) afforded evidence for at least three isomers in solution at low-temperature. The low temperature \(^{31}\text{P}\{^1\text{H}\} \text{n.m.r. spectrum and its } ^{31}\text{P} - ^{31}\text{P} \text{DQCOSY spectrum recorded at } -75 \text{ °C have been analyzed in terms of these conformational isomers. Further investigations of the tetrakis-phosphine complexes } [\text{IrCl}_2(PMe_3)_3(PMe_2Ph)][\text{ClO}_4] \text{ and } [\text{IrCl}_2(PMe_3)_3(PMePh_2)]\text{[ClO}_4]\text{ also showed the presence of rotational isomers.}

A controlled synthesis of the cluster \([\text{Os}_5(\mu-H)(\mu-PPhH)(CO)_{10}]\) is reported and the reactions of the anionic phosphinidene cluster \([\text{Os}_5(\mu-H)(\mu-PPh)(CO)_{10}]\) with electrophiles are included. Reaction of the anion with methylidene gave \([\text{Os}_5(\mu-H)(\mu-PPhMe)(CO)_{10}]\) characterised crystallographically and found to contain an endo phenyl group indicating inversion of stereochemistry at phosphorus. The crystal structure of \([\{\text{Os}_5(\mu_3-PPh)(CO)_{10}\}_{2}\text{Hg}]\) is described.
Reaction of the anionic phosphido complex [Mo(CO)$_5$(PPhH)] with the metal electrophiles [PtCl$_2$(dppe)] and [PtCl$_2$(PEt$_3$)$_2$] was seen to be simple nucleophilic substitution at the platinum(II) centres. A single major product isolated from the reaction of the [Mo(CO)$_5$(PPhH)] with [PtCl$_2$(dppe)] was isolated. The single-crystal X-ray structure of this compound revealed it to be [Pt(μ-PPhH)$_2$(Mo(CO)$_3$)$_2$(dppe)]. $^{31}$P{¹H} n.m.r. studies of this complex confirmed the existence of two diastereoisomers and these have been separated using preparative HPLC techniques. We have also shown that these complexes exist as several rotameric isomers in solution giving rise to broad n.m.r. signals in the $^{31}$P{¹H} n.m.r. spectrum. The synthesis of [Pt(μ-PPhH)$_2$(Mo(CO)$_3$)$_2$(PPh$_2$C$_2$H$_4$PPh$_2$)] and [Pt(μ-PPhH)$_3$(Mo(CO)$_4$)](dppe)] reinforced the above proposal regarding rotamers in solution and these compounds are observed to occur in both possible diastereoisomeric forms. Three products have been identified from the reaction of [Mo(CO)$_5$(PPhH)] with [PtCl$_2$] and extensive $^{31}$P{¹H} n.m.r. investigations carried out. The single-crystal X-ray structures of the two products [Pt(μ-PPhH)(Mo(CO)$_3$)Cl(PEt$_3$)$_2$] and trans-[Pt(μ-PPhH)$_2$(Mo(CO)$_3$)$_2$(PEt$_3$)$_2$] have been determined. Variable-temperature $^{31}$P{¹H} n.m.r. studies have shown the former complex to exist in three rotameric forms in solution and these are rapidly exchanging at room temperature. The trinuclear complex [Pt(μ-PPhH)$_2$(Mo(CO)$_3$)$_2$(PEt$_3$)$_2$] was identified in both cis and trans forms, the former isomer was identified by n.m.r. methods whilst the single-crystal X-ray structure of the trans isomer was determined. The $^{31}$P{¹H} n.m.r. spectrum of trans-[Pt(μ-PPhH)$_2$(Mo(CO)$_3$)$_2$(PEt$_3$)$_2$] revealed the existence of two diastereoisomeric forms.
Table of Contents

Abstracts 2

Table of Contents 4

Acknowledgements 11

Chapter 1 Introduction 13

1.1 Preparation and Properties of Phosphine and its Organic Derivatives 14
  1.1.1 Preparation of Phosphine 14
  1.1.2 Structure and Properties of Phosphine 15
  1.1.3 Spectroscopic Characterisation of the Complexes 17
  1.1.4 Structural Implication of $^{31}$P{'H} N.M.R. Parameters 20

1.2 Structural Survey of Phosphine Ligands and their Derivatives 21
  1.2.1 Interaction with One Metal Centre 21
  1.2.2 Interaction with Two Metal Centres 24
  1.2.3 Interaction with Three Metal Centres 27
  1.2.4 Interaction with Four Metal Centres 32
  1.2.5 Interaction with more than Four Metal Centres 35

1.3 Related Nitrogen Donor Ligands 37
  1.3.1 Amines and Dialkylamides 37
  1.3.2 Imides and Nitrides 40

Chapter 2 Thermal Reaction of Phenylphosphine with $\text{[Ru}_3\text{(CO)}_{12}]$ 42

2.1 Introduction 43
2.2 Results and Discussion

2.2.1 Thermal Reaction of [Ru₃(CO)₁₂] with an excess of Phenylphosphine

2.2.2 Mass Spectra of [Ru₃(μ-H)(μ-PPhH)₃(CO)₃]

2.2.3 Crystal Structure of [Ru₃(μ-H)(μ-PPhH)₃(CO)₃]

2.2.4 Identification of [Ru₃(μ-H)₃(μ-PPhH)₂(CO)₆]

2.2.5 Crystal Structure of [Ru₃(μ-H)₂(μ₂-PPh)(PPhH₂)(CO)₆]

2.2.6 Reaction of [Ru₃(μ-H)₂(μ₂-PPh)(CO)₆]

2.3 Results Using Cyclohexylphosphine

2.3.1 Reaction of [Ru₃(CO)₁₂] with Cyclohexylphosphine

2.3.2 Spectroscopic Characterisation of [Ru₃(μ-H)₂(μ-PCyH)₃(CO)₃]

2.3.3 Spectroscopic Characterisation of [Ru₃(μ-H)(μ-PCyH)₃(CO)₃]

2.3.4 Spectroscopic Characterisation of [Ru₃(μ-H)₂(μ₂-PCy)(PCyH₂)(CO)₆]

2.3.5 Mass Spectra of some Phosphido and Phosphinidene Clusters

2.3.6 Pyrolysis of [Ru₃(μ-H)₂(μ₂-PCy)(PCyH₂)(CO)₆]

2.4 Transformation of [Ru₃(μ₃-PPh)₂(CO)₆] to Higher Nuclearity Clusters

2.4.1 Attempted Hydrogenation of [Ru₃(μ-PPh)₃(CO)₆]

2.4.2 Crystal Structure of [Ru₆(μ-H)(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂]

2.4.3 Crystal Structure of [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂]

2.4.4 Structural Relationship between [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂], [Ru₆(μ-H)(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂], and [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂]

2.4.5 ¹H N.M.R. Studies of [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂] and [Ru₆(μ₃-PPh)₂(μ₄-PPh)(CO)₁₂]

2.4.6 Attempted Hydrogenation of [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂]

2.4.7 Pyrolysis of [Os₆(μ₃-PPh)₂(CO)₁₂]
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>Results and Discussion</td>
<td>172</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Reaction with Simple Electrophiles</td>
<td>172</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Reaction with Gold Phosphine Chloride Complexes</td>
<td>178</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Mass Spectra of $[{\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)}_2\text{Au}]\text{[ClO}_4] $</td>
<td>179</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Crystal Structure of $[{\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)}_2\text{Au}]\text{[ClO}_4] $</td>
<td>179</td>
</tr>
<tr>
<td>4.2.5</td>
<td>Spectroscopic Characteristics</td>
<td>184</td>
</tr>
<tr>
<td>4.2.6</td>
<td>Reaction of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PHR})] \ (R = \text{Ph, H})$ with Organomercury Compounds</td>
<td>191</td>
</tr>
<tr>
<td>4.3</td>
<td>Conclusions</td>
<td>194</td>
</tr>
<tr>
<td>4.4</td>
<td>Experimental</td>
<td>195</td>
</tr>
<tr>
<td>4.5</td>
<td>Spectroscopic data for the Complexes</td>
<td>199</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>203</td>
</tr>
<tr>
<td>5.2</td>
<td>Results and Discussion</td>
<td>207</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Synthesis of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4]\text{[ClO}_4] $</td>
<td>207</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Crystal Structure of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4]\text{[ClO}_4] $</td>
<td>209</td>
</tr>
<tr>
<td>5.3</td>
<td>N.M.R. Investigations</td>
<td>219</td>
</tr>
<tr>
<td>5.3.1</td>
<td>$^{31}\text{P}(^1\text{H})$ N.M.R. Investigations of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4]\text{[ClO}_4] $</td>
<td>220</td>
</tr>
<tr>
<td>5.3.2</td>
<td>$^1\text{H}$ N.M.R. Investigations of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4]\text{[ClO}_4] $</td>
<td>227</td>
</tr>
<tr>
<td>5.4</td>
<td>Studies of other Tetrakis-Phosphine Complexes of Iridium(III)</td>
<td>232</td>
</tr>
<tr>
<td>5.4.1</td>
<td>The Synthesis of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PMe}_2\text{Ph})]\text{[ClO}_4] $ and $[\text{IrCl}_2(\text{PMe}_2)_3(\text{PMePh}_2)]\text{[ClO}_4] $</td>
<td>232</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Crystal Structure of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PMe}_2\text{Ph})]\text{[ClO}_4] $</td>
<td>234</td>
</tr>
<tr>
<td>5.4.3</td>
<td>$^{31}\text{P}(^1\text{H})$ N.M.R. Studies of the Tetrakis-Phosphines Complexes</td>
<td>238</td>
</tr>
</tbody>
</table>
5.5 Conclusions

5.6 Experimental

5.7 Spectroscopic Data for the Complexes

Chapter 6 Reactions of the Phosphinidene Cluster Anion
[Os₃(μ-H)(μ₃-PPh)(CO)₁₀]⁻

6.1 Introduction

6.2 Results and Discussion
6.2.1 Reaction of [Os₃(μ-H)(μ-PPh)(CO)₁₀]⁻ with Organic Electrophiles
6.2.2 Crystal Structure of [Os₃(μ-H)(μ-PPhMe)(CO)₁₀]

6.3 Reactions with Metal Electrophiles
6.3.1 Reaction of [Os₃(μ-H)(μ-PPh)(CO)₁₀]⁻ and [Os₃(μ-PPhH)(CO)₁₀]⁻ with [Au(PMe₂Ph)Cl]
6.3.2 Reaction of [Os₃(μ-H)(μ-PPh)(CO)₁₀]⁻ with Organomercury Compounds
6.3.3 Crystal Structure of [{Os₃(μ-H)(μ₃-PPh)(CO)₁₀}₂Hg]

6.4 Details of Mass Spectra

6.5 Conclusions

6.6 Experimental

6.7 Spectroscopic Data for the Complexes

Chapter 7 Synthesis and Studies of Platinum-Molybdenum Phosphido Complexes
7.1 Introduction 308

7.2 Reaction of $[\text{Mo(CO)}_5 (\text{PPhR})]^- (R = \text{Ph, H})$ with Simple Electrophiles 318
   7.2.1 Preparation of $[\text{Mo(CO)}_5 (\text{PPhHR})]^- (R = \text{Ph, H})$ 318
   7.2.2 Reaction of $[\text{Mo(CO)}_5 (\text{PPhR})]^-$ with Methyl iodide 318
   7.2.3 Reaction of $[\text{Mo(CO)}_5 (\text{PPhR})]^-$ with Gold Phosphine Complexes 319

7.3 Reaction of $[\text{Mo(CO)}_5 (\text{PPhH})]^-$ with Platinum(II) Complexes 325
   7.3.1 Reaction of $[\text{Mo(CO)}_5 (\text{PPhH})]^-$ with $[\text{PtCl}_2 (\text{dppe})]$ 325
   7.3.2 Crystal Structure of $[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{dppe})]$ 330
   7.3.3 Separation of the SS/RR and SR9 Meso Isomers of $[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{dppe})]$ 336
   7.3.4 N.M.R. Studies of $[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{dppe})]$ 336
   7.3.5 Synthesis and $^{31}\text{P}(^{1}\text{H})$ N.M.R. Studies of $[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{dppe})]$ 341
   7.3.6 Thermolysis of $[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{dppe})]$ 347

7.4 Preparation of Di- and Trimetallic Phosphido Bridged Complexes 349
   7.4.1 Reaction of $[\text{Mo(CO)}_5 (\text{PPhH})]^-$ with $[\text{PtCl}_2 (\text{PEt}_3)_2]$ 349
   7.4.2 Crystal Structure of $[\text{Pt}(\mu-\text{PPhH}) \{\text{Mo(CO)}_5\}_2 \text{Cl(PEt}_3)_2]$ 350
   7.4.3 $^{31}\text{P}(^{1}\text{H})$ N.M.R. Studies of trans-$[\text{Pt}(\mu-\text{PPhH}) \{\text{Mo(CO)}_5\}_2 \text{Cl(PEt}_3)_2]$ 354
   7.4.4 Identification of cis and trans-$[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{PEt}_3)_2]$ 358
   7.4.5 Crystal Structure of trans-$[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{PEt}_3)_2]$ 362
   7.4.6 $^{31}\text{P}(^{1}\text{H})$ N.M.R. Studies of trans-$[\text{Pt}(\mu-\text{PPhH})_2 \{\text{Mo(CO)}_5\}_2 (\text{PEt}_3)_2]$ 367
   7.4.7 Correlation of $^1J(^{195}\text{PtP})$ and Pt-P Bond Distances 372

7.5 Conclusion 375
7.6 Experimental

7.7 Spectroscopic Data for the Complexes

References
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Chapter 1

Introduction and Review of
Phosphido and Phosphinidene Chemistry
1 Introduction and Review of Phosphido and Phosphinidene Chemistry

1.1 Preparation of Phosphine and its Organic Derivatives

1.1.1 Preparation of Phosphine

\( \text{PH}_3 \) is the most stable hydride of phosphorus, being the first of a homologous series \( \text{P}_n \text{H}_{n+2} \) (\( n = 1-6 \)), the members of which diminish in thermal stability. \( \text{PH}_3 \) is an extremely poisonous, highly reactive, colourless gas with a faint garlic odour. Phosphine can be made in a number of ways:

1. Reaction of a metallic phosphide with water.

\[
\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Ca(OH)}_2
\]

2. Alkaline hydrolysis of elemental phosphorus.

\[
\text{P}_4 + 3\text{KOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{KH}_2\text{PO}_2
\]

3. Alkaline hydrolysis of \( \text{PH}_4^+\text{I}^- \).

\[
\text{P}_4 + 2\text{I}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{PH}_4^+\text{I}^- + 2\text{HI} + 2\text{H}_3\text{PO}_4
\]

\[
\text{PH}_4^+\text{I}^- + \text{KOH} \rightarrow \text{PH}_3 + \text{KI} + \text{H}_2\text{O}
\]

4. Thermal decomposition of the lower oxyacids of phosphorus.

\[
4\text{H}_3\text{PO}_3 \xrightarrow{200^\circ \text{C}} \text{PH}_3 + 3\text{H}_3\text{PO}_4
\]
5. Reduction of PCl₃ with LiAlH₄ or LiH.

\[
\begin{align*}
\text{PCl}_3 + \text{LiAlH}_4 & \xrightarrow{\text{Et}_2O/0^\circ \text{C}} \text{PH}_3 \\
\text{PCl}_3 + 3\text{LiH} & \xrightarrow{\text{warm}} \text{PH}_3 + 3\text{LiCl}
\end{align*}
\]

Whilst using PH₃ gas for the synthesis of several phosphine complexes of iridium, it was noticed that the gas spontaneously ignited in the presence of air. Others have carefully demonstrated that this spontaneous flammability is due to the presence of diphosphine, P₂H₄.

Phosphines can be converted into phosphides by alkali metals in liquid ammonia or in ethers. Treatment of these with alkyl halides provides an efficient method of forming P-C bonds. Unsymmetrical phosphines, which are useful ligands in transition metal chemistry, can be prepared in this way.

6. \( \text{RPCl}_2 \rightarrow \text{RPH}_2 \rightarrow \text{RPNa}_2 \)

\( \text{RPNa}_2 \rightarrow \text{RR'}_2\text{P} \)

7. \( \text{PH}_3 \rightarrow \text{PHNa}_2 \rightarrow \text{PHMe}_2 \)

\( \text{PHMe}_2 \rightarrow \text{Me}_2\text{PNa} \rightarrow \text{Me}_2\text{P(CH}_2)_2\text{PMe}_2 \)

1.1.2 Structure and Properties of Phosphine

PH₃ has a pyramidal structure with HPH angles of 93.6 ° whilst angles of up to 100 ° are observed for the phosphorus halides. In comparison the bond angles of NH₃ are much greater. These angles suggest that phosphorus uses mainly p-orbitals with a small amount of s-character whilst in trivalent nitrogen compounds the central atom is mainly sp³ hybridised.

By virtue of the lone-pair of electrons on phosphorus, PH₃ can act as a proton acceptor and as an electron-pair donor. Table 1.1 shows some PK₆ values for phosphonium ions and their corresponding ammonium ions. A strong regular variation
Table 1.1 PK\textsubscript{a} values for ammonium and phosphonium ions

<table>
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<tr>
<th>Phosphonium PK\textsubscript{a}</th>
<th>Ammonium PK\textsubscript{a}</th>
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<tr>
<td>PH\textsubscript{4}\textsuperscript{+}</td>
<td>-14</td>
</tr>
<tr>
<td>MePH\textsubscript{3}\textsuperscript{+}</td>
<td>-3.2</td>
</tr>
<tr>
<td>Me\textsubscript{2}PH\textsubscript{2}\textsuperscript{+}</td>
<td>3.9</td>
</tr>
<tr>
<td>Me\textsubscript{3}PH\textsuperscript{+}</td>
<td>8.65</td>
</tr>
<tr>
<td>iBuPH\textsubscript{3}\textsuperscript{+}</td>
<td>-0.02</td>
</tr>
<tr>
<td>iBu\textsubscript{2}PH\textsubscript{2}\textsuperscript{+}</td>
<td>4.1</td>
</tr>
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<td>iBu\textsubscript{3}PH\textsuperscript{+}</td>
<td>7.976</td>
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<td>Ph\textsubscript{3}PH\textsuperscript{+}</td>
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</tr>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+}</td>
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<tr>
<td>Me\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}</td>
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<tr>
<td>Me\textsubscript{3}NH\textsuperscript{+}</td>
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</tr>
<tr>
<td>iBuNH\textsubscript{3}\textsuperscript{+}</td>
<td>10.52</td>
</tr>
<tr>
<td>iBu\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}</td>
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</tr>
<tr>
<td>iBu\textsubscript{3}NH\textsuperscript{+}</td>
<td>10.89</td>
</tr>
<tr>
<td>Ph\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}</td>
<td>0.79</td>
</tr>
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</table>

in base strength is found for the series PH\textsubscript{3} < PMe\textsubscript{2}H < PMe\textsubscript{2}H < PMe\textsubscript{3}.\textsuperscript{77} The variation in PK\textsubscript{a} is much greater for the phosphines than for the amines, although the PK\textsubscript{a} values of trimethylamine and PMe\textsubscript{3} are comparable. Phosphine is found to be an extremely weak Brønsted base. These PK\textsubscript{a} values will depend on the availability of the lone-pair of electrons on the central atom. The HPH angles of phosphine indicate that the lone-pair of electrons has substantial s-orbital character while the P-H bonds show mainly p-orbital character. The high percentage of s-character associated with the lone-pair of electrons causes it to be close to the nucleus. Both the phosphonium and ammonium ions will be sp\textsuperscript{3} in bonding to their four substituents. This requires little or no change in hybridisation for the amines whilst considerable rehybridisation is needed in the case of phosphine. By analogy with the PK\textsubscript{a} values of the phosphonium ions (Table 1.1) the
acidity of complexes containing PH₃, phenylphosphine and diphenylphosphine should decrease in the order MPH₃ > MPPhH₂ > MPPh₂H.

1.1.3 Spectroscopic Characterisation of the Complexes

³¹P(¹H) and ³¹P proton-coupled n.m.r. spectroscopy has been used extensively to identify the structures of transition-metal complexes containing PH₃ and primary and secondary phosphine ligands. The free ligands cover a larger chemical shift range with PH₃ occurring at high-field whilst successive substitution of the protons shifts the ³¹P n.m.r. resonance to lower field (Figure 1.1). The electronegativity of the

![Chemical shifts of various phosphines relative to 85% phosphoric acid.](image)

Figure 1.1 Chemical shifts of various phosphines relative to 85% phosphoric acid. Substituents at phosphorus and the angles between them are the two most important
variables determining $^{31}$P chemical shifts and coupling constants. Coordination chemical shifts ($\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$) depend on the nature of the metal and on the changes in SPS angles on coordination. The angle opening on coordination is consistent with the usually observed downfield shift. For example, the complex [Ir(CO)BrH(PEt$_3$)$_2$(PH$_2$)] contains a phosphido ligand for which $\delta(P) = -219.3$. Coordination to a metal centre affords the novel complex [Ir(CO)BrH(PEt$_3$)$_2$(PH$_2$RuCl$_2$η$^6$-MeC$_6$H$_4$CHMe$_2$-p)] with $\delta(P) = -125.6$.

In all the complexes reported thus far, the chemical shifts of the PH$_3$ and PPhH$_2$ are much more variable than those of tertiary phosphine ligands in the same complex. The chemical shifts of PH$_3$ and PPhH$_2$ become more negative as the coordination number changes from four to three (Figure 1.2).

\[
\begin{align*}
&\text{[Ir(CO)ClH(PEt$_3$)$_2$(PH$_3$)]}^+ & \rightarrow & \text{[Ir(CO)ClH(PEt$_3$)$_2$(PH$_2$)]}^+ \\
&1^J(PH) = 407 \text{ Hz} & 1^J(PH) = 172.4 \text{ Hz} \\
&\delta(P) = -138.9 & \delta(P) = -217.9 \\
&\delta(PH) = +4.6 & \delta(PH) = +1.1
\end{align*}
\]

\[
\begin{align*}
&\text{[Ir(CO)BrH(PEt$_3$)$_2$(PH$_3$)]}^+ & \rightarrow & \text{[Ir(CO)BrH(PEt$_3$)$_2$(PH$_2$)]}^+ \\
&1^J(PH) = 406.2 \text{ Hz} & 1^J(PH) = 172.8 \text{ Hz} \\
&\delta(P) = -139.4 & \delta(P) = -219.3 \\
&\delta(PH) = +5.0 & \delta(PH) = +1.4
\end{align*}
\]

\[
\begin{align*}
&\text{[Os(CO)$_2$Cl(PPh$_3$)$_2$(PH$_3$)]}^+ & \rightarrow & \text{[Os(CO)$_2$Cl(PPh$_3$)$_2$(PH$_2$)]}^+ \\
&1^J(PH) = 415.9 \text{ Hz} & 1^J(PH) = 175.3 \text{ Hz} \\
&\delta(P) = -121.9 & \delta(P) = -229.2 \\
&\delta(PH) = +3.34 & \delta(PH) = +0.87
\end{align*}
\]

\[
\begin{align*}
&\text{[Os(CO)Cl(PMe$_3$)(PPh$_3$)$_2$(PH$_3$)]}^+ & \rightarrow & \text{[Os(CO)Cl(PMe$_3$)(PPh$_3$)$_2$(PH$_2$)]}^+ \\
&1^J(PH) = 757.3 \text{ Hz} & 1^J(PH) = 179.6 \text{ Hz} \\
&\delta(P) = -123.3 & \delta(P) = -189.3 \\
&\delta(PH) = +2.80 & \delta(PH) = +0.70
\end{align*}
\]

\[
\begin{align*}
&\text{[IrCl$_2$(PMe$_2$Ph)$_3$(PH$_3$)]}^+ & \rightarrow & \text{[IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)]}^+ \\
&1^J(PH) = 381.0 \text{ Hz} & 1^J(PH) = 176.2 \text{ Hz} \\
&\delta(P) = -121.5 & \delta(P) = -150.2 \\
&\delta(PH) = +3.06 & \delta(PH) = +1.54
\end{align*}
\]
The $^{31}$P chemical shifts of neutral phosphido complexes resemble those of the parent phosphines, for example, the $^{31}$P{$^1$H} n.m.r. spectrum of [Ir(CO)BrH(PEt$_3$)$_2$(PH$_2$)] contains $\delta$(PH$_2$) = -217.9 whilst the chemical shift of PH$_3$ is ca -240 ppm. Reaction of these complexes with either organic or metallic electrophiles results in a down-field shift of the phosphorus atom resonance ([Ir(CO)BrH(PEt$_3$)$_2$(PH$_2$BH$_3$)] $\delta$(PH$_2$) = -125.6), similar to the down-field shift observed upon coordination of the parent phosphine to a transition-metal centre. This shift is a useful indication of the change in coordination at the phosphorus atom. There is a similar systematic change in $\delta$(PH), which is to lower field if P is three-coordinate and bound to a single metal centre than if it is four coordinate (Figure 1.2).

The values of $^1$J(PH) show some useful patterns too. $^1$J(PH) for PH$_3$ is 182.2Hz and we regard this coupling to be due to P-H bonds with a substantial amount of p-orbital character and a minor s-orbital contribution. N.m.r. studies of the protonation of PH$_3$ to PH$_4^+$ in 96% sulphuric acid revealed a much greater value of $^1$J(PH) 545.7 Hz. It is possible that J unlike $\delta$ depends mainly on the geometry of the molecule, which for PH$_4^+$ is probably a regular tetrahedron and therefore consists of bonds with sp$^3$
character. The increase in $^1J(PH)$ along the series $PH_2 < PH_3 < PH_4$ has been proposed to be the result of increasing 3s electron character in the P-H bonds.\textsuperscript{15,16} As expected, reported data for the complexation of $PH_3$ and $PPhH_2$ indicates an increase of $^1J(PH)$. When phosphorus is three-coordinate, $^1J(PH)$ is ca 175 Hz and, when the coordination is increased to four, $^1J(PH)$ values between 278 Hz and 430 Hz are common (Figure 1.2).\textsuperscript{8} This increase in $^1J(PH)$ is the result of opening the SPS angles thereby increasing the s-orbital character in the P-H bonds. (Figure 1.3).

### 1.1.4 Structural Implications of $^{31}$P N.M.R. Parameters

Phosphido groups bridging metals that are not bonded to each other have $^{31}$P n.m.r. resonances at very high-field.\textsuperscript{2,20} In comparison the $^{31}$P n.m.r. resonances of phosphido ligands bridging metal-metal bonds appear at much lower field.\textsuperscript{2,17,26} For example, conversion of $[Ru_3(CO)_9(\mu_3-C=C≡CPr)(\mu-PPh_2)]$\textsuperscript{281} into $[Ru_3(CO)_8(\mu-PPh_2)(C≡CPr)]$ (Figure 1.4) results in a large down-field shift of $\delta(P)$ to +113.0 from $\delta -65.4$ with a corresponding reduction in the P-Ru-P angle from 92.8° to 74.4°.\textsuperscript{25} These large differences in chemical shifts for the two types of phosphido bridge provide a useful spectroscopic probe for determining the presence or absence of metal-metal bonds. A $\delta(P)$ value of +62.3 for $[Co_2(\mu-PPh_2)_2(CO)_6]$ can be compared to a $\delta(P)$ of +134 for $[Co_4(\mu-PPh_2)_2(CO)_8]$\textsuperscript{150} which can be envisioned as having four three membered rings (Figure 1.5).\textsuperscript{23}
Phosphorus-phosphorus coupling constants provide additional useful information. Phosphines occupying sites trans to phosphido bridges on the same metal atom exhibit 

\[ \delta = +62.3 \]

\[ \delta = +134 \]

Figure 1.5

\( J(PP) \) of quite large values. For example, \( trans-[Ru_2(CO)_3(\mu_2-\eta^2-C≡CPr)\mu-PPh_2)(PPh_2C≡CPr)] \) was found to have \( J(PP) = 215 \) Hz. \( J(PP) \) values for a phosphido ligand trans to a phosphine are often smaller than those found for trans phosphine ligands. Cis coupling constants are much smaller. For example, \( J(PP) \) in \( cis-[Ru_2(CO)_3(\mu_2-\eta^2-C≡CPr)(\mu-PPh_2)(PPh_2C≡CPr)] \) is only 17 Hz.

1.2 Structural Survey of Phosphine Ligands and their Derivatives

1.2.1 Interaction with One Metal Atom

There are four possible forms of coordination of a phosphorus ligand to a single metal centre illustrated in Figure 1.6. Bonding mode (A) is a simple phosphine derivative and complexes containing \( PH_3, PPh_2 \) or \( PPh_3 \) have all been characterised. For example, \( [Os(CO)ClH(PPh_2)(PPh_3)]^{+1,11} [Ir(CO)BrH(PH_3)(PET_3)]^{+48} \) and \( [IrCl_2(PMe_2Ph)_3(PPh_2H)]^{+31} \) have all been reported. Because of the high reactivity of the P-H bond, synthetic routes to [M]-PHR'R' complexes usually requires mild conditions.\(^{22} \) For instance, \( [Os(CO)ClH(PPh_2)(PPh_3)] \) was prepared by substitution of
a bulky labile PPh₃ ligand in [Os(CO)HCl(PPh₃)₃]. Several examples of terminal secondary phosphine complexes have also been prepared following procedures previously developed for the synthesis of tertiary phosphine complexes (Equation 1.1-1.3).  

\[
\begin{align*}
[CpM(CO)$_2$] + PR$_2$H + AgBF$_4$ & \rightarrow [CpM(CO)$_2$(PR$_2$H)]$^+$BF$_4^-$ + AgI \\
(M = Ru, Fe; R = Ph, H) \\
[CpMn(CO)$_2$(NO)]$^+$PF$_6^-$ + PR$_2$H & \rightarrow [CpMn(CO)(NO)PR$_2$H]$^+$PF$_6^-$ \\
(R = Cy, Ph) \\
[CpFe(CO)I(PPh$_2$H)] + L + AgPF$_6$ & \rightarrow [CpFe(CO)L(PPh$_2$H)]$^+$PF$_6^-$
\end{align*}
\]

Equations 1.1 - 1.3

In bonding mode (B) the phosphido ligand can exist in either of two discrete amphoteric states: ²⁹ as a planar positive phosphenium ion ²¹⁶ or as a pyramidal phosphido ligand.³⁰ The former has a formal phosphorus double bond to the metal whereas the latter has a stereochemically active lone-pair on phosphorus. The tungsten complex [W(C≡CCMe₃)Cl₂(PEt$_3$)$_2$(PPhH)], structurally characterised by Schrock, ⁴⁰ contains a planar phosphenium ligand. This complex contains a short W-P bond (2.29(1) Å) indicating a π-n-π double bond and a large W-P-C bond angle (140 °). The homoleptic tungsten phosphido complex [W$_3$(PCy$_3$)$_3$]$^-$ ⁴¹ contains short W-P double bonds with substantial π-n-π bonding (2.346(4) Å), phosphido bridging ligands with partial multiple bond character, planar in nature and a bond length intermediate between double and single (2.381(4) Å) and pyramidal phosphido bridging ligands with formal single bonds (2.473(4) Å). This simple complex provides a useful comparison between all
three bonding types. The pyramidal geometry of the phosphido ligand in [Os(CO)$_2$Cl(PPh$_3$)$_2$(PPhH)] is indicated by the much smaller Os-P-C bond angle (113°) and the longer Os-P bond lengths (2.523(7) Å).\textsuperscript{3,29}

Several methods for preparing phosphido complexes are known. An important method involves deprotonation of a coordinated phosphine. Other methods for their synthesis involve: (A) nucleophilic attack of metal carbonylate anions halophosphines,\textsuperscript{37,42,43,49,50} (B) transmetallation of a metal halide with a metalated phosphine,\textsuperscript{39,41} (C) bisphosphine cleavage with metal-metal bonded dinuclear species,\textsuperscript{44,45} (D) oxidative addition of P-H or P-X (X = halogen) bond to low valent metal substrate.\textsuperscript{7,10,46-48}

The analogous arsenium ligands have been more thoroughly studied. The planar arsenido tungsten complex [CpW(CO)$_2$(AsR$_2$)] reversibly forms the tricarbonyl by CO addition and the AsR$_2$ group becomes pyramidal in order to avoid a 20e system (Figure 1.7).\textsuperscript{51-53}

Bonding mode (C) has been postulated as an intermediate both by Roper\textsuperscript{54,55} and Mathey.\textsuperscript{56-61} Mathey proposed that this terminal phosphinidene unit with a dicoordinated phosphorus atom and a formal phosphorus-metal double bond was generated from the stable 7-phosphanorbornadiene complex (Figure 1.8) upon pyrolysis in a mass spectrometer. Thermolysis of the 7-phosphanorbornadiene complex in the presence of trapping reagents established the intermediacy of the terminal phosphinidene complex (Figure 1.8). Terminal phosphides (bonding mode (D) remain unknown.
1.2.2 Interaction with Two Metal Centres

Three possible modes of coordination exist for interaction with two metal centres (Figure 1.9). Bonding mode (E) describes a $\mu_2$-phosphido ligand which can bridge metal-metal bonded complexes or nonbonding metal-metal complexes. These bridging phosphido ligands do not necessarily bridge the two metal centres symmetrically and many clusters containing unsymmetrical phosphido bridges have been structurally characterised. Several approaches to the synthesis of phosphido bridged species...
are available both for homo and heterometallic complexes. These methods include: (A) thermolysis of a metal carbonyl with an appropriate phosphine, \(^{63-70,170}\) (B) oxidative addition of the P-H bond of a primary or secondary phosphine complex to a 16e Group 10 complex, \(^{32,37,71-74}\) (C) nucleophilic substitution of a metal phosphido anion at a metal halide complex, \(^{75-78}\) (D) chloride substitution from a chlorophosphine complex, \(^{123}\) (E)

![Figure 1.10](image)

propene elimination resulting from the reaction of a \(\pi\)-allyl complex with a coordinated phosphine (Figure 1.10), \(^{67-69}\) (F) reaction of a mononuclear phosphido complex with a neutral metal carbonyl, \(^91\) (G) cleavage of a coordinated diphosphine (Me\(_2\)PPMe\(_2\)) ligand, \(^92\) (H) the reaction of PPh\(_2\)C=CR or vinylphosphine with metal clusters \(^93-96\) (Figure 1.11) and dehalogenation of a transition-metal halophosphine with [Co\(_2\)(CO)\(_4\)]. \(^{97}\)

![Figure 1.11](image)

Bridging phosphido ligands have been recognised as being capable of inhibiting fragmentation of dinuclear and polynuclear metal complexes in their reactions. \(^1\) However, recently it has been established that these ligands are not always inert. \(^70,104,105\)

For example, the dimethylphosphido bridge in \([\text{CpCo}(\mu-\text{PMe}_2)]_2\) reacts with the
alkyne,98,99 $C_6(CO_2Me)_2$ to give $C_6(CO_2Me)_6$ and a mixture of products (Figure 1.12) resulting from the insertion of alkyne molecules into Co-P bonds. Mays and co-workers have studied the reactions of μ-phosphido complexes with alkynes and have isolated complexes containing quaternised phosphole ligands 100 resulting from P-C and C-C bond formation and M-P bond cleavage. The reaction of $[Co_3(CO)_8(\mu-PPh_2)_3]$ and $[Mn_2(CO)_8(\mu-PPh_2)_2]$ with the alkynes $C_6(CO_2Me)_2$ and C$_2$H$_2$ gave $[Co_3(\mu-\eta^2:\eta^2-C_4(CO_2Me)_2)PPh_2](\mu-PPh_2)(CO)_4]$ and $[Mn_2(\eta^1-C_6H_4PPh_2)(\mu-PPh_2)(CO)_4]$ respectively.100 Carty has shown that the phosphido bridge in $[CoRu(CO)_6(\mu-PPh_2)]$ readily undergoes insertion by CO and acetylene to give the novel cluster $[RuCo(CO)_6(PPh_2COC(Ph))C(Ph)]$ which readily decarbonylates to $[RuCo(CO)_6(PPh_2C(Ph))C(Ph)]$.101,102 The phosphido-bridged σ-π acetylide cluster $[Fe_2(CO)_5(C=CR^1)(\mu-PPh_2)]$ reacts with acetylenes, $R^2C=CR^3$ leading to acetylene coupling and insertion into a Fe-P bond generating the new organometallic derivatives $[Fe_2(CO)_5(PPh_2C(O)C(R')CC(R')C(R'))]$ ($R^1 = 'Bu$, $R^2 = R^3 = CO_2Me$) and $[Fe_2(CO)_5(PPh_2C(R')C(R')CC(R')C(O))]$.103

Phosphinidene ligands bridging two metal centres can occur as either pyramidal
at phosphorus$^{110}$ (bonding mode F) or planar at phosphorus$^{111}$ (G). These phosphinidene ligands can be prepared by the reaction of $\text{RPCl}_2$ with a metal complex anion or by deprotonation of a bridging phosphido ligand. Huttner was first to report the synthesis and structure of the arsinidene complex $\text{PhAs[Cr(CO)}_3]$$_2$ in which the phenylarsinidene fragment was stabilised as a bridging ligand with trigonal planar coordination at arsenic.$^{106}$ The first evidence of a phenylphosphinidene intermediate was demonstrated by means of trapping reactions.$^{108}$ Huttner found that the phenylphosphinidene fragment could be stabilised as a ligand in transition metal complexes. He showed that the phosphorus atom of $\text{PhP[Cr(CO)}_3]$C$_2$ was planar and that the Mn-P bond lengths were unusually short, indicative of a substantial amount of $\delta\pi$-$\pi\delta$ bonding overlap.$^{107}$ More recently Cowley and co-workers have employed the method of metal carbonylate anion attack on halophosphines to prepare a planar bridging phosphinidene complex$^{109}$ (Figure 1.13). The V-P distances in this complex are considerably shorter than those found in other vanadium phosphine complexes. Together with trigonal planar geometry at phosphorus a structure with vanadium-phosphorus multiple bonding character was established.

**1.2.3 Interaction with Three Metal Centres**

Phosphinidene ligands capping three metal centres are shown in Figure 1.14. These clusters do not necessarily contain metal-metal bonds and heterometallic clusters are possible.$^{190}$ Clusters containing $\mu_3$-phosphinidene ligands occur frequently in cluster chemistry, and are often the product of prolonged reflux of a metal carbonyl with a
Much work has been reported in this area and clusters such as \([\text{M}_3(\mu_3-PPh)_2(\text{CO})_3], \quad [\text{M}_4(\mu-H)_2(\mu_3-PPh)(\text{CO})_3] \) \((\text{M} = \text{Ru, Os})\), \([\text{Ru}_3(\mu-H)_2(\mu_3-PPh)(\text{PPhH}_2)(\text{CO})_3]\) \(^{112}\) and \([\text{Os}_3(\mu-H)_3(\mu_3-BuP)(\text{Bu}_2\text{PH})(\text{CO})_3]\) \(^6\) have been structurally characterised. Examination of the condensation and degradation products from the thermolysis reactions of the bridged diphenylphosphido derivatives \([\text{Ru}_3(\mu-PPh)(\mu-H)(\text{CO})_3], \quad [\text{Ru}_3(\mu-PPh)(\mu-H)(\text{CO})_4]\) and \([\text{Ru}_3(\mu-PPh)(\mu-H)(\text{CO})_5]\) revealed that several of the products contained capping phosphinidene ligands both on trinuclear metal frameworks and higher nuclearity metal skeletons.\(^{115}\)

Dephenylation of \(\text{PPh}_3\) under forcing conditions can lead to phosphido and phosphinidene-bridged clusters. The reaction of \([\text{Ir}_4(\text{CO})_{12}]\) with triphenylphosphine in refluxing toluene yields a mixture of products one of which was identified by X-ray diffraction as \([\text{Ir}_4(\mu_3-PPh)(\mu-\text{CO})(\text{CO})_3(\text{PPh}_3)_4]\).\(^{117}\) The tripod ligand \(\text{CH}(\text{PPh}_2)_3\) is a source of \(\mu_3\)-phosphinidene ligands under appropriate conditions as, for example, in the attempted preparation of \([\text{Ir}_4(\text{CO})_9(\text{CH}(\text{PPh}_2)_3)]\) using the mononuclear complex \([\text{IrCl}(\text{CO})_2(\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2-p)]\) with zinc and CO, which gave the unusual product \([\text{Ir}_5(\text{CO})_6(\text{Ph})(\mu_3-PPh)(\mu-\text{dppm})]\) \(^{118}\) \((\text{dppm} = \text{Ph}_3\text{PCH}_2\text{PPh}_2)\). The source of the phosphinidene, dppm and aryl groups in this product was the tripod ligand \((\text{CH}(\text{PPh}_2)_3)\). Thermally induced loss of CO from \([\text{Os}_3(\text{CO})_9(\text{PPh}_2\text{R})]\) \((\text{R} = \text{Me, Ph})\) provides a vacant coordination site easily trapped by activation of a C-H bond to give \([\text{Os}_3(\mu-H)(\mu-P(\text{C}_6\text{H}_4\text{PhR})})(\text{CO})_3]\).\(^{120}\) Continued thermolysis afforded the final product, \([\text{Os}_3(\mu-P\text{Ph})(\text{CO})_9(\text{C}_6\text{H}_4)]\),\(^{119}\) after loss of a benzene molecule.

More controlled synthetic strategies for the preparation of \(\mu_3-\text{PR}\) containing clusters are available. For instance, halide displacement from coordinated halophosphines
can lead to $\mu_1$-PR clusters in good yield. Several heterometallic clusters have been prepared employing this procedure (Figure 1.15). Huttner found that dehalogenation of complexed dihalophosphine by $[\text{Fe}(\text{CO})_3]$ gave heterometallic $\mu_1$-PR bridged clusters. Conditions that result in the making and breaking of metal-metal bonds are of key interest to the chemistry of metal cluster complexes. The cluster $[\text{CpMn}(\text{CO})_2\text{Fe}(\text{CO})_6(\mu_1$-PPh)] is of special interest because it has been demonstrated to undergo reversible cleavage of metal-metal bonds on addition of small molecules (Figure 1.16). These clusters can be reversibly transformed into each other (Figure 1.16). $[\text{C}_3\text{H}_2\text{Co}(\text{CO})_3]$ has also been used successfully as a dehalogenating agent, yielding mixed cobalt clusters, analogous to the open cluster (I) in Figure 1.16. However, clusters formed by this procedure cannot be transformed to closed cluster systems analogous to (II) and (III).

Propene elimination resulting from the reaction of a $\pi$-allyl complex with a coordinated PR$_2$H ligand affords phosphido bridged complexes. Similarly propene elimination resulting from the reaction of a binuclear phosphido bridged complex with $[\text{Cr}(\text{CO})_3(\text{C}_3\text{H}_5)]$ has been used to prepare $\mu_1$-PR bridged complexes.
Vahrenkamp has developed the stepwise formation of \( \mu_2\)-PR trimetallic clusters via P-H compounds. [Fe(CO)\(_4\)(PRH\(_2\))] reacts with [Co\(_2\)(CO)\(_8\)] or [\(\pi\)-C\(_6\)H\(_6\)]Co(CO)\(_3\)] to yield [CoFe(CO)\(_3\)(\(\mu_2\)-PRH)]. This cluster reacts with [Co\(_2\)(CO)\(_8\)] to give [FeCo\(_2\)(CO)\(_9\)(\(\mu_2\)-PR)] and with [Ru\(_3\)(CO)\(_{12}\)] to form [FeRuCo(CO)\(_9\)(H)(\(\mu_2\)-PR)] and with [Fe\(_2\)(CO)\(_{12}\)] to give [Fe\(_2\)Co(CO)\(_9\)(H)(\(\mu_3\)-PR)]. Huttner has developed a similar procedure for the synthesis of heterometallic \( \mu_2\)-PR bridged clusters involving [Cp(CO)\(_2\)Mn(PRCl\(_2\))] and [Fe\(_2\)(CO)\(_3\)] to afford [CpMnFe\(_2\)(CO)\(_8\)(\(\mu_2\)-PR)]. Reaction of [Cp(CO)\(_2\)Mn(PRCl\(_2\))] with [Fe\(_2\)(CO)\(_{12}\)] was found to give the same compound and [Ru\(_3\)(CO)\(_{12}\)] gave the corresponding mixed MnRu\(_2\) cluster.

Phosphinidene bridged clusters can have been used as starting material for the preparation of new \( \mu_3\)-PR bridged complexes, for instance, metal carbonylate anions have been used effectively to displace metal groups from clusters such as [Co\(_2\)Fe(CO)\(_9\)(\(\mu_2\)-PR)] (Figure 1.17). \(^{128-130}\)

The \( \mu_3\)-PR groups have proved useful as building blocks for clusters. \(^{208}\) The metal atoms that they bridge are held together during the course of a reaction enabling the study of mechanisms that involve metal-metal bond cleavage and formation. However, recently it has been shown that under some conditions the P-M bonds can indeed be attacked. Huttner and co-workers reported the first example of a reversible acetylene insertion into a metal phosphinidene bond following its coordination to a metal. UV irradiation of the phosphinidene cluster [Fe\(_3\)(\(\mu_3\)-PPh)(CO)\(_{10}\)] in the presence of diphenylacetylene leads to the complex [Fe\(_3\)(\(\mu\)-PhPC(Ph)C(Ph))(CO)\(_9\)] resulting from the insertion of the diphenylacetylene into a Fe-P bond (Figure 1.18). \(^{131,132,136}\) A number of

\[\text{Figure 1.17}\]

\[
\begin{array}{c}
\text{R} \\
\text{P} \\
\text{(CO)₃Ru} \\
\text{Co(CO)₃} \\
\text{(CO)₃Co} \\
\text{(CO)₃Ru} \quad \text{Na[Cp(CO)₅W]} \\
\text{Co(CO)₃} \\
\text{(CO)₃W} \\
\text{W(Cp(CO)₂)}
\end{array}
\]

-30-
related phosphinidene-acetylene coupling reactions have now been observed \(^{137}\) a further example is provided by the UV-promoted addition of diphenylacetylene to the bis-phosphinidene cluster [Fe\(_3\)(µ-P(C\(_6\)H\(_4\)OMe))\(_2\)(CO)\(_9\)].\(^{133}\) The acetylene is inserted between the phosphorus atoms and is \(\pi\) bound to the metal and \(\sigma\) bound to both phosphorus atoms. The step-wise conversion of a capping phosphinidene ligand into an edge-bridging phosphido group has been demonstrated \(^{134,135}\) and is discussed more fully in Chapter 6. These examples demonstrate the nucleophilic character of the phosphinidene ligand but there is also evidence for electrophilic behaviour in neutral species as shown in the following examples. The bis-phosphinidene cluster [Fe\(_3\)(µ-PPh)\(_2\)(CO)\(_9\)] is attacked by H\(^+\) affording the mixed phosphido/phosphinidene anion [Fe\(_3\)(µ-PPh)(µ-PPhH)(CO)\(_9\)]\(^-\).\(^{138}\) A more complex reaction sequence indicating the electrophilic behaviour of the µ-phosphinidene fragment has been developed by Geoffroy.\(^{139}\) [Fe\(_3\)(µ-PPh)\(_2\)(CO)\(_9\)] reacts
with PhLi to yield the benzoyl cluster \([\text{Fe}_3(\mu_5-\text{PPh})_2(\text{CO})_6(\text{C(O)}\text{Ph})]\). Addition of EtOSO_2CF_3 to this species did not result in the expected phosphinidene-carbene cluster but instead phosphinidene-carbene coupling occurred to give \([\text{Fe}_3(\mu_3-\text{PPhC(OEt)}\text{Ph})(\text{CO})_9]\) (Figure 1.19).

Finally, Vahrenkamp has successfully used CpRh(CO)_2 and CpIr(CO)_2 as suitable precursors of CpM building blocks by which trinuclear \(\mu_1\)-PR bridged clusters could be expanded to tetranuclear (A) and pentanuclear (B) clusters (Figure 1.20). From \(\mu_1\)-PR-M\_3 complexes, RP-bridged tetranuclear clusters with FeCo_2Ru, RuCo_2Rh, Fe_2CoRh, Ru_2CoRh, FeRuCoRh, RuCoWRh and RuCo_2Ir frameworks and pentanuclear clusters with FeCo_2Rh_2, RuCo_2Rh_2, Fe_2CoRh_2 and Ru_2CoRh_2 frameworks have been formed.\(^{140}\)

![Figure 1.19](https://example.com/figure19.png)

**Figure 1.19**

Carbonyls omitted for clarity.

### 1.2.4 Interaction with Four Metal centres

Many \(\mu_4\)-phosphinidene containing clusters (Figure 1.21) have been isolated from the thermal reaction between \([\text{M}_3(\text{CO})_{12}]\) (M = Ru, Os) and primary phosphines.\(^{113,141,142}\) Clusters such as \([\text{Ru}_4(\mu_4-\text{PPh})_2(\mu-\text{CO})(\text{CO})_6]\) and \([\text{Ru}_5(\mu_4-\text{PPh})(\text{CO})_{13}]\) have been
structurally characterised and found to contain phosphinidene ligands capping a square face of the skeletal framework. More forcing conditions afforded higher nuclearity products through condensation reactions and many of the species isolated were found to contain \( \mu_4 \)-phosphinidene ligands. Section 1.2.3 revealed that trinuclear clusters containing diphenylphosphido ligands underwent condensation and degradation reactions upon prolonged thermolysis in xylene solvent. Many of the products isolated also contained \( \mu_4 \)-phosphinidene ligands as well as \( \mu_3 \)-capping ligands. Studies of the thermal behaviour of the linked cluster \([\{\text{Ru}_3(\text{CO})_{11}\}_2(\text{C}_2(\text{PPh}_2)_2)]\) was found to afford as the major product \([\text{Ru}_3(\mu_2-\text{C}_2\text{PPh}_2)(\mu-\text{PPh}_2)(\text{CO})_{11}]\) but several condensation products containing \( \mu_4 \)-phosphinidene ligands were also isolated some of which were \([\text{Ru}_4(\mu_4-\text{PPh})(\mu_3-\text{PhC}_2\text{PPh}_2)(\mu-\text{CO})_8(\text{CO})_2]\), \([\text{Ru}_4(\mu_4-\text{PPh})(\mu_2-\text{CCPh}(\text{PPh}_2))(\text{CO})_{12}]\), \([\text{Ru}_4(\mu_4-\text{H})(\mu_4-\text{CCPh}(\text{PPh})_{10})(\text{CO})_8]\) and \([\text{Ru}_5(\mu_4-\text{PPh})(\mu_4-\text{CCPh}(\text{C}_6\text{H}_4)\mu_3-\text{PPh})(\text{CO})_{10}]\) \([\mu_4-\text{PPh}(\text{OMe})](\text{CO})_{11}]\) .

Lewis and co-workers found that the phosphido-bridged cluster \([\text{Os}_3(\mu-H)(\mu-\)

\[\begin{align*}
\text{R} & \quad \text{M} \\
\text{P} & \quad \text{M}\end{align*}\]

\[\text{M'}(\text{CO})_2\text{Cp}\]

\[\begin{align*}
(\text{J}) & \\
(\text{K})
\end{align*}\]
PRH(CO)_{10} reacted with [M_x(CO)_{12}] (M = Ru, Os) at elevated temperatures to afford tetra-, penta-, and hexanuclear products containing μ₄-phosphinidene ligands. Lewis proposed that the triply-bridging phosphinidene ligand was readily converted to the edge-bridging intermediate resulting in the formation of a lone-pair of electrons on phosphorus \(^{147}\) (Equation 1.4). They believed that this process was involved in the condensation of [Os₃(μ-H)₂(μ₄-PR)(CO)₆] with the metal carbonyls. Clusters with the pentanuclear stoichiometry [M₅(CO)₁₅(μ₄-PPh)] \(^{148,149}\) were the most abundant products and crystallographic studies on similar clusters revealed a square based pyramidal arrangement of the metal atoms with the phosphinidene group occupying the sixth position of an idealised octahedron (μ₄-PPh capping the square face).

Phosphinidene ligands capping four metal atoms have also been prepared by reduction of a metal carbonyl complex in the presence of an appropriate halophosphine, for example, reduction of [Co₃(CO)₁₂] with zinc powder under a CO atmosphere followed by the addition of RPCl₂ afforded [Co₄(μ₄-PPh)₂(μ₄-CO)₂(CO)₂]. \(^{150}\) This cluster can also be prepared from the thermal reaction of [Co₃(CO)₁₂] with phenylphosphine \(^{151}\) or by reaction of [(C₅H₅)Mn(CO)₂(PPhBr₂)] with Na[Co(CO)₄]. \(^{152}\) The μ₄-PR bridged clusters [Ru₅(CO)₁₅(μ₄-PR)] arise in a similar manner during the reaction of [Cp(CO)₂Mn(PPhCl₂)] with [Ru₃(CO)₁₂]. The synthesis of phosphinidene clusters from the metal carbonyl or carbonylmetalates and dihalophosphines has only recently been employed as a synthetic route to μ₄-PR and μ₄-PR bridged clusters despite the fact that μ₃-X containing clusters have been prepared using this procedure for some time. The reaction of [Ni₃(CO)₁₂]²⁺ with PPhCl₂ forms the cluster [Ni₄(CO)₁₅(μ₄-PPh)₆] consisting of a cube of Ni(CO) units each face containing a μ₄-PPh capping ligand. \(^{155}\)

Condensation reactions of complexes containing phosphido bridges with reactive P-H bonds have been used to prepare clusters containing phosphinidene ligands. Suitable treatment of [Fe₂(μ₄-PPhH)₂(CO)₆] with [Fe₅(CO)₁₂] afforded the unsaturated cluster [Fe₄(μ₄-PPh)₂(μ₄-CO)(CO)₁₀] \(^{156}\) consisting of a square plane of metal atoms and two capping phosphinidene ligands occupying the remaining two vertices of an idealised octahedron.

The phosphinidene ligand in [Fe₄(μ₄-PPh)(μ₄-η²-C₅H₅)(CO)₆] \(^{156}\) can accommodate an additional metal fragment to give the tetranuclear cluster [Fe₄(μ₄-PPh)(μ₄-η²-C₅H₅)(CO)₁₁] \(^{157,159}\) containing a square-planar array of metal atoms. This type of condensation reaction resulting in the conversion of μ₄-phosphinidene to μ₄-
phosphinidene ligands has been described by Vahrenkamp.\textsuperscript{132} He successfully expanded trinuclear $\mu_3$-PR clusters with CpM(CO)$_2$ ($M = \text{Rh, Ir}$) units (see section 1.2.3 for further details).

Although clusters containing $\mu_4$-PR ligands are often prepared during high temperature reactions these clusters are capable of undergoing transformations in which metal-phosphorus bond cleavage is involved. For example, both clusters [M$_4$(\(\mu_4\)-PPh)$_2$(\(\mu\)-CO)(CO)$_{10}$] ($M = \text{Ru, Fe}$) are considered to be coordinatively unsaturated and add CO. In the case of the carbonylation of [Fe$_4$(\(\mu_4\)-PPh)$_2$(\(\mu\)-CO)(CO)$_{10}$], the product was found to be [Fe$_4$(\(\mu_4\)-PPh)$_2$(CO)$_{12}$] in which the four metal atoms are perfectly square planar with all carbonyl groups terminal. The similar carbonylation of the ruthenium analogue was found to be reversible but as established from X-ray crystallography the CO addition involved Ru-P and Ru-Ru bond cleavage \textsuperscript{159} (Figure 1.22). Treatment of closo-[Ru$_4$(\(\mu_4\)-PPh)$_2$(\(\mu\)-CO)(CO)$_{10}$] with acetylene under ambient conditions lead to the insertion of acetylene into the skeletal framework of the cluster and the formation of [Ru$_4$(\(\mu_4\)-PPh){\(\mu\}-PPhCHCH}(\(\mu\)-CO)(CO)$_{10}$] (Figure 1.22).

terminal carbonyl ligands omitted for clarity.

![Figure 1.22](image-url)
Bonding type (B) has been identified by Huttner. The trihalophosphine complex \( L_{\nu}M-PX_3 \) (\( L_{\nu}M = \text{CpMn(CO)}_2, \text{Cr(CO)}_3, \text{W(CO)}_5, X = \text{Br, Cl} \)) upon treatment with \([\text{Co}(\text{CO})_4]\) mainly yields clusters of the type \([\text{Co}(\text{CO})_6(\mu_4-P)ML_n]\) with the \([\text{Co}(\text{CO})_6(\mu_4-P)]\) group acting as a ligand \(^{152}\) (Figure 1.23).

1.2.5 Interaction with more than Four Metals

Phosphorus atoms are found bridging transition-metal atoms in many cluster complexes containing five or fewer metal atoms \(^{152,161-165}\) but clusters with fully encapsulated, interstitial phosphorus atoms are rare. In \([\text{Rh}_9(\mu_4-P)(\mu-\text{CO})_{12}(\text{CO})_9]^2\) and \(^{166}\) \([\text{Rh}_{10}(\mu_{10}-P)(\mu-\text{CO})_{12}(\text{CO})_{10}]^3\) the phosphorus atoms are encapsulated in mono and bicapped square antiprismatic arrangements of rhodium atoms respectively and in the hexacobalt cluster anion \(^{167}\) \([\text{Co}_6(\mu-\text{CO})_2(\text{CO})_nP]^\text{–}\) the phosphide atom is only partially encapsulated. Other clusters containing interstitial phosphides include \([\text{Os}_6(\mu_6-P)(\text{CO})_{18}]^\text{+}\),\(^\text{168}\) prepared from the prolonged reflux of a xylene solution of \([\text{Os}_6\text{H}_2(\text{CO})_n(\mu_2-PH)]^\text{+}\) \(^{169}\) and found to consist of a trigonal prismatic core of osmium atoms.\(^\text{296}\)

Prolonged reflux of a toluene solution of \([\text{Ru}_3(\text{CO})_{12}]\) with diphenylphosphine for up to 24 hours gave a complex reaction mixture which gave many clusters containing phosphido and phosphinidene ligands. One unique reaction product was isolated and characterised crystallographically as \([\text{Ru}_6(\mu_4-P)(\mu_2-\eta^1,\eta^4-\text{CH}_2\text{Ph})(\mu-\text{CO})_2(\text{CO})_n]\) \(^{113}\) in
which the eight ruthenium atoms adopt a square antiprismatic arrangement of metal atoms. This type of dephenylation reaction is not uncommon. Coordinated triphenylphosphine is known to readily lose a phenyl group under appropriate reaction conditions to give rise to products containing diphenylphosphido ligands. The latter can be dephenylated to afford compounds containing phenylphosphinidene ligands or encapsulated phosphides. Related to this cluster derivative is a product resulting from the thermolysis of \[ \text{[Ru}_3(\mu-\text{PPh}_2)(\mu-\text{H})_2(\text{CO})_{10}] \] in toluene. This cluster \[ \text{[Ru}_8(\mu_4-P)(\mu_4-P\text{Ph})(\mu_2-\text{PPh}_2)(\text{CO})_{22}] \] contains a partially interstitial phosphide ligand.

1.3 Related Nitrogen Donor Ligands

1.3.1 Amines and Dialkylamido Ligands

Ammonia and amines are classical ligands in coordination chemistry, but these are not often used with organo-transition-metal compounds. Compounds containing NR$_2$ (dialkylamido) ligands are well known. These dialkylamido ligands are more common among early than late transition-metals because the nitrogen forms both $\sigma$ and $\pi$ donor bonds to the metal centres. The early transition metal centres have vacant d-orbitals to serve as $\pi$ acceptors. Thus dialkylamido ligands should form stronger bonds with early transition-metals containing vacant d-orbitals than with the late transition metals which are electron rich. Similarly to the phosphonium ligand, the dialkylamido is required to exhibit planar MNC$_2$ units in order that it may form both $\sigma$ and $\pi$ bonds. These complexes contain short metal-nitrogen bond lengths and this geometry implies sp$^2$ hybridisation at N and $\pi$ donation to the metal from the remaining pair of electrons in the p-orbital.

As for early transition-metal phosphido complexes, dialkylamido complexes can also be prepared by a metathetical reaction (Equation 1.5 and 1.6). This procedure has been employed to prepare many homoleptic dialkylamido complexes, but in comparison
very few homoleptic phosphido complexes have been characterised. A direct comparison of a pair of homoleptic amido and phosphido complexes is possible for [Mo(NMe₂)₄] and [Mo(PCy₂)₄]. In both complexes Mo-P and Mo-N bond lengths are consistent with formal double bonds. These complexes are isostructural and both contain planar (at N and P) 4-electron donor (σ + π) ligands.

The mixed phosphido/amido complexes [Mₓ(Bu₃P)ₓ(NMe₂)₄] (M = Mo, W) have been successfully prepared. Structural evidence revealed planar geometry at the nitrogen atom whilst the phosphido ligands were pyramidal, a consequence of the competition of three donor ligands for two acceptor orbitals. Chisholm concluded a greater π donor ability of the amido ligand over the phosphido ligand (NR₂ > PR₂). He also suggested that that inversion at phosphorus in this complex was facile and not frozen out on the n.m.r. time-scale. Inversion barriers at three-coordinate nitrogen are well known to be much lower than those at three-coordinate phosphorus and consequently amido ligands become planar more readily than phosphido ligands.

More recently the mixed mononuclear phosphido/amido complexes [Mo(NMe₂)₂(PPh₂)₂] and [Mo(NMe₂)₃(PBu₃)] have been prepared. Both the Mo-N and Mo-P distances were short indicative of π bonding in both ligands. Evidently, since there are four available metal dₓπ orbitals, these are used equally well by both NMe₂ and PPh₂ ligands. Chisholm found little evidence for a difference between the bonding in the amido and phosphido ligands but subtle structural differences led him to conclude the same order of π donor ability as was found in the dinuclear mixed phosphido/amido complexes above. The difference between the bonding of the (M≡M)₄ and the Mo₄ centres reflects the relative number of available metal dₓπ orbitals.

Homoleptic amido compounds are very reactive, especially towards protonic acids such as alcohols (Equation 1.7). These substances also react with electrophilic molecules such as CO₂ and cyanides, isocyanides (Equation 1.8 and 1.9). Soon after

\[
\text{M(NR₂)ₙ + HL } \quad \text{MLₙ + nHNR₂ } \quad \text{Equation 1.7}
\]

\[
\text{(L = Cl, OR, OH)}
\]

\[
\text{LnM(NR₂) + CO₂ } \quad [\text{LnM(O₂CNR₂)}] \quad \text{Equation 1.8}
\]

\[
\text{(NMe₂)₅W-NMe₂ + CO₂ } \quad [(\text{NMe₂})₅\text{W(O₂CMe₅)}] \quad \text{Equation 1.9}
\]
Chisholm had established the relative π donor abilities of the phosphido and amido ligands, he compared the NR₂ and PR₂ ligands on the basis of their chemical reactivity. The conversion of amido ligands into carbamate (O₂CNR₂) ligands by reaction with CO₂ is well established.²⁷⁰ He found that reaction of 1,2-[Mo₂(Bu₂P)₂(NMe₂)₄] with CO₂ gave the expected formal insertion of carbondioxide to give the mixed carbamate/phosphinecarboxylate complex [Mo₂(O₂CPBu₂)₃(O₂CNMe₂)₃(NMe₂)] (Figure 1.24) but this product readily decomposed through ligand exchange and redox chemistry to give [Mo₂(O₂CPBu₂)₄]²⁷⁴ (Figure 1.24).

Tungsten(VI) neopentylidyne complexes react with water to give oxo neopentylidene complexes of the type [W(O)(CHCMe₃)(PEt₃)Cl₂]. If an amine is used in place of water the amido neopentylidyne complex [W(CCMMe₃)(NHR)(PEt₃)Cl₂] is isolated. These can be converted into the imido neopentylidene complexes [W(CCMMe₃)(NR)(PEt₃)Cl₂]. The analogous phosphido complex has also been prepared

\[
\text{1,2-[Mo₂(Bu₂P)₂(NMe₂)₄]} + 4\text{CO}_2 \xrightarrow{\text{hexane}} [\text{Mo₂(O₂PBU₂)₂(O₂CNMe₂)₂(NMe₂)₂}]
\]

![Figure 1.24](image)

[W(CCMMe₃)(PHR)(PEt₃)Cl₂] but can not be converted into the analogous neopentylidene phosphinidene complex.⁴⁰

-39-
1.3.2 Imides and Nitrides

When coordinated to a single metal centre, imido and nitrido ligands contain formal double and triple bonds to the metal, similar to those proposed for phosphinidene and phosphide ligands. Many organoimido complexes have been prepared, to date mostly for the second and third row transition metals.\textsuperscript{177} In contrast, the corresponding phosphinidene ligand has only been realised by trapping reactions with an appropriate organic substrate.\textsuperscript{55-60,108} Analysis of the final product established the intermediacy of the phosphinidene ligand. Examples of both types of terminal imido ligands are known; the terminal linear imido ligand is found in [Ta(BuN)(NMe$_2$)$_3$] whilst the bent form is found in [Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$].\textsuperscript{178} Doubly bridging imido ligands are common among the early transition-metal organoimido complexes, for example, [Zr(BuN)(NMe$_2$)$_2$]. The synthetic route to $\mu_3$-RX ($X = P$, As, Sb) complexes are in general not applicable to $\mu_2$-NR bridged clusters. The energy required to break the stable N-H bonds is usually not compensated for by the energy released upon
conversion of an amine to a $\mu_2$-bonded RN. The use of RNX$_2$ as a starting material is impossible because of its strongly oxidising nature although there are many synthetic equivalents for RN (RNO$_2$, RNO, RNC, (RN)$_2$S) that may be used to form $\mu_2$-NR bridges. For example, the cluster bonded nitrile [Fe$_3$(CO)$_9$(NCR)] has been converted to the $\mu_2$-NCH$_2$R ligand in [Fe$_3$(CO)$_9$(\(\mu\)-H)$_2$(\(\mu\)-NCH$_2$R)]$^{184}$ (Figure 1.25). Thermolysis of [Os$_3$(CO)$_{11}$(NH$_3$)] ($T = 170 \degree C$) produces only the $\mu_2$-NH$_2$ bridged complex [Os$_3$(CO)$_{10}$(\(\mu\)-H)(\(\mu\)-NH$_2$)]$^{189}$ (by a single H migration) whereas the analogous $\mu_2$-PHR bridged cluster is transformed under relatively mild conditions to the $\mu_2$-PR bridged cluster.$^{67,69}$

The $\mu_3$-NH cluster [Ru$_3$(\(\mu\)-H)$_2$(\(\mu\)-NH)(CO)$_3$] reacts with CO to give [Ru$_3$(\(\mu\)-H)(\(\mu\)-NH$_2$)(CO)$_{10}$] which, in contrast to its phosphorus analogue, does not undergo decarbonylation and H-migration to form the $\mu_4$-bridged cluster.$^{183}$

Nitrobenzene and aniline react with [Ru$_3$(CO)$_{12}$] to give clusters containing stable $\mu$-NPh bridges, [Ru$_3$(CO)$_{10}$(\(\mu\)-NPh)$_2$], [Ru$_3$(CO)$_{9}$(\(\mu\)-NPh)$_2$] and [Ru$_3$(CO)$_{9}$(\(\mu\)-H)$_2$(\(\mu\)-NPh)].$^{184}$ The bis-nitrene cluster [Fe$_3$(CO)$_9$(\(\mu\)-NPh)$_2$] reacts with Li[BHEt$_3$], MeLi, or PhLi to afford the corresponding formyl or acyl clusters [Fe$_3$(CO)$_9$(\(\mu\)-NPh)$_2$(C(O)R)].$^{139}$ The benzoyl cluster reacts with EtOSO$_2$CF$_3$ to yield the nitrene-carbene cluster [Fe$_3$(CO)$_9$(\(\mu\)-NPh)$_2$(C(OEt)Ph)] which undergoes carbene-nitrene coupling upon exposure to air to form the imidate PhN=C(OEt)Ph. In comparison the bis-phosphinidene cluster [Fe$_3$(CO)$_9$(\(\mu\)-PPh)$_2$] also reacts with PhLi to yield the benzoyl derivative [Fe$_3$(CO)$_9$(\(\mu\)-PPh)$_2$(C(OEt)Ph)]. However, addition of EtOSO$_2$CF$_3$ to this species does not result in the analogous carbene-phosphinidene cluster [Fe$_3$(CO)$_9$(\(\mu\)-PPh)$_2$(C(OEt)Ph)], but instead phosphinidene-carbene coupling occurs to give [Fe$_3$(CO)$_9$(\(\mu\)-PPh)$_2$(\(\mu\)-PhPC(OEt)Ph)]. The bis-nitrene and bis-phosphinidene clusters both react with H$_2$; the former to afford a formyl cluster [Fe$_3$(CO)$_9$(\(\mu\)-NPh)$_2$(CHO)]$^{1}$ whilst the latter is converted to the mixed phosphido/phosphinidene cluster [Fe$_3$(CO)$_9$(\(\mu\)-PPh)(\(\mu\)-PPhH)]$^{1}$ via hydride-phosphinidene coupling.
Chapter 2

Thermal Reactions of Phenylphosphine
with Ru₃(CO)₁₂
2 Thermal Reactions of Phenylphosphine with Ru₃(CO)₁₂

2.1 Introduction

The ability of primary and secondary phosphines (or transition metal complex phosphines[^298,300,301] to oxidatively add to metal clusters has been exploited for several years. These products often retain the metal cluster integrity and contain μ₂-phosphido and/or μ₃-phosphinidene ligands. The ease of formation of clusters containing carbon[^153,154], nitrogen[^184], sulphur[^303,179] and now phosphorus[^193,192,114,67] capping ligands has resulted in the preparation of a large number of these such compounds containing stable, non-fluxional, bridging and capping ligands, such that the integrity of the metal cluster framework is retained during a chemical reaction. Often it is face or edge-bridging phosphorus, arsenic or sulphur ligands that are employed to stabilise metal clusters and many such clusters have been reported e.g. [Co₃(μ-PPh₂)(μ-CO)(CO)₉][^312], [Co₃(μ-PMe₂)(μ-CO)(CO)₉][^399], [Fe₃(μ-S'Bu)(μ-S'Bu)(CO)₉][^310], [Os₃(μ-S)(μ-H)₂(CO)₉][^303], [Fe₃(μ₃-PPh)(μ-H)₂(CO)₉][^192], [Co₃(μ₃-PPh)(μ-CO)(CO)₉][^311], [Ru₃(μ₃-AsPh)(μ-H)₂(CO)₉][^302], [Fe₄(μ₄-PPh)(μ-CO)(CO)₁₀][^156] and [Ru₂Rh₂(μ₄-PPh)(μ-CO)(CO)₁₂]. The ability of these types of clusters to resist fragmentation under conditions commonly employed in catalytic processes means that they have potential uses as homogeneous catalysts. [Co₄(μ₄-PPh₂)(μ-CO)₂(CO)₈] has been found to homogeneously catalyse the hydroformylation of alkenes without any apparent fragmentation.[^301,150]

Mays and co-workers have prepared clusters containing μ₂-PPhR and μ₃-PPh bridging ligands from the reaction of phenylphosphine with [M₃(CO)₁₂] (M = Ru or Os). The capping phosphinidene clusters [M₃(μ-PPh₂)(CO)₉] were observed to be stable with respect to break up into mononuclear products and the capping ligand once in place was very difficult to remove. The reaction of [M₃(CO)₁₂] with phenylphosphine in refluxing solvents lead initially to the formation of edge-bridging PPhH and face-capping PPh ligands whilst longer reaction times and higher boiling solvents gave greater yields of the capped species. The resulting products are shown in Figure 2.1 and the crystal structure of [Ru₃(μ-H)(μ-PPh₂)(CO)₁₀] and [Ru₃(μ-H)₂(μ₃-PPh)(CO)₉] were determined.[^69]

Huttner has reported the reactions of the primary phosphines, RPH₂ (R = C₆H₅, p-CH₃OC₆H₄ or C₆H₁₁) with [Os₃(CO)₁₂] in the presence of trimethylamine oxide, to
afford the terminal phosphine complexes [Os₃(PPhH₂)(CO)]₁₁ and the phosphido-bridged cluster [Os₃(μ-H)(μ-PPhH)(CO)]₁₀. Thermolysis of the terminal phosphine complex, [Os₃(PRH₂)(CO)]₁₁, was reported to give under different conditions [Os₃(μ-H)(μ-PRH)(CO)]₁₀ and [Os₃(μ-H)₂(μ₂-PR)(CO)]₉ by subsequent hydrogen migration and CO dissociation processes. He also reported the conversion of the phosphido cluster [Os₃(μ-H)(μ-PRH)(CO)]₁₀ into the dihydride cluster [Os₃(μ-H)₂(μ₂-PR)(CO)]₉ by thermal decarbonylation in an appropriate hydrocarbon solvent (Figure 2.2).

![Figure 2.2](image)

The results obtained from the [Os₃(CO)]₁₂/PRH₂ system demonstrated the stepwise transformation of a terminally bonded PRH₂ ligand to a doubly bridging μ-PRH unit and finally to a triply bridging μ₂-PR group by successive hydrogen transfer and CO dissociation processes (Figure 2.3).

![Figure 2.3](image)

Shortly after these reports, Haines reported that condensation products were also formed in the reaction of [Ru₃(CO)]₁₂ with phenylphosphine under conditions slightly
Figure 2.1  Phosphido and Phosphinidene clusters of triruthenium 69
more forcing than those employed by Mays and Huttner.\textsuperscript{191} Treatment of $[{\text{Ru}}_3(\text{CO})_{12}]$ with an equimolar amount of phenylphosphine in toluene under reflux was reported to afford several new products. Initially five products were identified, two of which were

![Figure 2.4](image.png)

trinuclear clusters, one pentanuclear, and the fourth was tetranuclear, whilst the fifth remained uncharacterised but was thought to be a condensation product. Figure 2.4 shows the skeletal framework of the pentanuclear (A) and tetranuclear (B) condensation products.

Upon reinvestigation\textsuperscript{142} of the reaction of $[{\text{Ru}}_3(\text{CO})_{12}]$ with phenylphosphine in refluxing toluene Haines discovered that the reaction not only afforded a wide range of products, the nature and yields of which were dependent on the reaction times and molar ratios employed, but the majority of products isolated were of nuclearity greater than three. Longer reflux times afforded tri-, tetra-, penta-, and hexanuclear clusters and included the trinuclear derivatives $[{\text{Ru}}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]$, $[{\text{Ru}}_3(\mu-\text{H})_2(\mu-\text{PPh})(\text{CO})_9]$ and $[{\text{Ru}}_3(\mu_3-\text{PPh})_2(\text{CO})_9]$ and also the higher nuclearity clusters $[{\text{Ru}}_4(\mu_4-\text{PPh})_2(\mu-\text{CO})(\text{CO})_{10}]$, $[{\text{Ru}}_4(\mu_4-\text{PPhH})_2(\mu-\text{PPhH})(\text{CO})_9]$, $[{\text{Ru}}_5(\mu_4-\text{PPhH})_2(\text{CO})_{13}]$, $[{\text{Ru}}_6(\mu_4-\text{PPhH})_2(\text{CO})_n] \ (n = 14 \text{ or } 15)$ and $[{\text{Ru}}_4(\mu_4-\text{PPh})_2(\mu_4-\text{PPhH})_2(\text{CO})_{13}]$. Since this report, condensation and degradation products from the thermolysis reaction of the bridged diphenylphosphido derivatives $[{\text{Ru}}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]$, $[{\text{Ru}}_4(\mu-\text{H})_2(\mu-\text{PPhH})_2(\text{CO})_9]$, $[{\text{Ru}}_5(\mu-\text{H})(\mu-\text{PPhH})_2(\text{CO})_9]$ and $[{\text{Ru}}_6(\mu-\text{H})(\mu-\text{PPhH})_2(\text{CO})_6(\text{PPhH})]$ have been investigated by Haines.\textsuperscript{115,113} A variety of products containing tri-, tetra-, penta- and hexanuclear metal frameworks was observed and characterised crystallographically. Many of the reaction products involved the loss of benzene and the formation of the capping phenylphosphinidene ligands. These products were identified by comparison of similar products from the thermal reaction of $[{\text{Ru}}_3(\text{CO})_{12}]$ with phenylphosphine.
Homo and hetero-metallic clusters are potentially useful as homogenous catalysts, but one of the major limitations of their use is in their tendency to undergo fragmentation in solution in the presence of donor ligands. Phosphido bridged clusters stable to fragmentation have been investigated as homogenous catalytic systems. The homogenous catalytic properties of the cluster \([\text{Ru}_3(\text{PPh}_2)_n(\text{CO})_7] \) \((n = 1-3)\) were investigated; they exhibit good catalytic activity but during the catalysis the clusters were modified to give, as the main products, the trinuclear derivative \([\text{Ru}_3(\mu-H)(\mu-\text{PPh}_2)_3(\text{CO})_7] \) and the dinuclear compound \([\text{Ru}_2(\mu-\text{PPh}_2)_2(\text{CO})_6] \). These latter complexes were also found to be active catalysts for the selective hydrogenation of dienes \(^{196}\). All the clusters \([\text{Ru}_3(\mu-H)(\mu-\text{PPh}_2)(\text{CO})_7] \), \([\text{Ru}_3(\mu-H)_2(\mu-\text{PPh}_2)(\text{CO})_6] \), \([\text{Ru}_3(\mu-H)(\mu-\text{PPh}_2)_3(\text{CO})_7] \) and \([\text{Ru}_2(\mu-\text{PPh}_2)_2(\text{CO})_6] \) selectively hydrogenate \(\text{HC} = \text{CHBu} \) \(^ {194}\) to give \(\text{H}_2\text{C} = \text{CH} \text{Bu} \). These clusters also showed considerable activity in the selective hydrogenation of diphenylacetylene to stilbenes. The phosphine substituted derivatives were also found to be very effective in the isomerisation of cis-stilbene to trans-stilbene.\(^{195}\)

Jones and co-workers have examined the behaviour of metal complexes containing phosphido and arsenido ligands, particularly those with bulky substituents.\(^{63}\) He reported details of the reaction of \([\text{Os}_3(\text{CO})_3] \) with \(\text{Bu}_2\text{PH} \) and \(\text{Cy}_2\text{PH} \) (Scheme 2.1). The new complexes include the bis-phosphido cluster \([\text{Os}_3(\mu-H)_2(\mu-\text{PBu}_2)(\text{CO})_6] \) and the 46-electron cluster \([\text{Os}_3(\mu-H)_2(\mu-\text{PBu}_2)(\text{PBu}_2\text{H})(\text{CO})_2] \). Other clusters structurally characterised were \([\text{Os}_3(\mu-H)_2(\mu-\text{P'Bu})(\text{P'Bu}_2\text{H})(\text{CO})_2] \) and \([\text{Os}_3(\mu-H)(\mu-\text{P'Bu})_3(\text{CO})_2] \) and these clusters will be discussed later with respect to their relevance to clusters synthesised and reported in this chapter.

The thermal decomposition of \([\text{RhH}(\text{CO})(\text{PPh}_3)_3] \) in nonane at 120 °C has been reported to yield trinuclear \([\text{Rh}_3(\mu-\text{PPh}_2)_2(\text{CO})_5(\text{PPh}_3)_3] \) in the absence of carbon monoxide. Haines has isolated a closely related cluster, \([\text{Rh}_3(\mu-\text{PPh}_2)(\text{CO})_3] \) from the reaction of \([\text{Rh}(\mu-\text{Cl})(\text{CO})_2] \) with \(\text{PPh}_2 \). A X-ray crystallographic analysis confirmed that it contained an \(\text{Ru}_3 \overset{\text{P}}{\text{P}}_3 \) core geometry, similar to other known tris-phosphido bridged trinuclear clusters.\(^{305-307}\) Unlike other common \(\text{M}_2\text{P}_3 \) clusters the two \(\text{PPh}_2 \) groups coordinated to the unique rhodium atom were found to be essentially coplanar with the metal-atom plane. Haines has also successfully isolated the carbonylated product \([\text{Rh}_3(\mu-\text{PPh}_2)_2(\text{CO})_5] \) and the single-crystal X-ray structure showed it to contain an \(\text{Ru}_3\text{P}_3 \) core geometry but the Rh-Rh bond lengths \((3.048 \text{ Å - 3.223 Å})\) were found to be consistent.
with the Rh-P-Rh bridge bonding being of the open type.

The majority of the reactions of [Ru₆(CO)₁₂] with phenylphosphine investigated recently involve molar equivalents of both reactants. Our preliminary examinations of the reactivity of phenylphosphine with dodecacarbonyltriruthenium involved the use of slightly greater than three mole equivalents of the phosphine per triruthenium unit. Both phenylphosphine and cyclohexylphosphine afforded similar products and these are described in this chapter.
\[
\text{[Os}_3(\text{CO})_{12}] \xrightarrow{\text{tBu}_2\text{PH}} \text{[Os}_9(\text{tBu}_2\text{PH})_3] \\
\text{[Os}_3(\text{CO})_{12}] \xrightarrow{\text{tBu}_2\text{PH}} \frac{100 ^\circ \text{C}, 12\text{h}}{} \text{[Os}_{10}(\text{tBu}_2\text{PH})_2] \\
\]

Scheme 2.1
2.2 Results and Discussion

2.2.1 Thermal Reaction of [Ru₃(CO)₁₂] with an excess of phenylphosphine.

The reaction of [Ru₃(CO)₁₂] with slightly greater than three mole equivalents of phenylphosphine in refluxing n-hexane (b.p. 86 °C) for 95 minutes gave four compounds all in low yield. The first material isolated was characterised as a mixture of the trinuclear species [Ru₃(μ-H)(μ-PPhH)(CO)₁₀] and [Ru₃(μ-H)₂(μ₃-PPh)(CO)₉] by comparison of the spectroscopic data with those in the literature. A doublet of doublets and a doublet were observed in the hydride region of the ¹H n.m.r. spectrum for these two clusters. The former compound exhibits the characteristic one bond phosphorus-hydrogen coupling constant associated with a proton attached directly to a phosphorus centre.

Also isolated from this reaction mixture was the bisphosphido cluster [Ru₃(μ-H)₂(μ-PPhH)₂(CO)₉]. The i.r. spectrum in the carbonyl region is almost identical to that observed for the isostructural triad of phosphido bridged hydride clusters [M₃(μ-H)₂(μ-PPh₂)₂(CO)₉] (M = Fe, Ru, Os) (Figure 2.5). Figure 2.6 shows perspective views of the Ru₃P₂ skeletons for the three possible isomeric forms of [Ru₃(μ-H)₂(μ-PPhH)₂(CO)₉] with the phenyl rings and the carbonyl groups removed for clarity. Isomer (A) of C₂ symmetry contains both phosphorus-bound protons exo with respect to the triruthenium
ring whilst isomer (B), of lower symmetry $C_1$, contains one phosphorus-bound proton exo to the trinuclear core whilst the other proton is endo. An isomer with the same symmetry as that of (A) which contains both protons endo is also possible.

We believe that all three isomers are present in solution. The $^1$H n.m.r spectrum shows four virtual triplets to high-field ($\delta$ -16.78, -17.05 and -17.58, apparent $J(\text{PH})$ = 24.8 Hz, 24.5 Hz and 22.1 Hz respectively) which are assigned to the two hydride ligands for each isomeric form. Isomer (B) contains non-equivalent hydride ligands leading to two hydride resonances in the $^1$H n.m.r. spectrum for that isomer. Similar resonances have been observed in the $^1$H n.m.r. spectra of $[\text{Os}_3(\mu-\text{H})_2(\mu-P\text{Ph}_2)_2(\text{CO})_8]^6$, $[\text{Os}_3(\mu-\text{H})_2(\mu-P\text{Bu}_2)_2(\text{CO})_8]^6$ and $[\text{Ru}_3(\mu-\text{H})_2(\mu-P\text{Bu}_2)_2(\text{CO})_8]^6$ and they have been attributed to AAXX' type spectra. This coupling constant does not yield any information regarding the mode of coordination of the phosphorus nuclei (i.e. whether it is a phosphido or a phosphinidene type ligand) but the geometry of the cluster has been assigned by comparison of the i.r. spectrum with similar trinuclear clusters. These triplets were each split again into doublets of doublets due to coupling to the protons directly bound to the phosphorus. The hydride region of the $^1$H n.m.r. spectrum containing these three isomers is shown in Figure 2.7, two isomers containing magnetically equivalent hydride ligands and the third exhibiting non-equivalence of its hydrides. Absolute assignment of the isomers to each of the hydride resonances in the $^1$H n.m.r. spectrum has not been possible and attempted separation of these isomers

\[ \text{Figure 2.6} \]
Figure 2.7 400 MHz $^1$H n.m.r. spectrum of the hydride region of the cluster
[Ru$_3$(μ-H)$_2$(μ-PPhH)$_2$(CO)$_4$I]

chromatographically and by fractional crystallisation proved unsuccessful. We are
confident that these three species in solution are isomers each with two bridging
phosphido ligands and not clusters containing ligands with different modes of
coordination (i.e. terminal or capping ligands). These types of clusters have been shown
to have very different $R_f$ values as evidenced by t.l.c. Variable-temperature $^1$H n.m.r.
studies showed that these isomers do not exchange in solution. There was no observed
change in the composition of the solution after prolonged photolysis with white light.

The product isolated from the slowest moving band on the t.l.c. plate exhibited
a complicated i.r. spectrum. The $^1$H n.m.r. spectrum clearly consisted of a mixture of
two hydride containing compounds, evident from the two multiplets to high field of
TMS ($\delta$ -17.70 and -19.01). Fractional crystallisation of this mixture from n-hexane
afforded pure samples of each cluster (the purity confirmed by $^1$H n.m.r. spectroscopy)
and these two species have been identified crystallographically.

The major product crystallised first, affording a deep orange air-stable crystalline
solid, readily soluble in n-hexane and dichloromethane. This cluster was seen to contain
a hydride ligand, apparent from the multiplet at $\delta$ -17.70, corresponding to one of the
Figure 2.8 400 MHz 'H n.m.r. spectrum of [Ru(μ-H)(μ-PPH)](CO)₄]
multiplets in the original mixture. The multiplet contained a basic quartet splitting, indicating that the cluster contained three phosphorus nuclei, and the observed quartet splitting indicated a two-bond phosphorus-hydrogen coupling ($\text{J}(_{\text{PH}}) = 18.0 \text{ Hz}$). The $^1\text{H}$ n.m.r. spectrum of the pure compound is shown in Figure 2.8. There is a large number of geometric isomers possible, differing only in the stereochemistry at the phosphorus (i.e. whether the protons attached directly to the phosphorus are endo or exo with respect to the triruthenium ring) and/or the mode of coordination of the phosphorus-containing ligand (i.e. whether the phosphines are terminal, bridging, or capping, or a mixture of these). The $^1\text{H}$ n.m.r spectrum in Figure 2.8 clearly shows the presence of three sets of resonances in the region normally associated with P-H protons. The presence of three magnetically non-equivalent P-H protons implies that all the phosphorus-containing ligands are of the bridging phosphido type. The requirement of three magnetically non-equivalent P-H protons rules out several of the isomers containing three phosphido ligands although several possibilities remain. Each of these P-H resonances exhibits a one-bond phosphorus-hydrogen coupling constant of approximately 360 Hz. We believe that this cluster contains three bridging phosphido ligands although the phosphorus-hydrogen coupling constant and the chemical shifts of the P-H protons do not unequivocally establish the $\text{Ru}_3\text{P}_3$ core geometry.

![Figure 2.9 Structure of [Ru$_3$(µ-H)(µ-PPh$_2$)$_3$(CO)$_3$] determined by G. L. Geoffroy](image-url)
The trinuclear cluster $[\text{Ru}_3(\mu-H)(\mu-PPh_2)_3(\text{CO})_7]$, believed to be similar to that of ours except that no geometrical isomers are possible, was synthesised by Geoffroy several years ago and has been structurally characterised. The thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with diphenylphosphine afforded the trisubstituted cluster $[\text{Ru}_3(\text{CO})_9(PPh_2)_3]$ which, upon irradiation, gave the new phosphido bridged clusters $[\text{Ru}_3(\mu-H)(\mu-PPh_2)_3(\text{CO})_7]$ and $[\text{Ru}_3(\mu-H)_2(\mu-PPh_2)_2(\text{CO})_4]$. The structure of the trisphosphido complex has been characterised crystallographically by Geoffroy and is shown in Figure 2.9.

$^1$H n.m.r. evidence indicated that the cluster isolated from the reaction mixture contained three phosphido ligands, similar to the cluster prepared by Geoffroy but only one of the six possible isomers was observed by $^1$H n.m.r. spectroscopy.

2.2.2 Mass spectra of $[\text{Ru}_3(\mu-H)(\mu-PPhH)_3(\text{CO})_7]$  

The mass spectrum of this compound was measured at the London School of Pharmacy (ULIRS). Molecular ion peaks were observed at m/e = 826 (based on $^{101}$Ru)
for the compound [Ru₃(μ-H)(μ-PPh₂)(CO)₇]⁺ with the expected isotopic pattern for an Ru₃ compound (Figure 2.10). Fragmentation peaks corresponding to the loss of seven carbonyl groups were also observed. Although the parent molecular ion had been identified there are six possible isomers for [Ru₃(μ-H)(μ-PPh₂)(CO)₇]. It was therefore decided to undertake a single-crystal X-ray structure determination to unequivocally prove the nature of the coordination of the phosphorus containing ligands.

2.2.3 Crystal Structure of [Ru₃(μ-H)(μ-PPh₂)(CO)₇]

Suitable crystals of the cluster were grown by slow evaporation of an n-hexane solution of the compound at room temperature over a period of several days. The structure was solved by N. Powell at University College London. The cluster crystallises in the monoclinic space group P2₁/c with unit cell dimensions a = 8.4332 Å, b = 24.8517 Å, c = 14.6411 Å, β = 95.91 °, with four molecules per unit cell. The structure was refined to R = 0.0557 and R_w = 0.0494. Important bond lengths and angles are given in Table 2.1, and a view of the cluster is shown in Figure 2.11. The molecule has C₁ symmetry and it is apparent that each of the phosphido ligands bridging the Ru-Ru bonds is non equivalent. This is consistent with the ¹H n.m.r. evidence in which three separate signals were observed for the phosphorus-bound protons (Figure 2.8).

Geoffroy observed two crystallographically independent molecules of the cluster [Ru₃(μ-H)(μ-PPh₂)(CO)₇] differing only in the orientation of one of the phenyl rings (C(38)-P(23) in Figure 2.9). Each independent molecule had approximate C₅ symmetry, in contrast to the cluster [Ru₃(μ-H)(μ-PPh₂)(CO)₇] with C₁ symmetry. Inverting the stereochemistry at P(2) would afford a molecule with approximate C₅ symmetry and therefore two magnetically and chemically equivalent phosphido ligands, P(1) and P(2).

There are three terminal carbonyl groups bound to Ru(3) and two each to Ru(2) and Ru(1). Electron counting for this cluster predicts three metal-metal bonds (assuming that the phosphido bridging ligand is a 3e donor) which is confirmed by the bond lengths Ru(1)-Ru(2), Ru(2)-Ru(3) and Ru(1)-Ru(3). The Ru-Ru bonds bridged by only single phosphido ligands are within the range observed by Geoffroy for the cluster [Ru₃(μ-H)(μ-PPh₂)(CO)₇]. The Ru(2)-Ru(3) and Ru(1)-Ru(3) bond lengths are 2.965(1) Å and 2.957(1) Å respectively. [Ru₃(μ-H)(μ-PPh₂)(CO)₇]⁺ contained corresponding bond

-56-
Figure 2.11  Structure of $[\text{Ru}_3(\mu-\text{H})(\mu-\text{PPhH})_3(\text{CO})_3]$
Table 2.1 Selected bond lengths and angles for \([\text{Ru}_3(\mu-H)(\mu-\text{PPhH})_3(\text{CO})_7]\)

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-Ru(2) 2.800(1)</td>
<td>Ru(2)-Ru(1)-C(12) 117.3(3)</td>
</tr>
<tr>
<td>Ru(2)-Ru(3) 2.965(1)</td>
<td>Ru(1)-Ru(2)-C(21) 116.6(3)</td>
</tr>
<tr>
<td>Ru(1)-Ru(3) 2.957(1)</td>
<td>Ru(3)-P(3)-Ru(1) 74.2(1)</td>
</tr>
<tr>
<td>Ru(3)-P(2) 2.386(2)</td>
<td>Ru(3)-P(1)-Ru(2) 78.3(1)</td>
</tr>
<tr>
<td>Ru(3)-P(1) 2.388(2)</td>
<td>Ru(3)-P(2)-Ru(1) 78.1(1)</td>
</tr>
<tr>
<td>Ru(2)-P(1) 2.309(2)</td>
<td>Ru(2)-Ru(1)-P(2) 95.8(1)</td>
</tr>
<tr>
<td>Ru(2)-P(3) 2.320(2)</td>
<td>Ru(2)-Ru(3)-P(2) 89.9(1)</td>
</tr>
<tr>
<td>Ru(1)-P(2) 2.304(2)</td>
<td>Ru(1)-Ru(2)-P(1) 98.1(1)</td>
</tr>
<tr>
<td>Ru(1)-P(3) 2.325(2)</td>
<td>Ru(1)-Ru(3)-P(1) 92.3(1)</td>
</tr>
<tr>
<td>Ru(3)-C(32) 1.916(11)</td>
<td>Ru(3)-Ru(1)-P(3) 92.6(1)</td>
</tr>
<tr>
<td>Ru(3)-C(33) 1.925(10)</td>
<td>Ru(3)-Ru(2)-P(3) 92.5(1)</td>
</tr>
<tr>
<td>Ru(2)-C(21) 1.854(9)</td>
<td></td>
</tr>
<tr>
<td>Ru(2)-C(22) 1.879(9)</td>
<td></td>
</tr>
<tr>
<td>Ru(1)-C(11) 1.874(10)</td>
<td></td>
</tr>
<tr>
<td>Ru(1)-C(12) 1.871(10)</td>
<td></td>
</tr>
</tbody>
</table>
lengths ranging from 2.964(1) Å to 3.033(1) Å for both crystallographically independent molecules. In contrast the Ru(1)-Ru(3) bond, which is bridged both by the phenylphosphido ligand and a hydride ligand, has a bond length of 2.800(1) Å (2.814(1) Å and 2.801(1) Å for the corresponding bond lengths in the cluster \([\text{Ru}_3(\mu-\text{H})(\mu-\text{PPh}_2)_3(\text{CO})_7]\), much shorter than the other two ruthenium-ruthenium lengths in the molecule. In many, but not all, hydride bridged clusters the influence of the hydride bridge appears in the form of a lengthening of the bridged metal-metal bond, and this effect has been attributed to closed three-centre, two-electron bonding between the hydrogen atoms and the metals.\(^{197,198}\) Relative M-M distances, coupled with subtle variations in M-M-C(carbonyl) bond angles have been used with success to infer hydrogen atom location in clusters.\(^{197}\) The wide Ru(2)-Ru(1)-C(12) and Ru(1)-Ru(2)-C(21) angles, mean 116.9°, shows that these equatorial carbonyls bend away from the bridged Ru(1)-Ru(2) edge.

One of the phosphido bridges, P(3), is bent dramatically below the plane of the three ruthenium atoms, while the other two phosphido bridges P(1) and P(2) are well above the Ru\(_3\) plane. The Ru-P distances for the phosphorus atoms that are \textit{trans} to CO ligands \textit{i.e.} Ru(3)-P(2) and Ru(3)-P(1) linkages are 2.386(2) Å and 2.388(2) Å respectively. These bonding interactions are substantially longer than the remaining Ru-P distances all of which are \textit{trans} to phenylphosphido ligands and have bond lengths ranging from 2.304(2) Å to 2.325(2) Å. This asymmetry in the M-P-M bridging ligand

\[
\begin{array}{ccc}
\text{Figure 2.12} \\
\begin{array}{ccc}
2.400(3) & \text{Ru} & 2.388(2) \\
\text{Ru} & 2.430(2) & \text{P} \\
2.320(2) & \text{P} & 2.316(2) \\
\text{Ru} & 2.309(2) & \text{P} \\
2.327(2) & \text{P} & 2.304(2) \\
2.333(2) & \text{Ru} & 2.3403(8) \\
2.320(2) & \text{Ru} & 2.3929(8) \\
\end{array}
\end{array}
\]

\[\text{[Ru}_3(\mu-\text{H})(\mu-\text{PPh}_2)_3(\text{CO})_7] \text{ (A)} \]
\[\text{[Ru}_3(\mu-\text{H})(\mu-\text{PPhH})_3(\text{CO})_7] \text{ (B)} \]
\[\text{[Ru}_3(\mu-\text{H})_2(\mu-\text{PPh}_2)_2(\text{CO})_8] \text{ (C)} \]
(with Ru(1)-P and Ru(2)-P bond lengths shorter than the Ru(3)-P length) is not unusual in cluster chemistry. Figure 2.12 shows various cluster frameworks and the corresponding M-P bond lengths. The cluster, [Ru₃(μ-H)(μ-PPh₂)₃(CO)]₇, prepared by Geoffroy, exhibited similar asymmetry within the phosphido bridges [Ru(2)-P(12) 2.320(2) Å, Ru(3)-P(13) 2.316(2) Å, Ru(2)-P(23) 2.327(2) Å, Ru(3)-P(23) 2.332(2) Å trans to phosphido and Ru(1)-P(12) 2.400(3) Å and Ru(1)-P(13) 2.430(2) Å trans to CO]. The largest difference between M-P bond lengths within a phosphido bridge are on the phosphido ligands bridging the metal metal bonds without a hydride ligand.

All the Ru-P-Ru angles are acute, but the Ru(2)-P(3)-Ru(1) angle of the phosphido bridge spanning the metal-metal length with the hydride ligand is substantially more acute than the other two [Ru(2)-P(3)-Ru(1) 74.2 (1) ° compared with 78.3 (1) ° and 78.1 (1) ° for Ru(3)-P(1)-Ru(2) and Ru(3)-P(2)-Ru(1) respectively].

Most recently and after our work had been completed, Jones has focused on the unusual behaviour of metal clusters containing bulky phosphido and arsenido ligands. He has reported that the thermal reaction of [Os₃(CO)₁₂] with 'Bu₂PH and Cy₂PH affords a range of clusters with phosphido and phosphinidene ligands. Most interestingly he has crystallographically characterised a heptacarbonyl triosmium cluster containing three bridging phosphido ligands (Figure 2.13). Structural details similar to those of our cluster [Ru₃(μ-H)(μ-PPh₂)(μ-PPh)₃(CO)] were observed, the hydride was tentatively assigned to the shortest osmium-osmium edge consistent with our assignment of the bridging ligand.
hydride ligand in the analogous phenylphosphido cluster of ruthenium. The cluster structurally characterised by Jones also exhibited the asymmetry in the phosphido bridges that span the Os(CO)$_2$-Os(CO)$_3$ lengths. The phosphido bridge across the Os(CO)$_2$-Os(CO)$_2$ length is nearly symmetrical.

2.2.4 Identification of [Ru$_3$(μ-H)$_2$(μ$_r$-PPh)(PPhH)$_2$(CO)$_8$]

Fractional crystallisation of the mixture extracted from the slowest moving band afforded orange crystals of [Ru$_3$(μ-H)(μ$_r$-PPh)$_2$(CO)$_8$] (for crystal structure see section 2.2.3) and several yellow crystals of an unknown compound. These two sets of crystals were separated mechanically yielding pure samples of both products. The latter product exhibited a triplet of triplets in the hydride region of the $^1$H n.m.r. spectrum (δ = -19.01). Figure 2.14 shows the hydride region and the P-$\text{H}$ region of the $^1$H n.m.r. spectrum. The large coupling constant (J(PH) = 16.2 Hz) is indicative of two-bond coupling to phosphorus and the triplet splitting indicates that there are two phosphorus nuclei in the cluster. The P-H protons appear magnetically equivalent in the $^1$H n.m.r. spectrum, (Figure 2.14), as a simple doublet of quartets with the familiar large one-bond phosphorus-hydrogen coupling constant (J(PH) = 347.9 Hz) and smaller couplings to the hydride ligands and the remaining unique phosphorus nucleus. The quartet splitting is the result of the similar coupling of the hydride and the phosphorus nuclei. This quartet splitting implied that there were two different phosphorus environments, one terminal phosphine and the other capping the triruthenium face. A structure containing a μ$_r$-PPh ligand and a terminal phenylphosphine with both acidic protons attached was considered likely. This formulation implies that the yellow product is an isomer of the bisphosphido cluster, [Ru$_3$(μ-H)$_2$(μ-PPh)$_2$(CO)$_8$], although the significantly different R$_f$ values (i.e. [Ru$_3$(μ-H)$_2$(μ$_r$-PPh)(PPhH)$_2$(CO)$_8$] has a similar R$_f$ value to [Ru$_3$(μ-H)(μ$_r$-PPh)$_2$(CO)$_8$] and a significantly different value to [Ru$_4$(μ-H)$_2$(μ$_r$-PPh)$_2$(CO)$_8$]) of these two clusters implies that they are not structurally similar and the different modes of coordination proposed for the phospine ligands appears reasonable. The $^1$H n.m.r. spectrum showed a ddd resonance to low-field of the region normally associated with aromatic protons. This resonance is characteristic of the ortho protons of a phenyl ring that belongs to a μ$_r$-capping phosphinidene ligand. This downfield shift of the aromatic protons is apparently caused by the anisotropic magnetic
Figure 2.14 400 MHz $^1$H n.m.r. spectrum of [Ru$_3$(µ-H)$_2$(µ$_3$-PPh)(PPh$_2$)(CO)$_4$]
fields induced by the carbonyl ligands. The orientation of the ortho protons with respect to the carbonyl group is such that these protons are deshielded and come into resonance at lower fields than normal.

To confirm the nature of the bonding of the phosphine ligands in this cluster a single-crystal X-ray structure determination was undertaken at University College London by N. Powell.

2.2.5 Crystal Structure of \([\text{Ru}_3(\mu-\text{H})_2(\mu_3-\text{PPh})(\text{PPhH}_2)(\text{CO})_9]\)

Suitable crystals for single-crystal X-ray structure determination were grown by slow evaporation of an n-hexane solution of the cluster at room temperature over a period of several days. The compound crystallises in the monoclinic space group \(P2_1/n\) with unit cell dimensions \(a = 9.4933 \text{ Å}, b = 12.5566 \text{ Å}, c = 10.6138 \text{ Å}, \beta = 94.977^\circ\) and two molecules per unit cell. The structure was refined to \(R = 0.0339\) and \(R_w = 0.0416\). Important bond lengths and angles are given in Table 2.2 and views of the cluster are shown in Figure 2.15 and 2.16.

The molecule lies on a crystallographic mirror plane and only one half of the molecule is unique; the other coordinates have been generated by crystal symmetry. The molecule has \(C_s\) symmetry with the molecular symmetry plane containing the unique ruthenium atom and bisecting the Ru(2)-Ru(2a) bond. This molecule is similar to the ruthenium cluster, \([\text{Ru}_3(\mu-\text{H})_2(\mu_3-\text{PPh})(\text{CO})_9]\), prepared by Mays and co-workers,\(^6\) the only difference between these two molecules is the substitution of a carbonyl group trans to the phosphinidene ligand by a phenylphosphine ligand. Ru(2) and Ru(2a) each have three carbonyl groups and Ru(1) contains two carbonyl groups and a phenylphosphine ligand to complete the coordination sphere. The phenylphosphine ligand is located in an axial position, the thermodynamically preferred position. Figure 2.15 shows the molecular symmetry plane whilst Figure 2.16 shows clearly the position of the terminal phenylphosphine ligand. There are several related analogues of this compound, which include \([\text{Ru}_5(\mu-\text{H})_2(\mu_3-\text{PPh})(\text{CO})_9]\), \([\text{Ru}_3(\mu-\text{H})_2(\mu_3-\text{P(\text{CH}_3\text{OC}_6\text{H}_4)}_2)(\text{CO})_9]\) and \([\text{Os}_3(\mu-\text{H})_2(\mu_3-\text{P Bu})(\text{P Bu}_2\text{H}_2)(\text{CO})_9]\).

The hydridic protons and the \(\text{P-H}\) protons were located crystallographically, direct location of electron density above the M-M vector with successful refinement of the \(H\) atom position allowed the location of the bridging hydride site, although the
Figure 2.15 Structure of $[\text{Ru}_3(\mu-H)_2(\mu_2-PPh)(PPhH_2)(CO)_6]$
Figure 2.16 Structure of $[\text{Ru}_3(\mu-\text{H})(\mu_3-P\text{Ph})(\text{PPh}_3\text{H})(\text{CO})_3]$
Table 2.2 Selected bond lengths and angles for [Ru$_3$(μ-H)$_2$(μ$_3$-PPh)(PPhH$_2$)(CO)$_8$]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg.)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Ru(1)-Ru(2)-C(21)</td>
</tr>
<tr>
<td>Ru(1)-Ru(2)</td>
<td>2.948(1) 101.2(2)</td>
</tr>
<tr>
<td>Ru(2)-Ru(2a)</td>
<td>2.831(1) 145.9(2)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.360(2) 145.4(2)</td>
</tr>
<tr>
<td>Ru(2)-P(1)</td>
<td>2.288(1) 109.8(2)</td>
</tr>
<tr>
<td>Ru(2)-C(23)</td>
<td>1.915(6) 113.5(1)</td>
</tr>
<tr>
<td>Ru(2)-C(11)</td>
<td>1.882(6) 178.2(6)</td>
</tr>
<tr>
<td>Ru(2)-C(22)</td>
<td>1.954(6) 176.4(5)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.300(2) 178.2(6)</td>
</tr>
<tr>
<td>Ru(2)-P(1)</td>
<td>2.288(1) 178.4(6)</td>
</tr>
</tbody>
</table>
thermal parameters were idealised. The Ru(1)-Ru(2) and Ru(1)-Ru(2a) distances are 2.948(1) Å and these two distances are significantly different to that of the unique Ru(2)-Ru(2a) bond (2.831(1) Å). These longer distances are those that contain the Ru-H-Ru bridges and are similar in length to those observed by Mays in the structurally similar cluster [Ru$_3$(μ-H)$_2$(μ$_2$-PPh)(CO)$_9$]. A mean distance of 2.942(3) Å for the Ru-Ru bond lengths containing the hydride bridges is much shorter than the distance of 2.847(3) Å for the non bridged Ru-Ru bond. The equatorial carbonyl groups bend away from the Ru-Ru edges affording an increased Ru-Ru-C(carbonyl) angle, indicating the presence of a hydride ligand. The Ru(1)-Ru(2)-C(21) bond angle of 101.2 (2) ° is similar to the corresponding bond angles in [Ru$_3$(μ-H)$_2$(μ$_2$-PPh)(CO)$_9$], (mean value of 102.8 °) in comparison to the remaining Ru-Ru-C(carbonyl) angles which were much lower 95.6 °. The subtle variation of the bond angles and the lengthening of two of the Ru-Ru distances confirms that the two bridging hydride ligands are located along the Ru(1)-Ru(2) and Ru(1)-Ru(2a) edges. The Ru(2)-C(23) and Ru(2)-C(11) bonds (mean 1.888(6) Å) which are trans to the bridging hydride are shorter than those trans to the P atom (1.954(5) Å). The Ru-P (phosphinidene) distances for the ruthenium atom which bears the PPhH$_2$ ligand is slightly longer than those for the ruthenium atoms which bear three carbonyl units. The Ru(1)-P(1) distance of 2.300(2) Å compares with the Ru(2)-P(1) and Ru(2a)-P(1) distances of 2.288(1) Å.

Mays reported$^{69}$ that the capped cluster, [Ru$_3$(μ-H)$_2$(μ$_3$-PPh)(CO)$_9$], reacted with phenylphosphine in cyclohexane. He isolated a single cluster species in low yield with significant decomposition to non cluster species. This compound was proposed to be the phosphine substituted derivative of the starting material, [Ru$_3$(μ-H)$_2$(μ$_3$-PPh)(PPhH$_2$)(CO)$_9$]. Higher yields of this product could be obtained by treating [Ru$_3$(μ-H)$_2$(μ$_3$-PPh)(CO)$_9$] in dichloromethane with a 1:1 molar ratio of trimethylamine oxide in methanol at room temperature. He proposed a structure for the phenylphosphine substituted cluster and this structure is confirmed by our single-crystal X-ray structure determination.

### 2.2.6 Reaction of [Ru$_3$(μ-H)$_2$(μ$_3$-PPh)(CO)$_9$] with phenylphosphine.

A refluxing solution of [Ru$_3$(μ-H)$_2$(μ$_3$-PPh)(CO)$_9$] in n-decane reacted with phenylphosphine in the presence of CO gas. The reaction mixture was refluxed for 90
minutes to afford a deep yellow solution from which was isolated in 48% yield a bright yellow oil characterised by i.r. and 'H n.m.r. spectroscopy as the bisphosphinidene cluster \([\text{Ru}_3(\mu_2\text{-PPh})_2(\text{CO})_9]^{114}\) (Figure 2.17). The purge of CO gas was required during this preparation because in the absence of carbon monoxide at high temperatures, degradation and condensation reactions are known to occur. Even with the stabilising phosphinidene ligands, triruthenium clusters undergo decomposition to noncluster species at high temperatures. The presence of CO gas ensured that the trinuclear framework remained intact during the reaction. Two moles of \(\text{H}_2\) were eliminated per cluster unit during the reaction with no overall increase or decrease in carbon monoxide content. The cluster has been structurally characterised and is known to contain only two M-M bond with two \(\mu_2\text{-PPh}\) ligands.

On refluxing a solution of the cluster \([\text{Ru}_3(\mu_2\text{-PPh})_2(\text{CO})_9]\) in n-decane whilst purging with CO gas there was no reaction (i.r evidence) even after several hours at reflux in n-decane (b.p. 175 °C). No degradation or condensation products were observed and the starting material was retrieved in effectively quantitative yield after chromatographic work up.
2.3 Results with Cyclohexylphosphine

2.3.1 Reaction of \([\text{Ru}_3(\text{CO})_{12}]\) with Cyclohexylphosphine

A procedure similar to that used for the thermal reaction of \([\text{Ru}_3(\text{CO})_{12}]\) with phenylphosphine was employed. Slightly greater than three mole equivalents of cyclohexylphosphine was refluxed with \([\text{Ru}_3(\text{CO})_{12}]\) in n-hexane. After chromatographic work up three major well separated bands were observed, these were extracted from the t.l.c. plates and the products crystallised.

The products isolated from the reaction mixture were each identified spectroscopically and shown to be analogous to the products isolated from the reaction of \([\text{Ru}_3(\text{CO})_{12}]\) with phenylphosphine. The bis-phosphido cluster \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_8]\) was isolated as an air-stable orange crystalline material and was identified by comparison of its spectroscopic properties with those of the known clusters \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PPhH})_2(\text{CO})_8]\), \([\text{M}_3(\mu-\text{H})_2(\mu-\text{PPh}_2)(\text{CO})_8]\) \(^{65}\) and \([\text{Os}_3(\mu-\text{H})_2(\mu-\text{PR}_2)_2(\text{CO})_8]\) \(^{63}\) (\(R = \text{Bu}, \text{Cy}\)). Elemental analytical data obtained (C, H) were acceptable.

2.3.2 Spectroscopic Characterisation of \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_8]\)

The \(^1\text{H}\) n.m.r. spectrum consisted of four hydride resonances to high-field of TMS (\(\delta 17.38, -17.57, \) and \(-17.92, \) apparent \(J(\text{PH}) = 24.2\) Hz, \(23.4\) Hz and \(22.0\) Hz respectively) indicating the presence of three hydride containing clusters in solution in differing quantities. These three clusters in solution can be directly identified with the three geometric isomers possible for a cluster with the formulation \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PRH})_2(\text{CO})_8]\) (\(R = \text{alkyl or aryl}\)). The three possible isomers are shown in Figure 2.6 with \(R = \text{phenyl}\). Figure 2.18 shows the hydride region of the \(^1\text{H}\) n.m.r. spectrum for both bis-phosphido clusters, \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PRH})_2(\text{CO})_8]\) (\(R = \text{Ph and Cy}\)), and the close similarity between these two sets of isomers is particularly evident. The i.r. spectrum in the carbonyl region of \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_8]\) is almost identical to that observed for the phenylphosphido analogue and to those of the isostructural clusters \([\text{M}_3(\mu-\text{H})_2(\mu-\text{PPh}_2)(\text{CO})_8]\) \(^{65}\) (\(M = \text{Fe, Ru and Os}\)). Figure 2.19 shows the close similarity of the two i.r. spectra of the related clusters \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PRH})_2(\text{CO})_8]\) (\(R = \text{Ph and Cy}\)). The major difference is in the frequencies of absorption for identical i.r. stretches, as
Figure 2.18 400 MHz $^1$H n.m.r. spectrum of the hydride region of the clusters 
$[\text{Ru}_2(\mu-H)_2(\mu-PRH)_2(CO)_6]$ ($R = \text{Ph, Cy}$)

(a) $[\text{Ru}_3(\mu-H)_2(\mu-PCyH)_2(CO)_6]$

(b) $[\text{Ru}_3(\mu-H)_2(\mu-PPhH)_2(CO)_6]$
Figure 2.19  $\nu$(CO) i.r. spectra of (a) $[\text{Ru}_2(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_2]$ and (b) $[\text{Ru}_2(\mu-\text{H})_2(\mu-\text{PPhH})_2(\text{CO})_2]$

(a) $[\text{Ru}_2(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_2]$

(b) $[\text{Ru}_2(\mu-\text{H})_2(\mu-\text{PPhH})_2(\text{CO})_2]$
a result of the disparate electronic properties of the phosphines. The structures of the clusters, \([M_3(\mu-H)\mu(PPh_2)\mu(CO)_6]\) (\(M = \text{Fe, Ru, Os}\)), are well-established and are known to contain two phosphido bridging ligands, one above and one below the plane of the metals, with hydride ligands bridging the same metal-metal bonds as the phosphido ligands. The presence of similar bands in the i.r. spectrum of the cluster isolated from this reaction indicates that it should have a similar structure.

2.3.3 Spectroscopic Characterisation of \([\text{Ru}_3(\mu-H)(\mu-\text{PCyH})_3(CO)_7]\)

The second band isolated from the t.l.c. plates afforded air-stable deep orange crystals after slow evaporation of an n-hexane solution of the compound at room temperature. The i.r. spectrum in the carbonyl region compared favourably with the i.r. spectrum recorded for \([\text{Ru}_3(\mu-H)(\mu-PPhH)_3(CO)_7]\) (Figure 2.20). The different stretching frequencies for the equivalent i.r. bands in the two spectra is a consequence of the different electron-donating properties of the phosphines. Phenylphosphine can be seen to have greater electron donating properties \((\text{i.e. is a better sigma donor})\) than cyclohexylphosphine as evidenced by the lower stretching frequencies of the carbonyl groups of the cluster containing the phenylphosphido ligands.

From this i.r. evidence we proposed a similar structure to that of the tris-phosphido cluster \([\text{Ru}_3(\mu-H)(\mu-PPhH)_3(CO)_7]\). The i.r. spectrum did not afford any information regarding the presence of possible isomers, but from \(^1\text{H n.m.r. spectroscopy it became evident that there was more than one isomer in solution. The most convincing evidence for this came from the \(^1\text{H n.m.r. spectrum in the high-field hydridic region, although the P-H resonances did indicate that there was more than one species in solution and that these were not in exchange. Figure 2.21 shows the }\(^1\text{H n.m.r. spectrum in both the hydride and the }\text{P-H region. The four quartet resonances (δ - 18.50, -18.80, -19.20, -19.52) with coupling constants indicative of two-bond phosphorus-hydrogen coupling (}^{3}\text{J(PH) = 17.9 Hz, 17.1 Hz, 16.8 Hz and 16.7 Hz respectively}) identified that there were three phosphorus nuclei in the cluster. These isomers are observed to be present in vastly disparate concentrations as evidenced by }\(^1\text{H n.m.r. spectroscopy. The P-H resonances could not be unambiguously assigned to their appropriate hydride resonances, but each of the P-H resonances exhibited a one-bond phosphorus-hydrogen coupling constants ranging from 350 Hz to 370 Hz.}}\)
Figure 2.20 $v$(CO) i.r. spectra of (a) $[\text{Ru}_2(\mu-\text{H})(\mu-\text{PPhH})_3(\text{CO})_7]$ and (b) $[\text{Ru}_2(\mu-\text{H})(\mu-\text{PCyH})_3(\text{CO})_7]$.
Figure 2.21 $^1$H n.m.r. spectrum of the hydride & P-H region of the complex
$[\text{Ru}_2(\mu-H)(\mu-\text{PPhH})_2(\text{CO})_7]$
Figure 2.22 shows each of the six possible geometric isomers differing only in their stereochemistry at the phosphido phosphorus nuclei (i.e. whether the acidic phosphorus bound protons are exo or endo with respect to the plane of the metal atoms). Isomer (A) is that found in the equivalent crystal structure of \([\text{Ru}_3(\mu-\text{H})(\mu-\text{PPhH}^\text{CO})_3]\) and is of low symmetry, \(C_1\), with all phosphido ligands non-equivalent. Some of these isomers will be less favourable than others as a consequence of the steric requirements of the bulky cyclohexyl group. We know that isomer (A) is probably present because this is the isomer observed for the phenylphosphido analogue. Isomers (B) and (E) would be expected to be the least favourable geometric isomers because both bulky cyclohexyl groups are directed towards each other and are on the same side of the triruthenium plane. This endo arrangement of the phosphido ligands on the same side of the metal plane is the most sterically demanding geometry and these two isomers would be expected to be absent. With these two isomers eliminated there are four possible isomeric forms remaining and four sets of quartet resonances are observed in the hydride region of the \(^1\text{H} \text{n.m.r.}\) spectrum (Figure 2.21). These isomers may be tentatively assigned to (A), (C), (D), (F) (Figure 2.22) where each cluster has either one endo and one exo cyclohexyl group or has both cyclohexyl groups exo with respect to the metal plane.

The P-H region of the \(^1\text{H} \text{n.m.r.}\) spectrum is very complicated (Figure 2.21) and only assignment of pairs of resonances have been allocated. Although absolute assignment of the P-H resonances could not be made to their appropriate hydride signals consideration of the symmetry of the predicted isomers should allow the determination of the number of P-H signals expected and this should agree with the number observed in the spectrum. Some of the phosphido cluster have \(C_1\) symmetry whilst others have a mirror plane relating phosphido ligands on the same side of the metal plane and are of \(C_2\) symmetry. Those molecules with \(C_2\) symmetry should only exhibit two P-H resonances whilst those of \(C_1\) symmetry (such as that of the phenylphosphido cluster whose structure was determined crystallographically and whose \(^1\text{H} \text{n.m.r.}\) spectrum exhibited three sets of P-H signals confirming the \(C_1\) symmetry) should exhibit three P-H resonances per isomer. The four isomers that are expected to be present in solution should contribute ten P-H signals to the \(^1\text{H} \text{n.m.r.}\) spectrum. Figure 2.21 shows that there are ten different resonances attributable to the phosphorus-bound protons in agreement with our assignment of the isomers in solution.
Figure 2.22 Six possible geometric isomers of [Ru$_3$(µ-H)(µ-PPH)$_3$(CO)$_7$].
The high-temperature $^1$H n.m.r. (CDCl$_3$, +55 °C) spectrum showed no sign of broadening in the hydride region and no exchange of the isomers was observed on the n.m.r. time-scale. Photolysis of an n.m.r. sample with white light for several days did not alter the abundance of any of the isomers ($^1$H n.m.r. evidence). This inability of the isomers to exchange in solution is not unusual as exchange would require either cleavage of a metal phosphido bond or deprotonation followed by inversion with subsequent reprotonation.

2.3.4 Spectroscopic Characterisation of [Ru$_3$(μ-H)$_2$(μ-3-PCy)(PCyH$_2$)(CO)$_8$]

The slowest moving band extracted from the chromatographic plates afforded two sets of crystals after fractional crystallisation form n-hexane. The least soluble crystals were air-stable and red-brown in colour. Elemental analysis supported the formulation [Ru$_3$(μ-H)(μ-PCyH)(PCyH$_2$)(CO)$_8$]. The $^1$H n.m.r. spectrum exhibited two sets of P-H resonances with integral ratios of 2:1. The structure is expected to be a simple phosphine substituted derivative of [Ru$_3$(μ-H)(μ-PCyH)(CO)$_8$] (Figure 2.23).

Finally the yellow crystals isolated from this slow moving band exhibited a $^1$H n.m.r. spectrum that was very similar to that obtained for the cluster [Ru$_3$(μ-H)$_2$(μ-3-PPh)(PPhH$_2$)(CO)$_8$], whose structure was determined crystallographically. The resonance due to the bridging hydride ligand (δ -19.37) appeared as a triplet of triplets ($^3$J(PH) = 15.4 Hz and $^3$J(HH) = 3.4 Hz) representing two equivalent metal-bound hydrogen atoms coupled to two phosphorus nuclei with further coupling to two magnetically equivalent phosphorus-bound protons. This implies that the two hydride ligands are disposed symmetrically with respect to the PCyH$_2$ substituent.

The phosphorus-bound protons appeared as a doublet of doublets of quartets in
Figure 2.24 400 MHz $^1$H n.m.r. spectrum of (a) [Ru₂(μ-H)₂(μ-PCyH)₂(CO)₆] and (b) [Ru₂(μ-H)₂(μ-PPhH)₂(CO)₆]

(a) [Ru₂(μ-H)₂(PCyH)₂(CO)₆]

(b) [Ru₃(μ-H)₂(μ-PPhH)₂(CO)₆]
the $^1$H n.m.r. spectrum. The P-H resonances of both clusters $[Ru_3(\mu-H)_2(\mu_3-PR)(PRH_2)(CO)_8] \ (R = Cy, Ph)$ are very similar appearing as double quartets. Figure 2.24 shows the $^1$H n.m.r. spectra of both clusters and their similarity is extremely evident. The most significant difference between the two spectra is that there appears to be two sets of resonances in the spectrum corresponding to $[Ru_3(\mu-H)_2(\mu_3-PCy)(PCyH_2)(CO)_8]$. Careful consideration of the structure of this cluster shows that there is an extra proton, the $\alpha$ proton of the cyclohexyl ring, that is capable of coupling to the phosphorus-bound proton (Figure 2.25). This effect has been observed in the $^1$H n.m.r. spectra of the triosmium clusters $[Os_3(\mu-H)((\mu-PCyH)(CO)_{10}], [Os_3(PCyH_2)CO]_{11}$ and $[Os_3(PCy_2H)(CO)_{11}]$ prepared by Huttner and co-workers. He noticed an additional coupling, other than the familiar coupling to phosphorus, arising from the $\alpha$ hydrogen atom of the cyclohexyl group ($^3J(HH) = 4.4 \text{ Hz}$). The three-bond coupling constant to the P-H proton in the cluster $[Ru_3(\mu-H)_2(\mu_3-PCy)(PCyH_2)(CO)_8]$ is within the range expected for this type of coupling as evidenced from the known cluster documented in the literature.
Figure 2.26 Mass spectra of (a) \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_6]\)  (b) \([\text{Ru}_3(\mu-\text{H})(\mu-\text{PCyH})_3(\text{CO})_7]\)

(a) \([\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PCyH})_2(\text{CO})_6]\)

(b) \([\text{Ru}_3(\mu-\text{H})(\mu-\text{PCyH})_3(\text{CO})_7]\)
2.3.5 Mass Spectra of some Phosphido and Phosphinidene Clusters

Mass spectra were measured at the London School of Pharmacy (ULIRS). Metal carbonyl clusters characteristically show a fragmentation pattern with the successive loss of CO ligands. Molecular ion peaks for the cluster \([\text{Ru}_3(\mu_3-\text{H})_2(\mu_3-\text{PCyH})_2(\text{CO})_8]\) were found at around m/e 757 (based on \(^{101}\text{Ru}\)) with the expected isotopic pattern for an Ru\(_3\) species. Successive loss of eight CO groups was observed as we expected. The tris-phosphido cluster, \([\text{Ru}_3(\mu_3-\text{H})(\mu_3-\text{PCyH})(\text{CO})_7]\), shows the loss of seven CO groups in the mass spectrum fragmentation pattern and a parent molecular ion at around m/e 846 (based on \(^{101}\text{Ru}\)) corresponding to \([\text{Ru}_3(\mu_3-\text{H})(\mu_3-\text{PCyH})_2(\text{CO})_8]^+\) (Figure 2.26a). Finally the cluster \([\text{Ru}_3(\mu_3-\text{H})(\mu_3-\text{PCy})(\text{PCyH}_2)(\text{CO})_7]\) exhibited a parent molecular ion peak at m/e 757 in the mass spectrum, confirming that it was an isomer of the bis-phosphido cluster \([\text{Ru}_3(\mu_3-\text{H})(\mu_3-\text{PCyH})_2(\text{CO})_8]\). The successive loss of eight CO groups was observed in the fragmentation pattern as was expected (Figure 2.26b). The parent molecular ion for \([\text{Ru}_3(\mu_3-\text{H})(\mu_3-\text{PCy})(\text{PCyH}_2)(\text{CO})_9]\) is at around m/e 785 (based on \(^{101}\text{Ru}\)) consistent with the formulation. The successive loss of nine carbonyl groups was observed in the fragmentation pattern as was expected.

2.3.6 Pyrolysis of \([\text{Ru}_3(\mu_3-\text{H})_2(\mu_3-\text{PCy})(\text{PCyH}_2)(\text{CO})_9]\)

Refluxing the title complex in n-decane (b.p. 175 °C) whilst purging with CO gas for 300 minutes afforded a single major product identified spectroscopically as the cluster \([\text{Ru}_3(\mu_3-\text{PCy})_2(\text{CO})_9]\). The i.r spectrum in the carbonyl region is similar to that for the phenylphosphinidene analogue \([\text{Ru}_3(\mu_3-\text{PPh})_2(\text{CO})_9]\). Figure 2.27 shows the transformation that has occurred with the net loss of two molecules of hydrogen per molecule of cluster formed and the addition of one mole of CO per mole of product. A similar reaction performed in the absence of CO gas would most certainly lead to the production of high nuclearity clusters.

Mays reported\(^6\) that the cluster \([\text{Ru}_3(\mu_3-\text{H})(\mu_3-\text{PPh})(\text{PPhH}_2)(\text{CO})_9]\), a minor product from the thermal reaction of \([\text{Ru}_3(\text{CO})_{12}]\) with phenylphosphine in cyclohexane, did not undergo transformation to the capped phosphinidene cluster \([\text{Ru}_3(\mu_3-\text{H})_2(\mu_3-\text{PPh})(\text{PPhH}_2)(\text{CO})_9]\) by decarbonylation when thermolysed in high boiling hydrocarbon solvents as he had expected. He argued that substitution of a phosphine ligand for a
Figure 2.27

carbonyl group should increase the tendency of the metal atom to undergo oxidative addition. He suggested that the failure to undergo this transformation was kinetic since he was able to prepare the cluster by treatment of [Ru₃(μ-H)₂(μ₃-PPh)(CO)₉] with Me₃NO in methanol followed by phenylphosphine. Reasonable yields were obtained by this preparative route.

Ruthenium complexes containing a single terminally bound phosphine such as [Ru₃(PRH₂)(CO)₉] are readily converted into edge bridging species by decarbonylation and proton transfer. Once edge bridging, the phosphido complex will readily transfer another proton to the Ru-Ru bond with concomitant loss of CO to form the phosphinidene capped cluster [Ru₃(μ-H)₂(μ₃-PR)(CO)₉]. This transformation occurs rapidly in hydrocarbon solvents at 60 °C. This cluster is known to react with phenylphosphine under mild conditions, either at 60 °C in cyclohexane or at room temperature in the presence of trimethylamine oxide to afford the phosphine substituted cluster [Ru₃(μ-H)₂(μ₃-PPh)(PPhH₂)(CO)₉] by decarbonylation. We know that this complex can not be prepared from the phosphine substituted phosphido cluster, [Ru₃(μ-H)(μ-PPhH)(PPhH₂)(CO)₉], by thermolytic methods. A simple transformation carried out by us has shown that the complex [Ru₃(μ-H)₂(μ₃-PCy)(PCyH₂)(CO)₉] can be converted to the bisphosphinidene cluster [Ru₃(μ₃-PCy)(CO)₉] by thermal dehydrogenation with concomitant carbonylation. Reaction of [Ru₃(μ-H)₂(μ₃-PPh)(CO)₉] with phenylphosphine in a high boiling solvent affords the same complex presumably through the terminal
phosphine complex \([\text{Ru}_3(\mu_\text{-H})_2(\mu_\text{3-PPh})(\text{PPhH}_2)(\text{CO})_6]\) as established by Mays and coworkers.

Huttner's results obtained from the \([\text{Os}_3(\text{CO})_{12}]\text{PRH}_2\) system\(^{67,114}\) demonstrated the step-wise transformation of a terminally bound PRH\(_2\) ligand into a doubly bridging \(\mu\text{-PRH}\) unit and finally into a triply bridging \(\mu_3\text{-PR}\) group by successive hydrogen transfer and CO substitution processes. The transformations carried out on the phosphido and phosphinidene clusters demonstrate the stepwise synthesis of the cluster \([\text{Ru}_3(\mu_\text{3-PPh})_2(\text{CO})_9]\) (Scheme 2.2). Attempted hydrogenation of this final cluster back to the \([\text{Ru}_3(\mu_\text{-H})_2(\mu_\text{3-PPh})(\text{PPhH}_2)(\text{CO})_6]\) by decarbonylation failed and was seen to afford condensation products only, no trinuclear clusters were isolated from the thermal reaction of \([\text{Ru}_3(\mu_\text{3-PPh})_2(\text{CO})_9]\) with hydrogen. The chemistry of the bisphosphinidene cluster will be discussed fully in the following section.
Scheme 2.2
2.4 Transformations of [Ru₃(μ₃-PPh)₂(CO)₉] to High Nuclearity Clusters.

2.4.1 Attempted Hydrogenation of [Ru₃(μ₃-PPh)₂(CO)₉]

Since the transformation of [Ru₃(μ-H)₂(μ₃-PR)(PRH₂)(CO)₈] (R = Ph, Cy Figure 2.27) occurred readily in n-decane under an atmosphere of CO gas with the release of hydrogen we thought that it might be possible to add hydrogen to the cluster [Ru₃(μ₃-PPh)₂(CO)₉] with concomitant loss of CO to afford [Ru₃(μ-H)₂(μ₃-PPh)(PPhH₂)(CO)₈].

A refluxing solution of the title cluster in n-decane was purged with H₂ gas and the i.r. spectrum monitored. The solution was refluxed until there was no further change in the i.r. spectrum and chromatographic work-up of the deep brown solution afforded three well separated products. None of these products was the required cluster compound [Ru₃(μ-H)₂(μ₃-PPh)(PPhH₂)(CO)₈] and at no time during the reaction was there any i.r. evidence for its formation. Each of the products was obtained as air-stable crystalline materials by slow evaporation from an n-hexane solution overnight.

The first band isolated from the chromatographic plate afforded deep orange crystals. The FAB mass spectrum showed a parent molecular ion at 1372 which indicated a condensation product. The parent molecular ion at 1372 corresponded to the formulation [Ru₆(CO)₁₂(PPh)₄]₄²⁻ a cluster formed from the condensation of two [Ru₃(μ₃-PPh)₂(CO)₉] molecules with the concomitant loss of one CO molecule per ruthenium atom. Elemental analytical data (C, H) agreed reasonably well with those calculated for the proposed formulation. The ¹H n.m.r. spectrum recorded at room temperature displayed a single broad resonance in the hydride region; the only other signals present were aromatic resonances and no P-H resonances were observed. To low-field of the region normally occupied by aromatic resonances were two sets of signals integrating 1:1. One set appeared as a sharp multiplet (ddd) whilst the other signal was broad and appeared to be around coalescence and no fine structure was observed.

These features in the ¹H n.m.r. spectra were not unique to this cluster, since the other crystalline materials isolated from the reaction also showed similar properties. The second isolated cluster had a ¹H n.m.r. spectrum that was similar to the first with two sets of aromatic resonances appearing to low field of the region normally associated
with aromatic protons. One of these signals was sharp with a fine structure similar to
the previous sample whilst the other resonance was broad. The major difference
between the two samples was the absence of any hydride $^1$H n.m.r. resonance for the
second cluster. Elemental analytical data for the second product were not significantly
different to those for the first. As a result of the close similarity between their $^1$H
n.m.r. spectra, these clusters were expected to be similar in their geometries and
properties. It was decided to undertake single-crystal X-ray structure determinations of
these clusters to unequivocally determine the nature of these two species.

2.4.2 Crystal Structure of [Ru$_6$(μ-H)$_2$(μ$_2$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$]

The X-ray structural determination was performed by N. Powell at University
College London and confirmed the hexanuclear nature of the cluster metal core.
Suitable crystals of the compound were grown by slow evaporation of an n-hexane
solution overnight. The complex crystallises in the triclinic space group $P1$ with two
molecules per unit cell of dimensions $a = 10.144(3)$ Å, $b = 12.452(4)$ Å, $c = 18.204(6)$
Å, $\alpha = 88.02 (3)$ °, $\beta = 77.80 (2)$ °, $\gamma = 72.72 (2)$ °. The structure was refined to $R$
$= 10.74$ and $R_w = 11.93$. Important bond lengths and angles are tabulated (Table 2.3)
and a view of the cluster is given in Figure 2.28.

The six ruthenium atoms adopt a distorted trigonal prismatic geometry with both
of the triangular face capped by μ$_3$-PPh ligands and two of the three remaining square
faces capped by μ$_4$-PPh phosphinidene ligands. The coordination to each ruthenium
atom is completed by two terminal carbonyl groups. The distortions within the metal-
metal framework away from a regular trigonal prismatic geometry towards octahedral
are not as pronounced as in the hexanuclear cluster [Ru$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$]. There
is a small torsional twist of the Ru(1) Ru(2) Ru(3) plane through an angle of slightly
greater than 4 ° about the approximate three-fold axis. This twist is much less than in
the closely related cluster [Ru$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$]$^{113,115,142}$ and, as a result of the
small size of this twist, there are only small distortions of the square faces of the
trigonal prism. This is reinforced by the similar lengths of the two diagonals of each
quadrilateral face, [Ru(3)-Ru(5) 4.265(4) Å and Ru(2)-Ru(6) 4.244(4) Å, Ru(6)-Ru(4)
4.257(4) Å and Ru(4)-Ru(3) 4.267(4) Å, Ru(5)-Ru(1) 4.161(4) Å and Ru(2)-Ru(4)
4.374(4) Å]. There are much larger differences between the diagonal lengths of each

-86-
Figure 2.28  Structure of \([\text{Ru}_4(\mu-H)_2(\mu_2-PPh)_2(\mu_4-PPh)_2(CO)_12]\)
Table 2.3 Selected bond lengths and angles for \([\text{Ru}_6(\mu-H)_2(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_2])\)

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<th>Bond lengths (Å)</th>
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<tr>
<td>Ru(1)-Ru(4) 3.073(4)</td>
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quadrilateral face in the cluster $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$. The mean difference between the diagonal lengths of each quadrilateral face in the cluster $[\text{Ru}_6(\mu-H)_2(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ is 0.0831 Å whilst the equivalent mean difference in the related hexanuclear cluster $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ is 0.639 Å (nearly 10 fold bigger). The quadrilateral faces in the cluster $[\text{Ru}_6(\mu-H)_2(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ are very nearly planar, with only a small folding about the diagonals of each face. The folding about the Ru(2)-Ru(6) diagonal is 4.4 ° and about the Ru(5)-Ru(1) diagonal is 5.4 ° and that about the Ru(4)-Ru(3) diagonal is 6.1 °. These folding angles are much less than those observed for the cluster $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$. One of the intrabasal lengths is slightly longer than the other two, leading to further distortions of the skeletal framework, the long Ru-Ru distance is Ru(4)-Ru(5) 2.974(4) Å whilst the two shorter distances are Ru(4)-Ru(6) 2.835(4) Å and Ru(5)-Ru(6) 2.824(4) Å. Likewise the opposite triangular face contains a long metal-metal bond Ru(1)-Ru(2) [2.957(4) Å], and two short bonds Ru(2)-Ru(3) [2.853(4) Å] and Ru(1)-Ru(3) [2.874(4) Å]. These two long ruthenium-ruthenium bonds correspond to the approximately parallel lengths within each of the two triangular faces of the trigonal prismatic skeleton. The non-hydridic cluster $[\text{Ru}_6(\mu_3-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ in comparison contained intrabasal ruthenium ruthenium distances that were approximately the same, but the cluster $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ was found to contain bonds within the triangular faces of the prism that were lengthened to a greater extent than those in the hydridic cluster $[\text{Ru}_6(\mu-H)_2(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ [Ru(1)-Ru(3) 3.323(3) Å and Ru(4)-Ru(6) 3.509(3) Å]. A gradual increase in the lengths of these two intrabasal Ru-Ru bonds is apparent on progressing through the cluster series: $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$, $[\text{Ru}_6(\mu-H)_2(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ and $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$. There is effective no difference in the intrabasal bond lengths of the cluster $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ whilst the difference between the two short and one long Ru-Ru length in $[\text{Ru}_6(\mu-H)_2(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_2(\text{CO})_{12}]$ is 0.119 Å and the equivalent difference in the cluster $[\text{Ru}_6(\mu_2-P\text{Ph})_2(\mu_4-P\text{Ph})_3(\text{CO})_{12}]$ is even greater, 0.532 Å. Although the two triangular faces of the trigonal prism are not parallel (dihedral angle of 4.7 °) the difference in the interbasal distances between opposite ruthenium atoms is not as large as in the non hydridic hexanuclear cluster. The longest distance is Ru(3)-Ru(6) 3.269(4) Å whilst the two shorter distances are Ru(2)-Ru(5) 3.072(4) Å and Ru(1)-Ru(4) 3.073(4) Å. Only six of the ruthenium-ruthenium distances are considered as being short [2.824(4) Å-
These six short ruthenium-ruthenium bonds are contained within the triangular faces of the trigonal prismatic framework. There are no bonding interactions between the two triangular faces of the metal skeleton in contrast to the cluster \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\), although these three interactions are intermediate in length \([3.073(3) \text{ Å} - 3.268(4) \text{ Å}]\). The remaining six distances are very long \([4.161(4) \text{ Å} - 4.374(4) \text{ Å}]\), being the diagonal lengths of the quadrilateral faces. A regular trigonal prismatic framework should contain nine short and six long metal-metal interactions.

### 2.4.3 Crystal Structure of \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\)

A direct comparison of the \(^1\text{H}\) n.m.r. spectra of the two crystalline samples obtained from the high temperature reaction of \([\text{Ru}_3(\mu_3-\text{PPh})_2(\text{CO})_9]\) and \(\text{H}_2\) gas indicated that there was a close similarity between the two clusters. Having obtained the structure of \([\text{Ru}_6(\mu_3-\text{H})_2(\mu_4-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\), it was thought necessary to determine the single-crystal X-ray structure of the related compound. Suitable crystals of the cluster were grown by slow evaporation of an n-hexane solution of the compound overnight. Initially it was thought that the cluster was the related compound \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\) but the \(^1\text{H}\) n.m.r and i.r. spectra were inconsistent with the data reported in the literature. Preliminary examinations of the crystal revealed that it belonged to a different space group than that reported by Haines,\(^{142,115}\) and different unit cell dimensions were observed. As a result the X-ray structure was determined. The cluster crystallises in the monoclinic space group \(P2_1/c\) with two molecules per unit cell of dimensions \(a = 20.919(5) \text{ Å}, b = 20.262(2) \text{ Å}, c = 21.274(5) \text{ Å}, \beta = 110.68(2) ^\circ\). The structure was refined to \(R = 0.109\) and \(R_w = 0.107\). Important bond lengths and angles are given in Table 2.4 and a view of the cluster is shown in Figure 2.29. The cluster does appear to be \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\)\(^{142}\) in spite of the differences in the spectroscopic data reported. The difference between the unit cell parameters determined by Haines for \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\) and those reported here for a cluster with the same formulation can be explained by the presence of benzene molecules of crystallisation in the former cluster. Recently Haines carried out a structural determination of a non-solvated hexanuclear cluster \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\)\(^{115}\) and it appears that the structure is crystallographically indistinguishable form that determined by us.
Figure 2.29 Structure of \([\text{Ru}_4(\mu_3-P\text{Ph})_2(\mu_3-P\text{Ph})_2(\text{CO})_{12}]\)
Table 2.4 Selected bond lengths and angles for [Ru$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$]

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As for the previous cluster, both the triangular faces are capped by phosphinidene ligands and two of the square faces are also capped by these ligands. The coordination of each ruthenium is completed by two terminal carbonyl groups. The six ruthenium atoms adopt a distorted trigonal prismatic skeletal framework but the distortions are much more severe than those in the cluster \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\). The torsional twist of the Ru(1)Ru(2)Ru(3) atoms with respect to the Ru(4)Ru(5)Ru(6) atoms out of the idealised trigonal prismatic geometry is approximately 12°, much greater than in the related cluster already discussed (compare 4.7°). This torsional twist is shown clearly in Figure 2.30 where views of the two clusters down the triangular faces are shown, the greater twist within the cluster \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\) is evident. This twist away from the eclipsed geometry manifests itself in the considerable differences between the ruthenium atoms, for example the trigonal prismatic framework contains quadrilateral faces with extremely large differences between the two diagonals of each of these faces [Ru(3)-Ru(5) 3.954(4) Å and Ru(2)-Ru(6) 4.365(4) Å, Ru(6)-Ru(1) 3.942(4) Å and Ru(4)-Ru(3) 4.338(4) Å, Ru(5)-Ru(1) 3.227(3) Å and Ru(2)-Ru(4) 4.683(4) Å]. These values can be compared directly with those of the cluster \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\) in which the diagonals of each quadrilateral face are very nearly equal. In the non-hydridic cluster one short and one long diagonal distances is observed for each square face, a mean difference between the diagonals of 0.639 Å in comparison to a mean difference of 0.081 Å for the cluster \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\). The non-planarity of these quadrilateral faces is also more prominent in this cluster than the previous one. The folding about the Ru(2) Ru(6) diagonal is 15°, that about the Ru(5) Ru(1) diagonal is 11.8° and that about the Ru(3) Ru(4) diagonal is 18.8° (in comparison to 5.5° for \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]\)). The two triangular faces of the distorted prism are not parallel; the dihedral angle between the two faces (12.6°) is much greater than that (4.7°) in the hydridic cluster. This non-parallel arrangement of the triangular faces is reflected in the interbasal Ru-Ru distances where one is much larger than the other two [Ru(3)-Ru(6) 3.238(4) Å for the longest distance, the shorter lengths are Ru(2)-Ru(5) 2.865(4) Å and Ru(1)-Ru(4) 2.807(4) Å]. These short Ru-Ru lengths are within the range expected for metal bonding interactions. The difference between the longest and the average of the two short interbasal lengths (0.402 Å) is much greater than the equivalent difference of bond lengths in the hydridic cluster (0.196 Å). It must be
Figure 2.30 Metal atom skeletal framework of (a) $[\text{Ru}_4(\mu-H)_2(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]$ and (b) $[\text{Ru}_4(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_{12}]$
remembered that none of the interbasal distances in the cluster \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) are considered as metal-metal bonding, all being intermediate in length. The Ru-Ru distances within the triangular faces of the prism are all of similar length \([2.852(4) \text{ Å} - 2.892(4) \text{ Å}]\) whereas the intrabasal Ru-Ru distances in \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) consist of four short \([2.834(4) \text{ Å} - 2.874(4) \text{ Å}]\) and two long \([\text{mean } 2.965(4) \text{ Å}]\) bonds.

Eight of the ruthenium-ruthenium distances are less than 3 Å \([2.852(3) \text{ Å} - 2.892(3) \text{ Å}]\) and are considered as short, whilst two are intermediate \([3.227(3) \text{ Å} - 3.238(3) \text{ Å}]\) and the remaining five are long \([3.954(3) \text{ Å} - 4.683(4) \text{ Å}]\). There are too many short and intermediate interactions within this cluster to represent a trigonal prismatic framework and the distortions towards octahedral geometry is reflected in the number of short/intermediate bond lengths. In contrast the cluster \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) would only require a simple reduction in the interbasal lengths to afford a trigonal prismatic geometry with the correct number of long metal-metal interactions. The cluster framework of \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) contains too few long metal-metal distances and the distortions of the skeleton more closely represent the twelve short interaction required for an octahedral cluster. In conclusion the distortions within each framework discussed thus far can be related to the favoured geometry for that cluster \(i.e.\) the cluster \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) distorts towards octahedral geometry, reflected in the number of short metal-metal interactions, whilst the cluster \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) prefers a trigonal prismatic framework and this is reflected in the number of long metal-metal interactions.

2.4.4 Structural Relationship between \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\), \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) and \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\)

(a) Both clusters \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) and \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) can be seen to be based on trigonal prismatic metal skeletons. They differ only in the extent of the distortions from the regular geometry which have been described in the previous sections. The cluster \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_{12}]\) has also had its structure determined crystallographically and the major difference between this structure and those of the two clusters containing only four capping phosphinidene ligands is that all faces of the trigonal prism are capped. The distortions within the
skeletal framework of [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₃(CO)₁₂] can be described in terms of a simple expansion of the trigonal prismatic core. Figure 2.31 shows the metal skeletal frameworks for each of the three clusters for comparison. Haines described the expansion of the metal core of [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₂(CO)₁₂] as a lengthening of two of the basal edges, one to a greater extent than the other [Ru(1)-Ru(2) 3.323(3) Å and Ru(4)-Ru(6) 3.509(3) Å] and to an elongation of the axial edge opposite to the two long basal edges [Ru(2)-Ru(5) 3.241(3) Å]. In contrast to the cluster [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₃(CO)₁₂], there is no torsional twist of the triangular face about the three fold axis.

Haines reported that the low temperature ³¹P{¹H} n.m.r. spectrum of [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₂(CO)₁₂] displayed equivalence of the μ₃-phosphinidene ligands but that only two of the three μ₄-phosphinidene ligands were equivalent, the remaining one being unique. He reported that at high temperatures all the μ₄-phosphinidene ligands appeared to be equivalent by ³¹P{¹H} n.m.r. He dismissed the proposal that the ligands were migrating over the surface of the cluster and suggested that the process occurring involved elongation and contraction of the ruthenium-ruthenium edges.

Electron-counting for the cluster [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₃(CO)₁₂] revealed that there are 88-valence electrons (phosphinidene ligands donate four electrons to the skeletal bonding). There are many 86-electron octahedral clusters known, of which [Rh₆(CO)₁₂] is one, whose skeletal bonding can be described in terms of two-centre electron pair bonds if resonance of the eleven bonds dictated by the 18-electron rule is invoked. By analogy ten metal-metal bonds would be required for the 88-electron cluster [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₃(CO)₁₂]. An octahedral framework should contain twelve metal-metal distances and a regular trigonal prismatic skeleton nine. This requirement of ten metal-metal bonds for the cluster [Ru₆(μ₃-PPPh)₂(μ₄-PPPh)₃(CO)₁₂], clearly lies midway between these two ideal extremes and a metal core geometry midway between octahedral and trigonal prismatic would be expected. Careful examination of Figure 2.29 reveals the distortions away from the eclipsed trigonal prismatic geometry towards a staggered octahedral configuration and long bonding distances are apparent from the Ru(6)-Ru(3) and Ru(5)-Ru(1) contacts. The 88-electron polyhedral cluster can clearly be seen to adopt a geometry that lies between octahedral and trigonal prismatic as can be predicted from simple electron counting.

Applying the Polyhedral Skeletal Electron Pair approach, and on the basis that a capped polyhedral cluster has the same number of bonding skeletal molecular
Figure 2.31 Trigonal prismatic core geometries of (a) \([\text{Ru}_3(\mu_3-PPh)_3(\mu_4-PPh)_2(CO)]_3\) and (c) \([\text{Ru}_3(\mu_3-PPh)_3(CO)]_3\).
orbitals as the uncapped parent polyhedron, we may predict the possible core geometries for these clusters. The skeletal electron count on metal clusters allows us to deduce the number of electrons a particular cluster can contribute for skeletal bonding. Three atomic orbitals in the valence shell of the skeletal atom are required for cluster use and the number of electron available for cluster bonding will be those electrons remaining after allocation to the other valence shell orbitals (six for transition metals). These electrons, required for cluster bonding, are accommodated in the three atomic orbitals of the valence shell of the skeletal atoms. Considering \([\text{Ru}_6(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_1]\) an \([\text{Ru}(\text{CO})_3]\) unit will not contribute any electrons to the cluster for skeletal bonding (all twelve electrons are required to fill the six valence shell atomic orbitals) and therefore the only other electrons available for this purpose are those of the capping phosphinidene ligands (each phosphinidene ligand is capable of contributing four electrons for cluster bonding). These eight bonding-pairs required to hold the six skeletal atoms together should afford a cluster analogous to the \textit{nido} pentagonal bipyramidal boron hydride cluster \((\text{B}_5\text{H}_9)^-\). The polyhedral skeletal electron pair theory is not adequate in predicting the cluster geometries of these hexanuclear species.

A skeletal structure midway between octahedral and trigonal prismatic for the 88-electron cluster is reinforced by EHMO calculations for the \(\text{Co}_8\text{H}_8\) anions. The 86-electron cluster anion is predicted to adopt an octahedral geometry whilst the 90-electron cluster anion should have a trigonal prismatic geometry, an 88-electron cluster with six metal atoms would reasonably be expected to adopt a structure that was intermediate between these extremes.

(b) Electron counting on the cluster \([\text{Ru}_6(\mu-\text{H})_2(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_1]\) leads to 90-valence electrons of which 72 are required to fill the valence shell atomic orbitals (there are six valence shell atomic orbitals per metal atom) leaving 18 cluster-electrons for skeletal bonding. The polyhedral skeletal electron pair theory predicts an \textit{arachno} type polyhedral cluster geometry with \(n+3\) bonding pairs of electrons available to hold the metal framework together. The structure is predicted to be based on a polyhedron \((n+2\) vertices) with two of the vertices left unoccupied by the skeletal metal atoms. The polyhedron chosen is that based on the dodecahedron (Figure 2.32a) with two vertices missing (Figure 2.32b). Removal of the appropriate two vertices affords a skeletal framework that resembles a distorted trigonal prism. The distortions
within the metal core may be caused by the capped polyhedral cluster not having the same number of bonding skeletal molecular orbitals as the uncapped parent polyhedron. Mingos and Forsyth have calculated that capped metal cluster compounds containing a substantial number of capping ligands do not have the same number of bonding skeletal molecular orbitals as their uncapped parent clusters. Alternatively the cluster \([\text{Ru}_6(\mu_3-H)_2(\mu_4-PPh)_2(\mu_4-PPh)_2(\text{CO})_2]\) compound containing nine bonding pairs of electrons for cluster bonding would be predicted to have a regular dodecahedral geometry for the \(\text{Ru}_6(\mu_4-PPh)_2\) core (Figure 2.32a). This is contrary to what is observed and, although cluster geometries may be predicted by a variety of methods, the distortions within the skeletal metal atom framework cannot be accounted for so readily.

Extended Hückel molecular orbital calculations have been performed on the model cluster anions, \(\text{Co}_6\text{H}_6\), for octahedral, trigonal prismatic and bicapped tetrahedral geometries.\(^{200}\) These calculations showed high lying molecular orbital levels with predominantly 4s and 4p orbital character and which are bonding between the metal atoms. Cobalt-cobalt and boron-boron s-and p- overlap integrals are comparable for analogous polyhedral molecules and therefore give rise to similar molecular orbital splitting patterns. The calculated energies for the bonding molecular orbitals of the isopolyhedral boranes \(\text{B}_n\text{H}_6\) (octahedral, trigonal prismatic and bicapped tetrahedral) follow the same order as the cobalt s-p skeletal molecular orbitals. This is the theoretical basis of the polyhedral skeletal electron pair theory. Filling the energy levels
in the cobalt clusters leads to the hypothetical ions in which a 90-electron clusters requires a trigonal prismatic framework with nine skeletal electron pairs. This prediction is in agreement with clusters already isolated such as \([\text{Rh}_6\text{C(CO)}]^{2+}\) and now the cluster \([\text{Ru}_6(\mu_3-\text{P})_2(\mu_5-\text{PPh})_2(\text{CO})]^{2+}\).

Likewise for the 88-electron cluster, the 18-electron rule can be used to deduce the number of two-centre electron-pair metal-metal bonds present. The 90-electron cluster is 18-electrons short of that required to satisfy the 18-electron rule, and nine metal metal bonds are therefore predicted. The structural details of this cluster showed that there were six long metal metal distances the remaining interactions were either short or intermediate in length. Including the three intermediate interactions the correct number of metal-metal bonds is predicted for a trigonal prismatic geometry, although the rule does not explain the distortions observed within the cluster framework.

Lewis and co-workers have structurally characterised two 90-electron trigonal prismatic clusters, containing interstitial \(\mu_5\)-phosphide ligands (Figure 2.33). \([\text{Os}_6\text{H}(\text{P})(\text{CO})]^{2+}\) was isolated, as the only tractable product after prolonged reflux of a xylene solution of \([\text{Os}_6\text{H}_2(\text{CO})]^{2+}(\mu_2-\text{PH})\). [PPh_3Me][\text{Os}_6(\text{CO})_{18}(\mu_5-\text{P})] and [\text{Os}_6(\text{CO})_{18}(\mu_5-\text{P})(\text{AuPPh}_3)] both have trigonal prismatic core geometries with intrabasal lengths less

![Figure 2.33](image-url)

\[\text{Figure 2.33 Structure of (a) } [\text{Os}_6(\mu_5-\text{P})(\text{CO})]^{2+} \text{ and (b) } [\text{Os}_6(\mu_5-\text{P})(\text{AuPPh}_3)(\text{CO})]^{2+}\]
than 3 Å whilst the interbasal lengths are all slightly greater than 3 Å [3.101(1) Å - 3.151(1) Å]. The distortions observed within the skeletal framework of these two clusters are similar to those in the related cluster [Ru₆(μ-H)₂(μ₃-PPh)₂(μ₄-PPh)₂(CO)]₁₂.

The cluster [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)]₁₂, structurally characterised by Haines, contains 92-valence electrons. He explained the geometry of this skeletal framework as a trigonal prism which has been slightly opened up due to the occupancy of an antibonding skeletal molecular orbital by the two electron in excess of the 90-electrons required for a regular trigonal prismatic core. He was unable to oxidise this 92-electron cluster to the 90-electron species [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)]²⁺, which he predicted to contain the regular trigonal prismatic geometry. The 90-electron cluster examined by us confirms his belief that the skeletal metal core would have the geometry predicted. The use of the polyhedral skeletal electron pair theory would predict a regular tricapped trigonal prism for this cluster. The ten skeletal electron pairs for the Ru₆(μ₄-PPh)₂ core would predict this closo type structure and the Ru₆ core would as a consequence define a regular trigonal prism. The distortions within this framework have again not been accounted for through simple cluster geometry predictions. Although current bonding theories can predict the geometries of the metal atom frameworks of these compounds they can only do so to a first approximation and they do not account for the various distortions observed. These distortions are expected to be imposed by the capping phosphinidene ligands, most prominent in the 90 electron cluster where a regular core geometry was predicted. No conclusions as to whether these effects are steric or electronic have been made. An increase of electron density at metal complexes has been found to lead to an increase in the dihedral angle and to an unequal lengthening of some of the edges, although steric effects also play an important role in the geometry of metal clusters.

Figure 2.34 shows the trigonal prismatic core for the 88-, 90- and 92-electron related compounds along with their most important bond lengths. Average distances within the basal plane and between the triangular faces have been calculated for each of these clusters. The average of all nine metal-metal bond lengths for each of these clusters have also been calculated and the results are given in Table 2.5. Along the series from the 88-electron cluster to the 92-electron cluster there is an increase in the average bond length within and between the basal planes. As the electron count of the metal cluster increases the framework expands and the skeletal framework changes from
distorted octahedral (88e) to trigonal prismatic (90e) to an expanded trigonal prism (92e) but which bonds are elongated is somewhat unpredictable.
Figure 2.34  Trigonal prismatic bond lengths for [Ru$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$] (A) 
[Ru$_6$(μ-H)$_2$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$] (B) and [Ru$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_3$(CO)$_{12}$] (C)
Table 2.5  Ruthenium-Ruthenium interactions within the trigonal prismatic skeletal geometry.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of skeletal electrons for cluster bonding</th>
<th>Average of interbasal Ru-Ru distances (Å)</th>
<th>Average of intrabasal Ru-Ru distances (Å)</th>
<th>Average of 9 Ru-Ru distances in trigonal prism (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂]</td>
<td>88</td>
<td>2.860(3)</td>
<td>2.970(3)</td>
<td>2.897(3)</td>
</tr>
<tr>
<td>[Ru₆(μ-H)₂(μ₃-Ph)₂(μ₄-PPh)₂(CO)₁₂]</td>
<td>90</td>
<td>2.886(4)</td>
<td>3.139(4)</td>
<td>2.970(4)</td>
</tr>
<tr>
<td>[Ru₆(μ₃-PPh)₂(μ₄-PPh)₃(CO)₁₂]</td>
<td>92</td>
<td>3.062(3)</td>
<td>3.038(3)</td>
<td>3.054(3)</td>
</tr>
</tbody>
</table>
Prior to the X-ray crystallographic studies on these cluster compounds it was noticed that there was unusual behaviour in the aromatic region of the \(^1\text{H}\) n.m.r. spectrum. Both the title clusters exhibited downfield shifts of the aromatic signals that were assigned to the ortho protons. One set of downfield resonances was sharp at room temperature, whilst the other signal also for ortho protons of the phenyl rings was broad, implying that a fluxional process was occurring at room temperature. Figure 2.35 shows the variable-temperature \(^1\text{H}\) n.m.r. spectra in the aromatic region of the cluster \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_2]^{12}\) and Figure 2.36 shows the corresponding spectra of the 88 electron cluster \([\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_2]^{12}\).

(a) The downfield resonances in the \(^1\text{H}\) n.m.r. spectrum of \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_2]^{12}\) have been assigned to the ortho protons, each multiplet integrating for four protons. The sharp double double doublet signal (\(\delta 8.14, \; ^3J(\text{PH}) = 11.2\; \text{Hz}, \; ^3J(\text{HH}) = 6.4\; \text{Hz}\) and \(^4J(\text{HH}) = 1.2\; \text{Hz}\)) in the room temperature \(^1\text{H}\) n.m.r. spectrum can be identified with the ortho protons of both tricapping phosphinidene ligands. The phenyl rings of the phosphinidene ligand capping the triangular face of the cluster undergo rapid rotation about the phosphorus carbon bond rendering the ortho protons magnetically equivalent. The signals due to these protons remain sharp throughout the temperature range examined (as low as -75 °C in CD\(_2\)Cl\(_2\)). The broad resonance at \(\delta 7.96\) was assigned to the ortho protons of the phosphinidene ligands capping two of the three square face of the trigonal prismatic skeleton. At room temperature there is a process occurring that averages the environments of the ortho protons of these phenyl rings and the resonance appears as a broad singlet. This resonance was observed to broaden as the temperature was lowered. Broadening of the resonances assigned to the meta protons of the phosphinidene ligands that cap the square faces of the cluster framework was also observed. At -80 °C (CD\(_2\)Cl\(_2\)) the ortho protons become magnetically non-equivalent and give separate signals in the \(^1\text{H}\) n.m.r. spectrum. A chemical shift difference of 1 ppm between the ortho resonances was observed for the cluster \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_2]^{12}\) at the low temperature limit (\(\delta 8.32\) and 7.34 ppm). The meta protons of the phosphinidene ligands capping the square faces of
Figure 2.35 Variable temperature $^1$H n.m.r. spectra of the phenyl region of the complex $[\text{Ru}_6(\mu-H)_2(\mu_\gamma-\text{PPh})_2(\mu_\gamma-\text{PPh})_2(\text{CO})_n]$
Figure 2.36 Variable temperature $^1$H n.m.r. spectra of the phenyl region of the complex $[\text{Ru}_4(\mu_3-\text{PPh})_2(\mu_4-\text{PPh})_2(\text{CO})_8]$
the cluster also displayed magnetic non-equivalence at low temperature although the chemical shift difference between these two sets of signals was not as large as that observed for the \textit{ortho} protons. Increasing the temperature led to broadening of the signals for the \textit{meta} protons and coalescence of these signals occurs at approximately -15 °C. In this temperature range broadening of the signals of the \textit{ortho} protons of the same phenyl rings was observed, coalescence of these signals occurring between +5 and +20 °C. Throughout the whole temperature range there was no broadening of resonances associated with the \(\mu_3\)-PPh ligands. The solvent was then changed to d₄-toluene and spectra were recorded at higher temperatures, up to +105 °C. At this temperature there was rapid rotation of all four capping phosphinidene ligands about the phosphorus-carbon bonds rendering the \textit{ortho} and \textit{meta} protons of the \(\mu_4\)-PPh ligands magnetically equivalent. At this temperature two sets of \textit{ortho} resonances were observed, one set for each different bonding mode of phosphinidene ligand, both containing the familiar ddd splitting associated with \textit{ortho} protons.

(b) The variable-temperature \(^1\text{H} n.m.r.\) spectra of \([\text{Ru}_6(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})_2(\text{CO})_{12}]\) shown in Figure 2.36 are similar to those already discussed for \([\text{Ru}_6(\mu_3\text{-H})_2(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})_2(\text{CO})_{12}]\). Characteristically low-field signals are observed for the \textit{ortho} protons of both types of phenyl rings. The broad resonance at \(\delta\) 7.74 has been assigned to the \textit{ortho} protons of the \(\mu_3\)-PPh ligands and the sharp resonance at \(\delta\) 8.02 (\(^3\text{J}(\text{PH}) = 13.7 \text{ Hz}, ^3\text{J}(	ext{HH}) = 6.8 \text{ Hz} \text{ and } ^4\text{J}(	ext{HH}) = 1.2 \text{ Hz}\)) to the \textit{ortho} protons of the \(\mu_4\)-PPh ligands. The low temperature \(^1\text{H} n.m.r.\) spectrum (-80 °C in CD₂Cl₂) revealed the magnetic non-equivalence of the \textit{ortho} protons of the \(\mu_4\)-PPh ligands. This non-equivalence of the protons led to a large chemical shift difference between the protons in the different magnetic environments (\(\delta\) 8.46 and 6.90). This chemical shift difference between the signals of the \textit{ortho} protons is much larger than in the structurally similar cluster \([\text{Ru}_6(\mu_3\text{-H})_2(\mu_4\text{-PPh})_2(\mu_4\text{-PPh})_2(\text{CO})_{12}]\). These two sets of signals have equal integration as four protons per cluster. At this low temperature the separation of the resonances of the \textit{meta} protons is much more apparent (\(\delta\) 7.58 and 7.32) and the signals due to these magnetically non-equivalent nuclei are more easily identified than in the hydridic cluster. The signals due to the \textit{meta} protons coalesce at approximately -15 °C whilst those for the non-equivalent \textit{ortho} protons do not coalesce until room temperature. This difference in the coalescence temperature is the result of the greater
chemical shift difference between the signals of the non-equivalent ortho protons, a much faster rate of rotation being required to give coalescence. The much smaller difference in the chemical shifts of the meta protons at low temperature means that coalescence occurs at a much slower rate (i.e. at much lower temperatures). Similar to the variable-temperature $^1$H n.m.r. spectra of $[\text{Ru}_6(\mu_2\text{-H})_2(\mu_4\text{-PPh})_2(\mu_4\text{-PPh})_2(\text{CO})_{12}]$, the ortho and meta protons of the $\mu_3\text{-PPh}$ ligands remained equivalent on the n.m.r. time-scale.

A similar fluxional process was thought to be occurring in both of these high nuclearity clusters because of the close similarity in their variable-temperature $^1$H n.m.r spectra. Figure 2.37 shows the phosphinidene ligand that caps the square face of the cluster and the close approach of the ortho protons to the axial carbonyl groups is very apparent. These sterically unfavourable interactions will restrict the rotation about the carbon-phosphorus bond and this rotation will be slow on the n.m.r. time-scale at low temperatures, affording separate resonances for the ortho and meta protons. The rapid fluxionality for the phenyl ring resonances of the $\mu_4\text{-PPh}$ ligands can be explained in terms of a reduction of these unfavourable steric hinderances as a result of one less Ru(CO)$_2$ unit. Both clusters $[\text{Ru}_6(\mu_2\text{-H})_2(\mu_4\text{-PPh})_2(\mu_4\text{-PPh})_2(\text{CO})_{12}]$ and $[\text{Ru}_6(\mu_4\text{-PPh})_2(\mu_4\text{-PPh})_2(\text{CO})_{12}]$ shown no sign of restricted rotation about the carbon-phosphorus bond of...
Figure 2.38 Space filling model diagrams of \([\text{Ru}_6(\mu-H)_2(\mu_5-PPh)_2(\mu_4-PPh)_2(CO)_{12}]\)
the $\mu_3$-ligands.

Space filling diagrams of the two clusters show clearly the steric interactions of the phenyl protons with the carbonyl groups of the cluster framework as shown in Figure 2.38 for the cluster $[\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_6]$. 

A third product was isolated from the reaction $[\text{Ru}_6(\mu_3-PPh)_2(\text{CO})_6]$ with $\text{H}_2$ gas at high temperatures. This product corresponded to the slowest moving band on the chromatographic plate and after extraction and crystallisation from n-hexane was isolated as a brown air-stable crystalline material. The $^1\text{H}$ n.m.r. spectrum indicated that were no hydride ligands in the cluster, whilst the aromatic region of the spectrum exhibited resonances in the ration of 2:3. FAB mass spectra obtained for this sample showed parent molecular ions at around 1821 which is consistent with the formulation $[\text{Ru}_6(\mu_3-PPh)_6(\text{CO})_6]$. Elemental analytical data (C, H) showed reasonable agreement between calculated and the observed values for this formulation. The $^1\text{H}$ n.m.r. spectrum afforded extremely different characteristics to the spectra of $[\text{Ru}_6(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_6]$ and $[\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(\text{CO})_6]$. At room temperature only one set of resonances was observed to low-field of the region normally associated with the aromatic protons ($\delta$ 7.98 broad), as for the other two high nuclearity clusters, this resonance corresponds to the ortho protons of the $\mu_4$-PPh ligands. This down-field resonance appears as a broad signal similar to the broad resonances observed in the spectra already discussed and integrates as two protons whilst the remaining signals integrate as three protons.

Figure 2.39
This broad resonance at low-field has been assigned to the ortho protons of the \( \mu_r\)-PPh ligands by analogy with the examples already observed. There is only one set of ortho signals observed in the room temperature \( ^1H \) n.m.r. spectrum implying that there is only one type of phosphinidene ligand i.e. that of the type capping a square face of the cluster. To satisfy the requirements of eight metal atoms, and no triangular faces for the phosphinidene ligands to cap, a cubic structure is indicated, containing only square faces. The related cluster \([\text{Ni}_4(\mu_r\text{-PPh})_6(\text{CO})]\) has been structurally characterised\(^{193}\) and identified as a cubic arrangement of metal atoms with a phosphinidene ligand capping each of the square faces and one carbonyl ligand per metal atom completing the coordination sphere (Figure 2.39). This cluster contains 132 electrons whilst in comparison ours contains only 126 valence electrons although a similar structure cannot be dismissed. We have been unable to obtain crystals suitable for single-crystal X-ray structure determination.

2.4.6 Attempted Hydrogenation of \([\text{Ru}_4(\mu_r\text{-PPh})_2(\mu_r\text{-PPh})_2(\text{CO})_12]\)

\([\text{Ru}_6(\mu_r\text{-PPh})_2(\mu_r\text{-PPh})_2(\text{CO})_12]\) reacted with \( \text{H}_2 \) gas in refluxing mesitylene after 45 minutes. Chromatographic work up afforded at deep brown crystalline material identified spectroscopically as the starting material as well as a yellow oil identified as the 90-electron cluster \([\text{Ru}_4(\mu-H)_2(\mu_r\text{-PPh})_2(\mu_r\text{-PPh})_2(\text{CO})_12]\).

Refluxing a sample of the cluster \([\text{Ru}_6(\mu_r\text{-PPh})_2(\text{CO})_9]\) whilst purging with nitrogen gas afforded a deep brown solution after 150 minutes. There was no further change in the i.r. spectrum upon continued thermolysis. Chromatographic work-up led to separation of several of products, which were each identified spectroscopically and shown to be the same as the reaction products from the attempted hydrogenation of \([\text{Ru}_6(\mu_r\text{-PPh})_2(\text{CO})_9]\).

Recently Haines has investigated the condensation and degradation products from the thermolysis reaction of the bridged diphenylphosphido clusters \([\text{Ru}_3(\mu-H)(\mu-PPh)_2(\text{CO})_10], [\text{Ru}_3(\mu-H)_2(\mu-PPh)_2(\text{CO})_8], [\text{Ru}_3(\mu-H)(\mu-PPh)_3(\text{CO})_7]\) and \([\text{Ru}_3(\mu-H)(\mu-PPh)_3(PPh_2H)(\text{CO})_6]\) in xylene.\(^{113,115}\) These thermolysis reactions were found to afford a range of condensation and degradation products including tri-, tetra-, penta-, hexa- and hepta-nuclear clusters. Haines assumed that the trinuclear species \([\text{Ru}_6(\mu_r\text{-PPh})_2(\text{CO})_9]\) was an intermediate in the formation of the tetra and hexanuclear products, \([\text{Ru}_4(\mu_r\text{-PPh})_2(\text{CO})_9]\)
PPh₃(CO)(CO)₉ and [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂], in the thermolysis of [Ru₆(μ-H)₂(μ-PPh)₂(CO)₈]. It became apparent after several experiments that the pyrolysis of [Ru₆(μ-H)₆(μ-PPh)₂(CO)₈] was complex and the formation of [Ru₆(μ₃-PPh)₂(CO)₁₂] does not involve the simple loss of benzene from the octacarbonyl derivative together with the uptake of CO but rather some fragmentation and subsequent condensation process. The pyrolysis of [Ru₆(μ₃-PPh)₂(CO)₈] either under an inert atmosphere or under hydrogen was found to afford only the three high nuclearity clusters described. Even after short reaction times no other reaction products were observed, only starting material was evident, although the cluster [Ru₆(μ₃-PPh)₂(CO)₁₂] has now been shown to be intermediate in the formation of the hexanuclear clusters.

2.4.7 Pyrolysis of [Os₆(μ₃-PPh)₂(CO)₉]

A yellow solution of the cluster [Os₆(μ₃-PPh)₂(CO)₉] was refluxed in decahydronaphthalene (b.p 200 °C) whilst purging with H₂ gas. The reaction was monitored by i.r. spectroscopy and refluxing was continued until there was no further change in the spectrum. Chromatographic work-up afforded a single isolable compound whose i.r. spectrum was very similar in the pattern number and frequencies of absorptions, in the carbonyl region, to that of the related ruthenium cluster [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂]. Figure 2.40 shows the i.r. spectra of the two related clusters [M₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂] (M = Ru, Os). Elemental analysis of the crystalline sample afforded data with a reasonable agreement with the calculated values for [Os₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂].

The ¹H n.m.r spectrum recorded at room temperature only contained resonances in the aromatic region. As was observed in the ¹H n.m.r spectrum of the ruthenium analogue, two sets of signals were observed to low field of the region commonly associated with aromatic protons. Each of these resonances integrated as four protons. The broad resonance (δ 8.26), similar in nature to that observed in the ¹H n.m.r spectrum of [Ru₆(μ₃-PPh)₂(μ₄-PPh)₂(CO)₁₂], was assigned to the ortho protons of μ₄-PPh ligands. The down-field resonance at δ 7.98 (3J(PH) = 14.1 Hz, 3J(HH) = 7.8 Hz and 4J(HH) = 1.8 Hz) corresponds to the ortho protons of the phenyl ring of the μ₃-PPh ligands. These assignments have been made by a direct comparison with the spectra of the corresponding ruthenium cluster. At the low temperature limit of the solvent (-55 °C
Figure 2.40 $\nu$(CO) i.r. spectra of (a) $[\text{Os}_6(\mu_2\text{PPh})_2(\mu_4\text{PPh})_2(\text{CO})_{12}]$ and (b) $[\text{Ru}_6(\mu_3\text{PPh})_2(\mu_4\text{PPh})_2(\text{CO})_{12}]$
CDCl₃), the ¹H n.m.r. spectrum consisted of two sets of resonances for the ortho protons of the phenyl ring belonging to the μ₄-capping ligands, both these resonances integrating as two protons. A large chemical shift difference between these magnetically non-equivalent protons was observed at the low temperature limit (δ 8.26 and 6.96 for the two sets of ortho resonances). This magnetic non-equivalence of the protons is probably due to a similar restricted rotation as a result of steric crowding on the square faces of the cluster. The resonances of the ortho and meta protons of the phenyl rings of the μ₂-PPh ligand remain sharp throughout the temperature range examined. The separate signals due to the magnetically non-equivalent meta protons were less easily identified in the low temperature ¹H n.m.r. spectrum but were assigned through their behaviour as the temperature of the n.m.r. solvent was raised. The separate resonances of the meta protons appeared at δ 7.56 and δ 7.40. At -20 °C the signals corresponding to the meta protons had shifted together allowing unambiguous assignment of signals. Coalescence occurred between 0 °C and +10 °C whilst at these temperature the resonances due to the nonequivalent ortho protons remained broad and well separated.

A similar difference in the coalescence temperatures of these two sets of protons was observed in the analogous hexaruthenium cluster and was due to the large difference in the chemical shifts of the ortho protons in comparison to the chemical shift difference of the magnetically non-equivalent meta protons. Coalescence of these ortho protons does not occur until temperatures in the range of +40 ° to +60 °C are reached.

To clarify the situation several of the variable-temperature ¹H n.m.r. spectra of [Os₆(μ₂-PPh)₂(μ₄-PPh)₆(CO)₁₂] are shown in Figure 2.41. No evidence for hydride containing clusters was obtained.
Figure 2.41 Variable temperature $^1$H n.m.r. spectra of the phenyl region of the complex $\text{[Os}_6(\mu_2\text{-PPh})_2(\mu_4\text{-PPh})_2\text{(CO)}_{12}]$. 
2.5 Conclusion

[Ru₃(CO)₁₂] reacts with phenylphosphine under mild conditions to afford a range of trinuclear products consisting of two or three phosphine containing ligands. [Ru₃(µ-H)₂(µ-PPhH)₂(CO)₉] was identified spectroscopically by comparison with the reported data for the known complexes [Ru₃(µ-H)₂(µ-PPh₂)₂(CO)₉] and [Os₃(µ-H)₂(µ-PBu₂)₂(CO)₉]. [Ru₃(µ-H)₂(µ-PPhH)₂(CO)₉] can exist as three geometrical isomers and the high-field region of the ¹H n.m.r. spectrum revealed that all three isomers were present in solution. A triruthenium cluster containing two phosphorus bound ligands but with vastly different spectroscopic properties to [Ru₃(µ-H)₂(µ-PPhH)₂(CO)₉] was also isolated. A single-crystal X-ray structure determination showed this cluster to be [Ru₃(µ-H)₂(µ-PPh)(PPh₂)(CO)₈]. Finally, [Ru₃(µ-H)(µ-PPhH)₃(CO)₉] was also obtained as a minor crystalline product, initially identified from its similar spectroscopic properties to [Ru₃(µ-H)(µ-PPh₂)₃(CO)₉]. The single-crystal X-ray structure revealed a similar Ru₃P₃ core geometry to [Os₃(µ-H)(µ-PPh₂)₃(CO)₉] with three bridging phosphido ligands. This cluster should exist in six possible isomeric forms which are only interconvertible by deprotonation, inversion, reprotonation or M-P bond cleavage. However, it appears that one isomer is favoured substantially over the others.

A similar reaction of [Ru₃(CO)₁₂] with cyclohexylphosphine afforded identical products. Both [Ru₃(µ-H)₂(µ-PCyH)₂(CO)₉] (three isomers) and [Ru₃(µ-H)₂(µ-PCy)(PCyH₂)(CO)₉] were identified spectroscopically whilst [Ru₃(µ-H)(µ-PCyH)₃(CO)₉] displayed an i.r. spectrum identical to the phenylphosphido analogue but which existed as four of the six possible geometric isomers.

In the presence of CO gas a refluxing solution of [Ru₃(µ-H)₂(µ-PCy)(PCyH₂)(CO)₉] in n-decane loses two molecules of hydrogen and gains one molecule of CO resulting in the formation of [Ru₃(µ-PCy)₂(CO)₉].

Attempted hydrogenation of [Ru₃(µ-PPh)₂(CO)₉] in refluxing hydrocarbon solvent resulted in the formation of the high nuclearity clusters [Ru₆(µ-H)₂(µ₄-PPh)₂(µ₄-PPh)₂(CO)₁₂] and [Ru₆(µ₃-PPh)₂(µ₄-PPh)₂(CO)₁₂]. These clusters were identified by their single-crystal X-ray structures whilst a third minor product expected to be [Ru₆(µ₄-PPh)₆(CO)₁₃] remained unidentified crystallographically.

¹H n.m.r. studies on [Ru₆(µ-H)₂(µ₄-PPh)₂(µ₄-PPh)₂(CO)₁₂] and [Ru₆(µ₃-PPh)₂(µ₄-PPh)₂(CO)₁₂] indicated that there is a significant steric barrier to rotation about the P-
C bond of the $\mu_4$-PPh capping phosphinidene ligands. The low-temperature $^1$H n.m.r. spectrum of both these clusters revealed the presence of non-equivalent ortho and meta hydrogen atoms of the phenyl rings belonging to the $\mu_4$-PPh ligands whilst the ortho and meta hydrogen atoms belonging to the phenyl rings of the $\mu_4$-PPh ligands remained magnetically equivalent on the n.m.r. time-scale at low temperature.
2.6 Experimental

2.6.1 Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with phenylphosphine

To a refluxing solution of $[\text{Ru}_3(\text{CO})_{12}]$ (0.4038 g, 0.63 mmol) in n-hexane (80 cm$^3$) was added phenylphosphine (0.278 cm$^3$, 2.5 mmol) and the mixture heated under reflux for 95 minutes during which time the reaction mixture changed colour from deep orange to pale yellow. After cooling to room temperature the solvent was removed under reduced pressure to leave as deep yellow oily residue. Separation by chromatography [t.l.c., SiO$_2$; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (90:10 v/v)] gave three well separated bands.

The fastest moving band was identified spectroscopically as a mixture of $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{10}]$ and $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{9}]$ (0.106 g, 25%). Thermolysis of this mixture in refluxing heptane afforded a single product of the nonacarbonyl phosphinidene cluster $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{9}]$.

The next band to elute was extracted into dichloromethane and removal of the solvent under vacuum left a yellow oil. Crystallisation from n-hexane afforded red-orange crystals (0.013 g, 3%) identified as $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{9}]$ by comparison of its i.r. spectrum with those of the known clusters $[\text{M}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{9}]$ (M = Fe, Ru, Os).

The slowest band was identified as a mixture of two clusters one containing two phosphorus nuclei, the other three. Crystallisation of the oil from n-hexane afforded deep orange crystals of the trinuclear cluster $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{9}]$ (0.009 g, 3%) identified by its X-ray crystal structure, and the similarity of its i.r. spectrum to that of the known compound $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{CO})_{9}]$. MS (EI): m/e = 826 (M$^+$) based on $^{103}\text{Ru}$. Fragmentation pattern 826 - x(28) where x = 1-7. Attempted crystallisation of the remaining oil gave a mixture of orange and yellow crystals. Yellow crystals suitable for single-crystal X-ray determination were taken and the structure determined. The minor yellow species was identified as $[\text{Ru}_3(\mu^3\text{-H})(\mu^3\text{-PPh})(\text{PPhH})(\text{CO})_{9}]$ (0.007 g, 1.5%).

2.6.2 Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclohexylphosphine

To a solution of $[\text{Ru}_3(\text{CO})_{12}]$ (0.174 g, 0.27 mmol) in n-hexane (100 cm$^3$) was added cyclohexylphosphine (0.11 cm$^3$, 0.1 mmol). The reaction mixture was heated
under reflux for 95 minutes during which time there was a colour change from deep orange to pale yellow. The solvent was removed under reduced pressure and the oily residue remaining was chromatographed [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (90:5 v/v)] to afford three major bands.

The first band eluted was crystallised from n-hexane (-20 °C overnight) and afforded red crystals of $[\text{Ru}_3(\mu-H)_2(\mu-\text{PCy})_2(\text{CO})_8]$ (0.0098 g). [Found: C, 31.37; H, 3.22. $C_{20}H_{26}O_8P_2Ru_3$ requires C, 31.62; H, 3.42%]. MS (EI); m/e = 757 (M⁺) based on $^{101}\text{Ru}$. Fragmentation pattern: 757 - x(28) where x = 1-8.

The next band eluted was extracted from the t.l.c. plates with dichloromethane and gave a yellow oil after removal of the solvent under vacuum. Crystallisation of the oil from n-hexane (-20 °C) afforded deep orange microcrystals of $[\text{Ru}_3(\mu-H)(\mu-\text{PCy})_3(\text{CO})_7]$ (0.007 g). This compound was characterised by its similar i.r. spectrum to that of the phenylphosphine analogue. [Found: C, 35.05; H, 4.41. $C_{23}H_{17}O_7P_3Ru_3$ requires C, 35.8; H, 4.41%]. MS (EI): m/e = 846 (M⁺) based on $^{101}\text{Ru}$. Fragmentation pattern: 846 - x(28) where x = 1-8.

The slowest moving band was crystallised from n-hexane (-20 °C several days) and gave deep red air stable crystals of $[\text{Ru}_3(\mu-H)(\mu-\text{PCy})_3(\text{PCyH}_2)(\text{CO})_9]$ (0.014 g). [Found: C, 31.68; H, 3.35. $C_{21}H_{28}O_9P_3Ru_3$ requires C, 32.02; H, 3.30%]. Further crystallisation of the remaining residue afforded red-orange crystals of $[\text{Ru}_3(\mu-H)_2(\mu-\text{PCy})(\text{PCyH}_2)(\text{CO})_9]$ characterised by comparison of its spectroscopic properties with those of $[\text{Ru}_3(\mu-H)_2(\mu_3-\text{PPh})(\text{PPhH}_2)(\text{CO})_9]$ (0.008 g). [Found: C, 31.57; H, 3.52. $C_{20}H_{26}O_9P_3Ru_3$ requires C, 31.62; H, 3.42%]. MS (EI): m/e = 857 (M⁺) based on $^{101}\text{Ru}$. Fragmentation pattern: 857 - x(28) where x = 1-8.

### 2.6.3 Pyrolysis of $[\text{Ru}_3(\mu-H)_2(\mu_3-\text{PCy})(\text{PCyH}_2)(\text{CO})_9]$ 

A solution of $[\text{Ru}_3(\mu-H)_2(\mu_3-\text{PCy})(\text{PCyH}_2)(\text{CO})_9]$ (0.003 g, 0.0035 mmol) in n-decane (10 cm³) was heated at reflux whilst bubbling carbon monoxide gas. The i.r. spectrum was monitored and after 300 minutes of heating there was observed to be no further change in the i.r. spectrum. The reaction mixture was allowed to cool and the solvent removed under reduced pressure. The brown residue remaining was chromatographed [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, 3:1 v/v)] to give one major yellow band identified spectroscopically as the bisphosphinidene cluster $[\text{Ru}_3(\mu_2-\text{CyH})_2(\text{CO})_8]$ (0.006 g).
2.6.4 Preparation of $[\text{Ru}_3(\mu_3-P\text{Ph})_2(\text{CO})_9]$  

To a solution of $[\text{Ru}_3(\text{CO})_{12}]$ (0.269 g, 0.4 mmol) in n-decane (60 cm³) was added phenylphosphine (0.15 cm³, 1.36 mmol). The solution was heated at reflux for 70 minutes during which time the colour changed from deep orange to brown. The i.r. spectrum indicated that all the starting material had been consumed. The reaction solution was allowed to cool to room temperature and the solvent removed under high vacuum. The remaining residue was separated by chromatography [t.l.c., SiO₂; eluent: petroleum ether (b.p. 30-40 °C)/dichloromethane, 6:1 v/v] to give one fast moving yellow band. Extraction of the band into dichloromethane and removal of the solvent left a yellow oil. Crystallisation from n-hexane (-20 °C) afforded pale yellow air-stable crystals (0.047 g, 15%) of the title cluster. The product was characterised and its purity assessed by comparison of its spectroscopic data with that already published.

2.6.5 Reaction of $[\text{Ru}_3(\mu_3-H)_2(\mu_3-P\text{Ph})(\text{CO})_9]$ with phenylphosphine  

To a refluxing solution of $[\text{Ru}_3(\mu_3-H)_2(\mu_3-P\text{Ph})(\text{CO})_9]$ (0.023 g, 0.035 mmol) in n-decane (20 cm³) was added phenylphosphine (0.007 cm³, 0.035 mmol). Carbon monoxide gas was bubbled through the solution and the reaction mixture was heated at reflux for 90 minutes with the purge of carbon monoxide gas being maintained. The reaction was monitored by i.r. spectroscopy and the appearance of bands due to $[\text{Ru}_3(\mu_3-P\text{Ph})_2(\text{CO})_9]$ indicated that reaction was almost complete. Removal of the solvent under reduced pressure yielded a deep brown residue which was separated by chromatography [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (6:1 v/v)]. After several elutions a single major band was observed, identified spectroscopically as $[\text{Ru}_3(\mu_3-P\text{Ph})_2(\text{CO})_9]$ (0.0132 g, 48%).

2.6.6 Attempted reaction of $[\text{Ru}_3(\mu_3-H)_2(\mu_3-P\text{Ph})_2(\text{CO})_9]$ with $\text{H}_2$ gas  

A solution of $[\text{Ru}_3(\mu_3-P\text{Ph})_2(\text{CO})_9]$ (0.0132 g, 0.017 mmol) in n-decane (20 cm³) was heated to reflux whilst purging with hydrogen gas. The reaction was monitored by i.r. spectroscopy and after heating at reflux for 150 minutes only a small quantity of starting material remained. The dark brown reaction mixture was allowed to cool to room temperature and the solvent removed under reduced pressure. The deep brown residue remaining was chromatographed [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (3:1 v/v)] to give three well separated bands.
The fastest moving band, yellow in colour, was extracted into dichloromethane and removal of the solvent under reduced pressure followed by crystallisation from n-hexane by slow evaporation and drying under vacuum for several hours afforded deep orange-red air-stable crystals of \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(CO)_{12}]\) (0.003 g). Crystals suitable for single crystal X-ray determination were grown and the structure confirmed the hexanuclear nature of the product. [Found: C, 30.74; H, 1.65. \(C_{36}H_{22}O_{12}P_4\text{Ru}_6\) requires C, 31.42; H, 1.60%]. MS (FAB): \(m/e = 1374\) (M\(^{+}\)) based on \(^{101}\text{Ru}\). Fragmentation pattern: 1374 - x(28) where x = 1 - 12.

The second band eluted afforded deep brown air-stable crystals after crystallisation from n-hexane by slow evaporation at room temperature. Crystals suitable for structure determination were obtained and the product was identified as \([\text{Ru}_4(\mu_3-PPh)_2(\mu_4-PPh)_2(CO)_{12}]\) (0.005 g). [Found: C, 31.44; H, 1.39. \(C_{36}H_{22}O_{12}P_4\text{Ru}_6\) requires C, 21.44; H, 1.46%].

The slowest band afforded dark brown crystals after crystallisation from n-hexane. Unfortunately single crystals could not be grown. Positive identification of the product could not therefore be made.

### 2.6.7 Hydrogenation of \([\text{Ru}_3(\mu_3-PPh)_2(\mu_4-PPh)_2(CO)_{12}]\)

\([\text{Ru}_4(\mu_3-PPh)_2(\mu_4-PPh)_2(CO)_{12}]\) (0.0112 g, 0.008 mmol) was dissolved in mesitylene (20 cm\(^3\)) and heated to reflux whilst purging with hydrogen gas. The reaction was monitored by i.r. spectroscopy and the reaction was stopped as soon as the i.r. spectrum indicated that all the starting material had disappeared. The solution was refluxed for a total of 45 minutes during which time the purge of hydrogen gas was maintained. The deep brown reaction mixture was allowed to cool and the solvent was then removed under high vacuum. The oily residue remaining was chromatographed [t.l.c., SiO\(_2\); eluent: petroleum ether (b.p. 30-40 °C)/dichloromethane, (3:1 v/v)] to give two well separated bands.

The fastest moving band was identified spectroscopically to be the same as the product from the previous reaction \([\text{Ru}_6(\mu-H)_2(\mu_3-PPh)_2(\mu_4-PPh)_2(CO)_{12}]\) (0.0064 g, 57%). The slower moving band was identified as starting material (0.0025 g).
2.6.8 Thermolysis of [Ru$_3$(μ-PPh)$_3$(CO)$_9$] in n-decane

A solution of the title cluster (0.016 g, 0.02 mmol) in n-decane (20 cm$^3$) was heated under reflux for 150 minutes during which time the solution turned from deep yellow to dark brown. The solvent was removed under reduced pressure and the product separated chromatographically [t.l.c., SiO$_2$; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (3:1 v/v)] to yield three well separated bands. These bands were each identified spectroscopically and shown to be the same as the reaction products from 2.6.6.

2.6.9 Thermal Treatment of [Ru$_3$(μ-PPh)$_3$(CO)$_9$] with carbon monoxide gas

A sample of the title compound (ca. 0.005 g) was heated in n-decane (10 cm$^3$) to reflux whilst purging with carbon monoxide gas. After heating at reflux for several hours there was no observed change in the i.r. spectrum and the reaction mixture was still yellow in colour. Chromatographic work up as before afforded the starting material apparently in quantitative yield.

2.6.10 Thermolysis of [Os$_3$(μ-PPh)$_3$(CO)$_9$]

A similar procedure was followed with [Os$_3$(μ-PPh)$_3$(CO)$_9$] (0.0122 g, 0.012 mmol) in tetrahydronaphthalene (10 cm$^3$) for 180 minutes. A chromatographic procedure similar to that above afforded a single major brown band. Extraction of this band into dichloromethane and removal of the solvent and subsequent crystallisation by slow evaporation from an n-hexane solution afforded deep brown air stable crystals of [Os$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$_2$(CO)$_{12}$] (0.003 g). [Found: C, 19.26; H, 0.69. C$_{26}$H$_{20}$O$_{12}$Os$_6$P$_4$ requires C, 19.99; H, 1.04%].

-123-
2.7 Spectroscopic Data for the Complexes

Table 2.5 $^1$H n.m.r. data for phosphido and phosphinidene complexes of ruthenium

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift ($\delta$)$^a$</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
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<td>$^{[\text{Ru}<em>3(\mu-\text{H})(\mu-\text{PPH})(\text{CO})</em>{10}]}^b$</td>
<td>6.70 (dd)</td>
<td>PPh$_2$ (2H)</td>
<td>$^1$J(PPH)=390.0, $^3$J(HH)=3.1</td>
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<tr>
<td></td>
<td>7.40 (m)</td>
<td>phenyl (5H)</td>
<td>$^2$J(PPH)=28.1, $^3$J(HH)=3.1</td>
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<td></td>
<td>-16.62 (dd)</td>
<td>Ru-H-Ru (1H)</td>
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</tr>
<tr>
<td>$^{[\text{Ru}_3(\mu-\text{H})_2(\mu-\text{PPH})_2(\text{CO})_8]}^b$</td>
<td>6.64 (dm)</td>
<td>PPh$_2$ (2H)</td>
<td>$^1$J(PPH)=362.0</td>
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<tr>
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<td>7.40 (m)</td>
<td>phenyl (10H)</td>
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<td>-17.05 (tdd)$^c$</td>
<td>Ru-H-Ru (1H)</td>
<td>$^2$J(PPH)=24.5, $^3$J(HH)=3.03, $^2$J(HH)=2.51</td>
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<td>-16.78 (tm)$^c$</td>
<td>Ru-H-Ru (1H)</td>
<td>$^2$J(PPH)=24.8</td>
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<td>-17.37 (tm)$^c$</td>
<td>Ru-H-Ru (2H)</td>
<td>$^2$J(PPH)=22.4</td>
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<tr>
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<td>-17.58 (tdd)$^c$</td>
<td>Ru-H-Ru (1H)</td>
<td>$^2$J(PPH)=22.1</td>
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<td>$^{[\text{Ru}_3(\mu-\text{H})(\mu-\text{PPH})_3(\text{CO})_7]}^b$</td>
<td>4.98 (dm)</td>
<td>PPh$_2$ (1H)</td>
<td>$^1$J(PPH)=361.0</td>
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<tr>
<td></td>
<td>6.43 (d, broad)</td>
<td>PPh$_2$ (1H)</td>
<td>$^1$J(PPH)=350.0</td>
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<td>8.05 (dm)</td>
<td>PPh$_2$ (1H)</td>
<td>$^1$J(PPH)=350.1</td>
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<td>7.3-7.66 (m)</td>
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<td>-17.70 (qm)</td>
<td>Ru-H-Ru (1H)</td>
<td>$^2$J(PPH)=18.0</td>
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<tr>
<td>$^{[\text{Ru}_3(\mu-\text{H})_2(\mu_3-\text{PPH})(\text{PPhH}_2)(\text{CO})_8]}^b$</td>
<td>5.86 (dq)</td>
<td>PPh$_2$ (2H)</td>
<td>$^1$J(PPH)=347.6, $^3$J(PPH)=2.0, $^3$J(HH)=2.0</td>
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<td>7.45 (m)</td>
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<td>8.00 (ddd)</td>
<td>phenyl</td>
<td>$^3$J(PPH)=15.1, $^3$J(HH)=9.3, $^4$J(HH)=1.6</td>
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<td>-19.01 (tt)</td>
<td>Ru-H-Ru (1H)</td>
<td>$^2$J(PPH)=16.2, $^3$J(HH)=2.0</td>
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Table 2.5 continues overleaf
Table 2.5 continued...

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<tr>
<th>Compound</th>
<th>Chemical shift (δ)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
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<tbody>
<tr>
<td>[Ru&lt;sub&gt;3&lt;/sub&gt;(μ-H)&lt;sub&gt;2&lt;/sub&gt;(μ-PCyH)&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;8&lt;/sub&gt;]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.52 (dddd)</td>
<td>PCy&lt;sub&gt;H&lt;/sub&gt; (2H)</td>
<td>J(μ-H)=334.5, J(μ-H)=7.2, J(hh)=2.9</td>
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<td>1.3-2.1 (m)</td>
<td>cyclohexyl (22H)</td>
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<td>-17.57 (tdd)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Ru-H-Ru (2H)</td>
<td>2J(μ-H)=23.4, 3J(μ-H)=3.6, 3J(HH)=1.7</td>
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<tr>
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<td>-17.38 (tm)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Ru-H-Ru (2H)</td>
<td>2J(μ-H)=24.2</td>
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<tr>
<td></td>
<td>-17.92 (tdd)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Ru-H-Ru (2H)</td>
<td>2J(μ-H)=22.0</td>
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<td>-17.78 (tm)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Ru-H-Ru (2H)</td>
<td>2J(μ-H)=22.3</td>
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<tr>
<td>[Ru&lt;sub&gt;3&lt;/sub&gt;(μ-H)(μ-PCyH)&lt;sub&gt;3&lt;/sub&gt;(CO)&lt;sub&gt;7&lt;/sub&gt;]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-18.50 (qm)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Ru-H-Ru (1H)</td>
<td>2J(μ-H)=17.9</td>
</tr>
<tr>
<td></td>
<td>-18.80 (qm)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Ru-H-Ru (1H)</td>
<td>2J(μ-H)=17.1</td>
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<td>-19.20 (qm)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Ru-H-Ru (1H)</td>
<td>2J(μ-H)=16.8</td>
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<td>Ru-H-Ru (1H)</td>
<td>2J(μ-H)=16.7</td>
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<td>1.2-2.2 (m)</td>
<td>cyclohexyl (33H)</td>
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<tr>
<td></td>
<td>4.3-7.5 (dm)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>PCy&lt;sub&gt;H&lt;/sub&gt; (3H)</td>
<td></td>
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<tr>
<td>[Ru&lt;sub&gt;3&lt;/sub&gt;(μ-H)&lt;sub&gt;2&lt;/sub&gt;(μ&lt;sub&gt;2&lt;/sub&gt;-PCy)(PCyH&lt;sub&gt;2&lt;/sub&gt;)(CO)&lt;sub&gt;8&lt;/sub&gt;]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.56 (ddq)</td>
<td>PCy&lt;sub&gt;H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt; (2H)</td>
<td>1J(μ-H)=337.0, 3J(μ-H)=5.8, J(μ-H)=1.9</td>
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<td>1.2-2.0 (m)</td>
<td>cyclohexyl (22H)</td>
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</tr>
<tr>
<td></td>
<td>-19.37 (t)</td>
<td>Ru-H-Ru (2H)</td>
<td>2J(μ-H)=15.4, 3J(HH)=3.4</td>
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<tr>
<td>[Ru&lt;sub&gt;3&lt;/sub&gt;(μ-H)(μ-PCyH)(PCyH&lt;sub&gt;2&lt;/sub&gt;)(CO)&lt;sub&gt;9&lt;/sub&gt;]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.40 (dm)</td>
<td>PCy&lt;sub&gt;H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt; (2H)</td>
<td>1J(μ-H)=340.0</td>
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<tr>
<td></td>
<td>5.65 (ddd)</td>
<td>PCy&lt;sub&gt;H&lt;/sub&gt; (1H)</td>
<td>1J(μ-H)=362.0, 3J(μ-H)=8.9, 3J(HH)=2.8</td>
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<tr>
<td></td>
<td>1.3-2.2 (m)</td>
<td>cyclohexyl (22H)</td>
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<tr>
<td></td>
<td>-16.82 (ddd)</td>
<td>Ru-H-Ru (1H)</td>
<td>2J(μ-H)=25.2, 3J(HH)=3.2, 4J(μ-H)=1.2</td>
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Table 2.5 continues overleaf...
Table 2.5 continued .....  

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (δ)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
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<tbody>
<tr>
<td>$[\text{Ru}_6(\mu-\text{H})_2(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})]</em>{12}$&lt;sup&gt;b,f&lt;/sup&gt;</td>
<td>8.14 (ddd)</td>
<td>ortho Ph (4H)</td>
<td>$^3J(\text{PH})=11.2$, $^3J(\text{HH})=6.4$, $^4J(\text{HH})=1.2$</td>
</tr>
<tr>
<td></td>
<td>7.96 (s,broad)</td>
<td>ortho Ph (4H)</td>
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</tr>
<tr>
<td></td>
<td>7.56 (m)</td>
<td>phenyl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.38 (m)</td>
<td>phenyl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-22.60 (broad)</td>
<td>Ru-H-Ru (2H)</td>
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</tr>
<tr>
<td>$[\text{Ru}_6(\mu-H)_2(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})]</em>{12}$&lt;sup&gt;b,g&lt;/sup&gt;</td>
<td>8.32 (broad)</td>
<td>ortho Ph (2H)</td>
<td>$^3J(\text{PH})=11.7$, $^3J(\text{HH})=6.4$, $^4J(\text{HH})=1.3$</td>
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<td>8.06 (ddd)</td>
<td>ortho Ph (4H)</td>
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<td>7.48-7.6 (m)</td>
<td>phenyl (10H)</td>
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<td>7.38 (t)</td>
<td>meta Ph (2H)</td>
<td>$^3J(\text{HH})=5.9$</td>
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<td>7.34 (ddd, broad)</td>
<td>ortho Ph (2H)</td>
<td>$^3J(\text{PH})=13.3$, $^3J(\text{HH})=6.4$</td>
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<td>-22.60 (broad)</td>
<td>Ru-H-Ru (2H)</td>
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<tr>
<td>$[\text{Ru}_6(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})]</em>{12}$&lt;sup&gt;b,f&lt;/sup&gt;</td>
<td>8.02 (ddd)</td>
<td>ortho Ph (4H)</td>
<td>$^3J(\text{PH})=13.7$, $^3J(\text{HH})=6.8$, $^4J(\text{HH})=1.2$</td>
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<td>7.74 (broad)</td>
<td>ortho Ph (4H)</td>
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<td>7.56 (m)</td>
<td>phenyl (6H)</td>
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<td>7.44 (m)</td>
<td>phenyl (6H)</td>
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<td>$[\text{Ru}_6(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})]</em>{12}$&lt;sup&gt;b,g&lt;/sup&gt;</td>
<td>8.46 (broad)</td>
<td>ortho Ph (2H)</td>
<td>$^3J(\text{PH})=13.7$, $^3J(\text{HH})=6.9$</td>
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<td>ortho Ph (4H)</td>
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<td>7.52 (m)</td>
<td>phenyl (6H)</td>
<td>$^3J(\text{HH})=7.1$</td>
</tr>
<tr>
<td></td>
<td>7.58 (t)</td>
<td>meta Ph (2H)</td>
<td>$^3J(\text{HH})=7.1$</td>
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<td>7.43 (t)</td>
<td>para Ph (2H)</td>
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Table 2.5 continues overleaf .........
Table 25 $^1$H n.m.r. data for phosphido and phosphinidene complexes of ruthenium

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<tr>
<th>Compound</th>
<th>Chemical shift (δ)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
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<tr>
<td>$[\text{Ru}_6(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})</em>{12}]^{b,g}$</td>
<td>7.32 (t)</td>
<td>meta Ph (2H)</td>
<td>$^3J(\text{HH})=7.6$</td>
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<td>6.90 (broad)</td>
<td>ortho Ph (2H)</td>
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<td>$[\text{Os}_6(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})</em>{12}]^{b}$</td>
<td>8.26 (broad)</td>
<td>ortho Ph (2H)</td>
<td>$^3J(\text{PH})=14.1$, $^3J(\text{HH})=7.8$, $^4J(\text{HH})=1.8$</td>
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<tr>
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<td>7.98 (ddd, broad)</td>
<td>meta, para (6H)</td>
<td></td>
</tr>
<tr>
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<td>7.58 (m)</td>
<td>meta Ph (2H)</td>
<td>$^3J(\text{HH})=7.1$</td>
</tr>
<tr>
<td></td>
<td>7.56 (t)</td>
<td>meta Ph (2H)</td>
<td>$^3J(\text{HH})=7.1$</td>
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<tr>
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<td>7.40 (t)</td>
<td>meta Ph (2H)</td>
<td>$^3J(\text{HH})=7.0$</td>
</tr>
<tr>
<td></td>
<td>7.38 (t)</td>
<td>para Ph (2H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.96 (broad)</td>
<td>ortho Ph (2H)</td>
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<tr>
<td>$[\text{Os}_6(\mu_3\text{-PPh})_2(\mu_4\text{-PPh})<em>2(\text{CO})</em>{12}]^{b}$</td>
<td>7.74 (ddd)</td>
<td>ortho Ph (4H)</td>
<td>$^3J(\text{PH})=14.1$, $^3J(\text{HH})=8.6$, $^4J(\text{HH})=2.0$</td>
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<td>7.40 (v.broad)</td>
<td>ortho Ph (4H)</td>
<td></td>
</tr>
<tr>
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<td>7.28 (m)</td>
<td>phenyl (6H)</td>
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</tr>
<tr>
<td></td>
<td>7.16 (t, broad)</td>
<td>meta Ph (4H)</td>
<td>$^3J(\text{HH})=7.1$</td>
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<td>7.08 (t)</td>
<td>para Ph (2H)</td>
<td>$^3J(\text{HH})=7.0$</td>
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</table>

a: Spectra recorded in CDCl$_3$ and referenced internally to the solvent.
b: Spectra recorded at 400 MHz.
c: Four hydride resonances indicate the presence of four isomers of $[\text{Ru}_3(\mu-H)_2(\mu-\text{PPhH})_2(\text{CO})_8]$.
d: Four hydride resonances indicate the presence of four isomers of $[\text{Ru}_3(\mu-H)(\mu-\text{PPhH})_3(\text{CO})_7]$.
e: Overlapping PCy$_3$ signals lead to a complicated spectrum.
f: Spectra recorded in CD$_2$Cl$_2$ at +35 °C.
g: Spectra recorded in CD$_2$Cl$_2$ at -80 °C.
h: Spectra recorded in CDCl$_3$ at -55 °C.
Table 2.6 Infrared Data for the complexes

<table>
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<th>Compound</th>
<th>v (CO) / cm(^{-1})</th>
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</thead>
<tbody>
<tr>
<td>[Ru(<em>3)((\mu)-H)((\mu)-PPh)(CO)(</em>{10}))(^a)]</td>
<td>2098 m, 2058 s, 2048 s, 2025 s, 2013 s, 1999 m, 1989 m</td>
</tr>
<tr>
<td>[Ru(_3)((\mu)-H)(_2)((\mu)_3-PPh)(CO)(_9))(^a)]</td>
<td>2103 m, 2073 s, 2048 s, 2043 m, 2029 w, 2016 s, 1998 m, 1986 w</td>
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<tr>
<td>[Ru(_3)((\mu)-H)(_2)((\mu)-PPhH(_2))(CO)(_8))(^a)]</td>
<td>2080 m, 2046 s, 2035 s, 2014 s, 1991 m, 1983 w</td>
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<tr>
<td>[Ru(_3)((\mu)-H)((\mu)-PPhH(_3))(CO)(_7))(^a)]</td>
<td>2016 m, 2027 s, 2023 s, 2001 w, 1973 m</td>
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<tr>
<td>[Ru(_3)((\mu)-H)(_2)((\mu)_3-PPh)(PPhH(_2))(CO)(_8))(^a)]</td>
<td>2075 w, 2046 m, 2039 s, 2005 s, 1998 m, 1991 m, 1975 w</td>
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<tr>
<td>[Ru(_3)((\mu)-H)((\mu)-PCy(_3))(CO)(_7))(^a)]</td>
<td>2055 m, 2014 s, 1992 w, 1962 m</td>
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<tr>
<td>[Ru(_3)((\mu)-H)(_2)((\mu)-PCy(_3))(CO)(_8))(^a)]</td>
<td>2071 w, 2042 s, 2035 s, 2003 s, 1989 m, 1981 w</td>
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<tr>
<td>[Ru(_3)((\mu)-H)(_2)((\mu)_3-PCy)(PCy(_2))(CO)(_8))(^a)]</td>
<td>2069 w, 2034 s, 2031 s, 1993 s, 1991 m, 1979 m, 1966 w</td>
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<tr>
<td>[Ru(_6)((\mu)-H)(_2)((\mu)_3-PPh(_2))((\mu)_4-PPh(<em>2))(CO)(</em>{12}))(^a)]</td>
<td>2060 w, 2033 s, 2025 m, 2010 s, 1999 w, 1991 w, 1968 w, 1961 w</td>
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Table 2.6 continue overleaf .........
Table 2.6 continued.....

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$ (CO) / cm$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>[Ru$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$<em>2$(CO)$</em>{12}$]$^a$</td>
<td>2050 w, 2032 s, 2027 sh, 2010 w, 1994 w, 1988 w</td>
</tr>
<tr>
<td>[Os$_6$(μ$_3$-PPh)$_2$(μ$_4$-PPh)$<em>2$(CO)$</em>{12}$]$^a$</td>
<td>2057 w, 2027 s, 2019 m, 2007 s, 1998 w, 1982 w, 1963 w, 1951 w</td>
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<tr>
<td>[Ru$_3$(μ$_3$-PPh)$_2$(CO)$_9$]$^a$</td>
<td>2060 s, 2037 s, 2017 s, 2003 m, 1993 w, 1974 w</td>
</tr>
</tbody>
</table>

$a$: Spectra recorded in n-hexane
Chapter 3

Synthesis of Phosphine and Phosphido Complexes of Iridium(III)
3 Synthesis of Phosphine and Phosphido Complexes of Iridium(III)

3.1 Introduction

Terminal dihalophosphido complexes, LnM=PX₂ were among the first known examples of phosphido complexes. Ebsworth found that PF₂X (X = Cl, Br, I) reacted with trans-[PtHX(PEt₃)₂] to afford a binuclear complex in which two platinum atoms were bridged by PF₂. Although the mechanism was not clear he proposed that the initial step involved oxidative addition of PF₂X to the platinum(II) centre, leading to the formation of a complex containing Pt-PF₂ which reacted further (Figure 3.1).

![Figure 3.1](image)

The reaction of PF₂X with trans-[Ir(CO)X(PEt₃)₂] (X = Cl, Br, I) proceeds initially through coordination of PF₂X to the metal, and then by oxidative addition of PX to iridium, forming a derivative of iridium(III) with PF₂ bound to the metal. X-ray structural evidence for the pyramidal nature of the M-PF₂ group was not available but evidence from the n.m.r. parameters and from its chemical reactions left no doubt about the presence of a chemically active lone-pair of electrons. Before the successful syntheses of these dihalophosphido complexes three coordinate phosphorus in which one substituent was a transition-metal were relatively rare. Furthermore, their potential for the preparation of heterometallic complexes was recognised. Reaction of trans-[Ir(CO)Cl(PEt₃)₂] and PCl₃ gave trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂)]. The single-crystal X-
ray structure of this dichlorophosphido complex confirms the pyramidal nature of the phosphido ligand (Figure 3.2).

![Figure 3.2](image)

Typical methods for the synthesis of metal complexes of PR₂ ligands include nucleophilic attack by metal carbonylate anions on halophosphines,\(^{37,42}\) transmetallations of metal halides with metallated phosphines,\(^{41}\) bisphosphine cleavage with metal-metal bonded dinuclear species,\(^{44,43}\) oxidative addition of PX₃ to low valent metal substrates (Figure 3.3)\(^{7,10,46-48}\) and 1,2 elimination of hydrogen chloride from the complex [Cp(CO)₂MCl(PR₂H)]\(^{29}\) or 1,2 elimination of hydrogen chloride or dimethylamine from the complex [Cp(CO)₂M(H)(PR₂X)] (M = Mo, W; X = Cl, Me₂N).\(^{53}\) Each of these synthetic routes has been exploited but only the latter, oxidative addition, has been used for the synthesis of terminal phosphido complexes of the late transition-metal centres.

A synthetic route to cationic phosphine complexes,\(^{11}\) from which the corresponding terminal phosphido complexes may be obtained by deprotonation with a suitable base, has been developed by Roper. Substitution of a labile triphenylphosphine ligand in [OsHCl(CO)(PPh₃)₃] for the less sterically demanding PPhH₂ gave a high yield synthetic route to [OsHCl(PPhH₂)(CO)(PPh₃)₂]. The cationic complexes were derived from this neutral complex by replacement of the hydride ligand by MeCN on reaction with perchloric acid in the presence of acetonitrile. The precursor to the phosphido complex was obtained by subsequent replacement of this acetonitrile ligand for carbon monoxide. Roper assigned this complex as having a \textit{cis} dicarbonyl geometry (Figure 3.4). Treatment of this cationic complexes with DBU rapidly afforded the neutral terminal phosphido complex in high yield.
The reactions of platinum metals and their derivatives with tertiary phosphines have been extensively studied. The coordination chemistry of PH3 toward the platinum metals has received little attention. The discovery that phosphine forms stable complexes with transition metals214 led to the isolation and characterisation of many new species including; [V(Cp)(CO)3(PH3)]210, [Cr(CO)8x(PH3)x] (X = 1,2,3,4), [Mo(CO)6x(PH3)x] (x = 1,2,3), [Fe(CO)4(PH3)], [Ni(CO)3(PH3)], [Ni(PF3)2(PH3)], Ni(PF3)2(PH3)] and many more. With [PtClH(PEt3)2], PH3 reacted reversibly by displacement of chloride ion forming a cationic complex that was stable only at low temperature in solution214 (Equation 3.1). In contrast, [Ir(dppe)2]+ (dppe = 1,2 bis(diphenylphosphine)ethane) reacted with PH348 in an open vessel by coordination to give a cationic complex of five coordinate iridium(I), but in a sealed tube oxidative addition led to the formation of a PH3 complex of iridium(III) (Scheme 3.1).

\[
\begin{align*}
[\text{PtClH(PEt}_3\text{)}_2] + \text{PH}_3 & \quad 193 \text{ K} \\
& \quad 220 \text{ K} \rightarrow [\text{PtH(PEt}_3\text{)}_2(\text{PH}_3)]^+\text{Cl}^- \\
\end{align*}
\]

Equation 3.1
Ebsworth has described the reactions of trans-[Ir(CO)X(PEt₃)₂] (X = Br, Cl) with \( \text{PH}_3 \) and discovered them to be solvent dependent.\(^{10}\) The reaction in toluene\(^4\) led to

\[
\begin{align*}
[\text{Ir(dppe)}_2]^+ + \text{PH}_3 & \quad \xrightarrow{\text{open vessel}} \quad [\text{Ir(dppe)}_2(\text{PH}_3)]^+ \\
\text{closed vessel} & \quad \xrightarrow{\text{closed vessel}} \quad [\text{IrH(dppe)}_2(\text{PH}_2)]^+
\end{align*}
\]

Scheme 3.1

oxidative addition and formation of trans-[Ir(CO)XH(PEt₃)₂(\text{PH}_2)]. No evidence for the formation of a five coordinate intermediate iridium(I) was observed. The reactivity pattern as well as the n.m.r. parameters for trans-[Ir(CO)XH(PEt₃)₂(\text{PH}_2)] indicated a pyramidal geometry for the phosphido ligand. The reaction of \( \text{PH}_3 \) with trans-

![Figure 3.5](image)

trans-[Ir(CO)Cl(PEt₃)₂] in dichloromethane\(^8\) takes a different course. The product of the initial reaction at 180K gives [Ir(CO)(PEt₃)₂(\text{PH}_3)₂]. Internal oxidative addition converts this
five coordinate intermediate into [Ir(CO)H(P(t-Bu)_3)(PPh_2)(PPh_3)]^+ (Figure 3.5). [Ir(CO)H(P(t-Bu)_3)(PPh_2)(PPh_3)]^+ can be deprotonated with NMe_3 to give [Ir(CO)H(P(t-Bu)_3)(PPh_2)]^+. [Ir(CO)H(P(t-Bu)_3)(PPh_2)(PPh_3)]^+ can also be protonated with excess HCl to afford [Ir(CO)H(P(t-Bu)_3)(PPh_3)]^{2+} (Figure 3.6).

The structural evidence available for complexes containing terminal phosphido ligands [M-PR_x]^{216,41} suggests two possible bonding modes and two possible geometries at the phosphido phosphorus atom.^{29,215} These forms are either pyramidal at phosphorus, containing a chemically and stereochemically active lone-pair of electrons and exhibiting a long M-P bond length and a small M-P-R angle (<114°), or planar with a short M-P bond and a large M-P-R angle (approximately 130°). The bonding scheme in Figure 3.7 distinguishes both forms; the ligand in the pyramidal form is a 1e donor (A) and in the planar form a 3e donor (B). Type (A) would be expected for coordinatively saturated complexes and is expected to exhibit nucleophilic character. The formal charges found in (B) would be expected to lead to electrophilic nature at the phosphido ligand.

Examples of both planar and pyramidal terminal phosphido complexes have been crystallographically determined.^{216} Roper solved the structure of the neutral terminal phenylphosphido complex [Os(CO)_2Cl(PPhH)(PPh_3)]^{29,3} and a compact Os-P-C bond angle of 113° and a longer than average Os-P bond length were consistent with the pyramidal nature of the phosphido ligand. Comparison of this crystal structure with that obtained by Schrock for the alkylidyne tungsten complex [W(CCMe_3)(PPhH)Cl_2(P(t-Bu)_3)],^{40} which contains a planar phenylphosphido ligand (W-P-C = 140°), shows the two distinct bonding modes for this ligand (Figure 3.8).

Recent dynamic ^{31}P{^1}H n.m.r. studies suggest that there is a small but significant energy barrier (6 KCal mol^{-1}) separating the planar and pyramidal phosphido
geometries. A variable-temperature $^{31}$P{^1}H n.m.r. study of [Hf($\eta^5$-C$_5$H$_5$)$_2$(P(C$_6$H$_5$)$_2$)$_2$] showed two broad resonances at -126 °C. These two resonances were observed to coalesce at -100 °C giving the estimated activation energy of 6 KCal mol$^{-1}$.
This chapter describes the high-yield syntheses of simple cationic phosphine complexes of iridium(III) containing acidic P-H bonds and the deprotonation of these complexes to afford the neutral terminal phosphido PR₂, PRH, and PH₂ ligands. These complexes are expected to be pyramidal in nature at the phosphido ligand and are expected to exhibit nucleophilic character. The reactions of these complexes will be discussed in the next chapter. N.m.r. evidence is provided which reinforces our belief that the geometry of the phosphido ligand is pyramidal.
3.2 Results and Discussion

3.2.1 Synthesis of Phosphine Complexes of Iridium(III)

Deprotonation of the appropriate neutral transition metal phosphine complex in
the presence of base is known to afford anionic phosphido complexes which can be
reacted immediately with an appropriate electrophile (Equation 3.2-3.4).\textsuperscript{17,18,75,45,217} Few
examples of neutral terminal phosphido complexes of the late transition metals are
known, but provided these complexes are coordinatively saturated they would be
expected to undergo the familiar reactions of pyramidal phosphido ligands.\textsuperscript{227,30,4,8}

\[
\begin{align*}
[W(CO)_5(PPh_2H)] + MeLi & \rightarrow [WIr(\mu-PPh_2)(CO)_5(PPh_3)_2] \quad \text{Equation 3.2} \\
[Fe(CO)_4(t-Bu_2PH)] + n-BuLi & \rightarrow [(t-Bu_2PH)(CO)_2Fe(\mu-t-Bu_2P)Rh(COD)] \quad \text{Equation 3.3} \\
[W(CO)_4(PPh_2H)_2] + MeLi & \rightarrow [(CO)_4W(\mu-PPh_2)_2IrH(COD)] \quad \text{Equation 3.4}
\end{align*}
\]

This chapter describes a high-yield synthesis of complexes with the general
formula \([\text{IrCl}_3(\text{PMe}_2\text{Ph})_3(\text{PHR}_1\text{R}_2)][\text{ClO}_4]\) (\(R^1 = R^2 = H, R^1 = H, R^2 = \text{Ph}, R^1 = R^2 = \text{Ph}, \text{1a-c). The synthetic route to 1a-c is outlined in Scheme 3.2. A chloride ligand trans to PMe}_2\text{Ph in mer-}[\text{IrCl}_3(\text{PMe}_2\text{Ph})_3] is much more labile than the two chloride ligands that are trans to each other. This increased rate of substitution of a ligand trans to a phosphine is reflected in the ground state properties of the molecule, such as the iridium-chlorine bond length\textsuperscript{221} and its corresponding stretching frequency in the i.r. spectrum. Treatment of mer-\([\text{IrCl}_3(\text{PMe}_2\text{Ph})_3]\) \textsuperscript{219,220} with silver perchlorate in an acetone/water mixture afforded the aqua complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{H}_2\text{O})][\text{ClO}_4]\).\textsuperscript{218} Substitution of the water ligand in this cationic complex for a phosphine donor ligand (PHR\textsuperscript{1}R\textsuperscript{2}) was complete in under 10 minutes. A weakly bound ligand, such as water, trans to a ligand exhibiting a strong trans labilising effect results in this rapid substitution.

These cationic terminal phosphine complexes were isolated as yellow air-stable
crystalline materials after crystallisation from dichloromethane/diethylether mixtures.
This preparative route may be extended to include other related cationic tetrakis-

phosphine complexes such as [IrCl₂(PMe₃)₃(PR'R²)][ClO₄] which can be isolated as crystalline materials. The double salt [IrCl₆(PMe₂)₄][IrCl₆(PMe₂)₄] isolated from the reaction of [IrCl₄]²⁻ with PMe₃ used to synthesise the mer-tris-phosphine complex was characterised by its familiar ¹H n.m.r. spectrum and by conductimetric studies. Conversion of the double salt into the mer-trichloride, [IrCl₃(PMe₃)₃], was readily accomplished by thermolysis of the deep-brick solid in a high boiling (>125 °C) hydrocarbon solvent. This complex readily afforded the corresponding phosphine substituted species [IrCl₂(PMe₃)₃(PR'R²H)][ClO₄] using a similar procedure to that already discussed.

### 3.2.2 Spectroscopic Characterisation of the Complexes

[IrCl₂(PMe₂Ph)₃(PR'R²)][ClO₄]

The geometries of the new cationic phosphine complexes are firmly established by ¹H n.m.r. and ³¹P{¹H} n.m.r. spectroscopy. Phosphorus-phosphorus coupling confirms
the relative geometry of the chlorine and phosphines in complexes 1a-c. The unique phosphine was seen to resonate at a much higher field strength than the remaining tertiary phosphines (Figure 3.9). For example, when R1 = R2 = H the phosphorus nucleus comes to resonance at δ = -120 compared with a chemical shift of -55 ppm for the other tertiary phosphines. The up-field shift of the phosphorus resonance can be interpreted in terms of the inductive effects of the substituents directly bonded to the nucleus. The successive replacement of the hydrogen for alkyl or aryl groups in the cationic complex, [IrCl2(PMe2Ph)3(PH3)][ClO4], shifts the unique phosphine resonance to lower field, until the resonances of the dimethylphenylphosphine and the diphenylphosphine phosphorus nuclei are overlapping in the complex [IrCl2(PMe2Ph)3(PPh2H)][ClO4]. Hydrogen is more electropositive than carbon, with the

<table>
<thead>
<tr>
<th>δP</th>
<th>-121.5</th>
<th>-80.9</th>
<th>-50.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-PH3</td>
<td>M-PPhH2</td>
<td>M-PPh2H</td>
<td></td>
</tr>
</tbody>
</table>

| δH | 3.06 | 4.06 | 6.30 |

Figure 3.10

result that every replacement of a hydrogen for an alkyl group causes a downfield shift in the resonance of that phosphorus nucleus and any remaining hydrogens attached to it. This trend is also observed in the 1H n.m.r. spectrum for the P-H resonances in the series of complexes [IrCl2(PMe2Ph)3(PHR1R2)][ClO4]. Thus the ligands M-PH3, M-PH2R, M-PHR, and M-PR3 come to resonance at successively lower field (Figure 3.10).

Proton-coupled 31P n.m.r. spectra were recorded and revealed an increase in the multiplicity of the PHR1R2 resonance, as a result of coupling to extra nuclei with a large coupling constant. This extra splitting is observed as a result of the large one-bond phosphorus hydrogen coupling, (J(PH) = 380-400 Hz) to the proton directly bonded to the phosphine.14-16 For the case of [IrCl2(PMe2Ph)3(PH3)][ClO4] where the one bond P-H coupling (J(PH) = 381.0 Hz) and the trans phosphorus-phosphorus coupling are of comparable magnitude (J(PPH) = 403.0 Hz) the PH3 resonance appeared as a quintet further split by a small coupling to the cis phosphorus nuclei8 (Figure 3.11). The PMe2Ph resonances appeared as broad peaks a result of extra coupling to the ortho hydrogens of the attached phenyl and methyl groups. Similarly for the cationic complex
Figure 3.9 $^{31}$P($^1$H) n.m.r. spectra of (a) [IrCl$_2$(PMe$_2$Ph)$_3$(PH$_3$)][ClO$_4$] and (b) [IrCl$_2$(PMe$_2$Ph)$_3$(PPhH$_2$)][ClO$_4$]

(a) [IrCl$_2$(PMe$_2$Ph)$_3$(PH$_3$)][ClO$_4$]

(b) [IrCl$_2$(PMe$_2$Ph)$_3$(PPhH$_2$)][ClO$_4$]
Figure 3.11 $^{31}\text{P}['\text{H}]$ n.m.r. spectrum of the PH$_3$ region of the complex [IrCl$_2$(PMe$_2$Ph)$_3$(PH$_3$)][ClO$_4$]

(a) Proton decoupled

(b) Proton coupled to PH$_3$
[IrCl₂(PMe₂Ph)₃(PPh₂H)][ClO₄] the PPh₂ resonance showed a broad quartet in the ³¹P n.m.r. spectrum, a result of coupling to two protons directly bonded to phosphorus (Figure 3.11). The fine coupling was not observed because of additional coupling to the ortho hydrogens of the phenyl ring, unlike the PH₃ complex where there were no ortho hydrogens to couple.

The ¹H n.m.r. spectra of each of these mononuclear complexes gave rise to a distinctive pattern for the acidic protons directly bound to the phosphorus. Each complex showed a one-bond phosphorus-hydrogen coupling of approximately 380-400 Hz with further coupling to the cis and trans phosphines (Figure 3.12).

PH₃ exhibits a one-bond phosphorus-hydrogen coupling of 182.2 Hz¹⁴,¹⁵ and, when coordinated to a transition-metal centre this coupling increase to the familiar value of 381.0 Hz.¹⁴,⁹ This increase in coupling constant can be explained by considering the amount of s character within the phosphorus-hydrogen bond. Free phosphine is pyramidal in nature with a H-P-H angle of 93.7°. If the phosphorus atom of the PH₃ molecule were sp³ hybridised the lone-pair would reside in an orbital with only one quarter s character but the angles observed are near to those required for pure p orbitals (ideal p orbitals require H-P-H angle of 90°).¹²,¹⁴,¹⁶ Therefore in free phosphine we consider the lone-pair of electrons to reside in an orbital with a substantial amount of s-character, the value of the one-bond phosphorus-hydrogen coupling constant can then be considered as arising from a bond with high p-character with only a little s-character. The increase in coupling constant on coordination of the phosphine indicates that there is an increase in the percentage of s character within the phosphorus hydrogen bond. This is readily explained if the orbitals are required to rehybridise on coordination, possibly because the donor pair of electrons is required to exhibit a greater degree of p orbital character to form a strong M-P bond. This increase in p orbital character of the lone-pair of electrons is accompanied by a concomitant increase in the percentage of s-character in the phosphorus hydrogen bond, resulting in an increase in the one bond phosphorus hydrogen coupling constant. This increase in the coupling constant and the implication that the bonding orbitals are more closely sp³ would require the M-P-H angle to increase on coordination from the angle of 93.7° observed in free phosphine. In the complex [IrCl₂(PMe₂Ph)₃(PPh₂H)][ClO₄] the Ir-P-H angle was found to be 106.8° in agreement with the expected increase on coordination to a transition-metal centre. Increased H-P-C bond angles were also observed H(1)-P(4)-
Figure 3.12 \(^1\)H n.m.r. of the PH\(_3\) and PMe\(_2\)Ph region of the complex [IrCl\(_2\)(PMe\(_2\)Ph)\(_3\)PH\(_3\)]\([\text{ClO}_4\])\]
3.2.3 Attempted Deuteration of [IrCl₂(PMe₂Ph)₃(PH₃)][ClO₄]

These cationic complexes were expected to have labile phosphorus bound protons which would readily exchange with D⁺. Roper found that the isoelectronic complex [OsCl(CO)₂(PPhH₂)(PPh₃)₂][ClO₄] readily exchanges all phosphorus bound protons when treated with D₂O in CDCl₃ for three hours. This was evident from the disappearance of the n.m.r. resonance assigned to the phosphorus bound protons.

After dissolving a sample of [IrCl₂(PMe₂Ph)₃(PH₃)][ClO₄] in MeOD and shaking for three hours, isolation of the product showed that only partial exchange had occurred giving rise to two broad resonances in the ¹H n.m.r. spectrum for the protons directly bonded to the phosphorus. The sample was redissolved in MeOD and left overnight, there was no further change observed in the ¹H n.m.r. spectrum. No attempts were made to examine the exchange under base catalysed conditions. Roper showed that the neutral phosphine complexes [OsClH(CO)(PPh₃)₂(PPhH₂)] and [Os(Cl)₂(CO)(PPh₃)₂(PPhH₂)] did not undergo deuterium exchange under similar conditions. That charge is not the sole criterion for exchange of bound protons is demonstrated by our complexes [IrCl₂(PMe₂Ph)₃(PH₃)][ClO₄] and also by Roper’s complex trans-[RuH(CO)₂(PPhH₂)(PPh₃)₂][ClO₄].

3.2.4 Crystal Structure of [IrCl₂(PMe₃)₃(PPh₂H)][ClO₄]

N.m.r. studies have afforded all the information necessary to assign the relative geometry of the phosphines and chlorides in the cationic tetrakis-phosphine complexes. We decided to undertake a single crystal X-ray structure determination of one of the tetrakis-phosphine complexes. Single crystals of [IrCl₂(PMe₃)₃(PPh₂H)][ClO₄] were obtained by layering a dichloromethane solution of the salt with diethylether and allowing slow diffusion. The complex crystallises in the space group P2₁/c with one molecule of dichloromethane in the crystal for every molecule of the complex. The monoclinic unit cell had dimensions a = 10.314(2) Å, b = 17.253(3) Å, c = 19.092(3) Å, β = 103.19(2) °. The structure was refined to R = 0.0358 and selected bond lengths and angles are tabulated (Table 3.1) and views of the cation are shown in Figures 3.13.
and 3.14. The structure shows an approximate IrP₄ plane and is consistent with the ³¹P{¹H} n.m.r. spectrum. There are two possible isomers. The unsymmetrical rotamer with one phenyl above the IrP₄ plane and the other phenyl below this plane is the isomer seen in the crystal structure. The other possible isomer contains chemically and magnetically equivalent trans-PMe₃ ligands. The symmetrical arrangement arises from both phenyl rings being on the same side of the IrP₄ plane. There are quite large distortions of the P-Ir-P bond angle away from 180 °. A P-Ir-P angle of 168.5 ° and another of 170.0 ° were found for P(3)-Ir(1)-P(4) and P(1)-Ir(1)-P(2), respectively. These deviations from linearity are not uncommon and have been seen for many other complexes containing four phosphines coplanar, e.g. [IrCl₂(PMe₂Ph)₄][ClO₄] [223] [IrCl₂(PMe₂)₂(PMe₂Ph)][ClO₄], [Rh(PMe₃)₄][Cl] [215] and [ReCl(N₂)(PMe₂Ph)₄] [224]. These distortions of the square plane of the octahedron towards tetrahedral geometry are a consequence of the steric requirements of four phosphines contained in the same plane. This twisting of pairs of trans phosphines towards tetrahedral geometry relieves the strain within the plane containing the four phosphines, but causes smaller P-Ir-Cl angles which are unfavourable. This distortion is most apparent in Figure 3.14 which also shows the eclipsed conformations of the pairs of trans phosphines.
Figure 3.13 Structure of [IrCl₂(PMe₃)₃(PPh₂H)][ClO₄]
Figure 3.14 Structure of $[\text{IrCl}_2(\text{PMe}_3)_3(\text{PPh}_2\text{H})][\text{ClO}_4]$
Table 3.1 Selected bond lengths and angles for [IrCl₂(PMe₃)₃(PPh₂H)][ClO₄]⁻

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<thead>
<tr>
<th>Bond lengths (Å)</th>
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<tr>
<td>Ir(1)-Cl(1)</td>
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<tr>
<td>Ir(1)-Cl(2)</td>
<td>2.365(2)</td>
</tr>
<tr>
<td>Ir(1)-P(1)</td>
<td>2.365(2)</td>
</tr>
<tr>
<td>Ir(1)-P(2)</td>
<td>2.374(2)</td>
</tr>
<tr>
<td>Ir(1)-P(3)</td>
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<tr>
<td>Ir(1)-P(4)</td>
<td>2.387(2)</td>
</tr>
<tr>
<td>Cl(3)-O(1)</td>
<td>1.415(7)</td>
</tr>
<tr>
<td>Cl(3)-O(2)</td>
<td>1.405(6)</td>
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<td>1.417(6)</td>
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<td>P(4)-H(1)</td>
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</table>

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<tr>
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<tr>
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<td>Cl(1)-Ir(1)-P(1)</td>
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<td>Cl(2)-Ir(1)-P(1)</td>
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<td>Cl(2)-Ir(1)-P(2)</td>
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<td>Cl(1)-Ir(1)-P(3)</td>
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</tr>
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<td>Cl(1)-Ir(1)-P(4)</td>
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<tr>
<td>Cl(2)-Ir(1)-P(4)</td>
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</tr>
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<td>P(1)-Ir(1)-P(2)</td>
<td>170.0(1)</td>
</tr>
<tr>
<td>P(2)-Ir(1)-P(3)</td>
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</tr>
<tr>
<td>H(1)-P(4)-C(51)</td>
<td>100.9(34)</td>
</tr>
</tbody>
</table>
3.3 Synthesis of phosphido Complexes of Iridium(III)

3.3.1 Deprotonation of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PHR}^1\text{R}^2)]\text{[ClO}_4]\)

Roper found that attempted proton abstraction from his neutral phosphine complexes (Scheme 3.3) afforded intractable materials,\(^9\) so he employed the stratagery of forming cationic derivatives of the complexes in Scheme 3.3 prior to deprotonation. He found only a single example of a deprotonation reaction of a neutral complex that led to a tractable material. Deprotonation of \([\text{OsCl}_2(\text{CO})(\text{PPh}_3)_2(\text{PH}_3)]\) with base (DBU) in tetrahydrofuran at reflux affords the neutral dimer \([\text{Os}(\mu-\text{PH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]_2\), characterised crystallographically. He successfully deprotonated the cationic complexes with the organic base DBU (diazabicyclo[5,4,0]undec-7-ene) to afford the neutral terminal phosphido complexes (Figure 3.4).

![Scheme 3.3](image)

Treatment of a suspension of the cationic phosphine complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PHR}^1\text{R}^2)]\text{[ClO}_4]\) in ethanol with the non nucleophilic base DBU at room
temperature afforded the corresponding neutral terminal phosphido complex (Scheme 3.4). On addition of DBU to an ethanol suspension, it was common to observe a dramatic colour change. For the PH$_3$ complex a change from pale yellow to deep yellow accompanied addition of the base whilst for the phenyl and diphenyl phosphine complexes the suspensions turned deep orange. Crystallisation of the product from a dichloromethane-ethanol mixture afforded air-stable crystalline compounds, sparingly soluble in n-hexane and ethanol.

3.3.2 Spectroscopic Characterisation of the Phosphido Complexes

$^{31}$P{^1H} n.m.r. studies of the neutral phosphido complexes have shown that there is an up-field shift of the phosphido resonance compared with that of the parent molecule$^{9,4,8}$ (Figure 3.15). This upfield shift is observed for all the phosphido complexes, PH$_2$, PPhH and PPh$_2$, and is a consequence of the increased electron density at the phosphorus nucleus. The remaining PMe$_2$Ph resonances are unshifted. Figure 3.15 shows that the PH$_2$ group resonates at approximately $\delta = -150$ in comparison to $\delta = -120$ in the parent protonated molecule. An upfield shift of the protons directly bonded to the phosphido ligand is also observed in the $^1$H n.m.r. spectrum.

Accompanying the deprotonation was a reduction in the one-bond phosphorus-hydrogen coupling constant. The parent molecule showed a one bond coupling of 380-400 Hz and this was reduced to 176.2 Hz in the neutral complex, a coupling constant of comparable size to that found in free phosphines. The origin of the reduced one-bond coupling can be readily explained using simple arguments involving the quantity of s-orbital character in the bonds in the same way that the increase in the one-bond coupling on coordination of free phosphine was explained. Uncoordinated phosphine has a lone-pair of electrons in an orbital with a substantial amount of s character, and on
Figure 3.15. $^3\text{P}^2\text{H}^1$ n.m.r. spectra of $[\text{IrCl}_4(\text{PMe}_3\text{Ph})_2(\text{PH}_3)]$. (a) Proton coupled; (b) Proton decoupled.
coordination these electron exhibit greater p-character to favour bond formation. The orbitals (excluding d orbitals possibly required for \( \pi \) back bonding) on phosphorus will be more \( \text{sp}^3 \) like in nature giving rise to an increase in the s-orbital character of the P-H bond and a concomitant increase in the coupling constant. Deprotonation of the phosphine ligand will effectively cause the reverse process to occur. The resultant lone-pair of electrons (assuming a pyramidal phosphido ligand and not a planar one with \( \text{sp}^2 \) orbitals and a p-orbital available for \( \pi \) bonding to the metal centre) will preferentially reside in an orbital with predominately s-character as it does in the free ligand state.

This deprotonation should be accompanied with a reduction in the M-P-H bond angle as a result of the bonding orbitals having greater p-character (compare 93.7° in free phosphine). We have seen that in the complex \([\text{IrCl}_2(\text{PMe}_3)_3(\text{PPh}_2\text{H})][\text{ClO}_4]\) the Ir-P-H angle is as large as 106.8° implying orbitals nearer to \( \text{sp}^3 \) in character on deprotonation we expect this angle be reduced. Unfortunately no structural data is available for the M-P-H angles in terminal pyramidal phosphido complexes. It is not only the one bond phosphorus hydrogen coupling constant that is altered but also the \( \text{cis} \) and \( \text{trans} \) phosphorus-phosphorus couplings too. If the lone-pair of electrons prefer to reside in an orbital with predominately s-character then the above proposal explains the reduction in the phosphorus-phosphorus coupling, there being less s-character in the M-P bond. The \( \text{trans} \) coupling has been reduced from 403.0 Hz to 106.2 Hz and the coupling of the phosphido ligand to the \( \text{cis} \) phosphine has been reduced from 29.8 Hz to 7.7 Hz giving rise to the distortions observed for the phosphido resonance in the \( ^{31}\text{P}'\) n.m.r. spectrum (Figure 3.15). As a consequence of the reduction in the \( \text{cis} \) coupling constant, the pair of PMe\(_2\)Ph ligands \( \text{trans} \) to each other appear as a doublet of doublets in the \( ^{31}\text{P}'\) n.m.r. spectrum, in contrast to the parent cationic complex where the resonance was a triplet (Figure 3.15).

Restoring proton coupling to the \( ^{31}\text{P} \) n.m.r. spectrum established that there were two protons directly bonded to the phosphido ligand of \([\text{IrCl}_2(\text{PMe}_2\text{Ph}_3)(\text{PH}_2)][\text{ClO}_4]\) (Figure 3.15). A \( \text{trans} \) phosphorus-phosphorus coupling of 106.2 Hz gives rise to the doublet pattern whilst the additional triplet pattern was a result of a one-bond phosphorus-hydrogen coupling of 176.2 Hz.
3.3.3 Structural Considerations

Single-crystal X-ray structures are available for transition metal complexes containing both pyramidal and planar phosphido ligands (Figure 3.16). [OsCl(\text{CO})_3(PPhH)(PPhH)] exhibits a terminal phosphido ligand with pyramidal geometry at phosphorus as a result of having a stereochemically active lone-pair of electrons. Characteristic of this compound is the nucleophilic nature of the phosphido ligand.\textsuperscript{11,29} A planar phosphido ligand for the early transition metals has been structurally characterised by Schrock in the alkylidyne tungsten complex [W(\text{CCMe}_3)\text{Cl}_2(P\text{PhH})(\text{PEt}_3)].\textsuperscript{40} The nucleophilic nature of the phosphido ligand in the neutral complexes [IrCl_2(\text{PMe}_2\text{Ph})_3(PR\text{R}')_2] (R\text{'} = R\text{''} = \text{H}, R\text{'} = \text{Ph}, R\text{''} = \text{H}, R\text{'} = R\text{''} = \text{Ph}) is consistent with pyramidal geometry at the phosphido ligand (Figure 3.17).

\[31^P\text{[H]}\text{ n.m.r. investigations carried out on the cationic phosphine complex, [IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPh}_2\text{H})][\text{ClO}_4], and its corresponding phosphido complex, [IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPh}_2)\text{], reinforce our proposal of pyramidal geometry at the phosphido ligand in the iridium(III) complexes. The room temperature }31^P\text{[H]}\text{ n.m.r. spectrum of this complex exhibited an }A_2BC\text{ spin system, a result of rapid exchange of the two possible conformers in solution by virtue of rapid rotation about the M-P axis (Figure 3.18). Additon of DBU to an n.m.r. tube containing a \text{CDCl}_3 solution of the cation immediately afforded a deep orange solution which turned pale yellow over a period.\]
of time. The $^{31}$P($^1$H) n.m.r. spectrum was recorded again and showed an $A_2BC$ type spectrum implying rapid exchange of the rotamers in solution, with one branch of the multiplet broad at room temperature. Recording the spectrum at low temperature (-55 °C in CDC$_3$) resulted in an increase in complexity of the n.m.r. spectrum as a result of restricted rotation about the M-P bond resulting in the slow exchange of the rotamers on the n.m.r. time-scale. Although resonances could not be unequivocally assigned to the two expected conformers (expected $A_2BC$ and an $ABCD$ spin system) the presence of rotamers in solution confirms the pyramidal nature of the phosphido ligand. Different conformers would not be observed in solution if the phosphido ligand was planar in nature; an $A_2BC$ type spin system would be seen at both high and low temperature. On warming the sample to room temperature the signals were seen to coalesce affording the $A_2BC$ spins system already discussed.
3.4 Conclusion

We have successfully synthesised PH$_3$, PPh$_2$ and PPh$_2$H complexes of iridium(III) in high yield. These cationic complexes were found to deprotonate in polar solvent with the non nucleophilic base DBU, to afford the neutral terminal phosphido complexes with the general formula [IrCl$_2$(PMe$_2$Ph)$_3$(PR$_1^1$R$_2^2$)]. These complexes are expected to be pyramidal in nature and n.m.r. investigations lead us to believe that this is correct. Certainly these complexes show nucleophilic behaviour as described in the next chapter.
3.5 Experimental

3.5.1 Synthesis of [IrCl$_3$(PMe$_2$Ph)$_3$]

A solution of chloroiridic acid (0.6911 g, 1.7 mmol) in 2-methoxyethanol (25 cm$^3$) was refluxed with concentrated hydrochloric acid (0.5 cm$^3$) for ca. 15 minutes until deep green-brown in colour. The solution was cooled and dimethylphenylphosphine (1.1501 g, 8.3 mmol) added. The solution was refluxed under a nitrogen atmosphere for 8 hours during which time the solution turned yellow. On cooling overnight at -20°C a yellow crystalline material formed. This solid (0.732 g, 75%) was filtered and washed with diethylether. [Found: C, 39.95; H, 4.58; P, 13.3. C$_{24}$H$_{33}$Cl$_3$IrP$_3$ requires C, 40.43; H, 4.66; P, 13.03%].

3.5.2 Synthesis of [IrCl$_2$(PMe$_2$Ph)$_3$(H$_2$O)][BF$_4$]

A method similar to that described previously was used. To a suspension of [IrCl$_3$(PMe$_2$Ph)$_3$] (0.3070 g, 4.3 mmol) in acetone (20 cm$^3$) was added silver tetrafluoroborate (0.0896 g, 4.3 mmol) and the mixture was shaken for 20 minutes. The silver chloride was filtered off and the solvent removed under reduced pressure. Crystallisation of the oily residue from dichloromethane/diethylether gave yellow needles of the desired compound (0.300 g, 89%). [Found: C, 35.11; H, 4.35; P, 10.87. C$_{24}$H$_{33}$BCl$_2$F$_4$IrOP$_3$ requires C, 36.85; H, 4.51; P, 10.65%].

3.5.3 Synthesis of [IrCl$_2$(PMe$_2$Ph)$_3$(PH$_3$)][BF$_4$]

Phosphine gas was bubbled through a solution of [IrCl$_2$(PMe$_2$Ph)$_3$(H$_2$O)][BF$_4$] (0.241 g, 0.27 mmol) in dichloromethane (20 cm$^3$). The solution turned dark brown immediately and was left to stand overnight in a well ventilated fumehood. Decolourising charcoal was added and the suspension stirred under an atmosphere of nitrogen for 60 minutes. After filtering the resulting solution through celite a pale yellow filtrate remained, this was evaporated to dryness under reduced pressure to give a yellow oily residue. Crystallisation of the product from dichloromethane/diethylether gave the required product as yellow needles (0.176 g, 80%). [Found: C, 36.24; H, 4.48; P, 15.94. C$_{24}$H$_{38}$BCl$_2$F$_4$IrP$_4$ requires C, 36.11; H, 4.54; P, 15.52%].
3.5.4 Synthesis of [IrCl₂(PMe₂Ph)₃(PPhH₂)][BF₄]  
To a solution of [IrCl₂(PMe₂Ph)₃(H₂O)][BF₄] (0.2631 g, 0.34 mmol) in dichloromethane (20 cm³) was added phenylphosphine (0.044 cm³, 0.4 mmol). The initially pale yellow solution turned dark brown after a few minutes. After standing under an atmosphere of nitrogen gas overnight, a black residue was seen to settle out leaving a yellow solution. Decolourising charcoal was added and the solution stirred for 60 minutes. The mixture was filtered through celite to give a pale yellow solution. The filtrate was evaporated to dryness under reduced pressure to leave a green-yellow oil. The residue was recrystallised from dichloromethane/diethylether to give the pure product. (0.254 g, 86%). [Found: C, 41.01; H, 4.67; P, 14.17. C₃₆H₄₀BCl₂F₄Ir₂P₄ requires C, 41.21; H, 4.61; P, 14.17%].

3.5.5 Synthesis of [IrCl₂(PMe₂Ph)₃(PPh₂H)][ClO₄]  
To a solution of [IrCl₂(PMe₂Ph)₃(H₂O)][ClO₄] (0.206 g, 0.27 mmol) in dichloromethane (20 cm³) was added diphenylphosphine (0.049 cm³, 0.27 mmol). The solution was stirred under a nitrogen atmosphere for several hours then evaporated to dryness under reduced pressure to give a yellow oily residue. Crystallisation from dichloromethane/diethylether gave the pure product (0.201 g, 78%). [Found: C, 44.56; H, 4.58; P, 12.86. C₃₆H₄₄Cl₂IrO₄P₄ requires C, 44.92; H, 4.61; P, 12.87%].

3.5.6 Synthesis of [IrCl₂(PMe₂Ph)₃(PH₂)]  
To a suspension of [IrCl₂(PMe₂Ph)₃(PH₃)][ClO₄] (0.2194 g, 0.27 mmol) in ethanol (3 cm³) was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (0.0616 cm³, 0.4 mmol). The pale yellow suspension changed colour to deep yellow on addition of the base. The solution was stirred vigorously under an atmosphere of nitrogen for 90 minutes a deep yellow solid which precipitated from solution was collected by filtration and washed with 10 cm³ of ethanol. Crystallisation from dichloromethane/ethanol gave the product as a microcrystalline solid (0.163 g, 71%). [Found: C, 39.53; H, 4.70; P, 18.12. C₂₄H₃₅Cl₂IrP₄ requires C, 40.5; H, 4.96; P, 17.43%].

3.5.7 Synthesis of [IrCl₂(PMe₂Ph)₃(PPhH)]  
The reaction procedure above was repeated with [IrCl₂(PMe₂Ph)₃(PPhH₂)][ClO₄] (0.215 g, 0.24 mmol) suspended in ethanol (3 cm³).
Crystallisation of the product from dichloromethane/ethanol pave the required product as a deep orange microcrystalline solid (0.143 g, 76%). [Found: C, 45.43; H, 5.05; P, 16.03. C_{36}H_{39}Cl_{2}IrP_{4} requires C, 45.80; H, 5.00; P, 15.75%].

3.5.8 Synthesis of [IrCl_{2}(PMe_{2}Ph)_{3}(PPh_{2})]

A similar procedure was repeated with [IrCl_{2}(PMe_{2}Ph)_{3}(PPh_{2}H)][ClO_{4}] (0.167 g, 0.17 mmol) suspended in ethanol. Crystallisation of the resultant deep orange solid from dichloromethane/ethanol gave the desired product (0.111 g, 75%) [Found: C, 40.03; H, 5.09; P, 14.13. C_{36}H_{41}Cl_{2}IrP_{4} requires C, 50.16; H, 5.03; P, 14.29%].
3.6 Spectroscopic data for the Complexes

Table 3.2 \(^1\)H n.m.r. data for phosphine and phosphido complexes of Iridium(III)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ((\delta))a</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl(_2)(PMe(_2)Ph(_3))(PH(_3))][ClO(_4)](^b)</td>
<td>3.06 (ddt)</td>
<td>PH(_3) (3H)</td>
<td>(^1)J(PH)=381.0, (^3)J(PH)=7.0, (^3)J(PH)=4.5</td>
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<tr>
<td></td>
<td>1.71 (t)</td>
<td>PMe(_2)Ph(^1) (12H)</td>
<td>(^2)J(PH)=7.8(^f)</td>
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<tr>
<td></td>
<td>1.88 (dd)</td>
<td>PMe(_2)Ph(^c) (6H)</td>
<td>(^2)J(PH)=9.30, (^4)J(PH)=2.4</td>
</tr>
<tr>
<td></td>
<td>7.4-7.62 (m)</td>
<td>phenyl (15H)</td>
<td></td>
</tr>
<tr>
<td>[IrCl(_2)(PMe(_2)Ph(_3))(PPhH(_2))][BF(_4)](^b)</td>
<td>1.73 (t)</td>
<td>PMe(_2)Ph(^1) (12H)</td>
<td>(^2)J(PH)=7.50(^f)</td>
</tr>
<tr>
<td></td>
<td>1.89 (dd,broad)</td>
<td>PMe(_2)Ph(^c) (6H)</td>
<td>(^2)J(PH)=10.1, (^4)J(PH)=2.8</td>
</tr>
<tr>
<td></td>
<td>4.06 (dq)</td>
<td>PPh(_2)H(^1) (2H)</td>
<td>(^1)J(PH)=388.8, (^3)J(PH)=10.8</td>
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<tr>
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<td>7.0-7.65 (m,broad)</td>
<td>phenyl (20H)</td>
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</tr>
<tr>
<td>[IrCl(_2)(PMe(_2)Ph(_3))(PPh(_2)H)][ClO(_4)](^b)</td>
<td>1.70 (s,broad)(^e)</td>
<td>PMe(_2)Ph (18H)</td>
<td>half height line width=60Hz</td>
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<td></td>
<td>6.30 (dm)</td>
<td>PPh(_2)H(^1) (1H)</td>
<td>(^1)J(PH)=388.0</td>
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<td></td>
<td>7.4 (m)</td>
<td>phenyl (25H)</td>
<td></td>
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<tr>
<td>[IrCl(_2)(PMe(_2)Ph(_3))(PH(_2))(^b)</td>
<td>1.54 (dq)</td>
<td>PH(_2) (2H)</td>
<td>(^1)J(PH)=176.2, (^3)J(PH)=8.8</td>
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<td>1.18 (d)</td>
<td>PMe(_2)Ph(^c) (6H)</td>
<td>(^2)J(PH)=9.2(^f)</td>
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<td>1.79 (dt)</td>
<td>PMe(_2)Ph(^1) (12H)</td>
<td>(^2)J(PH)=8.2(^f), (^3)J(PH)=0.8</td>
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<tr>
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<td>6.95 (dt)</td>
<td>phenyl (2H)</td>
<td>(^3)J(HH)=9.7, (^4)J(PH)=2.1</td>
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<td>7.1-7.3 (m)</td>
<td>phenyl (9H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.55 (m)</td>
<td>phenyl (4H)</td>
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</tbody>
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Table 3.2 continues overleaf ..........
Table 3.2 continued ......

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<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ)\textsuperscript{a}</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl\textsubscript{2}(PMe\textsubscript{2}Ph)\textsubscript{3}(PPh\textsubscript{H})]\textsuperscript{b,d}</td>
<td>1.01 (d)</td>
<td>PMe\textsubscript{2}Ph\textsuperscript{c} (3H)</td>
<td>\textsuperscript{2}J(\textit{PH})=8.6</td>
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<tr>
<td></td>
<td>1.03 (d)</td>
<td>PMe\textsubscript{2}Ph\textsuperscript{c} (3H)</td>
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<tr>
<td></td>
<td>1.54 (t,broad)</td>
<td>PMe\textsubscript{2}Ph\textsuperscript{1} (6H)</td>
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<tr>
<td></td>
<td>1.76 (t,broad)</td>
<td>PMe\textsubscript{2}Ph\textsuperscript{1} (6H)</td>
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</tr>
<tr>
<td></td>
<td>3.84 (dq,broad)</td>
<td>PPh\textsubscript{H} (1H)</td>
<td>\textsuperscript{1}J(\textit{PH})=212.7, \textsuperscript{3}J(\textit{PH})=7.7</td>
</tr>
<tr>
<td></td>
<td>6.6-8.2 (m)</td>
<td>phenyl (20H)</td>
<td></td>
</tr>
<tr>
<td>[IrCl\textsubscript{2}(PMe\textsubscript{2}Ph)\textsubscript{3}(PPh\textsubscript{2})]\textsuperscript{b}</td>
<td>1.20 (d)</td>
<td>PMe\textsubscript{2}Ph\textsuperscript{c} (6H)</td>
<td>\textsuperscript{2}J(\textit{PH})=11.6</td>
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<td>1.66 (t)</td>
<td>PMe\textsubscript{2}Ph\textsuperscript{1} (12H)</td>
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<tr>
<td></td>
<td>6.9-7.9 (m)</td>
<td>phenyl (25H)</td>
<td>\textsuperscript{2}J(\textit{PH})=8.42</td>
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\textsuperscript{a}: Spectra recorded in CDCl\textsubscript{3} and referenced internally to the solvent.

\textsuperscript{b}: Spectra recorded at 400 MHz.

\textsuperscript{c}: PMe\textsubscript{2}Ph\textit{cis} to PMe\textsubscript{2}Ph

\textsuperscript{d}: PMe\textsubscript{2}Ph\textit{trans} to PMe\textsubscript{2}Ph.

\textsuperscript{e}: Spectra recorded at -50 °C.

\textsuperscript{f}: Broad as a result of different conformational isomers present in solution in exchange. The low temperature \textsuperscript{31}P{\textsuperscript{1}H} n.m.r. spectrum indicated the presence of different rotomers in exchange.

\textsuperscript{f}: J(\textit{PH}) = \textsuperscript{2}J(\textit{PH}) + \textsuperscript{4}J(\textit{PH}).
Table 3.3 $^{31}$P {$^1$H} n.m.r. data for phosphine and phosphido complexes of Iridium(III)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ($\delta$)$^a$</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PH$_3$)][ClO$_4$]$^b$</td>
<td>-121.5 (dt)</td>
<td>PH$_3$</td>
<td>$^2$J(PP)=403.0, $^2$J(PP)=29.8</td>
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<tr>
<td></td>
<td>-50.2 (dt)</td>
<td>PMe$_2$Ph$^c$</td>
<td>$^2$J(PP)=403.0, $^2$J(PP)=29.8</td>
</tr>
<tr>
<td></td>
<td>-51.0 (t)</td>
<td>PMe$_2$Ph$^t$</td>
<td>$^2$J(PP)=29.8</td>
</tr>
<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PPhH$_2$)][ClO$_4$]$^b$</td>
<td>-80.9 (dt)</td>
<td>PPhH$_2$</td>
<td>$^2$J(PP)=385.3, $^2$J(PP)=29.3</td>
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<tr>
<td></td>
<td>-50.1 (dt)</td>
<td>PMe$_2$Ph$^c$</td>
<td>$^2$J(PP)=385.3, $^2$J(PP)=29.3</td>
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<tr>
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<td>-50.5 (t)</td>
<td>PMe$_2$Ph$^t$</td>
<td>$^2$J(PP)=29.3</td>
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<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PPh$_2$H)][ClO$_4$]$^b$</td>
<td>-50.7 (m)</td>
<td>PMe$_2$Ph &amp; PPh$_2$H</td>
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<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)]$^b$</td>
<td>-150.2 (dt)</td>
<td>PH$_2$</td>
<td>$^2$J(PP)=106.2, $^2$J(PP)=7.0</td>
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<tr>
<td></td>
<td>-53.4 (dt)</td>
<td>PMe$_2$Ph$^c$</td>
<td>$^2$J(PP)=106.2, $^2$J(PP)=20.3</td>
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<td>-49.4 (dd)</td>
<td>PMe$_2$Ph$^t$</td>
<td>$^2$J(PP)=20.3, $^2$J(PP)=7.7</td>
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<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PPh)$_2$]$^b$</td>
<td>-64.8 (dt,broad)</td>
<td>PPhH</td>
<td>$^2$J(PP)=111.5, $^2$J(PP)=17.2</td>
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<td>-50.7 (dt)</td>
<td>PMe$_2$Ph$^c$</td>
<td>$^2$J(PP)=111.5, $^2$J(PP)=20.1</td>
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<td>-47.5 (t,broad)</td>
<td>PMe$_2$Ph$^t$</td>
<td>$^2$J(PP)=19.0</td>
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<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PPh)$_2$]$^b$</td>
<td>+5.1 (d,vbroad)</td>
<td>PPh$_2$</td>
<td></td>
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<tr>
<td></td>
<td>-50.8 (broad)</td>
<td>PMe$_2$Ph</td>
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</table>

$a$: Spectra recorded in CDCl$_3$ and chemical shifts are quoted relative to external 85% H$_3$PO$_4$ with downfield chemical shifts reported as positive.

$b$: Spectra recorded at 162 MHz

c: PMe$_2$Ph cis to PMe$_2$Ph

t: PMe$_2$Ph trans to PMe$_2$Ph.
Chapter 4

Reactions of Phosphido Complexes
of Iridium(III)
4 Reactions of Phosphido Complexes of Iridium(III)

4.1 Introduction

Transition-metal complexes containing pyramidal terminal phosphido ligands undergo nucleophilic attack, both at organic and transition metal centres. Generation of the phosphido complexes in situ and addition of the appropriate metal electrophile results in the isolation of heterobimetallic complexes. Geoffrey and co-workers have demonstrated the preparation of phosphido-bridged binuclear complexes by the bridge assisted synthetic method using the reaction of diphenylphosphido carbonylmetalates with the appropriate metal chloride (equation 4.1). Heterobimetallic complexes which link together metals with substantially different chemical properties are inherently interesting since they may lead to unusual bifunctional activation of organic substrates. Metal centres that are capable of undergoing oxidative addition, reductive elimination reactions are of particular importance in this respect.

The nucleophilic character of the pyramidal phosphido ligand is well documented. Such reactions of pyramidal phosphido ligands with organic substrates could be used to prepare new ligands that are unstable in the unbound state. Very curiously the pyramidal phosphido complex \([\text{OsCl(CO)}_2(\text{PPh}_3)_2(\text{PPhH})]\) was found to undergo both electrophilic (Figure 4.1) and nucleophilic (Equation 4.2) reactions.

\[
\text{[Li][Mo(CO)}_4(\text{PPh}_2\text{H})(\text{PPh}_2)] \xrightarrow{1/2[\text{Ir(μ-Cl}(\text{COD})]_2} \text{[(CO)}_4\text{Mo(μ-PPh}_2\text{)}_2\text{IrH(CO)}_2]\]
\]

Equation 4.1

Reaction with methyl iodide afforded the chiral cationic phosphine complex \([\text{OsCl(CO)}_2(\text{PPh}_3)_2(\text{PPhHMe})][\text{I}]\) and the neutral bimetallic complex \([\text{OsCl(CO)}_2(\text{PPh}_3)_2(\text{PPhH})(\text{AuCl})]\) is formed by the reaction of the neutral phosphido
complex with gold phosphine chloride \([\text{Au(PPh}_3\text{)Cl}]\). However electrophilic attack at the terminal phosphido ligand by the methoxide anion \(\text{MeO}^-\) afforded the complex \([\text{Os(CO)}_2\text{(PPh}_3\text{)}_2(\text{PPhHOMe})]\) after loss of chloride.\(^{29}\) This unexpected result for a pyramidal phosphido ligand was explained by Roper who proposed that there had to be a planar intermediate in order for nucleophilic attack to occur. He proposed that the conversion of the pyramidal phosphido into the planar phosphido ligand (Equation 4.2) was facilitated by the loss of chloride. The formation of the proposed cationic complex would be favoured in polar solvents such as methanol and the cation could then undergo the reactions expected for planar phosphido ligands. This reaction is an example of the synthesis of an unstable molecule which is only known to exist in the coordination sphere of a metal.\(^{37,56}\) The o-methylphenylphosphinite ligand rearranges to methanol and cyclopolyphosphine \((\text{PPh})_n\) when in the unbound state.

Roper was first to successfully prepare and characterise a terminal
monohalophosphido complex, \([\text{OsCl(CO)}_2(\text{PPh}_3)_2(\text{PPhI})]\). Complexes of this type are potential precursors of terminal phosphinidene complexes, \([\text{LnM=PR}]\), through the loss of a halide. Terminal phosphinidene ligands have been implicated as reaction intermediates but have eluded isolation to date. Reaction of \([\text{OsCl(CO)}_2(\text{PPhI})]\) with \(\text{AgSbF}_6\) in methanol/THF gives a product suggesting a cationic phenylphosphinidene complex intermediate (Figure 4.2).

![Diagram](image)

Figure 4.2

Ebsworth has investigated the reactions of several phosphido complexes of iridium(III), typically \([\text{Ir(CO)HBr(PEt}_3)_2(\text{PH}_2)]\). They found that the phosphido phosphorus atom was a weak donor and distinctly "soft" in character. \(\text{BF}_3\) was found not to interact with the phosphido ligand whereas \(\text{B}_2\text{H}_6\) formed a BH₃ complex with it. A tightly bound complex was also formed with \([\text{RuCl}_2(\pi^6\text{-MeC}_6\text{H}_4\text{CHMe}_2\text{-p})]\) (Figure 4.3). Furthermore, Ebsworth has successfully prepared the complexes \([\text{Ir(CO)H(PEt}_3)_2(\text{PH}_2)]\) and \([\text{Ir(CO)H(PEt}_3)_2(\text{PH}_2)]\). Reaction of these complexes with \(\text{BCl}_3\), \(\text{B}_2\text{H}_6\) and with the metal-based acceptors \([\{\text{RuCl}_2(\pi^6\text{-MeC}_6\text{H}_4\text{CHMe}_2\text{-p})\}_2], [\text{PtCl}_2(\text{COD})]\) (COD = cyclo-octa-1,5-diene) and \([\text{Mo(CO)}_6(\text{nbd})]\) (nbd = bicyclo[2.2.1]hepta-2,5-diene) showed that the phosphido ligands in these complexes act as bases to both first row main group and heavy transition-metal acceptors (Scheme 4.1).

N.m.r. parameters are important in identifying the complexes studied and show
Scheme 4.1  Reactions of [Ir(CO)H(PEt₃)₂(PH₂)₂] with main group and heavy transition-metal acceptors.
some useful patterns. The chemical shifts of the tertiary phosphine phosphorus nuclei fall within a small range and show no systematic changes from complex to complex. However, the chemical shifts of the phosphido phosphorus are much more variable. These fall well to low frequency in most cases studied for example, [IrCl₂(PMe₂Ph)₃(PH₂)], [Os(CO)₂Cl(PPh₃)₂(PH₂)] and [Ir(CO)BrH(PEt₃)₂(PH₂)]. The chemical shift of the phosphido phosphorus becomes more positive as the coordination at P changes from three to four.¹⁴⁻¹⁶

Terminal monohalo- and dihalophosphido complexes show a similar reactivity pattern.⁷ The reaction of [Ir(CO)X₂(PEt₃)₂(PF₂)] with O₂, S₈, Se; with B₂H₆; with [(RuCl₂(η⁶-C₆H₄CHMe₂-p))]₂; and with [PtCl₂(COD)] shows that the dihalophosphido phosphorus atom has a chemically active lone-pair of electrons (Figure 4.4) and compounds containing the M-PF₂ group can behave as a phosphine (i.e. they react with platinum complexes containing ligands that are readily displaced) and so can be used to synthesise mixed-metal complexes. Later the pyramidal nature of the dihalophosphido ligand was unequivocally proven by a single-crystal X-ray structure determination of [Ir(CO)Cl₂(PEt₃)₂(PCl₂)].⁶
Figure 4.4 Reactions of [IrCl₂(CO)(PE₃)₂(PF₂)] with electrophiles.
Finally, the monohalophosphido complex \([\text{Os(CO)}_2\text{ClPPh}_3\text{I}_2(\text{PPhI})]\), prepared by Roper, was assumed to contain a pyramidal phosphido ligand by analogy with the PPH ligand in \([\text{Os(CO)}_2\text{Cl(PPh}_3\text{I}_2(\text{PPhH})]\) (determined crystallographically). The nucleophilicity of the phosphido ligand in \([\text{Os(CO)}_2\text{Cl(PPh}_3\text{I}_2(\text{PPhI})]\) was demonstrated by methylation with MeI to produce \([\text{Os(CO)}_2\text{Cl(PPh}_3\text{I}_2(\text{PPhMeI})\text{]}^+\) and by the reversible protonation with perchloric acid to \([\text{Os(CO)}_2\text{Cl(PPh}_3\text{I}_2(\text{PPhIH})\text{]}^+\) \(^5\) (Scheme 4.2).

![Scheme 4.2](image)

Riera has prepared a series of gold-manganese heterobimetallic complexes with diphenylphosphido bridges.\(^3\)\(^0\) The formation of these mixed metal phosphido complexes will be discussed further in relation to the formation of iridium(III)-gold phosphido complexes described in this chapter.

We have generated the neutral mononuclear phosphido complexes \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PR}_1\text{R}_2)]\) in relatively high-yield and as air-stable crystalline solids. In Chapter 3 evidence of the pyramidal nature of the terminal phosphido ligand was presented and in this chapter we demonstrate further evidence of the pyramidal nature of the ligand through its reactions with organic and metallic electrophiles.
4.2 Results and Discussion

4.2.1 Reaction with Simple Electrophiles

The phosphido complexes \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PR}^1\text{R}^2)]\) all give deeply coloured solutions in dichloromethane and formation of paler colours is often a good indication that electrophilic addition has occurred. For example, the addition of \(\text{MeI}\) to a deep orange solution of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) in dichloromethane led to an immediate change to pale yellow indicating immediate reaction (Equation 4.3).

\[
\begin{align*}
\text{PMe}_2\text{Ph} & \quad \text{PMe}^h \quad \text{PM}^i\text{Ph} \\
\text{Cl} & \quad \text{Cl} \\
\text{Ir} & \quad \text{Ir} \\
\text{P}^*\text{Ph} & \quad \text{P}^*\text{Ph} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Equation 4.3

The counter ion was exchanged for the perchlorate anion to give a salt which crystallised more readily than the corresponding iodide, facilitating isolation. The chiral phosphine complex was isolated as a green-yellow crystalline material from a dichloromethane/diethylether mixture and was characterised by a reasonable agreement of elemental analytical data (C, H, Cl) with calculated values and also from \(^1\text{H}\) n.m.r. spectroscopy. The methyl group of the chiral phosphine, \(\text{PPhHMe}\), appeared as an eight-line multiplet (ddd) with coupling to the proton directly bound to the phosphorus as well as to the phosphorus nucleus of the same ligand and to that of the \textit{trans} phosphine. Decoupling experiments confirmed correct assignments (Figure 4.5). Decoupling at one branch of the P-H resonance collapsed one branch of the eight-line methyl multiplet and decoupling at the other branch collapsed the opposite branch. Two broad sets of triplet resonances were observed for the Me groups of the mutually \textit{trans} \text{PMe}_2\text{Ph} methyl protons; these methyl groups are diastereotopic because of the asymmetric P-centre. Rapid rotation about the metal-phosphorus axis will not average the field environment of the methyl groups and they remain magnetically non-
Figure 4.5 400 MHz $^1$H n.m.r. spectra of the methyl region of the complex 
$[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHMe})][\text{ClO}_4]$ 

(a) Decoupling at PH

(b) Decoupling at PH

(c) Without decoupling
equivalent even at high temperatures. Upon methylation of the terminal pyramidal phosphido ligand, $^1J(\text{PH})$ increases from 212.7 Hz to 393.0 Hz in the cationic complex. This increase in the coupling constant is consistent with the proposed increase in s orbital character in the phosphorus-hydrogen bond, as described for related compounds in the previous chapter. There is also an observed increase in the coupling of the phosphorus nucleus to the other phosphorus nuclei.

The P-H resonance appeared as a doublet of multiplets, a consequence of coupling to three phosphorus nuclei and also to the protons of the methyl group bound to the chiral phosphine. Decoupling at this methyl resonance simplified the appearance of this doublet of multiplets to a doublet of doublets of quartets, to give a spectrum similar to that of the corresponding resonance in the parent phosphine complex, $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH}_2)][\text{ClO}_4]$ (Figure 4.6). A noticeable difference between the two spectra is the significant upfield shift of the P-H resonance of the parent phosphine complex $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH}_2)][\text{ClO}_4]$ compared with that of the chiral phosphine complex $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHMe})][\text{ClO}_4]$ (δ 4.06 and δ 5.82 respectively).

A low temperature $^1\text{H}$ n.m.r. study showed that the broad methyl resonances at room temperature were a result of exchange of conformers in solution. A $^1\text{H}$ n.m.r. spectrum recorded at low temperature (CD$_2$Cl$_2$, -85 °C) indicated that there were rotamers in slow exchange on the n.m.r. time-scale.

The $^{31}\text{P} (^1\text{H})$ n.m.r. spectrum showed three distinct sets of resonances, the PMe$_2$Ph signals appeared in the familiar place but the PPhHMe resonance was seen to be shifted to much lower field than in the phosphido complex and also to lower field than in the parent phosphine complex. The inductive effects leading to a reduction in electron density at the phosphorus nucleus explains the origin of this downfield shift. The chemical shift of the phosphorus resonance of PPhHMe (δ -63.61) in comparison to that for the parent complex (δ -80.9) (Figure 4.7) is the result of alkylation at phosphorus. The electropositive character of the protons compared with that of the alkyl groups and the effect on the n.m.r. resonances of attached nuclei have been discussed in Chapter 3. The replacement of hydrogens for alkyl groups is known to shift the resonance of the phosphorus nucleus to lower field and also will move the chemical shift of any remaining protons directly bonded to the phosphorus to lower field. Comparison of the chemical shifts of the acidic protons of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH}_2)][\text{ClO}_4]$ (δ = 4.06) and of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHMe})][\text{ClO}_4]$ (δ
Figure 4.6 400 MHz $^1$H n.m.r. spectrum of the PH$_3$ region of the complex [IrCl$_2$(PMe$_2$Ph)$_2$(PH$_3$)][ClO$_4$]

(a) Coupled to PPhHMe

(b) Decoupled at PPhHMe
Figure 4.7: $^{31}$P($^1$H) spectra of the complexes (a) [IrCl$_2$(PMe$_2$Ph)$_3$][PPh$_4$][ClO$_4$] and (b) [IrCl$_2$(PMe$_2$Ph)$_3$][PPh$_4$H][ClO$_4$].
5.82) confirms that alkylation of the primary phosphine shifts the resonances of the remaining protons that are directly attached to the phosphorus nucleus to lower field. The coupling constants in both cationic complexes are nearly the same as would be expected from simple hybridisation models.

Further deprotonation of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHMe})][\text{I}]\) to give the corresponding neutral phosphido complex and treatment with methyl iodide afforded the tetrakis-dimethylphenylphosphine complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3][\text{ClO}_4]_2\) after counter ion exchange. This salt has been characterised by elemental analytical data (C, H, Cl) and there was an acceptable agreement between observed and calculated values. The \(^1\text{H}\) n.m.r. spectrum exhibited a broad resonance in the methyl region with a half height width of 60 Hz and broad resonances were also observed in the phenyl region.\(^3\) The room temperature \(^{31}\text{P}(^1\text{H})\) n.m.r. spectrum showed one broad resonance at \(\delta = -55\) indicating rapid exchange of conformers on the n.m.r. time-scale. The low temperature \(^1\text{H}\) and \(^{31}\text{P}(^1\text{H})\) n.m.r. spectra were recorded and have been analysed in terms of conformational isomers in slow exchange. A discussion of the variable-temperature n.m.r. spectra of this complex and of related tertiary phosphine complexes is deferred until Chapter 5.

Each of the neutral phosphido complexes \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PR}^1\text{R}^2)]\) was successfully protonated with perchloric acid as evidenced by \(^1\text{H}\) n.m.r. spectroscopy. The reaction shown in Figure 4.8 was seen to be fully reversible and the starting phosphine complex was recovered in quantitative yield.

Reaction of the phenylphosphido complex, \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\), with propargyl bromide in dichloromethane afforded a pale yellow solution of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PHPh(C}_3\text{H}_3))]\)[Br]. Isolation of the cation from methanol as the tetraphenylborate salt afforded a pale yellow solid with correct elemental analytical data.
(C, H, P). The solution i.r. spectrum (CDCl₃) of this complex showed a characteristic stretch at 2120 cm⁻¹ diagnostic of the C=O stretch. The ¹H n.m.r spectrum did not provide much information as a result of overlapping signals but resonances could be assigned to the tetraphenylborate anion confirming the cationic nature of the product. The ³¹P(¹H) n.m.r spectrum exhibits three sets of resonances due to the three different types of nuclei. The resonance due to the substituted phosphine could not be unambiguously assigned because the shift to lower field moved the PPh₃CH₃ resonance to the region containing the PMe₂Ph resonances. Assignment was unequivocally made after the proton-coupled spectrum was recorded. This spectrum showed an increase in the multiplicity of the resonance that was at lowest field (J(PH) = 388.0 Hz giving rise to an extra doublet coupling). This multiplet was therefore assigned to the PPh₃CH₃ ligand on the basis of the increased multiplicity.

4.2.2 Reaction with Gold Phosphine Chloride Electrophiles

[Au(PPh₃)Cl] reacted with a dichloromethane solution of the phenylphosphido complex, [IrCl₂(PMe₂Ph)_3(PPhH)], to generate a bridging heterobimetallic phosphido complex. The dramatic colour change from deep orange to pale yellow during the addition of the gold phosphine complex indicated that reaction was instantaneous. Yellow crystals of the product were obtained by layering a dichloromethane solution of the complex with diethylether and allowing slow diffusion. A similar reaction was observed for the phosphido complex [IrCl₂(PMe₂Ph)_3(PH₂)] with [Au(PPh₃Cl)]. In both cases colourless crystals were formed as a by-product.

Initially it was thought that the products formed were the bimetallic complexes [IrCl₂(PMe₂Ph)_3(μ-PPh)(AuPPh₃)][Cl]³⁺ (R = Ph, H) with a phosphido bridge between gold and iridium atoms. It became apparent from the ¹H n.m.r. spectra of these complexes, that loss of phosphine from the gold complex had occurred. Integral ratios of approximately 1:1 were observed for the methyl to phenyl resonances. If the phosphine had been retained by the gold complex during reaction the ratio would have been 18:30 (Me:Ph) for the complex [IrCl₂(PMe₂Ph)_3(μ-PH₂)(AuPPh₃)] and 1:2 for the analogous phenylphosphido complex. The observed integral ratio are therefore much too low to allow a formulation containing triphenylphosphine. A repeat reaction replacing the triphenylphosphine gold complex with [Au(PMe₂Ph)Cl], all other conditions
remaining the same, afforded exactly the same complex as evidenced by n.m.r. spectroscopy. Colourless crystals were again observed during crystallisation of the product. $^{31}$P($^1$H) n.m.r. spectra were recorded for the reaction mixture and signals corresponding to the bis-triphenylphosphine gold complex [Au(PPh$_3$)$_2$Cl] were observed to be present. This product is expected to account for the colourless crystals observed during the isolation of the major product, although complete confirmation of this was not obtained.

Reaction of the phosphido complexes with half mole equivalents of the gold complexes [Au(PPh$_3$)Cl] or [Au(PMe$_2$Ph)Cl] afforded the same product as above in similar yields (n.m.r. evidence). No colourless crystals were observed in either case although the reaction with [Au(PMe$_2$Ph)Cl] resulted in an obvious smell of the phosphine. The requirement of only a half mole equivalent of the gold complex for the reaction to proceed indicated that two moles of the phosphido complex reacted with each mole of the gold complex. The reaction product was therefore proposed to be the trinuclear compound [{IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)}$_2$Au][Cl] (R = Ph, R = H).

4.2.3 Mass Spectra of [{IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)}$_2$Au][Cl]

The mass spectra of this compound was measured at the London School of Pharmacy (ULIRS). The FAB mass spectrum showed molecular ion peaks at m/e 1617 for the compound [{IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)}$_2$Au][Cl] corresponding to [{IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)}$_2$Au]$^+$ with the expected isotopic pattern for an Ir$_2$Au species and the calculated molecular ion pattern is consistent with observed envelope of peaks. Fragmentation ions could not be assigned for all the observed peaks although some of the peaks such as [{Ir$_2$Cl$_4$(PMe$_2$Ph)$_3$(PH$_2$)}$_2$Au]$^+$ and [{IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)}$_2$Au]$^+$ were assigned.

4.2.4 Crystal Structure of [{IrCl$_2$(PMe$_2$Ph)$_3$(μ-PH$_2$)}$_2$Au][ClO$_4$]

Although evidence indicated that the reaction product was a trinuclear complex with the formulation [{IrCl$_2$(PMe$_2$Ph)$_3$(μ-PH$_2$)}$_2$Au][ClO$_4$], it was decided to undertake a single-crystal X-ray structure determination. Suitable crystals of the complex were obtained as the perchlorate salt from a dichloromethane/diethylether mixture and the
Figure 4.9 Structure of \([\{\text{IrCl}_3(\text{PMe}_2\text{Ph})_2(\text{PH}_3)\}_2\text{Au}]\text{[ClO}_4\text{]}\)
Table 4.1 Selected bond lengths and angles for [{IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)$_2$}Au][ClO$_4$]

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<th>Bond lengths (Å)</th>
<th>Bond angles (deg.)</th>
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<td>P(2)-Ir(1)-P(3) 85.8(2)</td>
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<tr>
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<td>P(1)-Ir(1)-P(4) 93.8(2)</td>
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<tr>
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<td>P(3)-Au-P(7)</td>
<td>P(3)-Au-P(7) 178.2(2)</td>
</tr>
</tbody>
</table>

-181-
structure was solved by N. I. Powell of University College London. The complex crystallises with one mole equivalent of water and of ether in the space group \(P2_1/c\); monoclinic unit cell of dimensions \(a = 18.292(3) \text{ Å}, b = 14.048(2) \text{ Å}, c = 25.657(6) \text{ Å} \beta = 90.4(2) ^\circ; \ Z = 4\). The structure was refined to \(R = 0.0640\). Important bond lengths and angles are given in Table 4.1, and a view of the cation is shown in Figure 4.9. There is an approximate but not crystallographic centre of symmetry with the gold atom on the inversion centre. The phenyl rings on adjacent cis PMe₂Ph ligands are close and parallel leading to the anomalous shifts observed in the \(^1\text{H} \text{n.m.r.} \) spectrum. These close and parallel rings have been observed for other structures which contain four phosphines ligands coplanar. One pair of phenyl rings has an angle of 3.4 \(^\circ\) between them and a separation of 3.67 \text{ Å}. The other pair of phenyl rings which are also close and parallel have an angle of 16.7 \(^\circ\) and a distance of 3.827 \text{ Å} between their centres. This orientation of the phenyl rings contrasts directly with the arrangement of the corresponding phenyl rings of the related trimetallic complex \([\{\text{RhCl}_2(\text{PMe}_2\text{Ph})_3(\mu-\text{CN})\}_2\text{Au}\}\text{[ClO}_4\text{]}\text{I}_2]^{99}\) which is also centrosymmetric with the gold atom on an inversion centre, but the phenyl rings attached to adjacent phosphine ligands are directed away from each other (Figure 4.10).

![Figure 4.10](image-url)
The P-Au-P angle is very nearly linear at 178.2°. In contrast, the phosphido bridged structures [Mn(CO)_4(μ-PPh_2)_2(AuC_6F_5)_2][PPN] and [Mn(CO)_4(μ-PPh_2)Au]_2 showed marked deviations from the ideally linear geometry expected for gold. Both these structures were seen to exhibit weak Au-Au interactions in the solid state. The iridium phosphido bond lengths in the complex [(IrCl_2(PMe_2Ph_2)Au)[ClO_4]] are slightly longer than those of other mixed metal phosphido bridged complexes containing iridium. Ir(1)-P(3) and Ir(2)-P(7) have bond lengths of 2.375(5) Å and 2.347(5) Å respectively. In comparison the iridium phosphido bond lengths in the heterobimetallic complex [(CO)_4W(μ-PPh_2)Ir(H)(COD)] are shorter (mean of the two iridium phosphido bond lengths is 2.299 Å). The related complex [(CO)_5Fe(μ-PPh_2)IrCl(COD)] exhibited iridium phosphido bond lengths in the same range (Ir-P = 2.304 Å). Although these latter complexes were prepared from iridium(I) complexes Goeffroy suggested these complexes were best formulated as containing iridium(III) centers. The difference in the bond lengths of these complexes must be due to the presence of a metal-metal interaction. The gold phosphido bond lengths are similar to those of the manganese gold complexes containing phosphido bridges. Gold-phosphorus bond lengths of 2.294(5) Å and 2.330(5) Å [Au-P(3) and Au-P(7)] interactions were observed. These values are in good agreement with those found by Riera in the complex [Au_2Mn(μ-PPh_2)_2(CO)_4(C_6F_5)_2][PPN] where the Au-P bond lengths are 2.313 Å and 2.322 Å. These bonds are long for Au-P interactions but are within the range expected for bridging phosphido ligands. Riera reported that the Au-P bond lengths in the tetracarbonyl complex [Au_2Mn(μ-PPh_2)_2(CO)_4] were slightly longer than those in the trinuclear complex. These bond lengths (mean = 2.336 Å) are very close to that observed for the Au-P(7) interaction in the trinuclear complex [(Ir_2Cl_2(PMe_2Ph_2)Au)[ClO_4]] although the remaining Au-P(3) length is shorter. These bonding interactions are not directly comparable because the trinuclear manganese gold phosphido complex is anionic and contains two neutral gold fragments, Au(C_6F_5), whilst the tetracarbonyl complex has no overall charge, although it contains two manganese centres bridged by an Au+ ion and should exhibit Au-P interactions that are more reliable for comparison with those of our compound.
4.2.5 Spectroscopic Characteristics

Both complexes \([\{\text{IrCl}_2(\text{PM}_{2}\text{Ph})_3(\mu-\text{PHR})\}_2\text{Au}\}][\text{ClO}_4] \) (R = H, Ph) showed broad resonances in the \(^1\text{H}\) n.m.r. spectrum in the methyl region. For R = H the \(^1\text{H}\) n.m.r. spectrum exhibited a broad triplet and a doublet of doublets indicating that Me groups are magnetically equivalent as a result of rapid rotation about the metal-phosphorus bonds. The phosphorus bound protons appeared as a complex multiplet in the \(^1\text{H}\) n.m.r. spectrum as a result of non first-order coupling to many different phosphorus nuclei. The spin system consists of a large one-bond phosphorus-hydrogen coupling \([\text{\(^1\)J(PH)} = 317.6 \text{ Hz}]\) and several large phosphorus phosphorus couplings through gold and iridium, with coupling of these phosphorus nuclei to the protons attached directly to the phosphido centre (Figure 4.11). A computer simulation was not possible since there were too many n.m.r. active nuclei involved in the spin system for the programs available, although a phosphorus decoupled \(^1\text{H}\) n.m.r. spectrum would have resolved the problem. The large line width in the \(^1\text{H}\) n.m.r. spectrum is a consequence of exchange; steric bulk at the phosphido centre is causing restricted rotation about the metal-phosphorus axis and as a result conformational exchange in solution is slow on the

Figure 4.11 400 MHz \(^1\text{H}\) n.m.r. spectrum of the PH\(_3\) region of the complex \([\{\text{IrCl}_2(\text{PM}_{2}\text{Ph})_3(\text{PH}_3)\}_2\text{Au}\}][\text{ClO}_4]\)

\[\text{Figure 4.11 400 MHz } ^1\text{H} \text{ n.m.r. spectrum of the PH}_3 \text{ region of the complex } \{\text{IrCl}_2(\text{PM}_2\text{Ph})_3(\text{PH}_3)\}_2\text{Au}[\text{ClO}_4]\]

\[\text{were too many n.m.r. active nuclei involved in the spin system for the programs available, although a phosphorus decoupled } ^1\text{H} \text{ n.m.r. spectrum would have resolved the problem. The large line width in the } ^1\text{H} \text{ n.m.r. spectrum is a consequence of exchange; steric bulk at the phosphido centre is causing restricted rotation about the metal-phosphorus axis and as a result conformational exchange in solution is slow on the}\]

\[\text{-184-}\]
n.m.r. time-scale.

For \( R = \text{Ph} \) steric bulk is greater and the \( ^1\text{H} \) n.m.r. confirms that there is exchange in solution at room temperature. Reaction of the phenylphosphido complex with \([\text{Au} (\text{PPh}_3 )\text{Cl} ] \) afforded a trinuclear complex with two chiral centres giving rise to two diastereoisomers, SR and RR, the latter having an enantiomeric counterpart, SS. We believe both these diastereoisomers are present in approximately equal proportions (n.m.r. evidence). The methyl groups belonging to the mutually trans \( \text{PMe}_2 \text{Ph} \) ligands are diastereotropic and appear as separate signals in the n.m.r. spectrum. This magnetic non-equivalence will remain even with rapid rotation about the metal-phosphorus axes and therefore at high temperature the \( ^1\text{H} \) n.m.r. spectrum will contain four sets of triplets and four sets of doublets for the two pairs of enantiomers. The phosphorus bound protons appear as a complex multiplet and should be treated as a second order spin system. A full conformational and stereochemical analysis by n.m.r. spectroscopy was not possible because of the large number of rotamers conceivable for each diastereoisomer.

The \( ^{31}\text{P} \{^1\text{H}\} \) n.m.r. spectrum of \([\{\text{IrCl}_2 (\text{PMe}_2 \text{Ph})_3 (\text{PH}_2 )\}_2 \text{Au}\}[\text{ClO}_4 ]\) displayed a large shift to low-field for the phosphido bridge when compared to the terminal phosphido precursor\(^4\)\(^8\) (Figure 4.12). Coupling constants for the phosphido resonance have been obtained from a reasonable spin simulation using a simplified spin system (\(\text{AA'XX'}\)) in which the smaller cis couplings have been ignored. The line intensities and positions were found to depend upon the large trans coupling constants both through

![Figure 4.13](image-url)

-185-
Figure 4.12  $^{31}\text{P}^{[\text{H}]}$ n.m.r. spectra of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_2(\text{PH}_2)_2\text{Au}]\text{[ClO}_4]$
iridium and through gold. Large deviations from the observed pattern were simulated if the coupling constants differed from the values quoted by a significant amount. Final coupling constants of $^2J(PP) = 311.0$ Hz and $^2J(PP) = 230.0$ Hz for the coupling through iridium and through gold respectively, gave simulated n.m.r. spectra whose line intensities and pattern matched reasonably well with the observed spectra.

Roper has shown that the isoelectronic osmium phosphido complex $[\text{OsCl(CO)}_2(\text{PPh}_3)_2(\text{PPhH})]$ reacts with $[\text{Au(PPh}_3\text{Cl})$ in a different manner by giving the neutral phosphido species $[\text{OsCl(CO)}_2(\text{PPh}_3)_2(\mu-\text{PPhH})(\text{AuCl})]^+$ (Figure 4.13) by the expulsion of triphenylphosphine. The formation of this phosphido bridged dinuclear complex is in marked contrast with the formation of the trimetallic complex that we have characterised structurally. Intuitively we would expect the neutral osmium(II) phosphido to be more nucleophilic than the neutral iridium(III) based on oxidation state differences, this is not what is observed, the osmium phosphido complex only appears to be nucleophilic enough to substitute the triphenylphosphine whereas the isoelectronic iridium(III) phosphido is nucleophilic enough to substitute the chloride as well. We have already observed significant differences between the parent phosphine complexes of these isoelectronic species. It was observed in the previous chapter that the complex $[\text{OsCl(CO)}_2(\text{PPh}_3)_2(\text{PPhH}_2)][\text{ClO}_4]$ readily exchanged all of its phosphorus bound protons with D$_2$O in three hours whereas $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_3)][\text{ClO}_4]$ under went partial exchange in MeOD.

The use of the gold(I) fragment $[\text{Au(PPh}_3\text{)]}^+$ as a replacement for H$^+$ has been widely exploited. Riera has prepared a series of di, tri and tetranuclear complexes with phosphido bridges between gold and manganese$^{80}$ (Figure 4.14). He showed that the complex $[\text{Mn(CO)}_3(\text{bipy})(\text{PPh}_2\text{H})][\text{PF}_6]$ reacts readily with the gold phosphine complex $[\text{AuCl(PPH}_3\text{)}]$ in the presence of Tl(acac) to afford the dinuclear phosphido bridged cationic complex $[\text{Mn(CO)}_3(\text{bipy})(\mu-\text{PPh}_2\text{})(\text{AuPPh}_3)] [\text{ClO}_4]$. In contrast the reaction of $[\text{Mn(CO)}_3(\text{PPh}_2\text{H})][\text{ClO}_4]$ and the complex $[\text{Au(PPh}_3\text{Cl})$ in the presence of Tl(acac) was found to yield the trimetallic complex $[[\text{Mn(CO)}_3(\mu-\text{PPh}_2\text{)})_2\text{Au}][\text{ClO}_4]$ with the bis-phosphine gold chloride complex as by product (Figure 4.14). This latter complex can be compared with our trimetallic compound. Riera suggested that the reaction of $[\text{Mn(CO)}_3(\text{PPh}_2\text{H})][\text{ClO}_4]$ with $[\text{Au(PPh}_3\text{Cl})$ and Tl(acac) gave the mixed product $[\text{Mn(CO)}_3(\mu-\text{PPh}_2\text{})(\text{AuPPh}_3)][\text{ClO}_4]$ analogous to $[\text{Mn(CO)}_3(\text{bipy})(\mu-\text{PPh}_2\text{})(\text{AuPPh}_3)][\text{ClO}_4]$ which was subsequently converted to the trimetallic phosphido.

-187-
Figure 4.14

\[
\begin{align*}
[Mn(CO)_5(PPh_2H)][ClO_4] & \xrightarrow{[Au(C_6F_5)\text{tht}]} K(\text{acac}) & \begin{array}{c}
\text{Au(C_6F_5)} \\
\text{PPh}_2 \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\text{Mn} \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\end{array} \\
[Mn(CO)_3(\text{bipy})(PPh_2H)][PF_6] & \xrightarrow{[Au(PR_3)\text{Cl}]} Tl(\text{acac}) & \begin{array}{c}
\text{Au(PR}_3) \\
\text{PPh}_2 \\
\text{N} \\
\text{N} \\
\text{Mn} \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\end{array} \\
[Mn(CO)_5(PPh_2H)][ClO_4] & \xrightarrow{[Au(PR_3)\text{Cl}]} Tl(\text{acac}) & \begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{Au} \\
\text{P} \\
\text{Ph} \\
\text{Mn} \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\text{CO} \\
\end{array} \\
[Mn(CO)_3(\text{bipy})(PPh_2H)][ClO_4] & \xrightarrow{[AuCl(\text{tht})]} K(\text{acac}), Tl(\text{acac}) & \begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{Au} \\
\text{P} \\
\text{Ph} \\
\text{Mn} \\
\text{N} \\
\text{N} \\
\text{CO} \\
\text{CO} \\
\end{array}
\end{align*}
\]
bridged complex and the bis-phosphine gold cation by a symmetrisation reaction of the type common in gold(I) chemistry. Possible pathways for the synthesis of the trinuclear complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2\text{AuPR}_3)]\) from the reaction of the appropriate iridium phosphido complex and \([\text{Au(PPh}_3\text{)Cl}]\) are shown in Figure 4.15. Examples of both types of intermediates, \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\mu-\text{PPhH})(\text{AuPPh}_3)]\) and \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\mu-\text{PPh HAuCl})]\), have been proposed in the literature. Although Roper proposed that the osmium(II) phosphido complex reacts with \([\text{Au(PPh}_3\text{)Cl}]\) to give a complex characterised as the latter type, the symmetrisation reaction common in gold(I) chemistry is favoured (A). It is also known that mixed phosphine complexes of the type \([\text{AuLL'}]^+\) are unstable with respect to \([\text{AuL}_2]^+\) and \([\text{AuL'}_2]^+\). We may consider the proposed heterobimetallic phosphido complex as such a mixed phosphine complex of gold(I), \(i.e\) \([\text{AuLL'}]\) (with \(L = \text{PPh}_3\) and \(L' = \text{PHR IrCl}_2(\text{PMe}_2\text{Ph})_3\)) which could undergo symmetrisation. Two possible reaction schemes are shown in Figure 4.16a and 4.16b assuming that the first complex formed is \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2\text{AuPR}_3)]\) and not \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2\text{AuCl})]\). Figure 4.16a shows a four-centre (either binuclear or assisted) mechanism operative (mechanism 1). Mechanism 2 involves dissociation of the phosphine ligand, which leads to the formation of a dinuclear phosphido complex with two triphenylphosphine ligands coordinated at a gold centre as well as affording a coordinatively unsaturated gold(I) complex. Loss of \([\text{Au(PPh}_3\text{)Cl}]\) from the former
Figure 4.16 (a) Four-centre mechanism

(b) Dissociation of phosphine
complex would afford a terminal phosphido as an intermediate which would readily combine with the unsaturated gold(I) fragment to give the observed trimetallic complex as the final product.

2.4.6 Reaction of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PHR})]\) with Organomercury Compounds

(a) Reaction with \([\text{HgClR}]\) (R = CH$_2$Ph, Et).

Solutions of the terminal phosphido complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) react with alkyl mercury halide complexes to afford the heterobimetallic phosphido-bridged complexes \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\mu-\text{PPhH})(\text{HgR})][\text{BPh}_4]\) (R = CH$_2$Ph, Et). Addition of the alkyl mercury halide to a deep orange solution of the terminal phosphido complex gave an immediate colour change to pale yellow. N.m.r. spectroscopic techniques were of limited use in identifying the nature of the complex in solution because of exchange processes occurring in solution. Steric bulk within the square plane containing the four phosphines resulted in slow exchange of conformers on the n.m.r. time-scale.

In both cases (R = CH$_2$Ph and R = Et) good FAB mass spectral data were obtained showing parent molecular ions consistent with the formulation of the phosphido-bridged bimetallic complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\mu-\text{PPhH})(\text{HgR})]^+\). The molecular ion peaks were found to contain the expected isotopic pattern for an iridium-mercury species (Figure 4.17). The calculated molecular ion pattern is consistent with the observed envelope of peaks. Although the fragmentation behaviour leading to some of

\[
\text{Figure 4.18}
\]
Figure 4.17 Mass spectra of some iridium-Mercury phosphido bridged complexes

(a) $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_5(\text{PPhHHgCH}_2\text{Ph})]^{+}[$BPh$_4$]

(b) $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_5(\text{PPhHHgC}_2\text{H}_4)]^{+}[$BPh$_4$]
the lower mass peaks could not be assigned, some of the peaks were assigned, i.e. 
[IrCl₂(PMe₂Ph)₂(μ-PPh)(HgC₂H₅)]⁺, [IrCl₂(PMe₂Ph)₃(PPhH)]⁺, [IrCl₂(PMe₂Ph)₃]⁺ and 
[IrCl₂(PMe₂Ph)₂]⁺ (R = C₂H₅) and [IrCl₂(PMe₂Ph)₂(μ-PPhH)(HgCH₂Ph)]⁺, 
[IrCl₂(PMe₂Ph)₃(PPhH)]⁺, [IrCl₂(PMe₂Ph)₃]⁺ and [IrCl₂(PMe₂Ph)₂]⁺ (R = CH₂Ph).

The complexes were isolated as tetraphenylborate salts from methanol. Each has 
been characterised as a simple dinuclear complex with a phosphido-bridge. These 
complexes are the product of electrophilic attack at the phosphido centre by the alkyl 
mercury halides (Figure 4.18).

(b) Reaction of [IrCl₂(PMe₂Ph)₃(PH₂)] with HgCl₂.

A deep yellow solution of the neutral phosphido complex reacted with HgCl₂ 
in dichloromethane. Addition of two mole equivalents of sodium tetraphenylborate to 
a solution of the product in methanol afforded a pale yellow precipitate whose 
elemental analytical data for (C, H and P) agreed reasonably well with the calculated 
values. A dicationic phosphido-bridged trimetallic complex similar to that observed for 
[[IrCl₂(PMe₂Ph)₃(PH₂)]₂Au][ClO₄] is expected (Figure 4.19).

Figure 4.19
4.3 Conclusion

Neutral iridium(III) complexes containing terminal phosphido ligands are easily prepared and are shown to be nucleophilic. The reactions of these phosphido complexes with organic electrophiles reinforces our belief that the phosphido ligand is pyramidal. Cationic complexes with chiral phosphine ligand have been prepared from the phosphido complex but no attempt was made to resolve the enantiomers.

Metal electrophiles were also observed to react with the neutral phosphido complex to afford a variety of dinuclear phosphido bridged complexes and also complexes that were trimetallic. The crystal structure of \(\left[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)\right]_2\text{Au}[\text{ClO}_4]\) confirmed that the complex is trimetallic. This complex contrasts directly with the product from a similar reaction of the osmium(II) phenylphosphido complex with \([\text{Au}(\text{PPh}_3)\text{Cl}]\), which was identified as dinuclear. An intermediate of the form, \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\mu-\text{PH}_2)(\text{AuPPh}_3)] [\text{ClO}_4]\), is expected to undergo a rapid symmetrisation reaction to give the observed trimetallic complex. Trimetallic complexes were also formed from the reaction of the phosphido complex with mercuric chloride, although dinuclear phosphido-bridged complexes were obtained from the reaction with alkyl mercury halides.
4.4 Experimental

4.4.1 Synthesis of [IrCl₂(PMe₃Ph)₃(PPhHMe)][I]

A solution of [IrCl₂(PMe₂Ph)₃(PPhH)] (0.054 g, 0.069 mmol) in dichloromethane (5 cm³) was treated with methyl iodide (0.008 cm³, 0.13 mmol) with stirring. The solution was stirred under a nitrogen atmosphere for 15 minutes. The solvent was removed under reduced pressure to leave a yellow oily residue. Crystallisation from dichloromethane/diethylether gave the product as yellow crystals (0.047 g, 73%). [Found: C, 40.13; H, 4.78; P, 13.1. C₃₅H₂₄Cl₁IrP₄ requires C, 40.1; H, 4.56; P, 13.3%].

4.4.2 Synthesis of [IrCl₂(PMe₃Ph)₄][ClO₄]

To a solution of [IrCl₂(PMe₂Ph)₃(PPhHMe)][I] (0.067 g, 0.072 mmol) in dichloromethane (5 cm³) was added base DBU (0.016 cm³, 0.11 mmol). After stirring the solution for ca. 15 minutes methyl iodide (0.009 cm³, 0.14 mmol) was added and the solution was shaken and left to stand for a further 30 minutes. The solution was evaporated to dryness under reduced pressure to yield a yellow oil. A solution of this oil in methanol (5 cm³) was treated with a solution of sodium perchlorate (0.008 g, 0.072 mmol) in methanol (2 cm³). After stirring the mixture for 10 minutes a yellow solid appeared. The solid was isolated by filtration and washed with portions of methanol (3x5 cm³) to yield the title complex (0.023 g, 34%). [Found: C, 41.85; H, 4.78; Cl, 11.74. C₃₂H₂₂Cl₃IrO₄P₄ requires C, 41.97; H, 4.83; Cl, 11.62%].

4.4.3 Synthesis of [IrCl₂(PMe₃Ph)₃(PPhHC₃H₃)][BPh₄]

To a stirred solution of [IrCl₂(PMe₂Ph)₃(PPhH)] (0.236 g, 0.3 mmol) in dichloromethane (20 cm³) was added freshly distilled propargyl bromide (0.042 cm³, 0.36 mmol). The solution was stirred under argon and after ca. 10 minutes the colour had changed from the initial deep orange to a pale yellow. The solvent was removed under reduced pressure to leave an oily residue. A solution of this oil in methanol (5 cm³) was treated with sodium tetraphenylborate (0.103 g, 0.3 mmol) in methanol (1 to 2 cm³). There was immediate formation of a yellow precipitate which was isolated by filtration. The solid collected was washed with portions of methanol (3x5 cm³) to yield a yellow solid identified as the title complex (0.243 g, 70%). [Found: C, 60.00; H, 5.32; P, 10.51. C₇₅H₄₂Cl₂IrP₄B requires C, 59.80; H, 5.40; P, 10.80%].
4.4.4 Synthesis of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]_2\text{Au}][\text{ClO}_4]\)

A solution of the phosphido complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]\) (0.0991 g, 0.14 mmol) in dichloromethane (10 cm³) was treated with \([\text{Au(PMe}_2\text{Ph})\text{Cl}]\) (0.065 g, 0.17 mmol) in dichloromethane (3 cm³). After stirring the mixture for several minutes the colour had changed from deep yellow to pale yellow. Stirring was continued for 30 minutes, after which time the solvent was removed under reduced pressure to leave a yellow oil. Crystallisation of the residue from dichloromethane/ethanol gave the product as fine yellow crystals of the chloride salt (0.080 g, 70%). [Found: C, 34.85; H, 4.34; Cl, 10.45; P, 14.86. \(\text{C}_{40}\text{H}_{76}\text{AuCl}_5\text{Ir}_2\text{P}_4\) requires C, 34.86; H, 4.27; Cl, 10.72; P, 14.99%].

A solution of the trimetallic complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]_2\text{Au}][\text{Cl}]\) (0.0318 g, 0.019 mmol) prepared by the above procedure in methanol (5 cm³) was treated with sodium perchlorate (0.003 g, 0.024 mmol) in methanol (2 cm³). After stirring for ca. 10 minutes a yellow precipitate formed and was collected by filtration and washed with methanol. Crystallisation of the product from dichloromethane/diethylether gave crystals of the title complex suitable for single-crystal X-ray structure determination.

4.4.5 Synthesis of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]_2\text{Au}][\text{Cl}]\)

The above reaction procedure was repeated for the terminal phosphido complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) (0.1086 g, 0.14 mmol) in dichloromethane (10 cm³) and \([\text{Au(PMe}_2\text{Ph})\text{Cl}]\) (0.0682 g, 0.14 mmol). Work up as before gave the title trimetallic complex as yellow crystals (0.076 g, 61%). [Found: C, 38.86; H, 3.95; Cl, 9.60; P, 13.76. \(\text{C}_{40}\text{H}_{76}\text{AuCl}_5\text{Ir}_2\text{P}_4\) requires C, 39.92; H, 4.35; Cl, 9.82; P, 13.73%].

4.4.6 Reaction of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]\) with \([\text{Au(PPh}_3]\text{Cl}]\)

A similar procedure was followed with the phosphido complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]\) in dichloromethane treatment with \([\text{Au(PPh}_3]\text{Cl}]\) gave a pale yellow solution which yielded the same trimetallic phosphido complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]_2\text{Au}][\text{Cl}]\) after crystallisation from dichloromethane/ethanol.

4.4.7 Reaction of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) with \([\text{Au(PPh}_3]\text{Cl}]\)

A procedure similar to that above was used with \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) in dichloromethane and \([\text{Au(PPh}_3]\text{Cl}]\). Crystallisation of the product as before gave the complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]_2\text{Au}][\text{Cl}]\).
4.4.8 Synthesis of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHHgEt})][\text{BPh}_4]\)

To a stirred solution of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) (0.0386 g, 0.049 mmol) in dichloromethane was added \([\text{HgC}_2\text{H}_2\text{Br}]\) (0.015 g, 0.049 mmol) in dichloromethane (5 cm³). The initial deep orange solution turned pale yellow immediately and the reaction mixture was stirred under nitrogen for ca. 30 minutes. The solvent was removed under reduced pressure to leave a yellow oily residue. The oil was dissolved up in methanol (5 cm³) and the resultant solution was treated with sodium tetrphenylborate (0.0167 g, 0.049 mmol) in methanol (1-2 cm³). A green-yellow precipitate formed immediately and was filtered and washed with methanol (3x5 cm³). The resultant yellow solid was dried under vacuum (0.035 g, 53%). [Found: C, 49.40; H, 4.33; P, 9.56. \(\text{C}_{56}\text{H}_{64}\text{BCl}_2\text{IrHgP}_4\) requires C, 50.38; H, 4.83; P, 9.28%]. MS (EI): M/e = 1017 (M⁺).

4.4.9 Synthesis of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHHgCH}_2\text{Ph})][\text{BPh}_4]\)

A solution of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) (0.040 g, 0.051 mmol) in dichloromethane (10 cm³) was treated with benzyl mercury bromide (0.0189 g, 0.05 mmol). The deep orange solution quickly turned pale yellow and, after being stirred under nitrogen for 30 minutes, the solution was evaporated to dryness under reduced pressure to give a pale yellow oil. A solution of the oil in methanol (3 to 4 cm³) was treated with sodium tetrphenylborate (0.0174 g, 0.05 mmol) in methanol (2 cm³). The yellow precipitate that formed was isolated by filtration and washed with methanol to yield the title complex (0.044 g, 62%). [Found: C, 53.44; H, 4.34; P, 9.54. \(\text{C}_{56}\text{H}_{66}\text{BCl}_2\text{HgIrP}_4\) requires C, 52.52; H, 4.77; P, 8.88%]. MS (EI): m/e = 1079 (M⁺).

4.4.10 Reaction of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]\) with mercury(II) halide.

A solution of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]\) (0.0506 g, 0.07 mmol) in dichloromethane (10 cm³) was treated with \(\text{HgCl}_2\) (0.0093 g, 0.035 mmol). An immediate colour change from deep orange to pale yellow indicated a quick reaction. The reaction mixture was left under nitrogen for ca. 30 minutes and then the solvent removed under reduced pressure to leave a green-yellow oil. The residue was dissolved up in methanol (5 cm³) and treated with a solution of sodium tetrphenylborate (0.0236 g, 0.07 mmol) in methanol (2 to 3 cm³). A green-yellow precipitate appeared immediately and was isolated by filtration. The solid was washed with methanol and dried under vacuum to give the trimetallic complex \([[[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PH}_2)]_3\text{Hg}][\text{BPh}_4]]\) (0.0161 g, 21%) as a
pale yellow solid. [Found: C, 54.31; H, 5.79. C_{98}H_{110}B_{2}Cl_{4}Ir_{2}HgP_{4} requires C, 56.30; H, 5.41%].
4.5 Spectroscopic data for the Complexes

Table 4.2 ^1H n.m.r. data for phosphine and phosphido complexes of Iridium(III)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ)^a</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl₂(PMe₂Ph)₃(PPhHMe)]I^b</td>
<td>1.32 (ddd)</td>
<td>PPhHMe (3H)</td>
<td>²J(PH)=11.5, ⁴J(PH)=6.0, ³J(HH)=2.4</td>
</tr>
<tr>
<td></td>
<td>1.64 (t,broad)</td>
<td>PMe₂Ph^1 (6H)</td>
<td>²J(PH)=7.8</td>
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<tr>
<td></td>
<td>1.75 (dt)</td>
<td>PMe₂Ph^c (3H)</td>
<td>²J(PH)=9.5, ²J(PH)=1.4</td>
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<tr>
<td></td>
<td>1.79 (dt)</td>
<td>PMe₂Ph^c (3H)</td>
<td>²J(PH)=9.8, ²J(PH)=2.4</td>
</tr>
<tr>
<td></td>
<td>1.91 (t,broad)</td>
<td>PMe₂Ph^c (6H)</td>
<td>²J(PH)=7.4</td>
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<tr>
<td></td>
<td>5.82 (dm)</td>
<td>PPhHMe (1H)</td>
<td>¹J(PH)=393, ³J(PH)=4.3^d</td>
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<tr>
<td>[IrCl₂(PMe₂Ph)₄][ClO₄]^b</td>
<td>1.80 (s,broad)</td>
<td>PMe₂Ph (24H)</td>
<td>half height line width =60 Hz</td>
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<tr>
<td>[IrCl₂(PMe₂Ph)₃(PPhC₃H₅)][BPh₄]^b</td>
<td>1.36 (s)</td>
<td>PMe₂Ph (6H)</td>
<td>²J(PH)=3.0^d</td>
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<td></td>
<td>1.50 (m)</td>
<td>PMe₂Ph (6H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.60 (s,broad)</td>
<td>CH (1H), CH₂ (2H)</td>
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</tr>
<tr>
<td></td>
<td>1.82 (m), 2.44 (m)</td>
<td>PPhHMe (1H)</td>
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<td></td>
<td>5.42 (dm)</td>
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<tr>
<td>[IrCl₂(PMe₂Ph)₃(PPhHgC₂H₅)][BPh₄]^b</td>
<td>1.55-1.64 (s,broad)</td>
<td>PMe₂Ph, C₅H₅ (23H)</td>
<td>¹J(PH)=348.0</td>
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<td>4.90 (dd,broad)</td>
<td>PPhH (1H)</td>
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<tr>
<td>[IrCl₂(PMe₂Ph)₃(PPhHgCH₂Ph)][BPh₄]^b</td>
<td>1.42 (s,broad)</td>
<td>PMe₂Ph^c (6H)</td>
<td>¹J(PH)=348.0</td>
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<td></td>
<td>1.60 (s,broad)</td>
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<td></td>
<td>2.82 (broad)</td>
<td>CH₂ (2H)</td>
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<td>5.05 (d,broad)</td>
<td>PPhH (1H)</td>
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Table 4.2 continues overleaf ........
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<th>Compound</th>
<th>Chemical Shift (δ)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
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</tr>
<tr>
<td>[{IrCl₂(PMe₂Ph)₃(PH₂)}_₂Au][ClO₄] (^b)</td>
<td>1.42 (d,broad) 1.76 (t,broad) 3.14 (dm) 7.1-7.5 (broad)</td>
<td>PMe₂Ph⁶ (6H) PMe₂Ph¹ (12H) PH₂ (2H) phenyl (15H)</td>
<td>(^{2}J(\text{PH})=9.3) (^{1}J(\text{PH})=317.6)</td>
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<tr>
<td>Diastereoisomer 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.36 (d,broad) 1.43 (d,broad) 1.87 (s,broad) 1.94 (d,broad) 4.90 (d,m) 7.0-8.2 (m)</td>
<td>PMe₂Ph⁶ (6H) PMe₂Ph¹ (6H) PMe₂Ph³ (3H) PMe₂Ph³ (3H) PPhH (1H) phenyl (20H)</td>
<td>(^{2}J(\text{PH})=8.0)</td>
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<td></td>
</tr>
<tr>
<td>[{IrCl₂(PMe₂Ph)₃(PPhH)}_₂Au][ClO₄] (^b)</td>
<td>1.28 (broad) 1.55 (broad) 4.95 (m)</td>
<td>PMe₂Ph (12H) PMe₂Ph (6H) PPhH (1H)</td>
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</tr>
<tr>
<td>Diastereoisomer 2</td>
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<td></td>
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</table>

\(^a\): Spectra recorded in CDCl₃ and referenced internally to the solvent.
\(^b\): Spectra recorded at 400 MHz.
\(^c\): PMe₂Ph cis to PMe₂Ph.
\(^d\): J(PH) = \(^{2}J(PH) + \(^{4}J(PH)\).
\(^e\): PMe₂Ph trans to PMe₂Ph.
Table 4.3 $^{31}$P {$^{1}$H} n.m.r. data for the phosphine and phosphido complexes of Iridium(III)

<table>
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<tr>
<th>Compound</th>
<th>Chemical shift ($\delta$)$^a$</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PPhHMe)]$\text{[I]}^b$</td>
<td>-63.61 (dm) &lt;br&gt;-50.00 (dt) &lt;br&gt;-48.81 (s, broad)</td>
<td>PPhHMe &lt;br&gt;PMe$_2$Ph$^c$ &lt;br&gt;PMe$_2$Ph$^t$</td>
<td>$^{2}$J(PP)=370.0 &lt;br&gt;$^{2}$J(PP)=370.0, $^{2}$J(PP)=25.0</td>
</tr>
<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_4$]$\text{[ClO}_4]^b$</td>
<td>-53.51 (s, broad)</td>
<td>PMe$_2$Ph</td>
<td>half height linewidth =120Hz</td>
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<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_4$]$\text{[ClO}_4]^b,d$</td>
<td>-51.60 (s) &lt;br&gt;-53.15, -49.46 (AA/BB)$^d$ &lt;br&gt;-54.37, -53.63 &lt;br&gt;-50.29, -49.02 (ABCD)</td>
<td>PMe$_2$Ph &lt;br&gt;PMe$_2$Ph</td>
<td>$^{2}$J(PP)=363.0, $^{2}$J(PP)=23.0</td>
</tr>
<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_3$(PPhHC$_3$H$_5$)]$\text{[BPh}_4]^b$</td>
<td>-41.80 (dt) &lt;br&gt;-51.60 (dt) &lt;br&gt;-50.72 (m)</td>
<td>PPhHC$_3$H$_5$ &lt;br&gt;PMe$_2$Ph$^c$ &lt;br&gt;PMe$_2$Ph$^t$</td>
<td>$^{2}$J(PP)=368.0, $^{2}$J(PP)=28.1</td>
</tr>
<tr>
<td>[[IrCl$_2$(PMe$_2$Ph)$_3$(PH$_2$)]$_2$Au]$\text{[ClO}_4]^b$</td>
<td>-118.5 (m) &lt;br&gt;-67.00 &lt;br&gt;-66.41 (dt)</td>
<td>PH$_2$ &lt;br&gt;PMe$_2$Ph &lt;br&gt;PMe$_2$Ph</td>
<td>$^{2}$J(PP)=311.1, $^{2}$J(PP)=230$^h$</td>
</tr>
<tr>
<td>[[[IrCl$_2$(PMe$_2$Ph)$_3$(PPh)]$_2$Au]$\text{[ClO}_4$</td>
<td>-66.60 (m)</td>
<td>PMe$_2$Ph &amp; PPhH</td>
<td></td>
</tr>
<tr>
<td>[[[IrCl$_2$(PMe$_2$Ph)$_3$(PPh$_2$)]$_2$Au]$\text{[BPh}_4$</td>
<td>-53.00 (v broad)</td>
<td>PMe$_2$Ph &amp; PPh$_2$</td>
<td></td>
</tr>
</tbody>
</table>

*a: Spectra recorded in CDC$_3$ and chemical shifts are quoted relative to 85% H$_3$PO$_4$ with downfield chemical shifts reported as positive.
*b: Spectra recorded at 162 MHz.
*c: PMe$_2$Ph cis to PMe$_2$Ph
*t: PMe$_2$Ph trans to PMe$_2$Ph.
*d: Spectra recorded in CD$_2$Cl$_2$ at -75 °C.
Chapter 5

Conformations of Tetrakis-Phosphine Complexes of Iridium(III)
5 Conformations of Tetrakisphosphine Complexes of Iridium(III)

5.1 Introduction

Unexplained features of the n.m.r. spectra of complexes containing four PMe₂Ph ligands in a plane have been described.²²² ²²³ ²²⁴ ²²⁵ ²²⁶ ²²⁷ ²³⁴ A broad 'H n.m.r. methyl singlet at room temperature has been reported for \( \text{trans-IrCl}_2(\text{PMe}_2\text{Ph})_4\)[\(\text{ClO}_4\)].²²³ Similar spectra have been observed for other complexes in which four phosphines are coplanar, e.g., \[\text{ReCl(CO)(PMe}_2\text{Ph)}_3\] and \[\text{RuCl(CO)(PMe}_2\text{Ph)}_4][\text{BPh}_3\]. Electrochemical reduction of \[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3\] (Figure 5.1) gave a five-coordinate intermediate after release of a chloride anion.²³⁶ This species was found to react with \(\sigma\) donors, in particular PMe₂Ph reacted with this unsaturated complex to afford a six-coordinate osmium(II) complex which was described as \(\text{trans-OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{P'Me}_2\text{Ph})\) containing a unique weakly bound phosphine. A 3:1 ratio of the signals for the methyl and phenyl resonances led Stephenson to conclude that the complex was not a simple \(\text{trans-OsCl}_2(\text{PMe}_2\text{Ph})_4\)[\(\text{ClO}_4\)] species but rather contained three phosphines bound in a conventional manner through the phosphorus. The fourth phosphine ligand was not

![Figure 5.1](image-url)
bound through the phosphorus but interacted through the π system of the phenyl ring (i.e. [M-arene] bound) or through an agostic hydrogen atom from the phenyl ring or methyl group.

Although Stephenson could not obtain reasonable crystals of the osmium tetrakis-phosphine complex to enable a single-crystal X-ray structure determination to be carried out, other tetrakis-phosphine complexes with unusual modes of bonding have been structurally characterised. For example, the iridium(I) tetrakis-dimethylphenylphosphine complex \([\text{Ir}(\text{PMe}_2\text{Ph})_4]^+\) undergoes intramolecular oxidative addition at 80 °C to give the iridium hydrido complex \([\text{IrH}(\text{PMe}_2\text{Ph})_3(\text{PMePhCH}_2)]\) (Figure 5.2) containing three conventionally bound phosphines and one bound in a unique manner. Furthermore, Stephenson's proposal of a [M]-arene complex was not unreasonable considering tetrakis-phosphine complexes with this mode of bonding have been identified. Upon heating \([\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]\), \(\text{N}_2\) is lost and \([\text{Mo}(\text{PMe}_2\text{Ph})_4]\) is formed. This complex appeared from its stoichiometry to be unsaturated but rather than having an electron count of 14 containing four M-P bound phosphines it has rearranged to an 18e complex in which one of the phosphines binds via an arene ring, not via phosphorus at all (Figure 5.3).

We now show in this Chapter that the iridium(III) complex \([\text{IrCl}_x(\text{PMe}_2\text{Ph})_4][\text{ClO}_4]_x\), isoelectronic with Stephenson's osmium complex, contains four phosphines all of which are conventionally bound through the phosphorus to the iridium centre. The unexplained features of the n.m.r. spectra result from the presence of rotamers in exchange, each containing at least two phenyl groups in a close parallel arrangement.
MoCNd^PMePh was found to contain coplanar methyldiphenylphosphine ligands. This complex undergoes a variety of unusual substitution reactions where the phosphine ligands are replaced by P-, N-, or S-donor ligands while the labile dinitrogen ligands are retained. The lability of the bulky phosphine ligands can be attributed to a weakening of the molybdenum-phosphorus bond by inter-ligand steric interactions.

Many transition metal complexes containing four phosphine ligands coplanar are known, these include [ReCl(N2)(PMe2Ph)4]224 [ReCl(H2)(PMe2Ph)4]225 and [ReH(N2)(PEt2Ph)4]241 each of which has been characterised crystallographically. [ReCl(N2)(PMe2Ph)4] reacts with [MoCl6(THF)3] in methanol to afford the dinuclear complex [(PMe2Ph)2ClRe(N2)MoCl4(OMe)].242 The four phosphine ligands coordinated to the rhenium atom remain coplanar and, similar to the parent complex, two of the phosphines are orientated such that their phenyl rings are aligned close and parallel. Furthermore, the trinuclear complex, [MoCl5(μ-N2){ReCl(PMe2Ph)4}]243 was also found to contain two parallel phenyl rings per rhenium atom whilst the two remaining pairs of phenyl rings are directed away from each other (Figure 5.4).

This chapter describes the single-crystal X-ray structure of the tetrakis-phosphine complex [IrCl2(PMe2Ph)4][ClO4], the low temperature 31P{1H} n.m.r. spectrum for this compound has been analysed and is consistent with at least three rotamers in solution. The complexes [IrCl2(PMe3)3(PMe2Ph)][ClO4] and [IrCl2(PMe3)3(PMePh2)][ClO4] were also found to undergo conformational exchange in solution which was rapid on the
n.m.r. time-scale at room temperature. The low temperature $^{31}$P{'H} n.m.r. spectra has been interpreted as resulting from two isomers in solution. A single-crystal X-ray structure of the major isomer of [IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph)][ClO$_4$] has been determined and will be reported.
5.2 Results and Discussion

5.2.1 Synthesis of \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_4][\text{ClO}_4]\)

In Chapter 4 the reaction of the phenylphosphido complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhH})]\) with methyl iodide to afford the chiral phosphine complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHMe})][\text{I}]\) was discussed. N.m.r. studies on this complex afforded evidence that there were different rotamers in solution. The low temperature \(^1\text{H}\) n.m.r. spectrum exhibited several methyl resonances indicating slow exchange of these isomers on the n.m.r. time-scale. The \(^{31}\text{P}\{^1\text{H}\}\) spectrum showed three sets of resonances but broadening of these peaks led us to expect exchange of conformers in solution. Repeat deprotonation and methylolation of the chiral phosphine complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{PPhHMe})][\text{ClO}_4]\) afforded a complex that analyzed as \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_4][\text{ClO}_4]\), after exchange of the iodide counter ion for perchlorate. The \(^1\text{H}\) n.m.r. spectrum of this compound exhibited a single broad resonance in the methyl region\(^{228,234}\) (half-height line-width = 60 Hz). A broad singlet of half-height line-width of approximately 120 Hz was observed in the room temperature \(^{31}\text{P}\{^1\text{H}\}\) n.m.r. spectrum.

The aqua complex \([\text{IrCl}_2(\text{PMe}_2\text{Ph})_3(\text{H}_2\text{O})][\text{ClO}_4]\) was synthesised as described in the experimental section.\(^{218,220,244}\) The combination of a trans bond-weakening tertiary phosphine and a weakly coordinated aqua ligand trans to it afforded substitutional lability at the iridium centre. The title complex was prepared by the addition of a slight excess of PMe_2Ph to a dichloromethane solution of the aqua complex (Scheme 5.1).

\[
\begin{align*}
\text{Ir} & \quad \text{Cl} & \quad \text{H}_2\text{O} & \quad +\text{ClO}_4^- \\
\text{PMe}_2\text{Ph} & \quad \text{Cl} & \quad \text{PMe}_2\text{Ph} & \quad +\text{ClO}_4^- \\
\text{PMe}_2\text{Ph} & \quad \text{PMe}_2\text{Ph} & \quad \text{PMe}_2\text{Ph} & \quad \text{PMe}_2\text{Ph}
\end{align*}
\]

Scheme 5.1
Figure 5.5 Variable temperature $^1$H n.m.r. spectra of the methyl and phenyl regions of the complex $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4][\text{BPh}_4]$.
The $^1$H n.m.r. spectrum was essentially identical with that observed for the complex prepared from the terminal phenylphosphido complex by methylation as described above. A single broad resonance was observed in the methyl region of the spectrum as well as broad resonances for the phenyl resonances.

A variable-temperature $^1$H n.m.r. study was undertaken to establish the origin of the exchange process that led to the broad n.m.r. spectrum. Figure 5.5 show the variable-temperature $^1$H n.m.r spectrum of [IrCl$_2$(PMe$_2$Ph)$_4$][BPh$_4$] in the phenyl and methyl regions. At low temperature a spread of resonances is observed for the phenyl protons, Resonances as high-field as $\delta$ 5.65 and as low as $\delta$ 8.50 are seen. Peaks corresponding to methyl protons were also observed at high-field, at least eight methyl resonances were observed at low temperature (-50 °C CDCl$_3$). This phenomena is not unprecedented as Stephenson observed high and low-field shifts for the phenyl protons of his osmium complex [OsCl$_2$(PMe$_2$Ph)$_4$], these resonances ranging from $\delta$ 5.65 to $\delta$ 8.46$^{236}$ (exactly the same chemical shift range observed in the low temperature $^1$H n.m.r. spectrum of [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$]). In the light of Stephenson’s proposal that the osmium complex contained three phosphines bound through phosphorus to the metal centre and one phosphine bound in a unique fashion, and considering the similarity between the low temperature $^1$H n.m.r. spectra of his compound and that of the iridium tetrakis-dimethylphenylphosphine complex, we decided to undertake a single-crystal X-ray structure determination to unambiguously determine the nature of the bonding of the four phosphine to the metal centre. The structure was determined by N.Powell and J.Marshall at University College London.

5.2.2 Crystal Structure of [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$]

Suitable crystals of the title complex were obtained by layering a dichloromethane solution of the complex with diethylether and allowing the solvents to diffuse slowly at room temperature. [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$] crystallises monoclinic in the space group $P2_1/c$ with unit cell dimensions $a = 11.185(2)$ Å, $b = 26.301(2)$ Å, $c = 12.557(2)$ Å, $\beta = 90.17$ °. The structure was refined to $R = 0.035$ and $R_w = 0.034$. Selected bond lengths and angles are tabulated (Table 5.1), and views of the cation are shown in Figures 5.6 and 5.7.

The structure shows that the four phosphines are contained in a square plane.
Figure 5.6 Structure of [IrCl₂(PMe₂Ph₂)][ClO₄]
Figure 5.7 Structure of $[\text{IrCl}_2(\text{PMe}_3\text{Ph})_3][\text{ClO}_4]$
Table 5.1 Selected bond lengths and angles for [IrCl₂(PMe₂Ph)₄][ClO₄]

<table>
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<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg.)</th>
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<td>Ir-P(4)</td>
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</table>
with all phosphines bound in the conventional manner through phosphorus. There are distortions of the square plane of the octahedron, containing the phosphine, towards tetrahedral with trans P-Ir-P angles less than 180 ° [P(1)-Ir-P(3) 172.4(1) ° and P(2)-Ir-P(4) 170.9(1) °]. The deviations of the P-Ir-Cl angle away from 90 ° reflect these distortions away from the ideal planar geometry expected for the IrP4 system [P(1)-Ir-Cl(1) 95.1(1) °, P(1)-Ir-Cl(2) 87.2(1) ° and P(1)-Ir-Cl(1) 84.6(1) °, P(2)-Ir-Cl(2) 94.2(2) ° and P(3)-Ir-Cl(1) 92.5(1) °, P(3)-Ir-Cl(20 85.2(1) ° and P(4)-Ir-Cl(1) 86.4(1) °, P(4)-Ir-Cl(2) 94.8(1) °]. These distortions from the regular square plane are the result of intramolecular phosphine-phosphine repulsions. This distorted octahedral geometry, with one pair of trans phosphorus atoms lying above and the other below the equitorial plane, has been observed in the closely related [ReCl(N2)(PMe2Ph)4]2+ as well as [ReH(N2)(PET2Ph)4]2+ [Mo(N2)2(PMePh2)4]20 [ReCl(H2)(PMePh2)4]235 and [RuCl(CO)(PMe2Ph)4][ClO4]. The four Ir-P distances (2.401(1) Å) are significantly longer than the majority of the Ir-P distances in the related compounds [IrCl2(H2O)(PMe2Ph)4][ClO4]295 (2.379(4) Å), and [IrCl2(PMe2Ph)3(PMe2Ph)][ClO4] (2.381(4) Å). The lengthening of the Ir-P bonds in [IrCl2(PMe2Ph)4][ClO4] is principally steric in origin. [Mo(N2)2(PMePh2)4]240 contains four Mo-P bonds, longer than those of related complexes, and the lengthening of the bonds was attributed to the steric requirements of the phosphine ligands. The two iridium phosphorus bonds to the ligands with the parallel phenyl rings are shorter than the remaining two metal phosphorus bonds which may be a consequence of the reduced repulsion between the two phenyl rings which are aligned parallel allowing a closer approach to the iridium atom. The crystal structure of [IrCl2(PMe2Ph)4][ClO4] shows that two substituents on each phosphorus atom, a methyl and a phenyl group lie on the same side of the approximate IrP4 plane and a methyl group on the other. Because of the way phenyl groups occupy available sites, all the phosphine ligands are different, with four magnetically non-equivalent phosphorus nuclei. The molecule has C1 symmetry as a result of the orientation of the phosphine ligands. The two close and parallel phenyl rings have a distance of 3.83 Å between their centres and an angle of 10.6° between the rings. The X-ray structure of [Mo(N2)2(PMePh2)4]240 revealed similar features in the symmetrical (approximately D2h) way in which the phenyl rings were arranged into four pairs of parallel phenyl rings (Figure 5.8): (11)-(31), (12)-(22), (21)-(42) and (32)-(41), with angles between pairs of planes of 8.4(5) °, 8.9(5) °, 1.6(5) ° and 11.1(5) °, respectively. The average
perpendicular inter-ring separations are 3.1-3.6 Å. [ReCl(N₂)(PMe₂Ph)₄],²²⁴
[RuCl(CO)(PMe₂Ph)₄] (Figure 5.9), [(PMe₂Ph)₂ClRe(N₂)MoCl₆(OMe)]²⁴² and [MoCl₄(μ-
N₂)(ReCl(PMe₂Ph)₄)]²⁴³ and many others contain close parallel phenyl rings.⁴⁶ These

separations are typical for such energetically favourable interactions and similar
interactions have been observed in [Mo(CO)₆(PMe₂Ph)₂], the [Au(PPh₃)₃]+¹⁳ cation,
[Pt(PC₆H₆)₂(CF₃C=CCF₃)]²⁶⁶ (Cy = cyclohexyl) and [Ir(PMe₂Ph)₄]+ and other
complexes.²⁴⁸²⁴⁹ The parallel arrangement of phenyl rings provides an efficient packing
arrangement of the bulky ligands and may explain the deviations of the P atoms from the octahedral geometry.

It is this close and parallel arrangement of the phenyl rings that causes the large up-field and down-field shifts in the low temperature $^1$H n.m.r. spectrum. Figure 5.10 shows an expansion of the low temperature $^1$H n.m.r. spectrum of [IrCl$_2$(PMe$_2$Ph)$_4$][BPh$_4$]. Chemical bonds are regions of high electron density and are capable of setting up magnetic fields. These fields are stronger in one direction than in the other (they are anisotropic) and the effect of the field on the chemical shift of nearby nuclei is dependant on the orientation of nucleus in question with respect to that bond. The $\pi$ system of aromatic rings are a source of these anisotropic effects. The $\pi$-electron delocalisation allows aromatic ring currents which create a magnetic field that is opposed to the applied field at the centre of the ring, but reinforce the applied field outside the ring (Figure 5.11). Protons attached to phenyl rings are commonly observed to resonate at about 6 7.0 as a result of this induced magnetic field but it can be seen that protons of one phenyl ring that lies close enough and parallel to another will be affected by its induced magnetic field. Protons already deshielded by the anisotropic magnetic field will be shifted either to higher or lower field depending on the relative position of the attached protons with respect to the parallel phenyl ring and its induced magnetic field. Protons that lie parallel to the phenyl ring (such as H$_a$ in Figure 5.12) and that do not lie directly above the ring, but lie within the vicinity of

![Diagram of aromatic ring currents and induced magnetic field](image-url)
Figure 5.10  Low temperature (-80 °C) $^1$H n.m.r. spectrum of the complex 
[IrCl$_2$(PMe$_2$Ph)$_4$][BPh$_4$]
the induced magnetic field will be shifted even further down-field as a result of the interaction with the nearby induced magnetic field. The shift to lower field will fall off with distance from the phenyl ring so it is not surprising that the chemical shift movement is only 1.5 ppm. Those protons that are parallel and lie directly over the nearby phenyl ring (such as H\textsubscript{o} in Figure 5.12) will be shifted to higher field with respect to the normal position of phenyl resonances as a result of the shielding effect of the induced magnetic field of the close and parallel ring, because the magnetic field inside the phenyl ring is opposed to the applied magnetic field B\textsubscript{0}. The shift of these protons is of approximately the same magnitude as the shift to lower field because the protons lie the same distance away from the centre of the induced field of the nearby phenyl ring.

The magnetic field induced by the phenyl rings therefore accounts for the large up and down-field chemical shifts of the phenyl resonances in the low temperature \textsuperscript{1}H n.m.r. spectrum by simple considerations of shielding and deshielding by the diamagnetic anisotropy of the rings. There is also a large chemical shift range observed for the methyl resonances of the phosphine ligands in [IrCl\textsubscript{2}(PMe\textsubscript{2}Ph)\textsubscript{4}][ClO\textsubscript{4}]. Signals as high-field as \( \delta \) 0.8 were observed at low temperature (Figure 5.5). The anomalously high-field shift of these methyl resonances can be explained if we consider a methyl group lying close to and directly above a phenyl ring of a phosphine ligand that is cis to it in the coordination sphere. The methyl protons will be shielded by the induced diamagnetic anisotropy of the magnetic field created by the circulating electrons if the
group lies directly over the ring. The shift to high-field of some of the methyl resonances in the low temperature $^1$H n.m.r. spectrum may be accounted for by these shielding effects.

By rotation about the metal phosphorus bond it is possible to generate several different conformational isomers for an octahedral complex with four coplanar PMe$_2$Ph ligands. With the restriction that the phosphines may only be orientated such that a phenyl and a methyl group have to be on the same side of the IrP$_4$ plane and a methyl on the other side (i.e. the two methyl groups of the same phosphine may not appear on the same side of the plane) the number of rotamers possible is limited. This arrangement of the substituents attached to the phosphorus is typical for tetrakis-dialkylphenylphosphine complexes similar effects have been observed for [RuCl(CO)(PMe$_2$Ph)$_4$][ClO$_4$], [ReCl(N$_2$)(PMe$_2$Ph)$_4$] 224 (Figure 5.9) as well as [(PMe$_2$Ph)$_4$ClRe(μ-N$_2$)MoCl$_4$(OMe)], 242 [MoCl$_4$(μ-N$_2$){ReCl(PMe$_2$Ph)$_4$}] 243 and also for

\[ \text{ReH}(N_2)(\text{PET}_3\text{Ph})_4 \] 241 (Figure 5.13). Only four possible rotamers (A) to (D) 229 (Figure 5.14) are accessible. Rotamer (A) is that found in the crystal with C$_1$ symmetry and all phosphines non-equivalent. Rotamer (B) contains two pairs of close and parallel phenyl rings and has D$_2$ symmetry. All phosphines are magnetically equivalent in this rotamer, and large diamagnetic anisotropic shifts are expected in the $^1$H n.m.r. spectrum. Rotamer (C) with symmetry S$_4$ has no phenyl rings that are close and parallel but, as in conformer (B), all phosphines are equivalent. High-field shifts are expected for the methyl resonances because these groups are seen to lie above the phenyl rings of
adjacent phosphines and would be shielded by the induced magnetic field. Rotamer (D)

![Figure 5.14](image)

Rotamer (D) of symmetry $C_2$ has two pairs of magnetically equivalent phosphines, one pair with close parallel phenyl rings, the other whose rings are directed away from each other, again anomalous shifts would be expected in the low temperature $^1H$ n.m.r. spectrum.

5.3 N.M.R. Investigation

A sample of $[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4][\text{ClO}_4]$ was dissolved up in CD$_3$CN and the $^1H$ n.m.r. spectrum was recorded immediately. A broad resonance characteristic of the starting material was observed but peaks due to free phosphine ($\delta 1.4$, $^3J(\text{PH}) = 1.8$ Hz) and coordinated acetonitrile were also observed. The solution was left to stand at room temperature for 60 minutes after which time the spectrum was recorded again. The broad resonance due to the tetrakis-phosphine complex had disappeared completely and new signals corresponding to the acetonitrile complex

-219-
[IrCl₂(PMe₂Ph)₃(MeCN)][ClO₄] were observed as well as a sharp doublet due to free phosphine. The acetonitrile complex was prepared independently from the aqua complex and was fully characterised. The ¹H n.m.r. spectrum of the pure sample was closely similar to that generated by the addition of [IrCl₂(PMe₂Ph)₄][ClO₄] to acetonitrile.

To a separate sample of the complex [IrCl₂(PMe₂Ph)₃][ClO₄] in CDCl₃ was added an excess of PMeaPh and the ¹H n.m.r. spectrum was recorded immediately. A separate resonance due to the tetrakis-phosphine complex was observed as the familiar broad peak in the methyl region and a separate peak corresponding to uncoordinated phosphine was also present. There was no exchange of the free phosphine with coordinated phosphine on the n.m.r. time-scale.

5.3.1 ³¹P{¹H} N.M.R. Investigations of [IrCl₂(PMe₂Ph)₄][ClO₄]

The ³¹P{¹H} n.m.r. spectrum of [IrCl₂(PMe₂Ph)₄][BPh₄] in acetone at room temperature contained a single broad resonance as a result of coalesced signals. There was no exchange with added phosphine. Variable-temperature n.m.r. studies (Figure 5.15) indicated that there were several isomers that existed in solution at low temperature and these exchange as the temperature is raised. At low temperature (-80 °C d₆-acetone) the signals for these isomers are frozen out and the isomers no longer exchange on the n.m.r. time-scale. The low temperature ³¹P{¹H} n.m.r. spectrum (Figure 5.16) is interpreted as containing three of the four possible isomers (A) to (D) (Figure 5.14) possibly with a very low concentration of the fourth isomer. The low temperature ³¹P{¹H} n.m.r. spectrum (-80 °C) contains a singlet at δ -51.6 due to a totally symmetrical rotamer, (B) or (C) an AA'BB' pattern due to two pairs of magnetically equivalent nuclei [δ = -53.15 and -49.46] and an ABCD pattern [δ = -54.37, -53.63, -50.29, -49.02]. The unassigned resonances may be due to the fourth isomer in low concentration. Each component of the n.m.r. spectrum was simulated separately with coupling constants of +363.0 Hz for the trans phosphorus-phosphorus coupling and a cis coupling of -23.0 Hz. There was a strict requirement for the cis and trans coupling constants to be of opposite sign. With coupling constants of the same sign the simulated spectrum had the appearance of being inside out but the shapes of the multiplets could be reversed by using coupling constants of opposite sign. Both components, the AA'BB' and ABCD, were simulated with these couplings and the
Figure 5.15 Variable temperature $^{31}$P{'H} n.m.r. spectra of the complex [IrCl$_2$(PMe$_3$Ph)$_4$][ClO$_4$]
Figure 5.16  Low temperature (-80 °C) $^{31}$P$\{^{1}H\}$ n.m.r. spectrum of the complex
$\left[\text{IrCl}_2(\text{PMe}_2\text{Ph})_4\right]\left[\text{ClO}_4\right]$
simulated spectra of each component and the sum of these two spectra are shown in Figure 5.17 along with the observed spectrum. The predominant ABCD pattern is assigned to rotamer (A) found in the crystal. All the phosphines are magnetically non-equivalent as a result of the C_1 symmetry and hence there are four distinct chemical shifts and second-order coupling. The next most abundant conformer giving the AA’BB’ pattern is believed to be rotamer (D). The C_2 axis affords two pairs of magnetically equivalent phosphorus nuclei (arranged mutually cis) and an AA’BB’ pattern is consistent with this. Rotamers (B) and (C) have all phosphorus nuclei magnetically equivalent; the singlet (A_4) pattern could result from either of these two rotamers.

The separation of the 31P{1H} n.m.r. spectrum into these three sets of resonances, A_4, AA’BB’ and ABCD, was confirmed by a 31P-31P DQCOSY (phosphorus-phosphorus double quantum filled correlation spectroscopy) experiment at -75 °C in CD_2Cl_2 (Figure 5.18). Off diagonal peaks confirm the internal coupling within the AA’BB’ and ABCD sets but appropriate peaks were also detected which were consistent with slow isomer exchange at this temperature. Further n.m.r. investigations were required to enable unequivocal assignment of the A_4 rotamer to either (B) or (C).

The reaction of the chiral tetradentate ligand L, (L = 'BuHP(CH_2)_3PMe(CH_2)_3PMe(CH_2)_3PHBu) with K_2[PdCl_4] has been investigated by Stelzer.251-253 The reaction was found to afford a complex formulated as [PdLCl_2] (Figure 5.19). Although conformationally rigid this complex was found to exist as two

![Diagram](https://via.placeholder.com/150)

**Figure 5.19**

-223-
Figure 5.17 $^{31}$P($^1$H) n.m.r. spectra (a) Simulated AA’BB’, (b) Simulated ABCD, (C) sum of (a) & (b) and the observed low temperature spectrum of the complex [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$]
Figure 5.18 $^{31}$P-$^{31}$P DQ COSY (phosphorus-phosphorus double quantum filled correlation) spectrum recorded at -75 °C
Figure 5.20 Simulated and observed $^3\!P\{^1\!H\}$ ABCD/AA'BB' spectra of the complex [Pd(tet)Cl][Cl]

configurational isomers. The $^3\!P\{^1\!H\}$ n.m.r. spectrum (Figure 5.20) was interpreted as containing an ABCD and AA'BB' spin system and the close similarity between this spectrum and the low temperature $^3\!P\{^1\!H\}$ n.m.r. spectrum of [IrCl$_2$(PMe$_2$Ph)$_2$][ClO$_4$] is apparent. A further striking similarity between these spin systems is the strict requirement for the $cis$ and $trans$ $^3\!P$-$^3\!P$ coupling constants to be opposite in sign. The spectrum in Figure 5.20 was simulated using $trans$ coupling constants of 291.6 Hz and 294.7 Hz whilst the $cis$ coupling constants varied from -27.8 Hz to -37.5 Hz.
5.3.2 N.M.R. Investigation of [IrCl₂(AsMe₂Ph)₄][ClO₄]

The \(^1\text{H}\) and \(^{13}\text{C}[^1\text{H}]\) n.m.r. spectra of the two complexes [IrCl₂(EMe₂Ph)₄][ClO₄] (E = P or As), (1) and (2), correspond but those of (2) without \(^{31}\text{P}\) coupling are more easily interpreted. The \(^1\text{H}\) n.m.r. spectrum of (2) recorded at room temperature (CD₂Cl₂) contains a methyl singlet at \(\delta 1.60 (\Delta v_s = 60 \text{ Hz})\) and phenyl resonances in the range \(\delta 7.24-7.50\). At low temperature (-85 °C) sharp signals have appeared to low and high-field of the normal range expected for aromatic protons (\(\delta 5.75\) to 8.30) and methyl resonances as high-field as \(\delta 0.70\) are also observed. The presence of signals shifted to high and low-field, both for the phenyl and methyl resonances, is consistent with the observations that were made for complex (1, E = P) at low temperature. The chemical shift anisotropy due to the induced magnetic field of neighbouring phenyl rings is not as large as that observed for complex (1). The origin of this smaller effect is probably the larger distance between the parallel phenyl rings. The larger covalent radius of the arsenic atom forces the phenyl rings to be further apart and therefore the protons that lie above nearby phenyl rings will not experience shielding or deshielding of the same magnitude as the protons in complex (1) that lie closer to the induced magnetic field.

We have established that the two major rotamers in solution are (A) and (D), rotamer (A) should contribute eight methyl resonances to the \(^1\text{H}\) n.m.r. spectrum at low temperature and (D) four methyl resonances. Rotamers (B) and (C) would both contribute two methyl resonances to the n.m.r. spectrum. From these simple considerations we expect to see fourteen methyl peaks in the low temperature \(^1\text{H}\) n.m.r. spectrum. At -85 °C we observe at least thirteen peaks in the methyl region of the spectrum with possible accidental coincidence of others. This is consistent with the presence of at least three isomers in solution.

The low temperature \(^{13}\text{C}[^1\text{H}]\) n.m.r. spectrum reinforces these ideas, several of the methyl resonances are shifted to low-field but because of such a large chemical shift range the movement is not as apparent as in the \(^1\text{H}\) n.m.r. spectrum. Fourteen different signals are observed in the methyl region and this corresponds with both the \(^1\text{H}\) n.m.r spectrum of [IrCl₂(AsMe₂Ph)₄][ClO₄] and the low temperature \(^{13}\text{C}[^1\text{H}]\) n.m.r. spectrum of [IrCl₂(PMe₂Ph)₄][ClO₄] although the latter spectrum is complicated by coupling to phosphorus.
Figure 5.21 Variable temperature $^1$H n.m.r. spectra of the phenyl region of the complex $[\text{IrCl}_2(\text{AsMe}_2\text{Ph})_4]^+$.
The variable-temperature $^1$H n.m.r. spectrum of [IrCl$_2$(AsMe$_2$Ph)$_4$][ClO$_4$] is shown in Figure 5.21 and 5.22 for the phenyl and methyl resonances respectively. On raising the temperature from -85 °C to -70 °C (Figure 5.23 shows the $^1$H n.m.r. spectrum recorded at -70 °C) the majority of the signals in the phenyl region have broadened considerably except for a single set of resonances at $\delta$ 8.04 (d, ortho), 7.37 (t, meta), 7.32 (t, meta), 6.85 (t, para), 6.09 (d, ortho) which remain sharp (Figure 5.23 shows the $^1$H n.m.r. spectrum recorded at -70 °C) and one set of methyl resonances were observed to remain sharp at $\delta$ 1.645 (s) and 1.695 (s). Because there is only one set of phenyl resonances and one set of methyl resonances (comprised of two singlets) that remain sharp whilst the others broaden these must belong to the totally symmetrical isomer (B) or (C). The symmetrical isomer was predicted to contribute two methyl signals to the n.m.r. spectrum from consideration of its symmetry. The symmetrical isomer therefore exchanges at a slower rate than the other two rotamers. Comparing the variable-temperature $^1$H n.m.r. spectra of both [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$] and [IrCl$_2$(AsMe$_2$Ph)$_4$][ClO$_4$] this idea of slower exchange of the symmetrical isomer present in solution is also observed for the phosphorus analogue although due to the extra coupling to phosphorus the spectra are less easily interpreted. Slower exchange of the symmetrical rotamer was also observed on careful examination of the low temperature $^{31}$P{H} spectrum of [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$] (Figure 5.15). Above -80 °C the AA'BB' and the ABCD patterns broaden first and only at higher temperatures is exchange of the A$_4$ conformer observed.

A close approach of a methyl group to a phenyl ring of a PMe$_2$Ph ligand cis to it leads to an up-field shift of that resonance as a consequence of the diamagnetic anisotropy of the induced magnetic field. The methyl resonances that remained sharp as the temperature was raised appeared at $\delta$ 1.645 and 1.695, in the normal range for an AsMe$_2$Ph ligand. Close and parallel alignment of phenyl rings gives large up and down-field shifts of the phenyl protons the direction of the shift being dependant on the relative position of the phenyl protons with respect to the parallel phenyl ring. The phenyl protons that were observed to exchange at a slower rate than the others showed a considerable chemical shift difference for the ring protons. There was a 2 ppm chemical shift difference between the ortho protons of adjacent rings. One ortho proton was seen to be deshielded and had a chemical shift of 8.5 ppm indicating that it was lying above but to the side of the parallel ring. In contrast the other ortho proton was
Figure 5.22 Variable temperature $^1$H n.m.r. spectra of the methyl region of the complex $[\text{IrCl}_2(\text{AsMe}_2\text{Ph})_4]^+$.
Figure 5.23 Low temperature (-70 °C) $^1$H n.m.r. spectra of the methyl and phenyl regions of the complex $[\text{IrCl}_2(\text{AsMe}_2\text{Ph})_4]$.
shielded and had a chemical shift of 6.09 ppm and was assumed to lie centrally above the phenyl ring. Since the phenyl rings of adjacent phosphines in rotamer (C) do not come into close alignment we can be sure that the conformer corresponding to the A₄ pattern in the ³¹P [¹H] n.m.r. spectrum is that of (B) not (C). Close and parallel phenyl rings in molecules would be expected to lead to energetically favourable interactions and therefore it is not unreasonable that isomer (B) should be the observed in solution. There are two pairs of close and parallel phenyl rings in this isomer in comparison to (C) which does not exhibit any such interactions.

The three predominant rotamers in solution are, (A) (56%), (B) (18%), (C) (26%), all have aligned phenyl groups and the intuitively attractive isomer (C) is present in very low concentration if at all (see the weak unassigned peaks in Figure 5.15).

Integration of the low temperature ³¹P[¹H] n.m.r. spectrum enabled approximate values for the relative energies of the rotational isomers to be calculated. The difference per mole in Gibbs free energy between the conformers has been established as ΔGₓₚ = +1.23 Kjmol⁻¹, ΔGₓₓ = +1.82 Kjmol⁻¹, ΔGₓₓ = +0.59 Kjmol⁻¹. These values are extremely small and are consistent with those found in the literature. The entropy term, ΔS, corresponding to the change in disorder, is expected to be negligible and we can assume ΔG = ΔH.

5.4 Studies of other Tetrakis-Phosphine Complexes of Iridium(III)

5.4.1 The Synthesis of [IrCl₂(PMe₃)₃(PMe₂Ph)][ClO₄] and [IrCl₂(PMe₃)₂(PMe₃Ph)][ClO₄]

A procedure similar to that used for the preparation of [IrCl₄(PMe₃Ph)₂] was employed. The use of trimethylphosphine as a ligand presented a few practical problems due to its volatility and spontaneous flammability in air. The reaction between chloroiridic acid and PMe₃ was carried out in a sealed Schlenk tube under an atmosphere of argon. After seven hours of reaction brick red crystals of the complex [IrCl₂(PMe₃)₄][IrCl₄(PMe₃)₂] came out of solution on cooling. This double salt was
Scheme 5.2 Preparation of [IrCl₂(PMe₃)₃(PMePh₃)](ClO₄) (R = Ph, Me).
identified by its characteristic 'H n.m.r. spectrum and its conductivity in nitrobenzene. The mass spectrum only showed peaks that corresponded to the trans-mer-[IrCl$_2$(PMe$_3$)$_3$] complex. Thermolysis of a solution of the deep red crystals in methoxyethanol afforded a deep yellow solution of the required product, whose elemental analytical data (C, H and P) were in good agreement with the calculated values. Treatment of a solution of [IrCl$_3$(PMe$_3$)$_3$] in acetone with silver perchlorate afforded a precipitate of silver chloride which was filtered off to leave a yellow solution of the aqua complex [IrCl$_3$(PMe$_3$)$_3$(H$_2$O)][ClO$_4$]. Replacement of the substitutionally labile water ligand for the phosphine donor ligands, PMe$_2$Ph or PMePh$_2$, was readily accomplished in dichloromethane at room temperature (Scheme 5.2). By this method we have prepared the tetrakis-phosphine complexes [IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph)][ClO$_4$] and [IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph$_2$)][ClO$_4$] as air-stable yellow crystalline materials in good yield.

5.4.2 Crystal Structure of [IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph)][ClO$_4$]

Many structures have been solved which contain four phosphines that are coplanar and all exhibit significant distortions from a regular square plane containing the phosphines. The trans-P-M-P bond angle is less than the 180° required for a square plane. In most cases the distortions toward tetrahedral geometry are a consequence of intramolecular phosphine-phosphine interactions. We decided to undertake a single-crystal X-ray structure determination of one of the tetrakis-phosphine complexes synthesised to determine any relevant structural or conformational features. The complex [IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph)][ClO$_4$] was chosen. Single crystals of this complex were readily obtained by layering a dichloromethane solution of the complex with diethylether and allowing the solvents to diffuse slowly for several days at room temperature. The complex crystallised with one mole equivalent of CH$_2$Cl$_2$ in the space group $Pcab$ with eight molecules per unit cell of dimensions: $a = 13.730(3)$ Å, $b = 20.715(5)$ Å, $c = 21.720(3)$ Å. The structure was refined to $R = 0.051$. Selected bond lengths and angles are given in Table 5.2 and views of the cation are shown in Figure 5.24 and 5.25.

There is a planar arrangement of the phosphines with the chlorides cis. There are large deviations of the P-Ir-P bond angle from the ideal linear value of 180°. P-Ir-P angles of 167.3° and 168.9° were observed for P(1)-Ir-P(2) and P(3)-Ir-P(4) respectively. The X-ray structure of [Ir(PMe$_3$)$_4$]$^+$ showed it to have significant distortions.
Figure 5.24 Structure of [IrCl₂(PMe₃)₃(PMe₂Ph)]ClO₄
Figure 5.25 Structure of $[\text{IrCl}_2(\text{PMe}_3)_3(\text{PMe}_2\text{Ph})][\text{ClO}_4]$
<table>
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<tr>
<th>Bond lengths (Å)</th>
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<tr>
<td>Ir-Cl(2) 2.366(4)</td>
<td>Cl(1)-Ir-P(1) 95.1(2)</td>
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<td>Cl(2)-Ir-P(1) 83.6(2)</td>
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<td>Ir-P(2) 2.357(5)</td>
<td>Cl(1)-Ir-P(2) 97.5(2)</td>
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<td>Ir-P(3) 2.381(4)</td>
<td>Cl(2)-Ir-P(2) 83.8(2)</td>
</tr>
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<td>Ir-P(4) 2.375(4)</td>
<td>Cl(1)-Ir-P(3) 86.5(2)</td>
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<td>P(2)-Ir-P(4) 90.2(2)</td>
</tr>
<tr>
<td></td>
<td>P(3)-Ir-P(4) 168.9(2)</td>
</tr>
</tbody>
</table>
from the ideal square planar geometry expected. It is clear that these distortions from the expected square geometry are due to intramolecular phosphine-phosphine (or to a smaller extent phosphine-chlorine) repulsions. It is interesting to note the effect these have on the geometry of the phosphine ligands themselves. The Ir-P-C angles are significantly greater than tetrahedral ranging from 113.6 ° to 119.8 °. The steric crowding does not, however, seem to have affected the Ir-P and Ir-Cl bond lengths, the bond lengths are shorter than those found in [IrCl₂(PMe₂Ph)₄][ClO₄] but similar in length to the Ir-P distances (trans to P) in [IrCl₂(PMe₃Ph)₄][ClO₄]. The isomer observed in the crystal is that of the unsymmetrical rotamer with C₃ symmetry and with non-equivalent cis PMe₃ ligands. [IrCl₂(PMe₄)(PMe₂Ph)][ClO₄] contains pairs of trans phosphine eclipsed (Figure 5.25). This eclipsed arrangement of trans phosphines is a common feature of complexes containing four phosphines coplanar, for example, [IrCl₂(PMe₂Ph)₄][ClO₄] (Figure 5.5), [ReCl(N₂)(PMe₂Ph)₄]²⁺ [RuCl(CO)(PMe₂Ph)₄] (Figure 5.9) and [ReH(N₂)(PEt₂Ph)₄]⁻ (Figure 5.13).

5.4.3 ³¹P{¹H} N.M.R. Studies of the Tetrakis-Phosphine Complexes

Restricted rotation is normally associated with bulky phosphine ligands such as t-butyl substituted ones.²⁵ However, we have found that even with phosphines of a small cone angle more than one conformational isomer is present in solution at low temperature.

(a) [IrCl₂(PMe₃)₃(PMe₂Ph)][ClO₄]: Figures 5.26 and 5.27 show the variable-temperature ¹H n.m.r. spectra of the title complex in the phenyl and methyl region respectively. The low temperature ¹H n.m.r. spectrum (-75 °C) indicated the presence of two isomers in differing abundance. The major isomer no longer possesses equivalent ortho protons; these are now magnetically non-equivalent and there is a large chemical shift difference between the two signals (δ 8.44 and 7.42). The minor isomer showed a single broad triplet resonance at δ 8.08 for the magnetically equivalent ortho protons because there is a plane of symmetry through the molecule which relates the two sites. The other signals due to this minor isomer are obscured by the peaks corresponding to the major rotamer and therefore remain unobserved. The low temperature ¹H n.m.r. spectrum in the methyl region shows to signals, δ 1.04 (d) and 1.12 (d), at higher field
Figure 5.26 Variable temperature $^1$H n.m.r. spectra of the phenyl region of the complex $\text{[IrCl}_2\text{PMe}_3\text{PMe}_2\text{Ph}][\text{ClO}_4]$
Figure 5.27 Variable temperature $^1$H n.m.r. spectra of the methyl region of the complex [IrCl$_2$(PMe$_3$)$_2$(PMe$_2$Ph)][ClO$_4$].
than the rest due to the major isomer. Confirmation of this arises from considering the two possible rotamers, these signals must correspond to the unsymmetrical one because the symmetrical isomer does not allow close approach of the methyl group to the phenyl ring and therefore should not exhibit any anomalous shifts. The unsymmetrical isomer has the PMe₂Ph ligand orientated in such a way that the methyl group of an adjacent phosphine would lie directly above the phenyl ring. The magnetic field induced by the circulating electrons then acts to shield the methyl protons, accounting for the large up-field shift of these protons. These observations confirm that the major isomer in solution is that found in the crystal. The complexity of the methyl region at low temperatures is only consistent with restricted rotation about the Ir-PMe₃ bonds as well as about the Ir-PMe₂Ph bond. Thus the mechanism shown in Figure 5.28a hides the fact that, as the PMe₂Ph rotates, there is rotation about the other Ir-P bonds. Presumably this is a cog-wheel type process which maintains the overall arrangement of substituents at the phosphines with two up and one down, alternating around the molecule. As the temperature is raised the spectrum broadens and the three ortho resonances finally coalesce. At room temperature one set of phenyl resonances δ 8.04 (broad coalesced ortho resonances), 7.55 (t, para), 7.48 (t, para) established that the two rotamers observed in the low temperature ¹H n.m.r. spectrum were in exchange. Exchange of the ortho protons could occur by rapid rotation about the P-C bond of the phenyl ring or during the process that interconverts the two trans PMe₃ ligands. Figure 5.28 shows a process in which the trans PMe₃ ligands and HA and HB exchange by the same mechanism, requiring the rate of exchange of HA and Hb to be at least equal to that of the phosphine exchange.

³¹P(¹H) n.m.r. studies were also carried out on the complex [IrCl₂(PMe₃)₃(PMe₂Ph)][ClO₄] (Figure 5.29). The low temperature (-75 °C, d₆-acetone) spectra showed more clearly the two rotameric forms of this complex. The low temperature ³¹P(¹H) n.m.r. spectra (Figure 5.30) of this compound contains an AB₂C component (δ = 21.2, 33.4, 29.4 ppm) and an ABCD pattern (δ = 28.3, 26.2, 30.0, 25.5 ppm). The predominant isomer in solution at this temperature is the unsymmetrical one (95%) with only a very small concentration of the symmetrical rotamer (5%). Good simulated n.m.r. spectra were obtained by fixing the cis coupling constants at -27 Hz and the trans ones at 366 Hz for the major isomer and cis couplings of -30 Hz and trans couplings of 366 Hz for the minor rotameric form (Figure 5.31 shows the
Figure 5.28

Scheme 1

Scheme 2
Figure 5.29 Variable temperature $^{31}$P('H) n.m.r. spectra of the complex [IrCl$_3$(PMe$_3$)$_2$(PMe$_2$Ph)][ClO$_4$]

-35 - 10 - 52
-20 - 25 - 60
-25 - 40 - 75
-30 - 20 - 40
Figure 5.30  Low temperature (-75 °C) $^{31}$P($^1$H) n.m.r. spectra of [IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph)][ClO$_4$]
Figure 5.31 Simulated, (a), and observed, (b), $^{31}\text{P}^{('H)}$ n.m.r. spectra of the complex $[\text{IrCl}_2(\text{PMe}_3)_3(\text{PMe}_2\text{Ph})][\text{ClO}_4]$
calculated and observed spectra for [IrCl₃(PMe₃)₃(PMe₂Ph)][ClO₄]. Simulated n.m.r spectra appear as approximate AB quartets with a smaller coupling to the cis phosphorus nuclei. The coupling constants remain the same regardless of the degree of the second order nature of the spectra, but as the chemical shift difference gets less the inner lines of the multiplets become more intense at the expense of the outer lines. The smaller the chemical shift difference the resonances the greater the second-order distortions will become. In an AX spin system the chemical shift is given by the midpoint of each doublet, but in an AB spin system such as that shown in Figure 5.30 this is no longer the case and the chemical shift is given by equation 5.1 and the

\[ \delta_A - \delta_B = [(v_4 - v_1)(v_3 - v_2)]^{1/2} \] \hspace{1cm} Equation 5.1

\[ I_2/I_1 = I_3/I_4 = (v_4 - v_1)/(v_3 - v_2) \] \hspace{1cm} Equation 5.2

relative intensities of the lines of an AB quartet are given by equation 5.2. The chemical shifts required for the spin simulation were obtained by application of equation 5.1. It is a strict requirement that the couplings were of opposite sign, since spectra simulated with couplings of the same sign had the appearance of being inside out. This situation may be compared with the simulation of [IrCl₅(PMe₂Ph)₂][ClO₄] in which cis and trans couplings of opposite sign were also required. The predominant isomer at low temperature is that observed in the crystal structure (Figure 5.32 A) whilst the minor species in solution is assigned to the unsymmetrical rotamer, (B) in Figure 5.32. A rotation of 120° about the metal-phosphorus bond would interconvert these two isomers. Above -75 °C the spectra of the two rotamers start to broaden and at 45 °C both rotamers are observed to be at the fast exchange limit. The spectrum can then be interpreted as an AB₂C pattern (δ = 25.98, 23.56, 28.65 ppm).

(b) [IrCl₃(PMe₃)₃(PMe₂Ph)][ClO₄]: As for [IrCl₃(PMe₃)₃(PMe₂Ph)][ClO₄], the

\[ ^3P^1H \] n.m.r. spectrum can be interpreted as an AB₂C pattern (δ = 20.50, 24.20, 29.80 ppm). The low temperature spectrum (-75 °C, d₆-acetone) (Figure 5.33) again indicates two isomers in unequal abundance. Both the major and the minor isomers can be analysed as AB₂C type spectra (accidental coincidence in the spectrum of the
unsymmetrical isomer). For example at -75 °C the $^{31}$P{^1}H n.m.r. spectrum contained a major AB$_2$C pattern ($\delta = 26.0, 16.9, 30.8$ ppm) and a minor AB$_2$C pattern ($\delta = 32.8, 26.0, 26.0$ ppm). Both components of the spectrum have been successfully simulated with cis coupling of -27 Hz and trans couplings of 366 Hz. Figure 5.34 shows the low temperature $^{31}$P{^1}H n.m.r. spectrum of [IrCl$_2$(PMe$_3$)$_3$(PMePh$_2$)][ClO$_4$] and its corresponding spin simulated spectra. Above -75 °C exchange occurs and at room temperature both isomers are in rapid exchange and the spectrum consists of an AB$_2$C spin system. The central peaks corresponding to the trans PMe$_3$ ligands and the right hand branch of the AC multiplet are sharp at this temperature. The left hand branch of the AC multiplet has remained broad at room temperature because of the large chemical shift difference of this multiplet at low temperature. Much higher temperatures are required to resolve the coupling for these resonances. Figure 5.32 (C) and (D)
Figure 5.33 Variable temperature $^{31}$P($^1$H) n.m.r. spectra of the complex

$[\text{IrCl}_3(\text{PMe}_3)_2(\text{PMePh}_2)][\text{ClO}_4]$
Figure 5.34  Observed, (a), and simulated, (b) low temperature $^{31}$P{H} n.m.r. spectra of the complex [IrCl$_2$(PMe$_3$)$_2$(PMePh$_2$)][ClO$_4$]
shows both possible rotameric forms within the IrP₄ plane. Rotamer (C) is the major unsymmetrical isomer whilst (D) is the minor conformer in solution at -75 °C.

It is possible that the unsymmetrical isomer is undergoing a rapid symmetrisation reaction which does not involve the symmetrical isomer (Figure 5.28 scheme 1). This process could be occurring rapidly without our knowing about it. The process in Figure 5.28 would exchange Ph₁ and Ph₂ but not P1 with P2 and would not undergo exchange of the major (Figure 5.28a) isomer with the minor isomer (Figure 5.28b). Any process that would exchange P1 with P2 must go through the symmetrical (Me lying on a plane of symmetry) rotamer therefore the two AB₂C³¹P spin systems at low temperature must be the result of accidental equivalence. The difference between [IrCl₂(PMe₂)₃(PMe₂Ph)][ClO₄] and [IrCl₂(PMe₂)₃(PMePh₂)][ClO₄] in this respect is that 1a can convert into 1b by a methyl group rotating past an adjacent cis PMe₃ ligand (Figure 5.28), where as (2a) can only convert to (2b) by a phenyl passing a cis PMe₃ ligand. It is expected that the latter would be associated with a higher energy barrier. On the other hand the enantiomerisation process for (2a) only requires a methyl group moving from above to below the IrP₄ plane past the PMe₃ ligand and can therefore occur rapidly.
5.5 Conclusion

The unexplained features of the \(^1\)H n.m.r. spectrum of several \textit{trans} octahedral complexes containing four PMe\(_2\)Ph ligands coplanar can now be interpreted in terms of exchange of conformational isomers in solution. For the complex [IrCl\(_2\)(PMe\(_2\)Ph)\(_4\)][ClO\(_4\)], four possible isomers have been proposed with the restriction that a methyl and a phenyl group have to lie on the same side of the approximate IrP\(_4\) plane. The low temperature \(^{31}\)P\(\{}^1\)H\) n.m.r. spectrum has been interpreted as consisting of three of these four possible isomers with possibly a low concentration of the fourth. No exchange with free phosphine was observed. The anomalously high and low field shifts of both the phenyl and the methyl resonances in the low temperature \(^1\)H n.m.r. spectrum can be interpreted as arising from the close approach of an adjacent phenyl rings to the appropriate group. Close parallel phenyl rings are responsible for the shift observed in the phenyl region.

Different conformational isomers have also been observed in the less sterically crowded octahedral complexes [IrCl\(_2\)(PMe\(_3\))\(_3\)(PMe\(_2\)Ph)][ClO\(_4\)] and [IrCl\(_2\)(PMe\(_3\))\(_3\)(PMePh\(_2\))P][ClO\(_4\)]. In each case the low temperature \(^{31}\)P\(\{}^1\)H\) n.m.r. spectrum was interpreted as consisting of two rotameric forms, a major symmetrical and a minor unsymmetrical form. Both spectra have been successfully simulated and the only requirement is that the \textit{cis} and \textit{trans} couplings are of opposite sign.
5.6 Experimental

[IrCl₂(PMe₂Ph)₃(H₂O)][ClO₄] was prepared as reported. Dimethylphenylarsine was prepared using the literature preparation.

5.6.1 Synthesis of [IrCl₂(PMe₂Ph)₃][ClO₄]

To a stirred solution of [IrCl₂(PMe₂Ph)₃(H₂O)][ClO₄] (0.1369 g, 0.17 mmol) in dichloromethane (20 cm³) was added dimethylphenylphosphine (0.0476 g, 0.14 mmol). The reaction mixture was left stirring under nitrogen for 2 hours the solvent was then removed under reduced pressure to give a green-yellow oil. Slow addition of diethylether to a dichloromethane solution of this oil gave the title complex as yellow crystals (0.133 g, 86%). [Found: C, 41.85; H, 4.78; Cl, 11.74; P, 13.77. C₅₅H₄₅Cl₄IrO₄P₄ requires C, 41.97; H, 4.83; Cl, 11.63; P, 13.54%].

5.6.2 Synthesis of [IrCl₂(PMe₂Ph)₃(CH₃CN)][BF₄]

A solution of the aqua complex [IrCl₂(PMe₂Ph)₃(H₂O)][BF₄] (0.167 g, 0.2 mmol) in acetonitrile (20 cm³) was left to stand overnight. Removal of the solvent under reduced pressure gave a yellow oil. Crystallisation of the residue from dichloromethane/diethylether gave the title complex as yellow needles (0.134 g, 78%) [Found: C, 35.93; H, 4.21; N, 1.42; P, 11.45. C₅₇H₅₇BCl₂F₄NP₃ requires C, 38.75; H, 4.51; N, 1.74; P, 11.54%].

5.6.3 Reaction of [IrCl₂(PMe₂Ph)₃][ClO₄] with acetonitrile.

The complex [IrCl₂(PMe₂Ph)₃][ClO₄] (0.012 g) was dissolved in CD₃CN (0.8 cm³) in a 5 mm n.m.r. tube. The ¹H n.m.r. spectrum was recorded immediately and there were seen to be signals corresponding to starting material, [IrCl₂(PMe₂Ph)₃][ClO₄], and a new complex was observed. The solution was allowed to stand at ambient temperature for 15 minutes and the ¹H n.m.r. spectrum was recorded again. Signals due to the starting material were now absent and comparison of the recorded ¹H n.m.r. spectrum with one corresponding to pure [IrCl₂(PMe₂Ph)₃(CH₃CN)][ClO₄] confirmed the new species in solution to be that of the acetonitrile complex. A separate peak corresponding to free dimethylphenylphosphine was observed.
5.6.4 Synthesis of \([\text{IrCl}_2(\text{PMe}_3)_2]\)[IrCl_4(\text{PMe}_3)_2]\\

Chloroiridic acid (1.5517 g, 3.6 mmol) was refluxed with concentrated hydrochloric acid (ca. 0.5 cm³) in 2-methoxyethanol (20 cm³) for 15 minutes. The solution was allowed to cool and trimethylphosphine (1.40 g, 18 mmol) added. The Schlenk tube was evacuated and filled with argon and sealed. The mixture was heated under reflux for 8 hours during which time the solution initially green in colour had turned deep orange-red. The solution was allowed to cool overnight and the brick red crystals formed were filtered and washed with diethylether and dried under vacuum (1.2072 g, 67%). [Found: C, 20.69; H, 5.07; P, 17.76. \(\text{C}_9\text{H}_{27}\text{Cl}_3\text{IrP}_3\) requires C, 20.52; H, 5.15; P, 17.64 %]. MS (EI): m/e = 526 (M⁺) corresponding to \([\text{IrCl}_3(\text{PMe}_3)_3]^+\).

5.6.5 Synthesis if \([\text{IrCl}_3(\text{PMe}_3)_3]\\

[\text{IrCl}_2(\text{PMe}_3)_2][\text{IrCl}_4(\text{PMe}_3)_2] (0.45 g, 0.43 mmol) in 2-methoxyethanol (50 cm³) was heated under reflux for 60 minutes. The solution initially deep red-orange in colour turned deep yellow. The volume was concentrated under reduced pressure to ca. 5 cm³ and was left in the fridge at -20 °C overnight. The solution was filtered and the solid washed with diethylether and dried under vacuum. The filtrate was concentrated further and left in the fridge to yield more product (0.411 g 91%). [Found: C, 20.44; H, 5.01; P, 16.14. \(\text{C}_9\text{H}_{27}\text{Cl}_3\text{IrP}_3\) requires C, 20.52; H, 5.16; P, 17.64%]. MS (EI): m/e = 526 (M⁺).

5.6.6 Synthesis of \([\text{IrCl}_2(\text{PMe}_3)_3(H_2O)]\)[ClO_4]\\

To a suspension of \([\text{IrCl}_4(\text{PMe}_3)_3]\) (0.0682 g, 0.13 mmol) in acetone (10 cm³) was added silver perchlorate (0.027 g, 0.13 mmol) and the mixture shaken for 30 minutes. The silver chloride precipitate formed was filtered off and the yellow filtrate evaporated to dryness under reduced pressure to give a yellow oil. The residue was crystallised from dichloromethane/diethylether to give the title complex as yellow needles (0.056 g, 71%). [Found: C, 17.76; H, 4.80; P, 17.47. \(\text{C}_9\text{H}_{27}\text{Cl}_3\text{IrO}_2\text{P}_4\) requires C, 17.76; H, 4.74; P, 17.23%].
5.6.7 Synthesis of [IrCl₂(PMe₃)₃(PMe₂Ph)][ClO₄]

To a solution of [IrCl₂(PMe₃)₃(H₂O)][ClO₄] (0.060 g, 0.1 mmol) in dichloromethane (5 cm³) was added dimethylphenylphosphine (0.024 cm³, 0.17 mmol). The solution was stirred for 60 minutes and then the solvent removed under reduced pressure to leave an oily residue. Slow addition of diethylether to a dichloromethane solution of the residue gave the product as pale yellow crystals (0.053 g, 73%). [Found: C, 26.57; H, 4.84; P, 15.77. C₁₈H₄₆Cl₂IrO₄P₄ requires C, 26.60; H, 4.95; P, 15.22%].

5.6.8 Synthesis of [IrCl₂(PMe₃)₃(PMePh₂)][ClO₄]

A procedure similar to the above was followed with [IrCl₂(PMe₃)₃(H₂O)][ClO₄] (0.0281 g, 0.053 mmol) and methyldiphenylphosphine (0.019 cm³, 0.053 mmol). Crystallisation as before gave the title complex in good yield (0.031 g, 86%). [Found: C, 33.40; H, 5.31; P, 13.54. C₂₂H₈₀Cl₂IrO₄P₄ requires C, 33.42; H, 5.10; P, 13.45%].

5.6.9 Synthesis of [IrCl₃(AsMe₂Ph)₃]

Chloroiridic acid (0.9528 g, 2.34 mmol) and concentrated hydrochloric acid (ca. 0.5 cm³) were heated under reflux in 2-methoxyethanol (20 cm³) for ca. 15 minutes. The dark green-brown solution formed was allowed to cool and freshly distilled dimethylphenylarsine (1.376 g, 8.2 mmol) was added and the mixture heated under reflux for a further 8 hours. During this time the initial green-brown solution turned clear orange. The solution was allowed to cool overnight and the yellow crystals formed were filtered and washed with diethylether and dried under vacuum. The filtrate was concentrated under reduced pressure to ca. 10 cm³ and left in the fridge at -20 °C to yield more crystals of the desired product (0.645 g, 35%). [Found: C, 34.30; H, 3.96; Cl, 12.84. C₂₉Hₑ₉As₂Cl₄Ir requires C, 34.10; H, 3.90; Cl, 12.60%].

5.6.10 Synthesis of [IrCl₃(NO₃)(AsMe₂Ph)₃]

To a suspension of [IrCl₃(AsMe₂Ph)₃] (0.136 g, 0.16 mmol) in acetone (12 cm³) was added silver nitrate (0.0301 g, 0.17 mmol) in an acetone/water mixture (2 and 0.5 cm³ respectively). The mixture was stirred for 5 days. The silver chloride produced was filtered off and the filtrate was evaporated to dryness under reduced pressure to leave on oily residue. Crystallisation of the product from dichloromethane/diethylether gave the title complex in good yield (0.125 g, 89%). The product was characterised and its
purity assessed by comparison of the $^1$H n.m.r. spectrum with the previously reported data.

5.6.11 Synthesis of $[{\text{IrCl}}_2{(\text{AsMe}_2\text{Ph})}_4][\text{ClO}_4]$

$[{\text{IrCl}}_2{(\text{AsMe}_2\text{Ph})}_3{(\text{NO}_3}_2)]$ (0.143 g, 0.16 mmol) in acetone (10 cm$^3$) was stirred with an excess of sodium perchlorate (0.420 g, 3.4 mmol). Freshly distilled dimethylphenylarsine (0.030 cm$^3$, 0.16 mmol) was added and the mixture was stirred under nitrogen at ambient temperature for 2 hours. The solvent was removed under reduced pressure to give a green oil. Slow addition of diethylether to a dichloromethane solution of the product gave yellow-green crystals of the desired product (0.140 g, 78%).

5.6.12 Synthesis of $[{\text{IrCl}}_2{(\text{PMe}_3}_3{(\text{AsMe}_2\text{Ph})}[\text{ClO}_4]$

A solution of $[{\text{IrCl}}_2{(\text{PMe}_3}_3{(\text{H}_2\text{O})}[\text{ClO}_4]$ (0.113 g, 0.19 mmol) in dichloromethane was treated with freshly distilled dimethylphenylarsine (0.04 cm$^3$, 0.22 mmol). The solution was stirred under nitrogen for 60 minutes and then evaporated to dryness under reduced pressure. The yellow oily residue that remained was crystallised by slow addition of diethylether to a solution in dichloromethane yielding the title complex (0.098 g, 68%). [Found: C, 25.75; H, 4.71; P, 14.98. $\text{C}_{19}\text{H}_{34}\text{AsCl}_4\text{IrO}_4\text{P}_3$ requires C, 26.43; H, 4.96; P, 13.76%].
5.7 Spectroscopic data for the Complexes

Table 5.3 $^1$H n.m.r. data for phosphine substituted complexes of Iridium(III)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift ($\delta$)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$]$^b$</td>
<td>1.80 (s, broad)</td>
<td>PMe$_2$Ph (24H)</td>
<td>half height linewidth = 120 Hz</td>
</tr>
<tr>
<td></td>
<td>7.41 (broad)</td>
<td>phenyl (12H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.10 (broad)</td>
<td>phenyl (8H)</td>
<td></td>
</tr>
<tr>
<td>[IrCl$_2$(PMe$_3$)$_4$][IrCl$_4$(PMe$_3$)$_2$]$^f$</td>
<td>1.45 (t)</td>
<td>PMe$_3$ (9H)</td>
<td>$^3$J(PH) = 8.40</td>
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<td></td>
<td>1.68 (t, broad)</td>
<td>PMe$_3$ (18H)</td>
<td>$^2$J(PH) = 6.80</td>
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<td>[IrCl$_3$(PMe$_3$)$_3$]$^f$</td>
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<td>PMe$_3$ (18H)</td>
<td>$^2$J(PH) = 7.76$^g$</td>
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<td>1.67 (d)</td>
<td>PMe$_3$ (9H)</td>
<td>$^2$J(PH) = 10.60</td>
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<td>[IrCl$_2$(PMe$_3$)$_3$(H$_2$O)][ClO$_4$]$^f$</td>
<td>1.63 (t)</td>
<td>PMe$_3$ (18H)</td>
<td>$^2$J(PH) = 7.80$^g$</td>
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<td>1.72 (d)</td>
<td>PMe$_3$ (9H)</td>
<td>$^2$J(PH) = 11.51</td>
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<td></td>
<td>6.80 (broad)</td>
<td>H$_2$O (2H)</td>
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<tr>
<td>[IrCl$_2$(PMe$_3$)$_3$(PMe$_2$Ph)][ClO$_4$]$^{b,d}$</td>
<td>1.08 (d)</td>
<td>PMe$_2$Ph (3H)</td>
<td>$^2$J(PH) = 8.0</td>
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<td>1.10 (d)</td>
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<td>$^2$J(PH) = 7.0</td>
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<td></td>
<td>1.56 (m)</td>
<td>PMe$_3$ (6H)</td>
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<td></td>
<td>1.60 (d)</td>
<td>PMe$_2$Ph (3H)</td>
<td>$^2$J(PH) = 7.21</td>
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<td>1.71 (m)</td>
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<td>1.86 (t)</td>
<td>PMe$_3$ (3H)</td>
<td>$^2$J(PH) = 9.0</td>
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<td>7.44 (m)</td>
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<td>8.40 (t)</td>
<td>PMe$_2$Ph (1H)</td>
<td>$^2$J(PH) = 9.1</td>
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<td></td>
<td>8.08 (t, broad)</td>
<td>PMe$_2$Ph (2H)</td>
<td>$^2$J(PH) = 9.0</td>
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Table 5.3 continues overleaf .........
Table 5.3 continued.....

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<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (δ)*</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
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<tbody>
<tr>
<td>[IrCl₂(PMe₃)₃(PMePh₂)][ClO₄]b,e</td>
<td>1.55 (s,broad)</td>
<td>PMe₃ (18H)</td>
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<td></td>
<td>1.86 (d,broad)</td>
<td>PMe₃ (9H)</td>
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<tr>
<td></td>
<td>2.48 (d,broad)</td>
<td>PMePh₂ (3H)</td>
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<td></td>
<td>8.02 (m)</td>
<td>PMePh₂ (4H)</td>
<td>²J(PH)=7.51</td>
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<td>7.54 (s,broad)</td>
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<td>²J(PH)=7.7</td>
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<td>1.81 (s)</td>
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<td>6.9-7.6 (m)</td>
<td>AsMe₂Ph (15H)</td>
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<td>[IrCl₂(AsMe₂Ph)₄][ClO₄]b</td>
<td>1.60 (s,broad)</td>
<td>AsMe₂Ph (24H)</td>
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<td>7.26 (t,broad)</td>
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<td>7.42 (t,broad)</td>
<td>AsMe₂Ph (4H)</td>
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<tr>
<td></td>
<td>7.46 (broad)</td>
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*a:* Spectra recorded in CDCl₃ and referenced internally to the solvent.  
*b:* Spectra recorded at 400 MHz.  
*c:* PMe₃ cis tp PMe₃  
*d:* PMe₃ trans tp PMe₃.  
*e:* Spectra recorded at -75 °C.  
*f:* Spectra recorded at +45 °C.  
*g:* Spectra recorded at 200 MHz.  
*h:* J(PH)=²J(PH)+⁴J(PH).
Table 5.4 $^{31}\text{P} \{^1\text{H}\}$ n.m.r. data for phosphine substituted complexes of Iridium(III)

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<th>Compound</th>
<th>Chemical shift (δ)$^a$</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
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<td>$[^\text{IrCl}_2(\text{PMe}_2\text{Ph})_4][\text{ClO}_4]^b$</td>
<td>-53.51 (s,broad)</td>
<td>$\text{PMe}_2\text{Ph}$</td>
<td>half height linwidth =120 Hz</td>
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<td>$[^\text{IrCl}_2(\text{PMe}_2\text{Ph})_4][\text{ClO}_4]^b$</td>
<td>-51.60 (s)</td>
<td>$\text{PMe}_2\text{Ph}$</td>
<td>$^2J(\text{PP})=363.0$, $^2J(\text{PP})=-23.0$</td>
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<td></td>
<td>-53.15, -49.46 (AA/BB$'$)</td>
<td>$\text{PMe}_2\text{Ph}$</td>
<td>$^2J(\text{PP})=363.0$, $^2J(\text{PP})=-23.0$</td>
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<tr>
<td></td>
<td>-54.37, -53.63</td>
<td>$\text{PMe}_2\text{Ph}$</td>
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</tr>
<tr>
<td></td>
<td>-50.29, -49.02 (ABCD)</td>
<td>$\text{PMe}_2\text{Ph}$</td>
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<tr>
<td>$[^\text{IrCl}_2(\text{PMe}_3)_3(\text{PMe}_2\text{Ph})][\text{ClO}_4]^b$</td>
<td>+28.30, +26.20</td>
<td>$\text{PMe}_3$</td>
<td>$^2J(\text{PP})=366.0$, $^2J(\text{PP})=-27.0$</td>
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<tr>
<td></td>
<td>+30.00, +25.50 (ABCD)</td>
<td>$\text{PMe}_3$ &amp; $\text{PMe}_2\text{Ph}$</td>
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<tr>
<td></td>
<td>+21.20, +33.40</td>
<td>$\text{PMe}_2\text{Ph}$ &amp; $\text{PMe}_3$</td>
<td>$^2J(\text{PP})=366.0$, $^2J(\text{PP})=-30.0$</td>
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<td></td>
<td>+29.40 (A$_2$BC)</td>
<td>$\text{PMe}_2\text{Ph}$</td>
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<tr>
<td>$[^\text{IrCl}_2(\text{PMe}_3)_3(\text{PMe}_2\text{Ph})][\text{ClO}_4]^b$</td>
<td>+25.98, +23.56</td>
<td>$\text{PMe}_3$ &amp; $\text{PMe}_2\text{Ph}$</td>
<td>$^2J(\text{PP})=366.0$, $^2J(\text{PP})=-25.0$</td>
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<tr>
<td></td>
<td>+28.65 (A$_2$BC)</td>
<td>$\text{PMe}_3$</td>
<td></td>
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<tr>
<td>$[^\text{IrCl}_2(\text{PMe}_3)_3(\text{PMePh}_2)][\text{ClO}_4]^b$</td>
<td>+26.00, 16.90</td>
<td>$\text{PMe}_3$ &amp; $\text{PMePh}_2$</td>
<td>$^2J(\text{PP})=366.0$, $^2J(\text{PP})=-27.0$</td>
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<td></td>
<td>+30.80 (ABCD)</td>
<td>$\text{PMe}_3$</td>
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Table 5.4 continues overleaf .........
Table 5.4 continued .....  

<table>
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<th>Compound</th>
<th>Chemical shift ($\delta$)*</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
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<tr>
<td>[IrCl$_2$(PMe$_3$)$_3$(PMePh$_2$)][ClO$_4$]$^b$</td>
<td>+32.80, +26.0 +26.80 (A$_2$BC)</td>
<td>PMe$_3$ &amp; PMePh$_2$ PMe$_3$</td>
<td>$^2$J(PP)=366.0, $^2$J(PP)=-27.0</td>
</tr>
<tr>
<td>[IrCl$_2$(PMe$_3$)$_3$(PMePh$_2$)][ClO$_4$]$^{b,c}$</td>
<td>+29.80, +24.20 +20.50 (A$_2$BC)</td>
<td>PMe$_3$ PMePh$_2$</td>
<td>$^2$J(PP)=366.0, $^2$J(PP)=-27.0</td>
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</table>

*a: Spectra run in CDCl$_3$ and chemical shifts are quoted relative to external 85 % H$_3$PO$_4$ with downfield chemical shifts reported as positive.  
*b: Spectra recorded at 162 MHz.  
*c: Spectra recorded at +45 °C.  
*d: Spectra recorded in CD$_3$OD$_3$ at -75 °C.
Chapter 6

Reactions of the Phosphido Cluster

\[ \text{[Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}] \]
6 Reactions of the Phosphido Cluster \([\text{Os}_3(\mu-H)(\mu-P\text{PhH})(\text{CO})_{10}]\)

6.1 Introduction

The direct reaction of \([\text{Os}_3(\text{CO})_{12}]\) with phenylphosphine\(^{67,69}\) leads to fairly low yields of the phenylphosphido cluster \([\text{Os}_3(\mu-H)(\mu-P\text{PhH})(\text{CO})_{10}]\) along with the phenylphosphinidene cluster \([\text{Os}_3(\mu-H)_2(\mu_2-P\text{Ph})(\text{CO})_9]\) and other products. The problem with this route is that high temperatures are required for reaction. More recently a high yield route to transition metal clusters stabilised by bridging phosphido ligands has been developed.\(^{255}\) Reaction of \([\text{Os}_3(\text{CO})_{11}(\text{MeCN})]\) with \(\text{PR}_1\text{R}_2\text{H}\) rapidly gives the corresponding phosphine substituted cluster \([\text{Os}_3(\text{CO})_{11}(\text{PR}_1\text{R}_2\text{H})]\) (\(\text{R}_1 = \text{R}_2 = \text{H}; \text{R}_1 = \text{H}, \text{R}_2 = \text{Ph}; \text{R}_1 = \text{R}_2 = \text{Ph}\)) which is easily handled and can be isolated in good yield (Scheme 6.1). Direct thermal decarbonylation might be expected to give \([\text{Os}_3(\mu-H)(\mu-P\text{PhH})(\text{CO})_{10}]\) but a very effective and better method of decarbonylation is to deprotonate \([\text{Os}_3(\text{CO})_{11}(\text{PR}_1\text{R}_2\text{H})]\) with base to afford \([\text{Os}_3(\text{CO})_{11}(\text{PR}_1\text{R}_2)^+]\) which readily decarbonylates to \([\text{Os}_3(\text{CO})_{10}(\text{PR}_1\text{R}_2)^+]\). This decarbonylation is facile because the

![Scheme 6.1](image)
terminal phosphido ligand in the undecacarbonyl has a strong tendency to bridge and displace CO. Reprotonation of the decacarbonyl anion gives good yields of \([\text{Os}_3(\mu-H)(\mu-\text{PR}_3^2)(\text{CO})_6]\).

Lewis and co-workers have proposed two reaction routes resulting in the formation of \([\text{Os}_3(\mu-H)(\mu-X)(\text{CO})_{10}]\) (X = main group three-electron donor) species from \([\text{Os}_3(\text{CO})_{11}(\text{MeCN})]^{256}\). The first route involves ligand substitution to produce \([\text{Os}_3(\text{CO})_{11}(X-H)]\) followed by CO loss and the concomitant insertion of osmium into the X-H bond. Alternately they propose the first step to involve insertion into the X-H bond to give a one-electron terminal X species. The lone-pair residing on this X ligand moiety replaces a CO to afford the three-electron X bridge. Following reports of the reaction of \([\text{Os}_3(\mu-H)(\text{CO})_{11}]^-\) with NO+ to give \([\text{Os}_3(\mu-H)(\text{NO})(\text{CO})_{10}]\) \(^{293}\) Lewis decided to use the undecacarboxyl anion to attempt the preparation of a terminally bound Group 15 moiety. They found that the reaction of \([\text{Os}_3(\mu-H)(\text{CO})_{11}]^-\) with \(\text{PPh}_2\text{Cl}\) afforded the phosphido bridged cluster \([\text{Os}_3(\mu-H)(\mu-\text{PPh}_2)(\text{CO})_{10}]\) with no evidence of a terminally bound \(\text{PPh}_2\) containing intermediate. A similar reaction with \(\text{SbPh}_2\text{Cl}\) afforded the novel cluster \([\text{Os}_3(\mu-H)(\mu-\text{SbPh}_2)(\text{CO})_{10}]\) again with no evidence of a terminal Group 15 intermediate (scheme 6.2). The absence of a terminally bound group 15 containing cluster was expected to be a consequence of the lone-pair basicity of the main group atom. Reactions were conducted with the Group 15 trihalides (thereby decreasing the electron density at the main group atom and enhancing the possible formation of a terminally bound intermediate) and the initial reactions indicated that the

\[
\begin{align*}
\text{(CO)}_4\text{Os} & \quad \text{Os} \quad \text{Os}(\text{CO})_3 \\
\text{Os} \quad \text{Os} \quad \text{H} & \quad \text{Os}(\text{CO})_3 \\
\text{(CO)}_3 & \quad \text{(CO)}_3 \\
\text{E} = \text{P, Sb} \\
\end{align*}
\]

Scheme 6.2
The activation of metal carbonyl cluster compounds and the preparation of high nuclearity clusters from low nuclearity precursors "via sensible routes" presents problems. Lewis and co-workers have used the readily accessible phosphido bridged cluster \([\text{Os}_3(\mu-H)(\mu-PHR)(\text{CO})_{10}]\) for the rational synthesis of higher nuclearity clusters, both homo- and heteronuclear. He proposed that cleavage of the phosphinidene ligand of \([\text{Os}_3(\mu-H)(\mu_3-PPh)(\text{CO})_9]\) would create a vacant coordination site at one metal and a chemically active lone-pair on the resultant bridging phosphido group, subsequent reaction with \([\text{M}_3(\text{CO})_{12}]\) \((\text{M} = \text{Ru, Os})\) afforded a high yield route to cluster expansion\(^{147}\) (Scheme 6.3). The major products isolated from these reactions were the pentanuclear clusters \([\text{M}_2\text{Os}_4(\text{CO})_{15}(\text{PR})]\) with low yields of tetra- and hexanuclear clusters.

\[\text{Os}_3(\mu-H)(\mu_2-PH_2)(\text{CO})_{10}\] can be prepared in a similar manner to the more stable \(\mu_2-\text{PR}^1\text{R}^2\) and \(\mu_2-\text{PR}^1\text{H}\) analogues, but because of the thermal instability of this cluster, high nuclearity clusters cannot be prepared by pyrolysis with \([\text{M}_3(\text{CO})_{12}]\). Addition of \([\text{Os}_3(\text{CO})_{11}(\text{MeCN})]\) to a cyclohexane solution of \([\text{Os}_3(\mu-H)(\mu_2-PH_2)(\text{CO})_{10}]\) at 50 °C afforded a cluster formulated as \([\text{Os}_3(\mu-H)_2(\text{CO})_{10}(\mu_2-\text{PH})]\) whilst reaction with \([\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]\) gave \([\text{Os}_6(\mu-H)_2(\text{CO})_{30}(\mu_2-H)(\text{MeCN})]\).\(^{169}\) The former cluster, and its corresponding anion, have been found to be useful precursors for the synthesis of high nuclearity clusters containing interstitial phosphides. Prolonged heating of a xylene solution of \([\text{Os}_6(\mu-H)_2(\text{CO})_{21}(\mu_3-\text{PH})]\) at reflux afforded as a single major product \([\text{Os}_6(\text{CO})_{18}(\mu-H)(\mu_3-\text{P})]\).\(^{168}\) The cluster was found to consist of a trigonal prismatic framework of metal atoms, and is formally a 90e-system (see chapter 2 for further details).

A very interesting feature of the chemistry of \([\text{Os}_3(\mu-H)(\mu_2-PPhH)(\text{CO})_{10}]\) is that deprotonation leads to the kinetically controlled anion \([\text{Os}_3(\mu-H)(\mu_2-PPh)(\text{CO})_{10}]^-\) which persists in THF solutions at room temperature but which isomerises to \([\text{Os}_3(\mu_2-PPhH)(\text{CO})_{10}]^-\) on heating at reflux for several minutes. We have studied the reactions of these, anions with electrophiles \([\text{MeI}, [\text{Au}(\text{PMe}_2\text{Ph})\text{Cl}], \text{HgX}_2, \text{and HgRX} \ (R = \text{Et, CH}_2\text{Ph})]\) with the intention of establishing the regioselectivity of addition (at metal or phosphorus atom) and the stereochemistry of products of the general type \([\text{Os}_3(\mu-H)(\mu_2-PPhR)(\text{CO})_{10}]\) and our results are presented here.
6.2 Results and Discussion

6.2.1 Reaction of [Os₃(μ-H)(μ-PPh)(CO)₁₀] with Organic Electrophiles

The cluster [Os₃(μ-H)(μ-PPhH)(CO)₁₀] was prepared as reported briefly by the conversion of [Os₃(CO)₁₀] to [Os₃(CO)₁₁(PPhH₂)] and subsequent deprotonation, decarbonylation and reprotonation of [Os₃(CO)₁₁(PPhH₂)] to form [Os₃(μ-H)(μ-PPhH)(CO)₁₀]. Also, as reported, the deprotonation of [Os₃(μ-H)(μ-PPhH)(CO)₁₀] with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in THF gave complete conversion to [Os(μ-H)(μ-PPhH)(CO)₁₀]. Treatment of this solution with methyl iodide (Scheme 6.4) leads to a single t.l.c. band on chromatographic work-up. A ¹H n.m.r. spectrum of this single band revealed that it consisted of a mixture of [Os₃(μ-H)(μ-PPhH)(CO)₁₀] and [Os₃(μ-H)(μ-PPhMe)(CO)₁₀], apparent from the corresponding hydride resonances (δ -19.27 (dd), ²J(PH) = 17.2 Hz, ³J(PH) = 4.4 Hz and δ -18.65 (d), ²J(PH) = 16.2 Hz). Repeat of this treatment on the mixture gave pure [Os₃(μ-H)(μ-PPhMe)(CO)₁₀] as a single isomer, the stoichiometry of which was established by i.r., ¹H and ³¹P{¹H} n.m.r. data. The ³¹P{¹H} n.m.r. spectrum consisted of a doublet resonance (²J(PH) = 16.2 Hz) because the proton-decoupling conditions used did not extend as far as the hydride signal which remained coupled to phosphorus. The absence of a P-H resonance in the ¹H n.m.r. spectrum confirmed complete conversion to the methylphenylphosphido cluster.

The ³¹P{¹H} n.m.r. spectrum of [Os₃(μ-H)(μ-PPhH)(CO)₁₀] consisted of a doublet (δ 38.26), whereas the phosphido resonance belonging to the methylated cluster [Os₃(μ-H)(μ-PPhMe)(CO)₁₀] appeared at δ 84.72. Similar shifts of phosphorus resonances to low-field have previously been observed upon methylation of phosphido complexes such as [IrCl₂(PMe₂Ph)₂(Ph₂)] and [Mo(CO)₅(PPhH)] (see Chapter 4 for a discussion).

Spectra did not, however, readily allow us to establish the stereochemistry at phosphorus, that is whether the structure is 6(a) or 6(b) in Scheme 6.4. The phenylphosphido bridged cluster is known to have the phenyl group exo with respect to the Os(CO)₄ unit, that is in the position corresponding to that in 6(b) (Scheme 6.4). This configuration prevents unfavourable repulsion between the phenyl group and an axial carbonyl group of the Os(CO)₄ unit. The reported ¹H n.m.r. spectrum of the related cluster [Os₃(μ-H)(μ-PPhH)(CO)₁₀] contains multiplets at δ 7.78 and δ 6.77.
assigned to the *ortho* hydrogen atoms of the two respective phenyl rings. The *ortho* hydrogen atoms of [Os₃(μ-H)(μ-PPhMe)(CO)]₀ appear at δ 7.77 so that an assignment of the *ortho* signals in the spectrum of [Os₃(μ-H)(μ-PPh₂)(CO)]₀ would allow us to establish the stereochemistry in [Os₃(μ-H)(μ-PPhMe)(CO)]₀. The *ortho* hydrogen atom signal is at δ 7.34 in [Os₃(μ-H)(μ-PPhH)(CO)]₀, almost exactly the average of the two values for [Os₃(μ-H)(μ-PPh₂)(CO)]₀. Assuming that the phenyl groups of [Os₃(μ-H)(μ-PPh₂)(CO)]₀ are perpendicular as shown in Figure 6.1 as found in the related derivatives such as [Os₃(μ-H)(μ-PPh₂)(CO)₃P(OMe)₃], the δ-value for H^A would have a lower value than for [Os₃(μ-H)(μ-PPhH)(CO)]₀. This is because the H^A atom making a close approach to the face of the other phenyl group would be shielded (i.e. at low δ), because the magnetic field induced by the circulating π-electrons acts to oppose B₀. Rotation about the P-C bonds would average the two sites for H^A so we examined the low temperature ^1^H n.m.r. spectrum of [Os₃(μ-H)(μ-PPh₂)(CO)]₀ but even at -80 °C (CDCl₃) rotation about the P-C bond was rapid. On the basis of the above arguments for [Os₃(μ-H)(μ-PPh₂)(CO)]₀ we have assigned the signal at δ 6.77 to H^A and that at δ 7.78 to H^B. In the absence of adjacent phenyl rings influencing chemical shifts, the δ-values for the *ortho* hydrogen atoms of the *exo* and *endo* phenyl groups will be at δ 7.3 and δ 7.8 respectively. This then requires [Os₃(μ-H)(μ-PPhMe)(CO)]₀ to have structure 6(a) in Scheme 6.4 since the *ortho* hydrogen atom signal is at δ 7.77.

The most apparent difference between the ^1^H n.m.r. spectra of [Os₃(μ-H)(μ-
PPhH(CO)_{10} and [Os_{3}(\mu-H)(\mu-PPhMe)(CO)_{10}] is the down-field shift of the ortho resonances (δ 7.34 and δ 7.77 respectively). This shift of the signals belonging to the ortho hydrogen atoms of the phenyl ring is a consequence of their interaction with the induced magnetic field of the axial carbonyl group of the Os(CO)_{4} unit. This close approach of the ortho hydrogen atoms of the phenyl ring to the CO group means that they experience a field greater than B_{0} and therefore have a higher precessional frequency (higher δ value). Similar down-field shifts have been observed for the resonances of the ortho hydrogen atoms in clusters where there is a close approach of these atoms to an axial CO group. For example, the ortho hydrogen atom resonances of the phenyl rings of [M_{6}(\mu-H)_{8}(\mu_{3}-PPh)(CO)_{8}]^{67,69} (M = Ru, Os) (δ 7.75 and δ 8.05 respectively), [Ru_{6}(\mu-H)_{2}(\mu_{3}-PPh)_{2}(\mu_{4}-PPh)_{2}(CO)_{12}] (δ 7.96) and [Ru_{6}(\mu_{3}-PPh)_{2}(\mu_{4}-PPh)_{2}(CO)_{12}] (δ 7.74) all appear at to lower field than resonances of normal aromatic protons, a consequence of the induced magnetic field of the axial CO group. All these cluster have been structurally characterised and show a close approach of the phenyl ring to the axial CO. These observations similarly reinforce our expectations that the phenyl ring in [Os_{3}(\mu-H)(\mu-PPhMe)(CO)_{10}] is endo.

Chemical reactivity also supports the endo stereochemistry 6(a) since thermal decarbonylation leads to the ortho metallated compound [Os_{3}(\mu-H)_{2}(\mu_{3}-PC_{6}H_{4}Me)(CO)_{8}] in Scheme 6.4. This assumes that inversion at phosphorus cannot occur at the reaction temperature (125 °C). A n-octane solution of [Os_{3}(\mu-H)(\mu-PPhMe)(CO)_{10}] was heated at reflux for 45 minutes, after which time the i.r. spectrum indicated that decarbonylation was complete. A single major product was isolated from the reaction mixture. The ¹H n.m.r. spectrum of this product consisted of a methyl resonance [δ 2.13(d), J(PH) = 10.4 Hz (3H)] and phenyl resonances in a 3:1 ratio [δ 7.77 (1H), and δ 7.23 (3H)]. A ratio of 4:3, phenyl : methyl, indicated that the product of decarbonylation was [Os_{3}(\mu-H)_{2}(\mu-P(C_{6}H_{4})Me)(CO)_{8}]. The high-field region of the spectrum of [Os_{3}(\mu-H)_{2}(\mu-P(C_{6}H_{4})Me)(CO)_{8}] showed a broad peak at δ -17.19 indicating fluxional behaviour for the two non-equivalent hydride ligands. On cooling, changes in this signal, which are typical for an ABX spin system with A, B exchanging were observed. At of -55 °C (CDCl_{3}) the fluxional process occurring was slow enough on the n.m.r. time-scale to observe both separate hydride resonances, and resolve all the coupling constants of the ABX spin system. A similar dynamic process has been reported for [Os_{3}(\mu-H)_{2}(\mu-P(C_{6}H_{4})Ph)(CO)_{8}] although it was found impossible to reach the
slow exchange limit for the dynamic process because the temperature range of the solvent was not large enough. Since it was important to have no doubt about the stereochemistry at phosphorus in $[\text{Os}_3(\mu-H)(\mu-PPhMe)(\text{CO})_{10}]$, its single-crystal X-ray structure was determined. The structure was solved by Professor A. J. Deeming and Professor K. I. Hardcastle at California State University, Northridge.

6.2.2 Crystal Structure of $[\text{Os}_3(\mu-H)(\mu-PPhMe)(\text{CO})_{10}]$

Crystals suitable for X-ray structure determination were grown by cooling a n-hexane solution of the cluster at -20 °C for several days. The cluster crystallises in the orthorhombic space group $Pnma$ with unit cell dimensions $a = 15.401(3)$ Å, $b = 14.241(3)$ Å, $c = 10.090(3)$ Å with four molecules per unit cell. The structure was refined to $R = 0.0477$ and $R_w = 0.056$. Important bond lengths and angles are given in Table 6.1 and the molecular structure is shown in Figure 6.2.

The overall structure is as expected and the phenyl group is shown to be endo to the Os(CO)$_4$ unit, in contrast to its exo stereochemistry in $[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$. $[\text{Os}_3(\mu-H)(\mu-PPhMe)(\text{CO})_{10}]$ has a crystallographic mirror plane passing through Os(1) and P and bisecting the Os(2)-Os(2a) vector and the cluster has $C_s$ molecular symmetry. Apart from the different substituents at phosphorus, the overall geometry relates closely to those of similar clusters $[\text{Os}_3(\mu-H)(\mu-PPh_2)(\text{CO})_9\{\text{P(OMe)}_3\}]$,$^{257}$ $[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$,$^{67}$ and $[\text{Os}_3(\mu-H)_2(\text{CF}_3\text{CO}_2)(\mu-PPh_2)(\text{CO})_9]$. The dihedral angle between the ring Os(2)Os(2a)P and the Os$_3$ ring is 67.8 ° which is smaller than the 73.4 ° found in $[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$. The structural determination of the closely related cluster $[\text{Os}_3(\mu-H)(\mu-PPh_2)(\text{CO})_9\{\text{P(OMe)}_3\}]$,$^{257}$ revealed a dihedral angle between the equivalent planes of 69.2 ° comparing favourably with that found in $[\text{Os}_3(\mu-H)(\mu-PPhMe)(\text{CO})_{10}]$. This increase in the dihedral angle reflects the effect of the repulsive interaction of the endo phenyl substituent in $[\text{Os}_3(\mu-H)(\mu-PPhMe)(\text{CO})_{10}]$ with the adjacent axial CO ligand. The closest contacts between the phenyl and CO are C(41)-C(14) 3.11 Å, C(41)-O(14) 2.94 Å and C(42)-O(14) 3.12 Å. The position of the axial CO also appears to have been affected by the close approach of the phenyl group since the angle Os(2)-Os(1)-C(14) is 93.0(4) ° larger than the corresponding angle for the CO trans to it which is 86.3(4) °. Although in the cluster $\text{exo-[Ru}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$ the equivalent bond angles and lengths are 91.2(1) ° and 83.5(1) ° not much different, so
Figure 6.2  Structure of \([\text{Os}_3(\mu-H)(\mu-PPhMe)(CO)]_{18}\)
Table 6.1 Selected bond lengths and angles for [Os₃(µ-H)(µ-PPhMe)(CO)₁₀]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1)-Os(2)</td>
<td>Os(1)-Os(2)-Os(2a)</td>
</tr>
<tr>
<td>Os(2)-Os(2a)</td>
<td>2.8749</td>
</tr>
<tr>
<td>Os(2)-P</td>
<td>Os(2)-Os(1)-Os(2a)</td>
</tr>
<tr>
<td>P-C(3)</td>
<td>59.6(2)</td>
</tr>
<tr>
<td>P-C(41)</td>
<td>Os(2)-P-Os(2a)</td>
</tr>
<tr>
<td>Os(1)-C(14)</td>
<td>2.907(1)</td>
</tr>
<tr>
<td>Os(1)-C(12)</td>
<td>Os(2)-P-C(3)</td>
</tr>
<tr>
<td>Os(1)-C(13)</td>
<td>2.368(3)</td>
</tr>
<tr>
<td></td>
<td>Os(2)-P-C(41)</td>
</tr>
<tr>
<td></td>
<td>1.83(2)</td>
</tr>
<tr>
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<td>199.2(7)</td>
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<td>1.77(2)</td>
</tr>
<tr>
<td></td>
<td>99.2(7)</td>
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<tr>
<td></td>
<td>1.92(1)</td>
</tr>
<tr>
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<td>114.6(4)</td>
</tr>
<tr>
<td></td>
<td>1.92(1)</td>
</tr>
<tr>
<td></td>
<td>126.6(3)</td>
</tr>
<tr>
<td></td>
<td>1.88(1)</td>
</tr>
<tr>
<td></td>
<td>99.2(7)</td>
</tr>
</tbody>
</table>

Os(2)-Os(1)-C(12)   86.3(4)
Os(2)-Os(1)-C(14)   93.0(4)
Os(2)-Os(1)-C(13)   99.5(4)
there may be a different reason for these angles being different.

The Os(2)-Os(2a) distance is significantly longer than Os(2)-Os(1) and Os(2a)-Os(1) [Os(2)-Os(2a) 2.907(1) Å and Os(2)-Os(1) 2.875(6) Å]. This is consistent with the fact that a μ-H bridge on a metal cluster normally causes a lengthening of the bridged metal-metal vector. The short Os-Os distances agree satisfactorily with the distance of 2.877 Å which is the average Os-Os bond length in [Os₃(CO)₁₂]. The two equatorial Os(2)-C(23) bonds (1.89(6) Å) which are trans to the bridging hydride are shorter than those trans to the phosphido phosphorus Os(2)-C(22) (1.94(1) Å). These distances are very similar to those in [Os₃(μ-H)(μ-PPhH)(CO)₁₀] (1.91(2) Å trans to hydride and 1.94(2) Å trans to the phosphido phosphorus). Os(1) has distorted octahedral coordination geometry with the equatorial Os-C(carbonyl) distances shorter (Os(1)-C(13) 1.88(1) Å) than the axial Os-C(carbonyl) distances (Os(1)-C(12) 1.92(2) Å and Os(1)-C(14) 1.92(1) Å). This is expected due to the greater competition between trans carbonyl groups for back donation from the same metal orbital, detrimental to the synergistic interaction and lengthening both Os-C bonds. As expected the carbonyl groups that exhibit shorter Os-C(carbonyl) bonds on Os(1) have longer C-O distances than those with longer Os-C(carbonyl) bonds [C(13)-O(13) 1.16(2) Å compared to C(14)-O(14) 1.13(2) Å]. However, these differences are not very significant in the light of the e.s.d.'s.

Although the phosphinidene ligand has been widely excepted as stabilising metal clusters, Huttner has shown through a series of chemical transformations of [Fe₃(μ-H)₂(μ-PPh)(CO)₉] that these ligands are considerably more reactive than originally speculated. Figure 6.3 shows the transformation of a triply bridging phenylphosphinidene ligand into a doubly bridging methylphenylphosphido ligand. The most apparent difference between this cluster and [Os₃(μ-H)(μ-PPhMe)(CO)₁₀] is the unsaturation caused by the loss of a CO ligand from the Fe(CO)₄ unit. This unsaturation is compensated for by a η²-interaction of the aryl substituent endo to the unsaturated unit. Carty originally prepared the ruthenium analogue of this electron deficient cluster by liberation of the olefin from [Ru₃(CO)₉(μ-η²-C≡CR)(μ-PPh₂)]. More recently he successfully synthesised this complex by treatment of [Ru₃(μ-H)(μ-PPh₂)(CO)₁₀] with trimethylamine oxide in ethanol/CH₂Cl₂. We might expect that as a result of the correct stereochemistry at phosphorus, the cluster [Ru₃(μ-H)(μ-PPhMe)(CO)₁₀] should decarbonylate readily to afford [Ru₃(μ-H)(μ-PPhMe)(CO)₉] with a η²-interaction of the
endo phenyl ring.

Whether the \( \mu_2 \)-phosphinidene in \([\text{Os}_3(\mu-H)(\mu-P\text{Ph})(\text{CO})_{10}]^+\) is planar or pyramidal is still open to question. If it is pyramidal, deprotonation of \([\text{Os}_3(\mu-H)(\mu-P\text{PhH})(\text{CO})_{10}]^-\) does not lead to any change in the number of electrons donated by the phosphorus.

There must be an inversion from exo to endo phenyl before nucleophilic attack of the methyl iodide takes place. If isomers of \([\text{Os}_3(\mu-H)(\mu-P\text{Ph})(\text{CO})_{10}]^+\) with pyramidal phosphorus and with exo and endo phenyl are in equilibrium, one would expect the endo isomer to be the less populous but more nucleophilic since the lone-pair is less crowded. This would react to give \([\text{Os}_3(\mu-H)(\mu-P\text{PhMe})(\text{CO})_{10}]^-\). A planar phosphinidene would donate 5 electrons and no osmium-osmium bond would be required between the bridged atoms (Figure 6.4). The formation of \([\text{Os}_3(\mu-H)(\mu-P\text{PhMe})(\text{CO})_{10}]^-\) would occur by electrophilic addition from the less crowded side. Protonation of \([\text{Os}_3(\mu-H)(\mu-P\text{Ph})(\text{CO})_{10}]^+\) leads to the opposite isomer to methylation, either because the protonation
is reversible and the thermodynamically more stable isomer is then accessible or because protonation is less sterically restrictive and fast direct *endo* protonation is possible.

![Diagram of molecular structure]

**Figure 6.4**

### 6.3 Reactions with Metal Electrophiles

#### 6.3.1 Reaction of $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}]^+$ and $[\text{Os}_3(\mu-\text{PPhH})(\text{CO})_{10}]^-$ with $[\text{Au}(\text{PMe}_2\text{Ph})\text{Cl}]$

Addition of DBU to a solution of $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]$ in THF followed immediately by the addition of $[\text{Au}(\text{PMe}_2\text{Ph})\text{Cl}]$ as soon as formation of the anion $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]^-$ was complete (i.r. evidence) gave the hydrido-cluster $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10}]$. Chromatographic work-up and crystallisation from n-hexane afforded a pure sample of this cluster as a deep-orange air-stable crystalline material whose elemental analytical data (C, H, and P) agreed reasonably well with the calculated values. The reaction product is consistent with the phosphorus being the most nucleophilic centre in $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}]^+$ (Scheme 6.5). From the $^3\text{P}[^1\text{H}]$ n.m.r. spectrum, $^2\text{J}(\text{PP})$ was found to be 327 Hz, a value that is only consistent with both phosphorus atoms being bonded to Au [$^\delta(\text{P})$ 18.80(d), $^2\text{J}(\text{PP}) = 327$ Hz (PMe$_2$Ph) and $^\delta(\text{P})$ 26.98(dd), $^2\text{J}(\text{PP}) = 327$ Hz, $^2\text{J}(\text{PH}) = 12.5$ Hz (µ-PPh)]. Furthermore there was no dynamic exchange. The presence of these two phosphorus signals in the spectrum eliminates the possibility of the product being two clusters linked through [Au]$^+$, unlike the formation of $[(\text{IrCl}_2(\text{PMe}_2\text{Ph})_2)(\text{PH}_2)]_2\text{Au}[\text{ClO}_4]$ in which the analogous
Scheme 6.5
intermediate \( \text{IrCl}_2(\text{PMe}_2\text{Ph})(\text{PH}_2\text{AuPMe}_2\text{Ph})[\text{Cl}] \) was formed but readily under went a symmetrisation reaction to afford the final product containing two iridium phosphido complexes linked through \( [\text{Au}]^+ \). No such reaction was evident for the cluster \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhMe})(\text{CO})_{10} \). The chemical shift of the ortho phenyl hydrogen atom is \( \delta 7.74 \), very similar to that in \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhMe})(\text{CO})_{10} \), so we believe that the phenyl group on phosphorus is endo to the Os(CO)_4 group. This requires a structure like 6(a) (Scheme 6.4) with the methyl replaced by AuPMe_2Ph. The methyl resonance in the \(^1\text{H} \) n.m.r. spectrum of \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10} \) appeared as a doublet of doublets (\( \delta 1.81, ^2\text{J} (\text{PH}) = 9.60 \text{ Hz} \) and \( ^4\text{J} (\text{PH}) = 2.0 \text{ Hz} \)). The best yields of \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10} \) at -40 °C, under which conditions the kinetically formed anion \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10} \) is the most abundant, very little conversion to the thermodynamically more stable \( \text{Os}_3(\mu-\text{PPhH})(\text{CO})_{10} \) having occurred.

If, however, \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10} \) is deprotonated with DBU in THF and the mixture refluxed for three minutes, the anion \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10} \) is converted to the thermodynamically favoured \( \text{Os}_3(\mu-\text{PPhH})(\text{CO})_{10} \) by migration of the hydrogen atom. Figure 6.5 shows the changes occurring in the i.r. spectrum upon addition of DBU to a THF solution of \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10} \) (a) forming \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10} \) (b) and subsequent heating at reflux to afford \( \text{Os}_3(\mu-\text{PPhH})(\text{CO})_{10} \) (c). On addition of \( \text{Au}(\text{PMe}_2\text{Ph})\text{Cl} \) to this solution \( \text{Os}_3(\mu-\text{AuPMe}_2\text{Ph})(\mu-\text{PPhH})(\text{CO})_{10} \) is obtained, a non-hydridic isomer of \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10} \). This product was obtained pure after chromatographic work-up (t.l.c.) and crystallisation by slow evaporation from a n-hexane solution affording deep-orange air-stable crystals whose elemental analytical data (C, H, and P) agreed with the data obtained for \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10} \). The \(^3\text{P} [\text{H}] \) n.m.r. spectrum now contains two doublets (\( \delta 30.67, ^2\text{J} (\text{PP}) = 10.2 \text{ Hz} \) (\( \mu-\text{PPh} \)), and \( \delta 96.92, ^2\text{J} (\text{PP}) = 10.2 \text{ Hz} \) (\( \mu-\text{AuPMe}_2\text{Ph} \)) and the small value of \( ^2\text{J} (\text{PP}) \) reveals that this isomer does not have both P-atoms bonded to the same metal atom and clearly \( \text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10} \) and \( \text{Os}_3(\mu-\text{AuPMe}_2\text{Ph})(\mu-\text{PPhH})(\text{CO})_{10} \) cannot be related as exo and endo isomers. The \(^1\text{H} \) n.m.r. spectrum of \( \text{Os}_3(\mu-\text{AuPMe}_2\text{Ph})(\mu-\text{PPhH})(\text{CO})_{10} \) contained a signal due to a P-H substituent (\( \delta 7.37, ^1\text{J} (\text{PH}) = 394.0 \text{ Hz} \)) with the familiarly large value of \( ^1\text{J} (\text{PH}) \). The absence of a hydride resonance in the n.m.r. spectrum and the loss of the \( ^4\text{J} (\text{PH}) \) splitting in the methyl signal (\( \delta 1.88 ^2\text{J} (\text{PH}) = 9.6 \text{ Hz} \)) leads us to believe that the
Figure 6.5 \( v(\text{CO}) \) i.r. spectra of \([\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]\), \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]\), and \([\text{Os}_3(\mu-PPhH)(\text{CO})_{10}]\)
Figure 6.6 ¹H n.m.r. spectra of the phenyl region of the complexes [Os₃(μ-AuPMe₂Ph)(μ-PPh)(CO)]₆ and [Os₃(μ-H)(μ-AuPMe₂Ph)(μ₂-PPh)(CO)]₆
[Au(PMe₂Ph)]⁺ fragment is a μ₂-ligand at osmium and behaves as a pseudo hydride as described previously. Figure 6.6a shows the ¹H n.m.r. spectrum of [Os₃(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀] in the phenyl region. The ortho hydrogen atom resonance at δ 7.71 has been assigned to the phenyl ring belonging to the phosphido bridge whilst the resonance at δ 7.46 to the ortho hydrogen atoms of the bridging [Au(PMe₂Ph)]⁺ fragment. On the basis of ortho hydrogen chemical shifts we believe that there is an endo phenyl group (Scheme 6.5).

The triosmium clusters [Os(μ-H)(μ-PPhAuPMe₂Ph)(CO)₁₀] and [Os₃(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀] both decarbonylate thermally to the same compound, [Os₃(μ-H)(μ-AuPMe₂Ph)(μ₃-PPhH)(CO)₁₀] (Scheme 6.5) formed by AuPMe₂Ph or H migration respectively from P to Os atoms. Figure 6.6b shows the ¹H n.m.r. spectrum of [Os₃(μ-H)(μ-AuPMe₂Ph)(μ₃-PPhH)(CO)₁₀] in the phenyl region. In comparison to the spectrum of [Os₃(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀] (Figure 6.6a) the P-H resonances have disappeared with the concomitant formation of a hydride resonance (δ -23.25(dd), ²J(PH) = 11.4 Hz and ³J(PH) = 1.5 Hz).

The assignment of the configurations at the phosphido phosphorus atom of [Os₃(μ-H)(μ-PPhAuPMe₂Ph)(CO)₁₀] and [Os₃(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀] have relied upon the correct assignment of the ortho resonances corresponding to the phenyl ring of the bridging phosphido ligand. The presence of two sets of signals belonging to ortho protons of the two phenyl rings offers the possibility of an incorrect assignment. Both ortho resonances have extremely different appearances as a result of the dissimilar meta couplings of the phenyl rings. The ¹H n.m.r. spectrum of a genuine sample of [Au(PMe₂Ph)Cl] enabled assignment of the resonance due to its phenyl ring to be made and by default that of the phosphido bridge. Although the different coupling patterns of the ortho resonances appears to be a reliable criterion for their assignment the possibility of an incorrect interpretation must be acknowledged.

Similar transformations have recently been observed on the cluster [Ir₄(CO)₁₁(PPh₂H)]. Deprotonation of [Ir₄(CO)₁₁(PPh₂H)] with DBU in the presence of [Au(PPh₃)]/[TIPF₆] was found to give [Ir₄(CO)₁₁(PPh₂AuPPh₃)] characterised crystallographically. Deprotonation of the terminal phosphine complex in the absence of [Au(PPh₃)] afforded [Ir₄(CO)₁₀(μ-PPh₂)(μ-AuPPh₃)], figure 6.7 shows the cluster transformations that were observed. [Ir₄(CO)₁₁(PPh₂AuPPh₃)] underwent thermal decarbonylation with [Au(PPh₃)] migration to an Ir-Ir bond. This decarbonylation
Figure 6.9 ν(CO) i.r. spectra of [Os₂(μ-H)(μ-PPhH)(CO)₁₀], [Os₂(μ-PPhH)(CO)₁₀]⁻ and [Os₃(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀]
reaction is similar to that observed for \([\text{Os}_3(\mu-H)(\mu-PPh\text{AuPMe}_2\text{Ph})(\text{CO})_{10}]\) but in the latter example the transformation involves a phosphido to a phosphinidene ligand. Both these examples represent replacement of H by [Au(PPh_3)] at the phosphorus and are additional examples of the isolobal analogy between the H and AuPPh/AuPMe_2Ph ligands. Since the \(a_1\) hy(s-z) orbital of the [Au(PPh_3)Cl] fragment is higher lying than the 1s orbital of the hydrogen atom the polarities of the Os-Au and Os-H bonds are not equivalent.\(^{267}\) This leads to a large contribution from the following ionic resonance form in the case of the gold complex (Figure 6.8). Infrared studies have shown that

\[
P\text{Ph}_3\text{Au-M}^{\text{(CO)}}_n \quad \leftrightarrow \quad P\text{Ph}_3\text{Au}^{+}\text{M}^{\text{(CO)}}_n^{-}
\]

(Figure 6.8)

the electron density on the transition metal carbonyl moiety is intermediate between that in \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^{-}\) and \([\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]\), consistent with this proposal. Figure 6.9 shows the i.r. spectra of the three species; \([\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}] \) (a), \([\text{Os}_3(\mu-PPhH)(\text{CO})_{10}] \) (b) and \([\text{Os}_3(\mu-\text{AuPMe}_2\text{Ph})(\mu-PPhH)(\text{CO})_{10}] \) (c).

Although the chemical transformations of \([\text{Os}_3(\mu-H)(\mu-PPh\text{AuPMe}_2\text{Ph})(\text{CO})_{10}]\) and \([\text{Os}_3(\mu-\text{AuPMe}_2\text{Ph})(\mu-PPhH)(\text{CO})_{10}]\) is similar to that of \([\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]\), it appears that the replacement of H by [Au(PMe_2Ph)] occurs with a structural change (i.e. the formation of \(\text{endo-}[\text{Os}_3(\mu-H)(\mu-PPh\text{AuPMe}_2\text{Ph})(\text{CO})_{10}]\) from \(\text{exo-}[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]\)). We expect this inversion of stereochemistry is the result of the greater steric requirements of the more bulky [Au(PMe_2Ph)] fragment. We have already found that replacement of H by CH_3 occurs with inversion of stereochemistry.

6.3.2 Reaction of \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^{-}\) with Organomercury Compounds

The anion \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^{-}\) reacts similarly with the organomercury compounds [HgBr(CH_2CH_3)] and [HgBr(CH_2Ph)] to give the clusters \([\text{Os}_3(\mu-H)(\mu-PPh\text{HgCH}_2\text{CH}_3)(\text{CO})_{10}]\) and \([\text{Os}_3(\mu-H)(\mu-PPh\text{HgCH}_2\text{Ph})(\text{CO})_{10}]\) (Scheme 6.6) which were characterised by their spectra, elemental analytical data and their EI mass spectra. The assignment of the phenyl rings as having \(\text{exo}\) stereochemistry is based on the chemical
Scheme 6.6
shifts of the ortho hydrogen resonance $\delta$ 7.44 for $[\text{Os}_3(\mu-H)(\mu-PPhHgCH_2CH_3)(CO)]_{10}$ and comparison with the stereochemistry established for the cluster $[\{\text{Os}_3(\mu-H)(\mu-PPh)(CO)]_{10}Hg\}$; see below.

Treatment of solutions of both $[\text{Os}_3(\mu-H)(\mu-PPhHgCH_2CH_3)(CO)]_{10}$ and $[\text{Os}_3(\mu-H)(\mu-PPhHgCH_2Ph)(CO)]_{10}$ in THF with HCl (gas) resulted in rapid formation of $[\text{Os}_3(\mu-H)(\mu-PPhH)(CO)]_{10}$ (i.r. evidence). When the reaction was complete the reaction mixture was chromatographed (t.l.c.) and $[\text{Os}_3(\mu-H)(\mu-PPhH)(CO)]_{10}$ was isolated in effectively quantitive yield (Scheme 6.6), the electrophilic attack by organomercury compounds is totally reversible.

In contrast to these two organomercury compounds, the anion $[\text{Os}_3(\mu-H)(\mu-PPh)(CO)]_{10}^{-}$ reacts with the ferrocenyl compound $[\text{Fe}(C_5H_5)(C_5H_4HgCl)]$ to give the cluster $[\{\text{Os}_3(\mu-H)(\mu-PPh)(CO)]_{10}Hg\}$ which does not contain the ferrocenyl group. This $^1H$ n.m.r. spectrum contained a hydride resonance as a virtual triplet ($\delta$ -18.69, $^3J(\text{PH})$ + $^4J(\text{PH}) = 12.0$ Hz), characteristically appearing as a broad central peak and sharp more intense outer peaks (Figure 6.10). Likewise the $^{31}P$ n.m.r. spectrum, proton decoupled except for the hydride, is also a virtual triplet ($\delta$ -10.6). The phosphorus and hydride nuclei constitute an AA'XX' spin system with a large $^2J(PP)$ leading to a virtual triplet coupling. The stereochemistry at phosphorus was assigned as having the phenyl groups exo to the Os(CO)$_4$ unit, evident from the absence of any low-field ortho hydrogen atom resonances in the aromatic region of the spectrum. The same compound was obtained from $[\text{Os}_3(\mu-H)(\mu-PPh)(CO)]_{10}^{-}$ and mercury(II) chloride, bromide and iodide and was found to be halide free.
To characterise the cluster \([\{\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}\}_{2}\text{Hg}]\) properly we determined its single-crystal X-ray structure which established the formula as \([\{\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}\}_{2}\text{Hg}]\). The structural determination was performed by Professor K. I Hardcastle at California State University, Northridge.

### 6.3.3 Crystal Structure of \([\{\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}\}_{2}\text{Hg}]\)

Suitable crystals for X-ray structure determination were grown by evaporation of a dichloromethane/n-hexane solution of the cluster. The cluster crystallises in the triclinic space group \(P1\) with unit cell dimensions \(a = 13.739(2)\ \text{Å}, b = 18.903(2)\ \text{Å}, c = 8.947(2)\ \text{Å}, \alpha = 89.77(2)\ ^\circ, \beta = 75.79(2)\ ^\circ, \gamma = 73.41(1)\ ^\circ\) with two molecules per unit cell. The structure was refined to \(R = 0.0474\) and \(R_w = 0.0509\). Important bond lengths and angles are given in Table 6.3 and the molecular structure is shown in Figure 6.11.

Figure 6.12 shows the triosmium unit are held together by a P-Hg-P bridge. The phenyl groups in each cluster are \(\text{exo}\) to the Os(CO)₄ units and the \(\text{ortho}\) protons have a \(^1\text{H}\) n.m.r. signal at \(\delta 7.40\) as expected for this \(\text{exo}\) arrangement. The P-Hg-P angle is 171.8(2) \(^\circ\). There is a fairly close approach of the axial CO groups to the Hg atom \([\text{Hg}—\text{O(14)} 2.88\ \text{Å and Hg—O(42)} 2.85\ \text{Å}]\). Although the Hg is essentially two-coordinate and linear, the O(14) and O(42) atoms cause a slight distortion towards a tetrahedral geometry. \([\{\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}\}_{2}\text{Hg}]\) contains asymmetric molecules with non-equivalent \([\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}]\) units differing notably in the conformations of the phenyl rings. The dihedral angle between the ring Os(1)Os(2)Os(3) and Os(2)Os(3)P(1) is 67.7(1) \(^\circ\) and that between Os(4)Os(5)Os(6) and Os(5)Os(6)P(2) is 69.3(1) \(^\circ\). The distortions of the axial CO of Os(1) [Os(2)-Os(1)-C(14) 90.1(7) \(^\circ\), Os(2)-Os(1)-C(12) 85.3(6) \(^\circ\) CO \(\text{cis}\) to the phosphido and Os(3)-Os(1)-(14) 91.5(7) \(^\circ\), Os(3)-Os(1)-C(12) 85.3(6) \(^\circ\)] are not significantly different to the distortions in other phosphidobridged complexes, for example \([\text{Os}(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]\), \([\text{Os}_3(\mu-\text{H})(\mu-\text{PPhMe})(\text{CO})_{10}]\) and \([\text{Os}_3(\mu-\text{H})(\mu-\text{PPh})_2(\text{CO})_{10}]\). Much greater distortions are observed on Os(4) in which the axial CO \(\text{cis}\) to the phosphido is directed towards Os(5) [Os(6)-Os(4)-C(42) 98.2(6) \(^\circ\), Os(5)-Os(4)-(42) 84.1(6) \(^\circ\)] and the CO \text{trans} to it has similarly large distortions to maintain the \text{trans} geometry of the carbonyl ligands [Os(6)-Os(4)-C(44) 83.6(6) \(^\circ\) and Os(5)-Os(4)-C(44) 89.3(6) \(^\circ\)]. The greatest distortions occur on
Figure 6.11 Structure of \([\{\text{Os}_3(\mu-H)(\mu_5-PPh)(CO)\}_2\text{Hg}\]
Figure 6.12 Metal atom framework of \( \{\text{Os}_3(\mu-H)(\mu_2-PPh)(\text{CO})_{10}\}_2\text{Hg} \)
Figure 6.13 Space filling diagram of \( [(\text{Os}_3(\mu-H)(\mu_2-PPh)(\text{CO})_{10})_2\text{Hg}] \)
Os(4), and careful examination of the space-filling diagram in Figure 6.13 reveals that these distortions occur to relieve the unfavourable steric interactions of the phenyl ring that lies roughly parallel to the Os₃ plane. The perpendicular phenyl ring appears to tilt the Os₃ cluster forming a close interaction between the parallel phenyl and the axial carbonyl ligands. Figure 6.14 shows details of both the phosphido bridges and the orientation of the attached phenyl ring. The dihedral angle between the least squares plane of the phenyl ring and the plane defined by the mercury, the phosphido P and the ipso carbon of that phenyl ring shows that these two phenyl rings lie approximately perpendicular. An angle close to zero indicates a perpendicular orientation of the ring whilst an angles close to 90 ° reveals a parallel arrangement. The angle between ring C81-C86 and the plane C81-P(2)-Hg is 2.9 ° and between the ring C71-C76 and C71-P(1)-Hg is 93.7 °.

The Os(2)-Os(3) bond is symmetrically bridged by the phosphido ligand [Os(2)-P(1) 2.388(4) Å, Os(3)-P(1) 2.389(4) Å] in comparison the Os(5)-Os(6) bond is slightly asymmetrically bridged [Os(5)-P(2) 2.421(4) Å, Os(6)-P(2) 2.403(4) Å]. The metal cluster ring Os(1)Os(2)Os(3) contains two short bonds [Os(1)-Os(2) 2.870(2) Å, Os(1)-Os(3) 2.875(1) Å] and one long bond [Os(2)-Os(3) 2.8956(9) Å] whereas Os(4)Os(5)Os(6) contains one short [Os(4)-Os(5) 2.873(1) Å] and two long [Os(4)-Os(6) 2.897(1) Å and Os(5)-Os(6) 2.900(1) Å] bonds. These distortions reflect the steric requirements of the parallel phenyl ring. It has already been mentioned that the cis axial carbonyl of the [Os(4)(CO)₄] unit is severely distorted towards Os(5) avoiding interactions with the closely approaching phenyl ring, it is not just the axial CO that is distorted but the whole [Os(4)(CO)₄] unit evident from the large difference in Os-Os bond lengths of the unbridged vectors and the asymmetry of the phosphido bridge. That it is the complete [Os(4)(CO)₄] unit that is distorted is shown by the difference in the Os-Os-C angles of the trans equatorial CO ligands on Os(1) compared to Os(4) [Os(2)-Os(1)-C(11) 158.4(1) °, Os(3)-Os(1)-C(13) 161.4(1) ° compared to Os(6)-Os(4)-C(43) 167.0 °, Os(5)-Os(4)-C(41) 149.9(1) °].

The tilt within the cluster framework is reflected in the Os-P-Hg angles. For example, Os(3)-P(1)-Hg 124.5(2) °, Os(2)-P(1)-Hg 132.7(2) ° and Os(6)-P(2)-Hg 120.4(2) °, Os(5)-P(2)-Hg 128.9 °. The first pair of angles are larger because of the repulsion between the perpendicular phenyl ring and the carbonyl ligands, in the latter case the phenyl ring is parallel and the expansion of the angles at P(1) result in a
Figure 6.14 Perpendicular, (a), and parallel, (b), arrangements of the phosphido bridge phenyl rings
Table 6.2 Selected bond lengths and angles for [\{Os_5(\mu-H)(\mu_3-PPh)(CO)_{10}\}_2Hg]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1)-Os(2)</td>
<td>2.870(1)</td>
</tr>
<tr>
<td>Os(2)-Os(3)</td>
<td>2.8956(9)</td>
</tr>
<tr>
<td>Os(1)-Os(3)</td>
<td>2.875(1)</td>
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<tr>
<td>Os(4)-Os(5)</td>
<td>2.873(1)</td>
</tr>
<tr>
<td>Os(5)-Os(6)</td>
<td>2.900(1)</td>
</tr>
<tr>
<td>Os(4)-Os(6)</td>
<td>2.897(1)</td>
</tr>
<tr>
<td>Hg-P(1)</td>
<td>2.402(2)</td>
</tr>
<tr>
<td>Hg-P(2)</td>
<td>2.390(4)</td>
</tr>
<tr>
<td>Os(2)-P(1)</td>
<td>2.388(4)</td>
</tr>
<tr>
<td>Os(3)-P(1)</td>
<td>2.389(4)</td>
</tr>
<tr>
<td>Os(5)-P(2)</td>
<td>2.421(4)</td>
</tr>
<tr>
<td>Os(6)-P(2)</td>
<td>2.403(5)</td>
</tr>
<tr>
<td>P(1)-C(71)</td>
<td>1.84(2)</td>
</tr>
<tr>
<td>P(2)-C(81)</td>
<td>1.81(2)</td>
</tr>
<tr>
<td>C(71)-C(72)</td>
<td>1.36(2)</td>
</tr>
<tr>
<td>C(81)-C(82)</td>
<td>1.41(4)</td>
</tr>
<tr>
<td>C(72)-C(73)</td>
<td>1.42(3)</td>
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<tr>
<td>C(82)-C(83)</td>
<td>1.47(7)</td>
</tr>
<tr>
<td>C(73)-C(74)</td>
<td>1.38(3)</td>
</tr>
<tr>
<td>C(83)-C(84)</td>
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</tr>
<tr>
<td>C(74)-C(75)</td>
<td>1.43(3)</td>
</tr>
<tr>
<td>C(84)-C(85)</td>
<td>1.18(5)</td>
</tr>
<tr>
<td>C(75)-C(76)</td>
<td>1.41(3)</td>
</tr>
</tbody>
</table>
concomitant reduction/contraction of those at P(2) (see the space filling diagram in Figure 6.13 to clarify the situation). Accompanying this expansion of the Os-P-Hg angles is an increase in the Hg-P-C(ipso) angles. The perpendicular phenyl ring exhibits a large Hg-P(2)-C(81) angle, 100.0(5) ° whilst the contracted angle at Hg-P(1)-C(71) is only 92.5(5) °. Consideration of these angles and a careful examination of the space filling diagram reveals that it is sterically impossible to achieve two perpendicular phenyl rings in the cluster framework.

In spite of the rather open appearance of \([(\text{Os}_3(\mu-H)\mu-P\text{Ph})(\text{CO})_{10}]_2\text{Hg}\)], in Figure 6.11, the two Os₃ clusters are closely compacted and this has a consequence on the phenyl conformations. All known structures of similar types contain phenyl groups perpendicular to the Os₃ plane and bisecting the two equatorial CO ligands. However, in \([(\text{Os}_3(\mu-H)\mu-P\text{Ph})(\text{CO})_{10}]_2\text{Hg}\] the phenyl group at P(2) has the perpendicular conformation while the other at P(1) has the ring roughly parallel to the Os₃ plane. Lewis and co-workers have determined the structure of \[\text{[Os}_3(\mu-H)_2(\mu-\text{PC}_6\text{H}_4\text{Ph})(\text{CO})_6]\], they have shown that the nonmetallated phenyl ring lies away from the Os₃ triangle and approximately parallel to the Os-Os edge bridged by the phosphido-P atom. In this cluster the phosphido bridge bends back towards the Os₃ ring and the dihedral angle between the Os₃ plane and the plane defined by P and the two osmium atoms it bridges is 86.6 °. We think that there is only room for one phenyl ring to adopt the perpendicular arrangement since the Os₃ clusters tilt with respect to each other to make space on one side of the molecule for the perpendicular phenyl group. Figure 6.13 shows the steric crowding in this molecule. Because of the different conformations, the Os₃ units are different but n.m.r. spectra at room temperature and even down to -75 ° C (CD₂Cl₂) show them to be equivalent; an AA'XX' spectrum is observed for the phosphorus and hydride ligands. The most likely explanation is that the solid state structure persists in solution but a rapid fluxional exchange of the clusters is occurring.

6.4 Details of Mass Spectra

The mass spectra of several of the compounds prepared in this chapter have been recorded at the London School of Pharmacy (ULIRS). The source of ionisation employed was electron impact (EI). Unfortunately, in many instances the parent molecular ion was not the strongest peak, often being very weak due the rapid
fragmentation of the cluster. The use of a desorption technique such as fast atom bombardment (FAB) might have been preferable because this technique is known to give high concentrations of the parent molecular ion. Once the parent molecular ion had been identified in the EI mass spectrum the fragmentation pattern was easily interpreted, showing the characteristic decay by successive loss of CO ligands.

Molecular ion peaks for $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}_2\text{Ph})(\text{CO})_{10}]$ were found at around m/z 1299 ($M^+$) (based on $^{192}\text{Os}$) with the expected isotopic pattern for an Os$_3$ cluster. Details of the assignment of peaks due to fragmentation are given in the experimental section. Correspondingly a parent molecular ion with the same m/z value was observed in the EI mass spectrum of $[\text{Os}_3(\mu-\text{AuPMe}_2\text{Ph})(\mu-\text{PPhH})(\text{CO})_{10}]$.

The orthometallated cluster $[\text{Os}_3(\mu-\text{H})_2(\mu-\text{PMeC}_6\text{H}_4)(\text{CO})_9]$ was identified from its EI mass spectrum. A parent molecular ion peak at m/z 952 (based on $^{192}\text{Os}$) corresponding to $[\text{Os}_3(\mu-\text{H})_2(\mu-\text{PMeC}_6\text{H}_4)(\text{CO})_{10}]^+$ and the successive loss of only nine CO ligands was consistent with the product formulated.

The mass spectra of the alkylmercury substituted clusters $[\text{Os}_3(\mu-\text{H})(\mu-\text{PPhHgR})(\text{CO})_{10}]$ both contained extremely weak molecular ion peaks due to a very low concentration of the parent ion [$R = \text{Et}$, m/z ($M^+$) 1193 (based on $^{192}\text{Os}$, $^{199}\text{Hg}$) and $R = \text{CH}_2\text{Ph}$, m/z ($M^+$) 1255 (based on $^{192}\text{Os}$, $^{199}\text{Hg}$)]. In both cases, the initial fragmentation involved loss of the alkyl substituent from the parent molecular ion, followed by loss of mercury and only then was the successive loss of CO groups observed.
6.5 Conclusion

The phosphinidene anion \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^+\) is readily prepared by deprotonation of \([\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]\) with base (DBU) in tetrahydrofuran. Reaction of the preformed anion with methyliodide afforded the novel methylphenylphosphido cluster \([\text{Os}_3(\mu-H)(\mu-PPhMe)(\text{CO})_{10}]\). \(^1\)H n.m.r. evidence indicated that the phenyl ring of the phosphido bridge adopted endo stereochemistry with respect to the Os(CO)\(_4\) unit. Chemical reactivity supported this stereochemistry since thermal decarboxylation led to the ortho-metallated cluster \([\text{Os}_3(\mu-H)_2(\mu-P\{C_6\text{H}_4\}_\text{Me})(\text{CO})_{9}]\). The single-crystal X-ray structure of this cluster confirmed our belief that inversion at phosphorus had occurred during the deprotonation methylation steps and the endo stereochemistry was correct.

Deprotonation of \([\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]\) and subsequent reaction with [Au(PMe\(_2\)Ph)Cl] gave two isomeric clusters. Deprotonation at low temperature afforded the kinetically stable anion \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^+\) and reaction with [Au(PMe\(_2\)Ph)Cl] gave \([\text{Os}_3(\mu-H)(\mu-PPhAuPMe\(_2\)Ph)(\text{CO})_{10}]\). Refluxing a tetrahydrofuran solution of the anion \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^+\) gave the thermodynamically favoured cluster \([\text{Os}_3(\mu-PPhH)(\text{CO})_{10}]\), subsequent reaction with [Au(PMe\(_2\)Ph)Cl] gave \([\text{Os}_3(\mu-AuPMe\(_2\)Ph)(\mu-PPhH)(\text{CO})_{10}]\). On the basis of ortho hydrogen atom chemical shifts we believe that these clusters contain endo phenyl groups. Both clusters \([\text{Os}_3(\mu-H)(\mu-PPhAuPMe\(_2\)Ph)(\text{CO})_{10}]\) and \([\text{Os}_3(\mu-AuPMe\(_2\)Ph)(\mu-PPhH)(\text{CO})_{10}]\) decarboxylate thermally to the same compound \([\text{Os}_3(\mu-H)(\mu-AuPMe\(_2\)Ph)(\mu-PPh)(\text{CO})_{9}]\) formed by AuPMe\(_2\)Ph or H migration respectively from P to Os.

The anion \([\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^+\) reacts similarly with the organomercury compounds [HgBr(CH\(_2\)Ph)] and [HgBr(CH\(_2\)CH\(_3\))] to give the clusters \([\text{Os}_3(\mu-H)(\mu-PPhHgCH\(_2\)Ph)(\text{CO})_{10}]\) and \([\text{Os}_3(\mu-H)(\mu-PPhHgCH\(_2\)CH\(_3\))(\text{CO})_{10}]\) respectively. Examination of the \(^1\)H n.m.r. spectra of these clusters led to the assignment of the phenyl rings as having exo stereochemistry, based on the chemical shifts of the ortho hydrogen atom resonances, \(\delta 7.44\), and the stereochemistry for the cluster \([\{\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}\}_2\text{Hg}\]\. The formation of the clusters \([\text{Os}_3(\mu-H)(\mu-PPhHgCH\(_2\)Ph)(\text{CO})_{10}]\) and \([\text{Os}_3(\mu-H)(\mu-PPhHgCH\(_2\)CH\(_3\))(\text{CO})_{10}]\) are reversible, treatment of a tetrahydrofuran solution of these clusters with HCl(g) generated the starting material in quantitative yield.
Finally, treatment of \([\text{Os}_3(\mu-H)(\mu-PPh)(CO)_{10}]^-\) with \(\text{HgX}_2\) (\(X = \text{Cl, Br, I}\)) gave the linked cluster \([\text{Os}_3(\mu-H)(\mu-PPh)(CO)_{10}]_2\text{Hg}\] as did reaction of the anion with \([\text{Fe}(\text{C}_3\text{H}_2)(\text{C}_3\text{H}_4\text{HgCl})]\). A single-crystal X-ray structure showed that the cluster contained non-equivalent \([\text{Os}_3(\mu-H)(\mu-PPh)(CO)_{10}]^-\) units differing notably in the conformations of the phenyl rings, one being perpendicular to the Os$_3$ ring and the other parallel. We think that there is only room for one phenyl ring to adopt the perpendicular arrangement since the Os$_3$ clusters tilt with respect to each other to make space on one side of the molecule for the perpendicular phenyl group.
6.6 Experimental

The compounds \([\text{Au(PMe}_2\text{Ph)Cl}]\) and \([\text{Fe(C}_2\text{H}_5)(\text{C}_2\text{H}_5\text{HgCl})]\) were prepared as described in the literature. The mercury compounds \([\text{HgCl(C}_2\text{H}_5)]\) and \([\text{HgCl(CH}_2\text{Ph)}]\), and DBU were used as purchased from Aldrich p.l.c. Tetrahydrofuran was dried over sodium and distilled from potassium/benzophenone under nitrogen before use.

6.6.1 Synthesis of \([\text{Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]\)

A preparation similar to that indicated earlier in a communication was used. A solution of dodecacarbonyltriosmium (0.36 g, 0.4 mmol) in dichloromethane (400 cm³) and acetonitrile (4 cm³) was treated with a solution of Me₂NO.2H₂O (0.142 g, 1.1 mmol) in methanol (1 cm³). After being stirred at room temperature for 30 minutes, the reaction mixture was filtered through a small silica column (60-120 mesh). The resulting solution was treated directly with phenylphosphine (0.044 cm³, 0.4 mmol) and stirred for 60 minutes under nitrogen. The solvent was removed under reduced pressure to leave a yellow oily residue which was separated by chromatography [t.l.c., SiO₂; eluant: petroleum ether (b.p 30-40 °C)/dichloromethane (9:1 v/v)] to give a small amount of dodecacarbonyltriosmium near the solvent front and a major following band yielding \([\text{Os}_3(\text{CO})_{11}(\text{PPhH}_2)]\) as bright yellow crystals (0.306 g, 76%), spectroscopically characterised.

A sample of \([\text{Os}_3(\text{CO})_{11}(\text{PPhH}_2)]\) (0.177 g, 0.12 mmol) in dry THF (20 cm³) was treated with the base DBU (0.013 cm³, 0.12 mmol) to give an immediate colour change from pale yellow to deep orange as \([\text{Os}_3(\text{PPhH})(\text{CO})_{11}]\) is formed. The solution quickly turned to pale yellow as decarbonylation to \([\text{Os}_3(\mu-\text{PPhH})(\text{CO})_{10}]\) occurred and this was treated with HCl gas. The solution quickly became cloudy and the i.r. spectrum confirmed the formation of the title compound. The solvent was removed under reduced pressure to leave an oily residue which on chromatographic work up as above gave a single major yellow band which afforded \([\text{Os}_3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})_{10}]\) as yellow crystals (0.074 g, 43%), characterised by spectroscopic data.
6.6.2 Synthesis of \([\text{Os}_3(\mu-H)(\mu-PPhMe)(CO)]_{10}\)

A solution of \([\text{Os}_3(\mu-H)(\mu-PPhH)(CO)]_{10}\) (0.0609 g, 0.063 mmol) in dry THF (50 cm³) was treated with DBU (0.014 cm³, 0.095 mmol) at room temperature and when the i.r. spectrum indicated complete formation of the anion \([\text{Os}_3(\mu-H)(\mu-PPhH)(CO)]_{10}\) a large excess of methyl iodide (0.4 cm³, 6 mmol) was added and the solution stirred for 30 minutes. Removal of the solvent left a yellow oily residue which on chromatographic work-up [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane (19:1 v/v)] gave one major yellow band. Removal of the solvent left a yellow oil (0.055 g) which was shown to contain starting material (minor) and the required product \([\text{Os}_3(\mu-H)(\mu-PPhMe)(CO)]_{10}\). Retreatment of the yellow oil with DBU then methyl iodide as above and a similar work up gave the pure product as deep yellow-orange crystals from dichloromethane/n-hexane mixture. [Found: C, 20.95; H, 0.95; P, 3.15. \(\text{C}_{19}\text{H}_{39}\text{O}_{10}\text{P}\) requires C, 20.9; H, 0.7; P, 3.3%]. Crystals suitable for single crystal X-ray structure determination were obtained by slow evaporation from n-hexane at room temperature.

6.6.3 Thermolysis of \([\text{Os}_3(\mu-H)(\mu-PPhMe)(CO)]_{10}\)

A solution of \([\text{Os}_3(\mu-H)(\mu-PPhMe)(CO)]_{10}\) (0.020 g, 0.020 mmol) in n-octane (20 cm³) was refluxed under nitrogen. After 45 minutes the i.r. spectrum showed complete reaction and the solvent was removed under reduced pressure and the resultant oil chromatographed [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane (4:1 v/v)] to yield two bands. The first band was identified as \([\text{Os}_3(\mu-H)_2(\mu_3-PPh)(CO)]_{9}\) (minor) and the major band gave \([\text{Os}_3(\mu-H)_2(\mu_3-PC_6H_{14}Me)(CO)]_{9}\) as yellow crystals (0.011 g, 56%). MS(EI): m/e = 950 (M⁺-2H) (based on \(^{192}\text{Os}\)), 922 (M⁺-2H-CO), 894 (M⁺-2H-2CO), 866 (M⁺-2H-3CO), 838 (M⁺-2H-4CO), 810 (M⁺-2H-5CO), 782 (M⁺-2H-6CO), 754 (M⁺-2H-7CO), 726 (M⁺-2H-8CO), 698 (M⁺-2H-9CO), 683 (M⁺-2H-9CO-CH₃).

6.6.4 Reaction of \([\text{Os}_3(\mu-H)(\mu-PPhH)(CO)]_{10}\) with base followed by \([\text{Au}(\text{PMe}_3\text{Ph})\text{Cl}]\)

(a) A solution of the cluster \([\text{Os}_3(\mu-H)(\mu-PPhMe)(CO)]_{10}\) (0.0147 g, 0.015 mmol) in dry THF (15 cm³) was treated with DBU (0.0023 cm³, 0.015 mmol) at room temperature under argon. As soon as the i.r. spectrum indicated that all the starting material had been consumed, i.e when deprotonation was complete, \([\text{Au}(\text{PMe}_3\text{Ph})\text{Cl}]\)
(0.0056 g, 0.015 mmol) in THF (2 cm³) was added leading to an immediate colour change from pale yellow to deep yellow. The solvent was removed under reduced pressure and the oily residue chromatographed [t.l.c., SiO₂; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (9:1 v/v)] to give a small amount of fast moving [Os₄(μ-H)(μ-PPhH)(CO)₁₀] and the major band which gave [Os₄(μ-H)(μ-PPhAuPMe₂Ph)(CO)₁₀] as orange crystals (0.010 g, 53%).

(b) By a similar procedure but allowing 10 minutes between complete deprotonation and the addition of the gold complex, two closely moving bands were resolved by t.l.c. One was the hydride [Os₄(μ-H)(μ-PPhAuPMe₂Ph)(CO)₁₀] and the other its non-hydridic isomer [Os₄(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀].

(c) An improved yield of [Os₄(μ-H)(μ-PPhAuPMe₂Ph)(CO)₁₀] was obtained by carrying the reaction out at -40 °C and adding the gold complex immediately. Chromatographic work up as in (a) gave one major band identified as the cluster [Os₄(μ-H)(μ-PPhAuPMe₂Ph)(CO)₁₀]. [Found: C, 22.25; H, 1.15; P, 5.25. C₂H₁₇AuO₉Os₄P requires C, 22.9; H, 1.30; P, 4.75 %]. MS(El): m/e = 1299 (M⁺) (based on ¹⁹²Os), 1271 (M⁺-CO), 1133 (M⁺-CO-PMe₂Ph), 940 (M⁺-CO-AuPMe₂Ph), 912 (M⁺-2CO-AuPMe₂Ph), 884 (M⁺-3CO-AuPMe₂Ph), 856 (M⁺-4CO-AuPMe₂Ph), 828 (M⁺-5CO-AuPMe₂Ph), 800 (M⁺-6CO-AuPMe₂Ph), 772 (M⁺-7CO-AuPMe₂Ph), 744 (M⁺-8CO-AuPMe₂Ph), 716 (M⁺-9CO-AuPMe₂Ph), 688 (M⁺-10CO-AuPMe₂Ph).

(d) A better yield of the non-hydridic isomer was obtained by refluxing a mixture of [Os₄(μ-H)(μ-PPhH)(CO)₁₀] (0.014 g, 0.14 mmol) and DBU (0.003 cm³, 0.014 mmol) in THF (20 cm³) for 3 minutes by which time the initially formed anion [Os₄(μ-H)(μ-PPhH)(CO)₁₀] had been fully converted into the isomeric anion [Os₄(μ-PPhH)(CO)₁₀] (i.r. evidence). The solution was cooled to room temperature and the gold complex (0.0056 g, 0.015 mmol) in THF (1 cm³) was added. The solution turned from pale yellow to deep orange immediately and chromatographic work up as before gave a small quantity of the cluster [Os₄(μ-H)(μ-PPhH)(CO)₁₀] but mainly the cluster [Os₄(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀]. Removal of the solvent from a dichloromethane extract of this band under reduced pressure and crystallisation from n-hexane (-20 °C overnight) and vacuum drying for several hours gave the non-hydridic isomer in good yield.
6.6.5 Reaction of $[\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^+$ with HgCl$_2$

A solution of the cluster $[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$ (0.024 g, 0.025 mmol) in THF (25 cm$^3$) at 40 °C was treated with DBU (0.0038 cm$^3$, 0.025 mmol). As soon as the i.r. spectrum showed that all the starting material had been consumed, HgCl$_2$ (0.0068 g, 0.025 mmol) was added and the colour changed immediately to yellow-orange. The reaction mixture was stirred for 30 minutes under argon and the oily residue remaining, after the solvent had been removed under reduced pressure, was chromatographed [t.l.c., SiO$_2$; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane, (4:1 v/v)] to give a trace amount of starting material and a slower moving band which gave yellow microcrystals (0.0095 g) from a dichloromethane/n-hexane at -20 °C. The product was characterised by its i.r. spectrum and an X-ray crystal structure determination as $[\{\text{Os}_3(\mu-H)(\mu-2-PPh)(\text{CO})_{10}\}_{2}\text{Hg}]$.

6.6.6 Reaction of $[\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]$- with mercury(II) iodide and mercury(II) bromide

A similar procedure was followed with $[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$ in THF with DBU. Treatment of the resultant anion with mercury(II) bromide or mercury(II) iodide and chromatographic work up as above led to products that were indistinguishable from the above cluster $[\{\text{Os}_3(\mu-H)(\mu-3-PPh)(\text{CO})_{10}\}_{2}\text{Hg}]$ by i.r. and $^1$H n.m.r. spectroscopy.

6.6.7 Reaction of $[\text{Os}_3(\mu-H)(\mu-PPh)(\text{CO})_{10}]^+$ with alkyl mercury(II) halides

(a) [HgEtBr].- A solution of the cluster $[\text{Os}_3(\mu-H)(\mu-PPhH)(\text{CO})_{10}]$ (0.028 g, 0.029 mmol) in THF (25 cm$^3$) was treated with DBU (0.005 cm$^3$, 0.029 mmol) at -30 °C. [HgEtBr] (0.009 g, 0.029 mmol) was added and the solution was stirred at this temperature until there was no further change in the i.r. spectrum. Since the starting material was still observed to be present, more of the mercury compound was added (0.101 g, in total) until all of the starting material had been consumed. Removal of the solvent under reduced pressure gave a yellow-brown oily residue. Separation of the oil by chromatography [t.l.c., SiO$_2$; eluant: petroleum ether (b.p. 30-40
°C)/dichloromethane, (3:1 v/v)] gave one broad diffuse band which gave deep orange crystals of [Os$_3$(μ-H)(μ-PPhH$_2$CH$_3$)(CO)$_{10}$] (0.025 g, 75%). [Found: C, 19.2; H, 0.85; P, 3.15. C$_{18}$H$_{2}$HgO$_{10}$Os$_3$P requires C, 18.2; H, 0.95; P, 2.6%]. MS(EI): m/e = 1193 (M$^+$) (based on $^{192}$Os, $^{199}$Hg), 1164 (M$^+$-Hg), 965 (M$^+$-HgEt), 937 (M$^+$-HgEt-CO), 909 (M$^+$-HgEt-2CO), 881 (M$^+$-HgEt-3CO), 853 (M$^+$-HgEt-4CO), 825 (M$^+$-HgEt-5CO), 797 (M$^+$-HgEt-6CO), 769 (M$^+$-HgEt-7CO), 741 (M$^+$-HgEt-8CO), 713 (M$^+$-HgEt-9CO), 685 (M$^+$-HgEt-10CO), 608 (M$^+$-HgEt-10CO-C$_4$H$_3$).

(b) [Hg(CH$_2$Ph)Br]. - A similar procedure using the cluster [Os$_3$(μ-H)(μ-PPhH)(CO)$_{10}$] (0.031 g, 0.023 mmol), DBU (0.0049 cm$^3$, 0.032 mmol), [Hg(CH$_2$Ph)]Br (0.12 g, 0.32 mmol) gave [Os$_3$(μ-H)(μ-PPhH$_2$CH$_2$Ph)(CO)$_{10}$] as orange crystals (0.027 g, 60%) after chromatographic work up. [Found: C, 23.2; H, 0.88; P, 2.55. C$_{25}$H$_{33}$HgO$_{10}$Os$_3$P requires C, 22.1; H, 1.05; P, 2.5%]. MS(EI): m/e = 1255 (M$^+$) (based on $^{192}$Os, $^{199}$Hg), 1227 (M$^+$-CO), 1164 (M$^+$-CH$_2$Ph), 961 (M$^+$-HgCH$_2$Ph), 933 (M$^+$-HgCH$_2$Ph-CO), 905 (M$^+$-HgCH$_2$Ph-2CO), 877 (M$^+$-HgCH$_2$Ph-3CO), 849 (M$^+$-HgCH$_2$Ph-4CO), 821 (M$^+$-HgCH$_2$Ph-5CO), 793 (M$^+$-HgCH$_2$Ph-6CO), 765 (M$^+$-HgCH$_2$Ph-7CO), 737 (M$^+$-HgCH$_2$Ph-8CO), 709 (M$^+$-HgCH$_2$Ph-9CO), 681 (M$^+$-HgCH$_2$Ph-10CO), 608 (M$^+$-HgCH$_2$Ph-10CO-C$_4$H$_3$).

(c) [(C$_5$H$_9$)$_2$Fe(C$_2$H$_5$HgCl)]. - A similar treatment using [Os$_3$(μ-H)(μ-PPhH)(CO)$_{10}$] (0.0406 g, 0.042 mmol), DBU (0.006 cm$^3$, 0.042 mmol) and the ferrocenyl-mercury compound (0.0177 g, 0.0422 mmol) gave a single yellow t.l.c. band which gave yellow crystals (0.012 g, 27%) of the linked cluster [(Os$_3$(μ-H)(μ-PPh)(CO)$_{10}$)$_2$Hg], spectroscopically identical to the samples obtained from mercury(II) halides. Recrystallisation from a dichloromethane/n-hexane mixture gave crystals suitable for single crystal X-ray structure determination.

6.6.8 Treatment of the clusters [Os$_3$(μ-H)(μ-PPhH$_2$R)(CO)$_{10}$](R= Et, CH$_2$Ph) with dry HCl gas

A sample of the cluster [Os$_3$(μ-H)(μ-PPhH$_2$R)(CO)$_{10}$] (R= Et, CH$_2$Ph) (ca. 0.005 g) in dry THF (5 cm$^3$) was treated with HCl gas until the i.r. spectrum showed that the reaction was complete. Removal of the solvent under reduced pressure and chromatography (t.l.c., SiO$_2$; eluant: petroleum ether (b.p. 30-40 °C)/dichloromethane,
(9:1 v/v)] gave a single major yellow band in each case. 'H n.m.r. and i.r. measurements showed total conversion to [Os₃(μ-H)(μ-PPhH)(CO)₁₀] for both R = Et and R = CH₂Ph.
### 6.7 Spectroscopic data for the Complexes

**Table 6.3** $^1$H n.m.r. data for osmium phosphido clusters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift ($\delta$)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Os$<em>3$(µ-H)(µ-PPhH)(CO)$</em>{10}$]$^b$</td>
<td>7.05 (dd)</td>
<td>P-H</td>
<td>$^1$J(PH)=410.0, $^3$J(HH)=4.4</td>
</tr>
<tr>
<td></td>
<td>7.34 (m)</td>
<td>PPhH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-19.27 (dd)</td>
<td>Os-H-Os (1H)</td>
<td></td>
</tr>
<tr>
<td>[Os$<em>3$(µ-H)(µ-PPhMe)(CO)$</em>{10}$]$^b$</td>
<td>1.92 (d)</td>
<td>PPhMe (3H)</td>
<td>$^2$J(PH)=10.2</td>
</tr>
<tr>
<td></td>
<td>7.38 (m)</td>
<td>PPhMe (3H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.77 (m)</td>
<td>PPhMe (2H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-18.65 (d)</td>
<td>Os-H-Os (1H)</td>
<td></td>
</tr>
<tr>
<td>[Os$_3$(µ-H)$_2$(µ-PMc$_6$H$_4$)(CO)$_9$]$^{b,c}$</td>
<td>2.13 (d)</td>
<td>PC$_6$H$_4$Me 3H</td>
<td>$^2$J(PH)=10.4</td>
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<tr>
<td></td>
<td>6.94 (m)</td>
<td>PC$_6$H$_4$Me 3H</td>
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</tr>
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<td></td>
<td>7.75 (m)</td>
<td>PC$_6$H$_4$Me 1H</td>
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<tr>
<td></td>
<td>-17.12 (dd)</td>
<td>Os-H-Os (1H)</td>
<td>$^2$J(PH)=9.7, $^4$J(PH)=1.6</td>
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<tr>
<td></td>
<td>-17.26 (dd)</td>
<td>Os-H-Os (1H)</td>
<td>$^2$J(PH)=6.2, $^4$J(PH)=1.6</td>
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<tr>
<td>[Os$_3$(µ-H)(µ-PPhAuPMc$<em>2$Ph)(CO)$</em>{10}$]$^b$</td>
<td>1.81 (dd)</td>
<td>PMc$_2$Ph (6H)</td>
<td>$^2$J(PH)=9.6, $^4$J(PH)=2.0</td>
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<tr>
<td></td>
<td>7.17 (m)</td>
<td>phenyl (3H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.52 (m)</td>
<td>phenyl (3H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.60 (dd)</td>
<td>phenyl (2H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.74 (dd)</td>
<td>phenyl (2H)</td>
<td>$^3$J(PH)=11.1, $^3$J(HH)=7.8, $^4$J(HH)=1.7</td>
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<tr>
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<td>-18.02 (dd)</td>
<td>Os-H-Os (1H)</td>
<td>$^2$J(PH)=14.4, $^4$J(PH)=2.1</td>
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</tbody>
</table>

Table 6.3 continues overleaf ..........
Table 6.3 continued 

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (δ)*</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Os₅(μ-AuPMe₂Ph)(μ-PPhH)(CO)₁₀]ᵇ</td>
<td>1.88 (d) AuPMe₂Ph (3H)</td>
<td>²J(PH)=9.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.37 (dd) PPhH (1H)</td>
<td>²J(PH)=394.0, ⁴J(PH)=4.8</td>
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<tr>
<td></td>
<td>7.30 (m) phenyl (3H)</td>
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<tr>
<td></td>
<td>7.46 (ddd) AuPMe₂Ph (2H)</td>
<td>³J(PH)=14.7, ³J(HH)=8.6, ⁴J(HH)=1.7</td>
<td></td>
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<tr>
<td></td>
<td>7.50 (m) phenyl (3H)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>7.71 (ddd) PPhH (2H)</td>
<td>³J(PH)=12.9, ³J(HH)=7.5, ⁴J(HH)=2.2</td>
<td></td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-AuPMe₂Ph)(μ₃-PPh)(CO)₉]ᵇ</td>
<td>1.94 (d) AuPMe₂Ph (6H)</td>
<td>²J(PH)=9.1</td>
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<tr>
<td></td>
<td>7.44 (m) phenyl (3H)</td>
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</tr>
<tr>
<td></td>
<td>7.48 (m) phenyl (3h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.70 (ddd) ortho (2H)</td>
<td>³J(PH)=13.1, ³J(HH)=7.3, ⁴J(HH)=2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.93 (ddd) ortho (2H)</td>
<td>³J(PH)=14.5, ³J(HH)=7.3, ⁴J(HH)=1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-23.25 (dd) Os-H-Os (1H)</td>
<td>²J(PH)=11.4, ³J(PH)=1.5</td>
<td></td>
</tr>
<tr>
<td>[[Os₃(μ-H)(μ₃-PPh)(CO)₁₀]₂Hg]ᵇ</td>
<td>7.40 (m) phenyl (2H)</td>
<td>²J(PH)=12.0ᵈ</td>
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</tr>
<tr>
<td></td>
<td>7.26 (m) phenyl (2H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-18.69 (t) Os-H-Os (1H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-PPhHgC₂H₅)(CO)₁₀]ᵇ</td>
<td>1.42 (dt) CH₂CH₃ (3H)</td>
<td>³J(HH)=8.5, ⁴J(PH)=10.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.72 (m) CH₂CH₃ (2H)</td>
<td></td>
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<tr>
<td></td>
<td>7.26 (m) phenyl (3H)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>7.44 (m) phenyl (2H)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>-18.45 (d) Os-H-Os (1H)</td>
<td>²J(PH)=15.1</td>
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Table 6.3 continued …..

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (δ)a</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Os₃(µ-H)(µ-PPhHgCH₂Ph)(CO)₁₀]b</td>
<td>2.97 (d)</td>
<td>CH₂ (2H)</td>
<td>³J(PH)=7.5</td>
</tr>
<tr>
<td></td>
<td>7.0-7.4 (m)</td>
<td>phenyl (10H)</td>
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</tr>
<tr>
<td></td>
<td>-18.53 (d)</td>
<td>Os-H-Os (1H)</td>
<td>²J(PH)=15.5</td>
</tr>
</tbody>
</table>

a: Spectra recorded in CDCl₃ and referenced internally to the solvent.
b: Spectra recorded at 400 MHz.
c: Spectra recorded at -55 °C.
d: J(PH) = ²J(PH) + ⁴J(PH).
Table 6.4 \(^{31}P\{^1\text{H}\} \text{n.m.r. data for osmium phosphido clusters}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift ((\delta))^a</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Os}<em>3(\mu-\text{H})(\mu-\text{PPhH})(\text{CO})</em>{10}]^b)</td>
<td>38.26 (d)</td>
<td>PPhH</td>
<td>(^2J(\text{PH})=17.2)</td>
</tr>
<tr>
<td>([\text{Os}<em>3(\mu-\text{H})(\mu-\text{PPhMe})(\text{CO})</em>{10}]^b)</td>
<td>84.72 (d)</td>
<td>PPhHMe</td>
<td>(^2J(\text{PH})=16.2)</td>
</tr>
<tr>
<td>([\text{Os}_3(\mu-\text{H})_2(\mu-\text{PMeC}_6\text{H}_4)(\text{CO})_9]^b)</td>
<td>7.50 (broad)</td>
<td>PMeC(_6)H(_4)</td>
<td>half height width =100 Hz</td>
</tr>
<tr>
<td>([\text{Os}_3(\mu-\text{H})(\mu-\text{PPhAuPMe}<em>2\text{Ph})(\text{CO})</em>{10}]^b)</td>
<td>18.80 (d)</td>
<td>PMe(_2)Ph</td>
<td>(^2J(\text{PP})=327.0)</td>
</tr>
<tr>
<td></td>
<td>26.98 (dd)</td>
<td>PPhAuPMe(_2)Ph</td>
<td>(^2J(\text{PP})=327.0, , ^2J(\text{PH})=12.5)</td>
</tr>
<tr>
<td>([\text{Os}_3(\mu-\text{AuPMe}<em>2\text{Ph})(\mu-\text{PPhH})(\text{CO})</em>{10}]^b)</td>
<td>30.67 (d)</td>
<td>PMe(_2)Ph</td>
<td>(^3J(\text{PP})=10.2)</td>
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<td></td>
<td>96.92 (d)</td>
<td>PPhH</td>
<td>(^3J(\text{PP})=10.2)</td>
</tr>
<tr>
<td>([\text{Os}<em>3(\mu-\text{H})(\mu_3-\text{PPh})(\text{CO})</em>{10}]_2\text{Hg}]^b)</td>
<td>-10.60 (t)</td>
<td>PPh</td>
<td>(^2J(\text{PH})=12.0^c)</td>
</tr>
</tbody>
</table>

^a: Spectra recorded in CDCl\(_3\) and chemical shifts are quoted relative to 85% H\(_3\)PO\(_4\) with downfield chemical shifts reported as positive.

^b: Spectra recorded at 162 MHz.

^c: \(J(\text{PH}) = \left|^{2}J(\text{PH})\right|-\left|^{4}J(\text{PH})\right|\).
Table 6.5 Infrared Data for the complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>v (CO) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Os₃(μ-H)(μ-PPPh)(CO)₁₀]ᵃ</td>
<td>2108 w, 2053 m, 2036 m, 2020 s, 20002 w, 1989 m, 1976 m</td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-PPMe)(CO)₁₀]ᵃ</td>
<td>2102 m, 2060 s, 2052 s, 2020 sh, 2017 m, 2007 w, 1992 m, 1985 m</td>
</tr>
<tr>
<td>[Os₃(μ-H)₂(μ-PC₆H₄Me)(CO)₁₀]ᵃ</td>
<td>2105 m, 2075 s, 2048 s, 2038 m, 2022 m, 2010 s, 1995 m, 1977 m</td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-PPAuPMe₂Ph)(CO)₁₀]ᵇ</td>
<td>2088 m, 2043 s, 2035 m, 2004 m, 19898 m, 1974 m</td>
</tr>
<tr>
<td>[Os₃(μ-AuPMe₂Ph)(μ-PPPh)(CO)₁₀]ᵇ</td>
<td>2085 m, 2013 s, 2007 m, 1998 m, 1968 w, 1960 m</td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-AuPMe₂Ph)(μ₃-PPPh)(CO)₁₀]ᵇ</td>
<td>2071 m, 2050 s, 2022 s, 1997 m, 1987 m, 1975 m, 1962 w, 1942 w</td>
</tr>
<tr>
<td>[[Os₃(μ-H)(μ₃-PPPh)(CO)₁₀]₂Hg]ᵇ</td>
<td>2094 m, 2058 s, 2047 m, 2018 m, 1988 m, 1959 w</td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-PPHgC₂H₅)(CO)₁₀]ᵇ</td>
<td>2094 m, 2050 s, 2039 m, 2028 m, 2010 m, 1981 s, 1965 w</td>
</tr>
<tr>
<td>[Os₃(μ-H)(μ-PPHgCH₂Ph)(CO)₁₀]ᵇ</td>
<td>2095 m, 2055 s, 2044 m, 2018 s, 1990 s, 1962 w</td>
</tr>
</tbody>
</table>

(a) Spectra recorded in n-hexane.

(b) Spectra recorded in tetrahydrofuran.
Chapter 7

Synthesis and Studies of Platinum-Molybdenum Phosphido Complexes
7 Synthesis and Studies of Platinum-Molybdenum Phosphido Complexes

7.1 Introduction

Binuclear and polynuclear transition-metal complexes have been widely considered as having the potential to induce unique catalytic and stoichiometric transformations as a result of the cooperative interaction between adjacent metals. The synthesis of heterometallic complexes has received considerable attention during the last decade, more recently complexes containing Group 8 metals bonded to early transition metals have been examined. This interest in complexes containing Group 8 metals stems from their relevance to catalysis and the ease with which they undergo oxidative addition and reductive elimination reactions. However, under the forcing conditions employed for the chemical transformations, many heterometallic molecules undergo fragmentation, destroying the initial integrity of the complex. The use of bridging phosphido ligands has proved successful in retarding the fragmentation tendencies of these complexes, although increasingly it has been realised that the phosphido bridge can behave as a reactive centre and undergo chemical transformations.

Typical methods for the preparation of phosphido bridged complexes involves:

1. *In situ* lithiation of a coordinated secondary phosphine followed by reaction with a complex containing a halide (bridge-assisted synthetic approach);

\[
[(\text{CO})_5\text{Cr}(\text{P}^\text{tBu}_2\text{Li})] \xrightarrow{[\text{NiCl}_2(\text{PMe}_3)_2]} \text{THF, -100 °C} \rightarrow
\]

![Diagram](image-url)
(2) Thermal reaction of $[\text{Mo}_2(\text{CO})_6(\eta\text{C}_5\text{H}_5)_2]$ with tetraphenylphosphine;

$$[\text{Mo}(\text{CO})_3\text{Cp}]_2 \xrightarrow{\text{P}_2\text{Ph}_4} \text{Mo} \equiv \text{Mo} \equiv \text{Mo}$$

(3) Dehalogenation of mononuclear ruthenium complexes with $[\text{Co}_2(\text{CO})_8]$;}

$$[(\text{arene})\text{RuCl}_2(\text{PPh}_2\text{X})] \xrightarrow{[\text{Co}_2(\text{CO})_8]} \text{P}$$

(4) Oxidative addition of a coordinated secondary phosphine to a zero valent metal complex;

$$[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{H})] \xrightarrow{[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]} \text{Mo} \equiv \text{Pt}$$

(5) Reaction of a carbonylmetallate with a P-Cl bond of a PPh$_2$Cl complex;

$$[\text{PtCl}_2(\text{PPh}_2\text{Cl})_2] \xrightarrow{\text{Na}[\text{Mn}(\text{CO})_5]^+} \text{Pt}$$

Geoffroy and co-workers have prepared several heterobimetallic phosphido bridges complexes using the bridge-assisted approach. Among those are the related
complexes \([\text{Fe}(\mu-PPh_2)_2\text{IrH(COD)}]\) and \([\text{Fe}(\mu-PPh_2)_2\text{IrH(COD)}]\) prepared from \([\text{Ir(\mu-Cl)(COD)}]_2\) and the appropriate diphenylphosphido carbonyl complex. Studies performed on these complexes revealed that the reactivity at the iridium centre is dependent on the nature of the heterometallic moiety bonded to it. The iron-iridium complex underwent reaction with \(\text{CO/PPh}_3\) under quite mild conditions to give \([\text{Fe}(\mu-PPh_2)_2\text{IrH(CO)PPh}_3]\) (Equation 7.1). In contrast, much more forcing conditions are required for the tungsten-iridium complex to undergo the analogous reaction. X-ray structures of these two complexes revealed that replacement of the \([\text{W(CO)}_4]\) fragment by \([\text{Fe(CO)}_3]\) causes significant changes in the metal-metal bonding and it was suggested that this difference accounted for the change in reactivity.

The coupling of acetylene molecules across a dimetal centre is a process of potential relevance to a number of catalytic processes such as Reppe cyclisation of

-310-
acetylene to form cyclooctatetraene and benzene. Numerous examples of two acetylene molecules coupling at dimetallic centres have been reported. More recently Jones has investigated the reactivity of heterobimetallic complexes with acetylenes and found that they react with these unsaturated organic fragments. For example, [(Bu₂PH)(CO)₂Fe(μ-CO)(μ-Bu₂P)Rh(COD)] reacts with phenylacetylene with head-to-head coupling of two organic fragments to give a metallacyclopentadiene iron unit (Figure 7.1).

The formation of heterometallic phosphido bridged complexes is often accompanied by CO labilisation processes. For example, the oxidative addition of the P-H bond of [M(CO)₅(PPh₂H)] (M = Cr, Mo, W) to the zero valent platinum complexes, [Pt(C₂H₄)(PPh₃)₂] affords [(CO)₅M(μ-PPh₂)Pt(PPh₃)₂H] which rapidly loses CO to give [(CO)₅M(μ-PPh₂)(μ-H)Pt(PPh₃)₂] via a "platinum-assisted mechanism" involving PPh₃ dissociation, formation of a carbonyl-containing complex [(CO)₅M(μ-PPh₂)(μ-CO)Pt(PPh₃)H], subsequent rearrangement to [(CO)₅M(μ-PPh₂)(μ-H)Pt(PPh₃)(CO)] followed by the substitutional loss of CO from platinum by PPh₃ (Scheme 7.1).
The phosphido bridge in many complexes is strongly bound and capable of maintaining the integrity of the polynuclear metal framework during chemical transformations. Many examples of potentially significant reversible metal-metal bond cleavage have been reported. However, the phosphido bridge, although widely accepted as a stabilising ligand, has been found to have a chemical reactivity associated with it. This chemical reactivity might be accentuated by the presence of heterometals in the complexes. A comparison of the reactivity of the binuclear complexes [Co₅(CO)₈] and [RuCo(CO)₅(μ-PPh₂)] towards alkynes revealed significant reactivity differences between the two complexes, the dominant reaction pathway was found to be CO and acetylene insertion into the μ-PPh₂RuCo bridge leading to [RuCo(CO)₅(μ-CO)(μ-PPh₂COC(Ph)C(Ph))], which underwent subsequent decarbonylation to give [RuCo(CO)₅(μ-CO)(μ-PPh₂C(Ph)C(Ph))]. (Figure 7.2).

The phosphido bridge has been found to undergo chemical transformations under quite mild conditions. Evidence of chemical reactivity of phosphido bridges in heterometallic complexes has been provided by Geoffroy and co-workers. During studies of the synthesis, stability, and reactivity properties of the tungsten-osmium formyl complexes [(CO)₄W(μ-PPh₂)₂Os(CO)₂(CHO)(PMePh₂)][Li], Geoffroy discovered that the carbene ligand, formed by the methylation of the formyl complex, coupled with
the bridging phosphido ligand (Figure 7.3) to afford the novel $[\eta^2-(P,C)\mu-$
PPh$_2\text{CH(OMe)}]$ bridging ligand. Protonation of the formyl complex converts one of the
bridging phosphido ligands into a terminal PPh$_2\text{H}$ ligand. Phosphido bridge cleavage

\[
\begin{align*}
\text{Os} & \quad \text{Os} \\
\text{CO} & \quad \text{CO} \\
\text{P} & \quad \text{P} \\
\text{Ph} & \quad \text{Ph} \\
\text{W} & \quad \text{W} \\
\text{CO} & \quad \text{CO} \\
\text{P} & \quad \text{P} \\
\text{Ph} & \quad \text{Ph} \\
\text{CO} & \quad \text{CO} \\
\text{P} & \quad \text{P} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

**Figure 7.3**

in $[(\text{CO})_4\text{W(\mu-PPh}_2\text{)}_2\text{RhH(CO)(PPh}_3\text{)}]$ occurs readily in the presence of ethylene to afford
a terminal PPh$_2\text{Et}$ ligand by insertion of the ethylene into the Rh-H bond and
subsequent reductive coupling of the Rh-Et ethyl group.83

In our work we have investigated the synthesis and reactivity of platinum-
molybdenum phosphido bridged complexes contains the $\mu$-PPh$_2$H ligand. We have found
that nucleophilic substitution at platinum(II) complexes by $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{H})]$ is a
convenient route to these heterometallic complexes. Other known procedures for the
syntheses of platinum-molybdenum phosphido-bridged complexes include reaction of
PPh$_2\text{H}$ or PCy$_2\text{H}$ with the linear trinuclear complex $[\text{Pt}\{\text{Mo}\,(\text{CO})_3(\text{Cp})\}_2(\text{PhCN})_2]$ [274
(Scheme 7.2). Braunstein has prepared similar complexes by reaction of cis-
$[\text{PtCl}_2(\text{PPh}_2\text{Cl})_2]$ with the carbonylmetallate $[\text{Na}][\text{Mn}\,(\text{CO})_5]$; $[\{\text{Mn}(\text{CO})_4(\mu-\text{PPh}_2)$]$_2$Pt(CO)].
trans-[Pt(Mo(CO)₃Cp)₂(PhCN)] + PPh₂H → THF, 40 °C

Scheme 7.2
$[({\text{Mn(CO)}_4}(\mu-\text{PPh}_2))_2\text{Pt(}\mu-\text{PPh}_2)\text{H}]$ and $[(\text{Mn(CO)}_4)(\mu-\text{PPh}_2)_2\text{Pt(}\mu-\text{PPh}_2)_2]$ are the major products. In comparison to this synthetic procedure in which the heterometallic complex is preformed, followed by addition of the phosphido bridge, Powell and co-workers have exploited the acidity of the P-H of several metal complexes contains the secondary phosphine, PPh$_2$H. Oxidative addition of this bond to the zero-valent platinum complex [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] affords the heterometallic phosphido-bridged complexes (Scheme 7.3). Many mixed metal complexes have been prepared using this procedure, several of which are shown in Scheme 7.3. Complexes formed using this procedure contain direct metal-metal bonds bridged by phosphido ligands or weak metal-metal interactions. The more acidic cationic secondary phosphine complexes react with the platinum(0) complexes via initial deprotonation of the coordinated secondary phosphine which then substitutes a ligand at platinum followed by CO transfer to platinum. Subsequent reprotonation gives the required complex.

Carty has attempted to correlate structural change with $^{31}$P n.m.r. chemical shifts.
and coupling constants. Phosphido groups bridging nonbonding metals have $^{31}\text{P}$ resonances at very high-field. For example, the phosphido bridge in $[\text{Ru}_3(\text{CO})_9(\mu-\text{PPh}_2)(\text{C}≡\text{CPr})]$ appears at $\delta -51.8$ in the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum. Decarbonylation with concomitant metal-metal bond formation shifts this phosphido resonance to low-field $\delta +113.0$ consistent with the decrease in Ru-P-Ru bond angle (92.8° to 74.4°). $^{31}\text{P}$-$^{31}\text{P}$ coupling constants also provide additional information. Phosphines occupying coordination sites $\text{trans}$ to phosphido bridges on the same metal atom exhibit quite large $^2\text{J}(\text{PP})$ values (around 200 Hz) whilst $\text{cis}$ couplings are much smaller. Heterometallic phosphido-bridged complexes without metal-metal bonds exhibit high-field phosphorus resonances and upon metal-metal bond formation large downfield shifts occur (Figure 7.4). These observations imply that Cartys predictions hold for heterometallic systems, however, some exceptions to these correlations have been found so caution must be exercised in their use.

We have used the general route of nucleophilic substitution at a metal halide to prepare and examine several platinum-molybdenum phosphido-bridged complexes. Reaction of $[\text{Mo}(\text{CO})_5(\text{PPhH})]$ with cis-$[\text{PtCl}_2(\text{PET}_{3})_2]$ and $[\text{PtCl}_2(\text{dppe})]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) afforded a range of complexes each existing as pairs of stereoisomers. Examination of the low temperature $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra of several of these complexes revealed that these heterometallic complexes existed in several conformational forms in solution. The crystal structures of $[\text{Pt}(\mu-\text{PPhH})_2(\text{Mo}(\text{CO})_3)_2(\text{dppe})]$, $\text{trans}$-$[\text{Pt}(\mu-\text{PPhH})(\text{Mo}(\text{CO})_3)\text{Cl(PEt}_{3})_2]$ and $\text{trans}$-$[\text{Pt}(\mu-\text{PPhH})_2(\text{Mo}(\text{CO})_3)_2(\text{PET}_{3})_2]$ will be reported along with the results of several n.m.r. investigations.
7.2 Reactions of [Mo(CO)₅(PPhR)]⁺ (R = Ph, H) with Simple Electrophiles

7.2.1 Preparation of [Mo(CO)₅(PPhRH)] (R = Ph, H)

The primary and secondary phosphine complexes [Mo(CO)₅(PPhRH)] (R = Ph, H) were prepared using a modified procedure from that described by Stelzer and co-workers²⁷ (Equation 7.2). Molybdenum hexacarbonyl reacted with phenylphosphine in refluxing octane (b.p. 123 °C) to afford in 60-70% yield the monosubstituted product [Mo(CO)₆] + PRHz → [Mo(CO)₅(PPhH₂)] after column chromatography. Varying quantities of the disubstituted product were also obtained depending on the reaction time. Typically 20 minutes at reflux afforded the highest yields of the required products. The monosubstituted product was isolated as a colourless crystalline material (from n-hexane -20 °C) and could be stored for several months in the refrigerator.

7.2.2 Reaction of [Mo(CO)₅(PPhH)]⁺ with Methyl iodide

Addition of a one molar equivalent of DBU (diazabicyclo[5.4.0]undec-7-ene) to a tetrahydrofuran solution of the complex [Mo(CO)₅(PPhH₂)] afforded an immediate colour change from colourless to intense yellow. After being stirred for ten minutes, an excess of methyl iodide was added. Chromatographic work-up afforded a high yield of the chiral complex [Mo(CO)₅(PPhHMe)]. The formation of this complex was evident from the ¹H n.m.r. spectrum, the P-H resonance (δ 5.60, ¹J(PH) = 328.0 Hz, ³J(HH) = 6.7 Hz) appeared as a doublet of quartets and the methyl resonance as a simple triplet (³J(HH) = 6.7 Hz and ²J(PH) = 6.7 Hz). The P-H resonance of the methylated complex was shifted to lower field relative to that of the parent complex [Mo(CO)₅(PPhH₂)], δ 5.40 compared with δ 5.60 for [Mo(CO)₅(PPhH₂)] and [Mo(CO)₅(PPhHMe)] respectively. This shift to lower field is consistent with the observations made in Chapters 3 and 4 of substituent effects at phosphorus on the chemical shifts of the protons remaining directly bonded to the phosphorus and on the chemical shift of the...
phosphorus nucleus itself.

7.2.3 Reaction of \([\text{Mo(CO)}_5(\text{PPhR})]^- (R = \text{Ph, H})\) with Gold Phosphine Chloride Complexes

(a) Reaction with \([\text{Au(PMe}_2\text{Ph})\text{Cl}]\) and \([\text{Au(PPh}_3\text{)}\text{SCN}]\)

\([\text{Au(PMe}_2\text{Ph})\text{Cl}]\) was added to a tetrahydrofuran solution of \([\text{Mo(CO)}_5(\text{PPhH}_2)]\) and DBU. The reaction was monitored by i.r. spectroscopy; an immediate shift of the carbonyl absorptions to lower frequency indicated that reaction was instantaneous. Chromatographic work-up of the reaction mixture afforded a single major product and a minor fast moving band that was identified spectroscopically as starting material. Crystallisation of the major product from n-hexane at -20 °C overnight afforded a colourless air-stable crystalline material. The \(^1\text{H} \text{n.m.r.}\) spectrum of the product contained resonances due the methyl group of the gold fragment [\(\delta 2.06 \text{ (d), } J(\text{PH}) = 8.9 \text{ Hz}\)]. A simple doublet of doublets was expected for the methyl resonance if there were two phosphorus nuclei present. The doublet coupling observed revealed a rapid exchange of phosphine accompanied by the loss of phosphorus-hydrogen coupling. The \(^{31}\text{P}{'\text{H}}\) n.m.r. spectrum contained two well-separated resonances [\(\delta 28.5 \text{ (PMe}_2\text{Ph} \text{) and } \delta -65.0 \text{ (µ-PPhH)}\)], both signals appeared as broad singlets (\(\Delta v_s = 100 \text{ Hz}\)) due to rapid exchange leading to the loss of the \(^{31}\text{P}^{'\text{H}}\) coupling. From the n.m.r. evidence alone we propose the compound to be the simple phosphido bridged molybdenum-gold complex \([\text{Mo(CO)}_5(\mu-P\text{PhH})(\text{AuPMe}_2\text{Ph})]\) with rapid dissociation of either the phosphine or the gold-phosphine fragment leading to the loss of the \(^{31}\text{P}^{'\text{H}}\) coupling (Equation 7.3).

\[
[\text{Mo(CO)}_5(\text{PPh}_2\text{H})] \xrightarrow{\text{DBU}} [\text{Mo(CO)}_5(\mu-P\text{Ph}_2)(\text{AuPPh}_3)] \quad \text{Equation 7.3}
\]

A similar reaction of \([\text{Mo(CO)}_5(\text{PPh}_2\text{H})]\) with DBU and \([\text{Au(PPh}_3\text{)}\text{SCN}]\) afforded \([\text{Mo(CO)}_5(\mu-P\text{Ph}_2\text{AuPPh}_3)]\) as the major product. The \(^{31}\text{P}{'\text{H}}\) n.m.r. spectrum of this product contained two broad resonances [\(\delta = 22.0 \text{ (µ-PPh}_2\text{), and } \delta = 43.0 \text{ (PPh}_3\text{)}\)]. The FAB mass spectrum of this compound was measured at the London School of
Pharmacy (ULIRS). Parent molecular ion peaks were observed at m/e = 880 corresponding to [Mo(CO)₅(μ-PP₃AuP₃)]⁺. Fragmentation peaks corresponding to the loss of five carbonyl groups were also observed. Elemental analytical data obtained for (C, H, and P) showed an acceptable agreement with the calculated values for the proposed formulation.

The gold complexes [Au(P₃Cl)] and [Au(PMe₃Ph)Cl] have different reactivity patterns towards different nucleophilic phosphido centres evident from the reactions of these gold phosphine complexes with the phosphido complexes [IrCl₂(PMe₃Ph)₃(R¹R²)], [OsCl(CO)₂(PP₃H)₃(PP₃H)], and [Mo(CO)₅(PP₃H)]⁺. All three complexes react differently the latter two complexes give neutral metal-gold bimetallic complexes whilst the former affords the cation [{IrCl₂(PMe₃Ph)₃(PP₃H)}₂Au]⁺.

In Chapter 6 it was established that the anionic phosphido complex [Os₃(μ-H)(μ-PP₃)(CO)i₀]⁻ reacted with [Au(PMe₃Ph)Cl] at low temperature to afford the phosphido-bridged cluster [Os₃(μ-H)(μ-PP₃AuP₃Me₂Ph)(CO)₁₀] in a similar manner, to the molybdenum phosphido complex. Although these two anionic phosphido ligands react in a similar manner the n.m.r. properties of the final product are significantly different. The ³¹P{¹H} n.m.r. spectra of [Mo(CO)₅(μ-PP₃AuP₃)] and [Mo(CO)₅(μ-PP₃H)(AuP₃Me₂Ph)] contain broad singlets for both phosphorus nuclei, no ³¹P-³¹P coupling being observed. In comparison the ³¹P{¹H} n.m.r. spectrum of [Os₃(μ-H)(μ-P₃AuP₃Me₂Ph)(CO)₁₀] consisted of sharp resonances due to the P₃Me₂Ph and phosphido ligands [δ = +18.80 (d), 2J(PP) = 327.0 Hz (P₃Me₂Ph) and δ + 26.98 (dd), 2J(PP) = 327.0 Hz, 2J(PH) = 12.5 Hz (μ-P₃AuP₃Me₂Ph). The presence of ³¹P-³¹P coupling in this spectrum indicated that any exchange occurring in solution was very slow on the n.m.r. time-scale, much slower than the process occurring for [Mo(CO)₅(μ-PP₃H)(AuP₃Me₂Ph)]. No evidence of line-broadening due to exchange was apparent in the high temperature ³¹P{¹H} n.m.r. spectrum of the triosmium cluster. Having noted the significant reactivity differences between different phosphido complexes towards gold phosphine complexes and the marked difference in the properties of the final product it was decided to undertake a variable-temperature ³¹P{¹H} n.m.r. study.

(b) ³¹P{¹H} N.M.R Studies of [Mo(CO)₅(μ-PP₃)(AuP₃)]

The results of the variable-temperature n.m.r. study are shown Figure 7.5. At
Figure 7.5 Variable temperature \(^{31}\)P('H) n.m.r. spectra of [Mo(CO)$_5$(µ-PPh$_3$)(AuPPh$_3$)] and [Mo(CO)$_5$(µ-PPh$_3$)(AuPPh$_3$)] + PPh$_3$.
room temperature the spectrum consists of two broad singlets, indicating that sufficiently rapid exchange was occurring to cause the loss of $^{31}\text{P}-^{31}\text{P}$ coupling. Lowering the temperature of the n.m.r. solvent broadened the two singlets (-10 °C, CD$_2$Cl$_2$). At -35 °C the expected doublet coupling was evident with the inner peaks more intense than the outer ones. At -75 °C the two signals appeared as doublets with the inner lines remaining more intense than the outer indicating slight second order (AB) distortions.

Recording the $^{31}\text{P}$$^{1}\text{H}$ n.m.r. spectrum after the addition of a small quantity of triphenylphosphine resulted in the loss of $^{31}\text{P}-^{31}\text{P}$ coupling, even at -75 °C. The addition of triphenylphosphine effected an increase in the rate of exchange of free and coordinated phosphine. Raising the temperature of the n.m.r. solvent caused the coalescence of the resonances due to free and coordinated phosphine (δ 34 broad singlet).

Gold(I) has a strong tendency to form linear two coordinate complexes LAuX (L = neutral lewis base; X = halide or pseudohalide). These complexes are usually formulated as neutral complexes, LAuX, but since gold(I) is generally labile there exists the possibility of ligand scrambling to form the symmetrically substituted complexes [AuL$_2$]$^+$ and [AuX$_2$]$^+$e.g (tetrahydrothiophene)gold iodide in the solid state contains [Au(tht)$_2$]$^+$[AuI]$.^{277}$ and cyano(thiolate)gold(I)complexes RSAuCN$^-$ in aqueous solution are in equilibrium with substantial amount of [Au(CN)$_2$]$^+$ and [Au(SR)$_2$]$^+$. The $^{31}\text{P}$ n.m.r. spectrum of Et$_3$PAuCN$^{390}$ contained two peaks supporting the proposed dissociation (Scheme 7.4).

$$2 [(\text{PET}_3)\text{AuCN}] \rightleftharpoons [(\text{PET}_3)\text{Au}]^+ + [\text{Au(CN)}_2]^-$$

Scheme 7.4

The related (triphenylphosphine)goldcyanate complex showed only one broad resonance at room temperature but resolved into two peaks at low temperature. Similarly the room temperature $^{31}\text{P}$ n.m.r. spectrum of [(Mo(CO)$_5$(PPh$_3$))AuPPh$_3$] was broad at room temperature and therefore we could not rule out a similar equilibrium. However, at low temperature there were only two peaks (AB quartet) ruling out the possibility of an equilibrium similar to Scheme 7.4, an equilibrium of this sort would require four resonances. The absence of a $^{31}\text{P}$$^{1}\text{H}$ n.m.r. signal due to [Au(PPh$_3$)$_3$]$^+$ unequivocally ruled out the possibility of this equilibrium. A solution of [Mo(CO)$_5$(μ-
PPh\textsubscript{2})(AuPPh\textsubscript{3})\] in CDCl\textsubscript{3} was left to stand for several days, and there was no evidence for the symmetrisation reaction that might occur in solution. In Chapter 4 we reported the reaction of \([\text{IrCl}_{2}(\text{PMe}_{2}\text{Ph})_{3}(\text{PH}_{2})]\) with [Au(PPh\textsubscript{3})Cl] to give the trinuclear complex \([\{\text{IrCl}_{2}(\text{PMe}_{2}\text{Ph})_{3}(\text{PH}_{2})\}_{2}\text{Au}\}][\text{ClO}_{4}]\), the product of rapid symmetrisation of \([\text{IrCl}_{2}(\text{PMe}_{2}\text{Ph})_{3}(\text{PH}_{2}\text{AuPPh}_{3})]^{+}\). Riera found no evidence for the symmetrisation of \([\text{Mn(CO)}_{3}(\text{bipy})(\mu-\text{PPh}_{2}\text{AuPPh}_{3})]^{+}\) (Figure 7.6) in solution but he was able to prepare the required symmetrisation product by a different route. That he was able to prepare the trinuclear complex by a different route indicates that the failure of \([\text{Mn(CO)}_{3}(\text{bipy})(\mu-\text{PPh}_{2}\text{AuPPh}_{3})]^{+}\) to symmetrise to \([\{\text{Mn(CO)}_{3}(\text{bipy})(\mu-\text{PPh}_{2})\}_{2}\text{Au}\}][\text{ClO}_{4}]\) is kinetic in origin rather than thermodynamic. He also observed that the neutral complexes \([\text{Mn(CO)}_{3}(\mu-\text{PPh}_{2}\text{AuC}_{6}\text{F}_{5})]\) and \([\text{Mn(CO)}_{3}(\text{bipy})(\mu-\text{PPh}_{2}\text{C}_{6}\text{F}_{5})]\) did not undergo symmetrisation in solution at least at an appreciable rate.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_6.png}
\caption{Figure 7.6}
\end{figure}

(c) Reaction with [HgEtBr]

Gold(I) fragments such as [AuPR\textsubscript{3}]\textsuperscript{+} and [AuC\textsubscript{6}F\textsubscript{5}] are often chosen as candidates to replace H\textsuperscript{+}. We have found that the fragment [HgR]\textsuperscript{+} can also be exploited as an electrophile. We have already seen that \([\text{IrCl}_{2}(\text{PMe}_{2}\text{Ph})_{3}(\text{PR}_{2})]\) and \([\text{Os}_{6}(\mu-\text{H})(\mu-\text{PPh})(\text{CO})_{10}]\) react with alkylmercury halides to afford products containing the fragment [HgR]\textsuperscript{+}. 

-323-
A 1:1 tetrahydrofuran solution of [Mo(CO)$_5$(PPh$_2$H)] and DBU reacted with [HgBrEt], as evident from the significant shift of the i.r. carbonyl absorptions to lower frequency. This change in the i.r. spectrum occurred immediately on addition of the mercury compound and no further changes were observed over a 20 minute period. Chromatographic work-up afforded a single major band on the t.l.c. plate, extraction into dichloromethane and crystallisation form n-hexane at -20 °C afforded the product as a colourless crystalline material. Elemental analytical data (C, H, and P) obtained on the crystalline sample agreed with the proposed formulation [Mo(CO)$_5$(μ-PPh$_2$)(HgEt)].
7.3 Reactions of [Mo(CO)$_5$(PPhH)]$^-$ with Platinum(II) Complexes

Many platinum(II) phosphido bridged complexes containing early transition-metals have been prepared by Powell using the familiar method of oxidative addition to platinum(0) complexes such as [Pt(C$_2$H$_4$)(PPh$_3$)$_2$]. Either cationic or neutral complexes containing a secondary phosphine can be employed$^{32,71-74}$ (Scheme 7.3). The phosphido-bridged complexes formed in this manner contain metal-metal bonding interactions. Braunstein has utilised the bridge-assisted synthetic approach of displacement of ligand substituents. Halide displacement from coordinated halophosphines and arsines can lead to phosphido/arsenido bridged clusters in good yield. For example, the reaction of [PtCl$_2$(PPh$_2$Cl)$_2$] with [Mn(CO)$_3$]$^-$ afforded three major products all containing phosphido bridges across metal-metal bonds or across non-bonding distances$^{272}$ (Figure 7.7). This procedure has been employed to build heterometallic clusters with phosphido and phosphinidene bridges. Braunstein found that secondary phosphines undergo oxidative addition at preformed heterometallic complexes, exemplified by the reaction of [Pt{Mo(CO)$_3$Cp}$_2$(PhCN)$_2$] with diphenylphosphine to afford platinum-molybdenum complexes containing phosphido bridges$^{714}$ (Scheme 7.2).

Recently we have examined the reactions of the anionic phosphido complex [Mo(CO)$_5$(PPhH)]$^-$ with the platinum(II) complexes [PtCl$_2$(P$_3$E$_3$)$_2$]$^{287}$ and [PtCl$_2$(dppe)]$^{286}$ [dppe = 1,2-bis(diphenylphosphino)ethane]. The phosphido anion was found to undergo nucleophilic attack at the platinum centre, resulting in the substitution of one or both the chloride ligands, affording heterometallic complexes containing either two or three metal centres bridged by the phosphido ligand μ-PPhH.

Systems containing phosphine ligands and platinum atoms are particularly amenable to n.m.r. spectroscopic investigation,$^{279}$ facilitating identification of possible heterometallic systems and with considerable potential for the investigation and analysis of fluxional processes that may be occurring in solution.

7.3.1 Reaction of [Mo(CO)$_5$(PPhH)]$^-$ with [PtCl$_2$(dppe)]

A 1:1 solution of [Mo(CO)$_5$(PPhH$_2$)] and DBU in tetrahydrofuran reacted with [PtCl$_2$(dppe)], evident from the appearance of low frequency carbonyl absorptions in the i.r. spectrum. The completion of the reaction was established from i.r. evidence (a total
cis-[PtCl₂(PPh₂Cl)₂] $\xrightarrow{\text{Na}^+\text{[Mn(CO)₅]}^-}$ THF 0-25 °C

Figure 7.7
reaction time of 2 hours). Chromatographic work-up of the reaction mixture afforded three products: one major and two minor. A fast moving band was spectroscopically identified as a minor amount of the molybdenum starting material, whilst the other minor product remained unidentified until much later when it was discovered to be \([\text{Mo(CO)}_6(\mu-\text{PPhH})_2\text{Pt(dppe)}]\).

Very little information was obtained from the \(^1\text{H}\) n.m.r. spectrum of the major product, complicated signals due to the \(\text{CH}_2\) protons of the dppe backbone and of the \(\text{P-}H\) protons were present. The \(^{31}\text{P}\{^1\text{H}\}\) n.m.r. spectrum consisted of two sets of resonances (Figure 7.8), each set of phosphorus resonances consisting of signals due to the dppe ligand \([\delta = +44.8, ^2J(\text{PP}) = 213.0 \text{ Hz and } \delta = +46.0, ^2J(\text{PP}) = 216.0 \text{ Hz}] and signals at much higher field \([\delta = -33.6, ^2J(\text{PP}) = 213.0 \text{ Hz and } \delta = -53]\). These resonances at high-field have been assigned to the bridging phosphido ligand. Previous literature correlations of M-P-M angles

![Figure 7.9](image)

Figure 7.9

with \(^{31}\text{P}\) chemical shifts, indicated that the assignment of the high-field resonance to the phosphido bridge is correct. Binuclear phosphido bridged WPt, WPd, and WNi\(^{85}\) complexes prepared by Geoffroy and co-workers were found to contain direct metal-metal bonds. Figure 7.9 shows the X-ray structure of \([(\text{CO})_6\text{W(\mu-PPh}_2\text{)Pt(PPh}_3\text{)}]\). The \(^{31}\text{P}\) chemical shift of the bridging phosphido ligand in this complex appears at significantly lower field \((\delta = +173.8)\) than that of the bridge in \([\text{Pt(\mu-PPhH)}(\text{Mo(CO)}_5)_2(\text{dppe})]\) \((\delta = -33.6)\). This high-field shift of the phosphido resonance for the major product indicates that the complex does not contain M-M interactions. Many other heterometallic phosphido-bridged complexes have been prepared and these reveal...
Figure 7.8 $^{13}$P($^{1}$H) n.m.r. spectra of the complex [Pt(μ-PPPh$_2$)$_2$(Mo(CO)$_5$)$_2$](dppe)]
that downfield (δ 50-300) resonances are generally found for μ-PPh₂ ligands bridging metal-metal bonds and the high-field (δ +50 to -200) resonances occur when the phosphido ligand bridges two metals not joined by a metal-metal bond.²²⁰,²⁸¹

Both sets of resonances appeared as simple doublets with their corresponding satellites but careful examination of the signals revealed second-order structure on each of the peaks indicating that the lines were broadened by dynamic exchange. This broadening was most apparent in the spectrum of the minor species (Figure 7.8) where the large doublet coupling due to the phosphido phosphorus was absent. The presence of platinum satellites indicated that there was a single platinum centre in the complex. Restoring proton coupling to the spectrum resulted in an increase in the multiplicity of the high-field resonances [1^J(\text{PH}) = 330 Hz and 1^J(\text{PH}) = 295 Hz for the major and minor species respectively] confirming their assignment to the phosphido bridging ligands. Approximate integrals for the phosphido and phosphine resonances show a 1:1 correspondence and we believe that the species present in solution are stereoisomers of [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)] where both chloride ligands in the parent platinum complex have been replaced by [Mo(CO)₅(PPhH)]⁻ ligands.

Most apparent was the large differences in 1^J(¹⁹⁵PtP) for the phosphido and phosphine ligands [1^J(¹⁹⁵PtP(dppe))] > 1^J(¹⁹⁵PtPμ)]. 1^J(¹⁹⁵PtP) depends largely on the ligand occupying the trans position in the coordination sphere.²⁸²,²⁸⁴,²⁸⁵ For example, in the ³¹P{¹H} n.m.r. spectra of cis-[PtCl₂(PEt₃)₂] and [PtCl₂(dppe)] 1^J(¹⁹⁵PtP) is approximately 3500 Hz.²⁸³ The values of 1^J(¹⁹⁵PtP) for the dppe ligand trans to a phosphido ligand are significantly reduced [1^J(¹⁹⁵PtP) = 2323.0 Hz and 2187.0 Hz for the minor and major stereoisomers respectively]. These values compare favourably with those found in other Pt-metal heterometallic complexes where phosphido ligands are located trans to dppe ligands.³⁷,²⁻ For example, in the complex [(CO)₄M(μ-PPh₂)(μ-H)Pt(dppe)] (M = Cr, Mo, W) the values of 1^J(¹⁹⁵PtP(dppe)) range from 2170 Hz to 2306 Hz. The major stereoisomer of [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)] revealed a much smaller platinum-phosphorus coupling to the phosphido ligand [1^J(¹⁹⁵PtPμ) = 1450] than normally found for simple trans tertiary phosphine complexes of platinum. Coupling constants of similar size to those of the phosphido ligands were observed in the complex [(CO)₄M(μ-PPh₂)(μ-H)Pt(dppe)] (1360 Hz to 1570 Hz).²² These small 1^J(¹⁹⁵PtPμ) coupling constants are not just a consequence of the ligands occupying the trans coordination site because small values of 1^J(¹⁹⁵PtPμ) are observed in complexes which contain chloride trans to
phosphido. In these complexes we would expect larger coupling constants than observed. In trans-[Pt(μ-PPhH){Mo(CO)_3}Cl(PEt_3)_2], \(^{1}J(\text{^{195}PtP})\) is 2135 Hz when trans to a chloride ligand, smaller than expected on the basis of platinum-phosphorus coupling constants in simple phosphine-containing complexes such as cis-[PtCl_2(PEt_3)_2] in which \(^{1}J(\text{^{195}PtP})\) is 3500 Hz. In trans-[Pt(μ-PPhH)_2{Mo(CO)_3}Cl(PEt_3)_2], \(^{1}J(\text{^{195}PtP})\) (2526 Hz and 2431 Hz) is similar in size to \(^{1}J(\text{^{195}PtP})\) for trans-[PtCl_2(PEt_3)_2] (2400 Hz) but the Pt-Pμ coupling constant to the phosphido ligand is much smaller in magnitude \(^{1}J(\text{^{195}PtP})\) = 1110.0 Hz.

Trans phosphorus-phosphorus couplings in these phosphido complexes are much smaller than those of simple tertiary phosphine complexes of platinum(II). For example, [Pt(μ-PPhH)_2{Mo(CO)_3}_2(dppe)] contains \(^{3}J(PPμ)\) = 213.0 Hz and for [Pt(μ-PPhH)_2{Mo(CO)_4}(dppe)] \(^{3}J(PPμ)\) = 222.0 Hz. In comparison trans-[Pt(μ-PPhH){Mo(CO)_4}Cl(PEt_3)_2] contains much larger phosphorus-phosphorus coupling constants, \(^{3}J(PEt_3PEt_3)\) = 366.0 Hz, and for trans-[Pt(μ-PPhH)_2{Mo(CO)_4}(PEt_3)_2], \(^{3}J(PEt_3PEt_3)\) = 340.0 Hz. This reduction in the coupling constant suggests a lower phosphorus s orbital contribution to the PtPμ bond than that of simple tertiary phosphines.

Crystallisation of the major product from dichloromethane/ethanol afforded a pale yellow air-stable crystalline material and elemental analytical data obtained on this sample for (C, H, and P) agreed reasonably well with the values calculated for the formulation [Pt(μ-PPhH)_2{Mo(CO)_3}_2(dppe)]. It was decided to undertake a single-crystal X-ray structure determination to determine any relevant structural features. The structural determination was carried out at University College London by Professor A. J. Deeming.

7.3.2 Crystal Structure of [Pt(μ-PPhH)_2{Mo(CO)_3}_2(dppe)]

Crystals suitable for structure determination were grown from dichloromethane/ethanol by slow evaporation. The complex crystallises in the monoclinic space group \(P2_1/n\) with unit cell dimensions \(a = 14.294(4)\) Å, \(b = 19.439(6)\) Å, \(c = 18.318(5)\) Å, \(β = 101.30(2)°\) with four molecules per unit cell. The structure was refined to \(R = 0.057\) and \(R_w = 0.057\). Important bond lengths and angles are given in Table 7.1 and views of the complex are shown in Figures 7.10 and 7.11.
Figure 7.10 Structure of [Pt(μ-PhH)₂Mo(CO)₅]₂(dppe)
Figure 7.11 Structure of $\text{[Pt(\mu-\eta^5-PPhH)(Mo(CO)_5)_2(dppe)]}$
Table 7.1 Selected bond lengths and angles for \([\text{Pt(μ-PPH)}_2\{\text{Mo(CO)}_5\}_2(\text{dppe})]\)

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<th>Bond lengths (Å)</th>
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<td>Mo(2)-C(25)</td>
<td>2.047(12)</td>
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The geometry at platinum(II) is essentially planar [P(1)-Pt-P(3) 177.4(1) ° and P(2)-Pt-P(4) 178.0(1) °]. In the final cycles of refinement the difference maps indicated H-atom positions close to the phosphido phosphorus atoms but these were not distinct and were not included in the final model. The location of H-atoms attached to the bridging phosphido ligands is consistent with the observed ¹H n.m.r. data. The bridging phosphido ligand exhibits large Pt-P-Mo angles, [Pt-P(1)-Mo(1) 123.5(1) ° and Pt-P(2)-Mo(2) 122.1(1) °], much larger than other phosphido bridged heterometallic complexes structurally characterised where the Pt-P-M (M = Re, Cr) angles are much more acute. For example, the complex [(CO)₄Cr(μ-PPh₂)(μ-H)Pt(PEt₃)₂]²⁺ contains a Pt-P-Cr angle of 75.9 ° and the equivalent angle in [Cp(NO)Re(μ-PPh₂)(μ-H)Pt(PPh₃)₂]³⁺ is 77.21(7) °. These acute angles are due to the short Pt-M interactions in these complexes (usually less than 3 Å) in comparison to the much longer Pt-Mo distances observed in [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)]. These chromium-platinum and rhenium-platinum phosphido-bridged complexes with small Pt-P-M angles exhibit low-field chemical shifts for the phosphido ligands (δ = 136 and 128.7 respectively) these δ(P) values are consistent with the presence of a metal-metal bond. In comparison, the large Pt-P-Mo angles in the complex [Pt(μ-PPhH)(Mo(CO)₅)₂(dppe)] and therefore the long metal-metal interactions are consistent with the high-field values of δ(P) (δ -53) for the phosphido resonance, consistent with previous literature correlations. The two molybdenum-platinum distances [Pt-Mo(1) 4.349(2) Å, Pt-Mo(2) 4.320(2) Å] are asymmetrically bridged by the two μ-PPhH ligands [Pt-P(1) 2.361(3) Å, Pt-P(2) 2.363(2) Å and Mo(1)-P(1) 2.574(2) Å, Mo(2)-P(2) 2.571(2) Å].

The largest P-Pt-P angles are those between the dppe and the phosphido ligands, not between adjacent phosphido ligands [P(1)-Pt-P(4) 96.6(1) ° and P(2)-Pt-P(3) 96.3(1) ° whereas between the phosphido ligands P(1)-Pt-P(2) 82.6(1) ° and for the dppe P(3)-Pt-P(4) 84.5(1) °]. This last value fixed by the presence of the chelating ligand is consistent with values found in other Pt(dppe) systems. The large angles between the dppe and the phosphido ligands compared with the angle between adjacent phosphido ligands is reflective of the larger steric requirements of the former ligands. The Pt-P(phosphido) bonds are longer than the Pt-P(dppe) bonds [Pt-P(1) 2.361(3) Å and Pt-P(2) 2.363(2) Å compared with Pt-P(3) 2.300(3) Å and Pt-P(4) 2.301(2) Å]. These increased bond lengths are the result of the trans-influence of the dppe ligand. This large trans-influence of the dppe ligand is also reflected in the values of ¹J(¹⁹⁵PtP) in
the $^{31}\text{P}[^1\text{H}]$ n.m.r. spectrum. The Pt-P(phosphido) bond distances are considerably shorter when the ligand in the \textit{trans} coordination site exerts only a weak \textit{trans}-influence. For example, when the \textit{trans} ligand is chloride, the Pt-P distance is reduced to 2.288(2) Å as in \textit{trans}-[Pt\text{Cl}(\text{PET}_{3})_{2}(\mu-\text{PPhH})\text{Mo(CO)}_{5}]_{2}.

Application of the Cahn, Ingold, Prelog system for naming enantiomers according to their handedness established the relative configuration of each chiral phosphorus centre in the crystal. The diastereoisomer found in the crystal is \((P,S,P_{2}S)\)-[Pt(\mu-\text{PPhH})_{2}\{\text{Mo(CO)}_{5}\}_{2}(\text{dppe})]. This stereoisomer has an enantiomeric counterpart \((P,R,P_{2}R)\)-[Pt(\mu-\text{PPhH})_{2}\{\text{Mo(CO)}_{5}\}_{2}(\text{dppe})], and they are related as mirror images. Figure 7.12 shows the Fischer projections for both these stereoisomers and their relation to one-another: they are non-superimposable mirror images. Two further stereoisomers can be drawn for this compound. These are the RS and SR stereoisomers. They are not enantiomeric with respect to the RR and SS stereoisomers and are therefore
diastereoisomeric. Careful consideration of this second pair of stereoisomers reveals
that the RS and its mirror image SR are superimposable and are therefore identical. The SR diastereoisomer of [Pt(μ-PPh)₂{Mo(CO)₅}₂(dppe)] is achiral and not optically active and we refer to this stereoisomer as the *meso* stereoisomer.

7.3.3 Separation of SS/RR and SR (Meso) Isomers of [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)]

The two products observed in the ³¹P¹H n.m.r. spectrum of [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)] can now be related to the two possible diastereoisomeric forms of the complex, the major product is the SS/RR pair of enantiomers whilst the minor product is the *meso* diastereoisomer. Although fractional crystallisation afforded pure samples of the major diastereoisomer [³¹P¹H n.m.r. evidence], this was not a satisfactory procedure for the purification of both diastereoisomeric forms. We were unable to obtain a pure sample of the minor isomer by using this procedure. All attempts of separation using thin layer chromatography proved unsuccessful. Pure samples of both diastereoisomers were obtained by separation using an analytical HPLC column and 30% ethyl acetate and 70% n-hexane mixture as eluant. By application of preparative HPLC we were able to separate and collect enough of each isomer to characterise and check the purity of both diastereoisomers by ³¹P¹H n.m.r. spectroscopy. Figure 7.13 shows the ³¹P¹H n.m.r. spectra of both fractions from the HPLC column.

7.3.4 N.M.R. Studies of [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)]

On the basis of the solid-state structure, the ³¹P¹H n.m.r. spectrum of each isomer should result from the superposition of two spin systems, AA’XX’ and AA’XX’M (A = P¹, A’ = P³, X = P³, X’ = P³, M = Pt¹⁹⁵), because of the presence of one magnetically active platinum nucleus²⁷⁹ (¹⁹⁵Pt, I = 1/2, abundance 33.8%). Thus, 66.2% of the molecules will contain no magnetically active platinum and will belong to the AA’XX’ spin system. Furthermore 33.8% of the molecules contain ¹⁹⁵Pt (AA’XX’M spin system) and analysis of this spectrum allows the evaluation of J(¹⁹⁵PtP). This spin system appears similar to that of the AA’XX’ one but with an extra doublet coupling of magnitude J(¹⁹⁵PtP), rendering each branch only 1/4 the intensity
Figure 7.13 $^{31}{\text{P}}^{(1)}$ n.m.r. spectra of pure (a) SS/RR and (b) Meso diastereoisomers of [Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_2$(dppe)]
of those of the AA’XX’ signals. The room temperature $^{31}\text{P}^{(1}\text{H})$ n.m.r. spectrum of $[\text{Pt}(\mu-\text{PPh})_2\{\text{Mo(CO)}_5\}_2(\text{dppe})]$ contained broad resonances corresponding to the dppe and phosphido ligands. Each resonance appeared as a broad doublet with its corresponding $^{195}\text{Pt}$ satellites. Initially we thought that the line broadening was the result of restricted conformational exchange of the dppe backbone. At the limit of slow exchange we expected to observe resonances for three species in solution. Figure 7.14 shows the four possible conformational isomers expected at the slow exchange limit. The two isomers giving rise to the two $A_2B_2$-type spectra are derived from the SS/RR diastereoisomers which have a $C_2$ axis of rotation and therefore equivalent phosphido ligands. The two isomers are magnetically non-equivalent and should give rise to two sets of resonances in the low temperature spectrum. Isomers (C) and (D) are derived from the meso stereoisomer at the slow exchange limit. The phosphido ligands of these isomers are magnetically non-equivalent, but the two isomers are related by their mirror images and are enantiomeric, therefore only one set of ABCD resonances should be observed in the low temperature $^{31}\text{P}^{(1}\text{H})$ n.m.r. spectrum.

The low temperature $^{31}\text{P}^{(1}\text{H})$ n.m.r. spectrum was recorded and three species were observed in the spectrum but it appeared that two were derived from the meso stereoisomer and only one from the SS/RR pair of enantiomers. These observations directly contradict our predictions and further studies were required to resolve these inconsistencies.

To probe further into the dynamic process occurring in solution we:
(a) synthesised the corresponding diphenylarsinoethane analogue \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{dpae})\),
(b) prepared the analogous compound containing an unsaturated backbone within the chelating ligand, \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{PPh}_2\text{CH}=\text{C} \text{PH}_2\text{H})\), and
(c) prepared the bis-chelating complex \([\text{Pt(\(\mu\)-PPhH)}_2\text{Mo(CO)}_4(\text{dppe})]\).

\([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{dpae})\] (dpae = Ph\(_2\)AsCH\(_2\)CH\(_2\)AsPh\(_2\)) was prepared from the \([\text{PtCl}_2(\text{dpae})]\) and \([\text{Mo(CO)}_5(\text{PPhH})]\) and was found to exist as two diastereoisomers. The \(^{31}\text{P}{'\text{H}}\) spectrum contained two sets of phosphido resonances, one major (\(\delta\) -30.1) and the other minor (\(\delta\) -43.1), and both were broadened by exchange. The major stereoisomers were assigned to the SS/RR pair of enantiomers whilst the minor was assigned as the meso form. The low-temperature \(^{31}\text{P}{'\text{H}}\) n.m.r. spectrum (-75 °C, CD\(_2\)Cl\(_2\)) contained three sets of resonances but two were derived from the minor stereoisomer (\(\delta\) -61.0, -36.0) whilst the resonance due to the major diastereoisomer appeared broader. Raising the temperature led to coalescence of the two singlets due to the minor stereoisomer (-20 °C) and at room temperature a singlet midway between the two low temperature singlets appeared indicating equal population of the two isomers at low temperature. These results reinforce the observations made in the \(^{31}\text{P}{'\text{H}}\) n.m.r spectrum of \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{dppe})\) and further provide evidence contradicting our predictions for the appearance of the spectrum at the slow exchange limit based on restricted conformational exchange of the chelating ligand.

The \(^{31}\text{P}{'\text{H}}\) n.m.r. spectrum of \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{Ph}_2\text{PCH}=\text{C} \text{PH}_2\text{H})\) should contain sharp resonances providing that the line broadening in the spectra of \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{dppe})\) and of \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{dpae})\] was the result of the dynamic behaviour of the chelating ligand. \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{Ph}_2\text{PCH}=\text{C} \text{PH}_2\text{H})\] was readily prepared in an analogous manner to the previous trimetallic complexes and the \(^{31}\text{P}{'\text{H}}\) n.m.r. spectrum of the product is shown in Figure 7.15. This spectrum was found to contain two sets of resonances \([\delta\] +54.0, -33.0 (major diastereoisomer) and \(\delta\) +56.5, -54.0 (minor diastereoisomer)] each with significant line broadening exactly analogous to the complexes already described. The similarity between the \(^{31}\text{P}{'\text{H}}\) n.m.r. spectra of \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{dppe})\) and \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{Ph}_2\text{PCH}=\text{C} \text{PH}_2\text{H})\) is quite apparent by comparison of Figures 7.8 and 7.15. All three complexes \([\text{Pt(\(\mu\)-PPhH)}_2\{\text{Mo(CO)}_5\}]_2(\text{L-L})\] (L-L = dppe, dpae,
Figure 7.15  $^{31}$P($^1$H) n.m.r. spectra of the complex [Pt(μ-
PPhH)$_2$(Mo(CO)$_3$(Ph$_3$PhC$_2$H$_2$PPh$_3$))]
Ph$_2$PCH=CHPPh$_2$ exhibit similar behaviour in the $^3$P{$^1$H} n.m.r. spectrum and we conclude that the observed line-broadening is not the result of the non-rigid chelating ligand.

In Chapter 5 the variable-temperature $^3$P{$^1$H} n.m.r. spectra of several tetrakis-phosphine complexes of iridium(III) were interpreted in terms of several conformational isomers in equilibrium at low temperature. It appeared that a general requirement for the occurrence of these rotamers was the presence of four phosphines coplanar and that pairs of trans phosphines were eclipsed. The complex [Pt($\mu$-PPhH)$_2$(Mo(CO)$_3$)$_2$(dppe)] also contains four phosphines coplanar and careful examination of the orientation of each phosphine reveals that the alternating two up and one down arrangement of substituents is maintained. The similarity between the structures of [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$] and [Pt($\mu$-PPhH)$_2$(Mo(CO)$_3$)$_2$(dppe)] indicates the latter may exist in several conformational isomeric forms. We believe that the fluxional process observed by $^3$P{$^1$H} n.m.r. spectroscopy is the exchange of rotamers in solution and at low temperature rotation about the M-P bond is slow on the n.m.r. time-scale affording various conformational isomers, of which the sterically least hindered are the most populated. Beyond this, it is difficult to make any more detailed analysis.

7.3.5 Synthesis and $^3$P{$^1$H} N.M.R. Studies of [Pt($\mu$-PPhH)$_2$Mo(CO)$_4$(dppe)]

In the complex [Pt($\mu$-PPhH)$_2$(Mo(CO)$_3$)$_2$(dppe)] only two M-P bonds are free to rotate whilst those of the chelating ligand are locked into position, restricting the number of possible conformational isomers. The title complex, whilst containing phosphido bridges, has two chelating ligands and all M-P bonds are locked in fixed orientations. Free rotation about their axis is not possible and we expect the low temperature $^3$P{$^1$H} n.m.r. spectrum to contain two sets of sharp resonances due to the two magnetically nonequivalent rigid stereoisomers.

Scheme 7.4 shows the proposed synthesis of [Pt($\mu$-PPhH)$_2$Mo(CO)$_4$(dppe)]. The major difficulty incurred during the synthesis of cis-[Mo(CO)$_4$L$_2$] derivatives is the ready thermal isomerisation to the trans isomer, and if the preparation is carried out at high temperature the major product is often the thermodynamically more stable trans isomer. A convenient and inexpensive route for the preparation of cis derivatives of [Mo(CO)$_4$L$_2$] involves the use of piperidine as a ligand that is readily substituted. Once
Scheme 7.4
prepared, [Mo(CO)$_4$(NC$_5$H$_5$)$_2$] readily substitutes the piperidine ligands at room temperature under conditions that are not strenuous or lengthy enough to effect the cis-trans isomerisation. This procedure results in up to 40% yields of [Mo(CO)$_4$(PPh$_3$)$_2$] as a colourless crystalline material.

Addition of two equivalents of methyl-lithium to a tetrahydrofuran solution of [Mo(CO)$_4$(PPh$_3$)$_2$] afforded an immediate colour change accompanied by the formation of [Mo(CO)$_4$(PPh$_3$)$_2$][Li]$_2$ as evidenced by i.r. spectroscopy. These transition-metal phosphido anions readily undergo nucleophilic attack at metal chlorides with the formation of a metal-phosphorus bond and the concomitant elimination of LiCl. Addition of [PtCl$_2$(dppe)] to the reaction mixture resulted in immediate reaction which was evident from the shift of the carbonyl absorptions in the i.r. spectrum. No further change was apparent after ten minutes and the presence of insoluble LiCl indicated that nucleophilic attack at the platinum centre had occurred. The reaction mixture was worked-up chromatographically to yield a single major product identified spectroscopically as [Pt(μ-PPPh)$_2${Mo(CO)$_4$}(dppe)]. The i.r. spectrum in the carbonyl region was almost identical to that observed for the closely related complexes\(^{290}\) \[(CO)$_4$W(μ-PPPh)$_2$M(PPPh$_3$)\] (\(M = \text{Ni, Pd, Pt}\), \[(CO)$_4$Mo(μ-PPPh)$_2$E(Cp)$_2$\] (\(E = \text{Ti, Zr}\) and \(R = \text{H, SiMe$_3$}\)).

Figure 7.16 shows the $^{31}$P($^1$H) n.m.r. spectrum of [Pt(μ-PPPh)$_2$Mo(CO)$_4$(dppe)]. The signals due to the dppe ligand appear in the familiar region whilst those of the phosphido bridge appear at high-field consistent with the absence of a platinum-molybdenum bond and also with spectra of other related complexes. The phosphido resonance in [Pt(μ-PPPh)$_2${Mo(CO)$_4$}(dppe)] appears at lower field than the phosphido resonance of [Pt(μ-PPPh)$_2$Mo(CO)$_4$(dppe)] (δ -33.6 and -140 respectively). Stelzer and Johannsen have synthesised a variety of complexes \[(CO)$_4$Mo(μ-PPPhE)(ECp)$_2$\] (\(E = \text{Ti, Zr}\) and \(R = \text{H, SiMe$_3$}\)\(^{299}\) and a range of high-field signals corresponding to the phosphido bridge were observed (δ -75.5 to -144.62). The SS/RR enantiomeric pair and the meso stereoisomer are easily identified in the high-field phosphido region (δ -134.5 and -141.8 for the major and minor stereoisomers respectively), whereas accidental coincidence of the dppe resonances makes assignment of the magnetically non-equivalent stereoisomers difficult (δ +47.04 and 47.14 for the major and minor stereoisomers respectively). Most apparent in the $^{31}$P($^1$H) n.m.r. spectrum is the large difference in $^1J(^{195}$PtP$\mu$) compared with $^1J(^{195}$PtP(dppe)) in the same complex.
Figure 7.16 $^{31}$P($^1$H) n.m.r. spectrum of [Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_2$(dppe)]
$J(^{195}\text{PtP(dppe)})$ is much larger (2063.0 Hz and 2066.0 Hz) than the corresponding coupling to the phosphido ligand (1280.0 Hz and 1304.0 Hz). These values are very similar to those found in the closely related complex $[\text{Pt(μ-PPPPh)}_2(\text{Mo(CO)}_5)_2(\text{dppe})]$ [compare 2320.0 Hz and 2187 Hz for $J(^{195}\text{PtP(dppe})$ and 1450.0 Hz for $J(^{193}\text{PtP})$].

Careful examination of the $^{31}\text{P}[^1\text{H}]$ n.m.r. spectrum (Figure 7.16) reveals that the phosphido and phosphine signals are not simple triplets of doublets with the corresponding $^{195}\text{Pt}$ satellites, the outer separation of the triplet resonances is much larger than the inner separation. Coupling constants for both sets of resonances have been obtained from reasonable spin simulations. Figure 7.17 shows the coupling constants used for the final spin simulation. The $\text{trans}$ couplings were measured directly from the spectrum and were kept constant at +216 Hz whilst the $\text{cis}$ couplings were varied until a reasonable agreement between the observed and simulated spectra was obtained. Altering these coupling constants produced significant distortions from the required spectrum. Figure 7.18 shows the close agreement between the observed and the simulated spectra using the coupling constants in Figure 7.17. Stelzer has synthesised several metal complexes containing four phosphines coplanar using chiral tetradentate ligands$^{251-259}$ (Figure 7.19). The presence of two chiral phosphorus centres results in two disatereoisomeric forms for these complexes. The $^{31}\text{P}[^1\text{H}]$ n.m.r. spectra of these complexes have been interpreted as containing $\text{AA'}XX'$ and $\text{ABCD}$ spin systems. N.m.r. simulations performed by Stelzer revealed the requirement of $\text{cis}$ and $\text{trans}$ coupling constants of opposite sign (see Chapter 5 for further details).
Figure 7.18 Simulated, (a), and observed, (b), $^{31}$P{H} n.m.r. spectra of the complex $[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_4\}](\text{dppe})]$. 
The sharp resonances observed in the $^3$P{$^1$H} n.m.r. spectrum of [Pt($\mu$-PPhH)$_2$Mo(CO)$_4$(dppe)] implied that there was no line broadening as a result of the exchange of conformers in solution. A low temperature $^3$P{$^1$H} n.m.r. spectrum was recorded (-75 °C, CD$_2$Cl$_2$) and no broadening was observed indicating that the dynamic behaviour of the dppe ligand was rapid even at low temperature. The absence of any dynamic process evident in the n.m.r spectrum is the result of restricting the possible formation of conformational isomers thereby confirming that the fluxional process evident in the $^3$P{$^1$H} n.m.r. spectrum of [Pt($\mu$-PPhH)$_2$Mo(CO)$_5$$_2$(dppe)] was a consequence of rotamer exchange.

7.3.6 Thermolysis of [Pt($\mu$-PPhH)$_2$Mo(CO)$_5$$_2$(dppe)]

The title complex, as a mixture of stereoisomers, was refluxed in tetrahydrofuran and the reaction was monitored by i.r. spectroscopy. The gradual appearance of i.r. bands to low frequency of those corresponding to the starting material indicated that a transformation was occurring. No further change was seen after 45 minutes, after which time i.r. absorptions in the carbonyl region corresponding to the product and [Mo(CO)$_6$] were evident. The thermolysis reaction was repeated and the course of the reaction was monitored by $^3$P{$^1$H} n.m.r. spectroscopy. Examination of the spectra every ten minutes indicated that the meso stereoisomer underwent rapid transformation (evident from the appearance of resonances at $\delta$ -134.5 and -141.8) whilst the SS/RR
The enantiomeric pair underwent transformation only very slowly. Although the product of the thermolysis of the SS/RR stereoisomers of \[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_3\}_2\text{(dppe)}\] remain unidentified the product isolated from thermolysis of the meso stereoisomer has been identified spectroscopically as the bimetallic complex \[\text{Pt}(\mu\text{-PPhH})_2\text{Mo(CO)}_4\text{(dppe)}\] discussed above. The transformation of the title complex would lead to \[\text{Mo(CO)}_6\] as by-product explaining the presence of its i.r. absorptions during the reaction. The transformation of the meso stereoisomer upon thermolysis is shown in Figure 7.20. Only the RS stereoisomer underwent this transformation consistent with the appropriate stereochemistry at the phosphido phosphorus, i.e. the two molybdenum substituents at phosphorus are orientated favourably for interaction and transfer of a carbonyl ligand. No intermediates were apparent in the n.m.r. spectrum during the thermolysis and therefore no further information regarding the mechanism of the transformation is available. \[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_3\}_2\text{(dppe)}\] was isolated as a minor product from the reaction of \[\text{Mo(CO)}_6\text{(PPhH)}\] and \[\text{PtCl}_2\text{(dppe)}\]. That we find this bimetallic complex in the reaction mixture indicates that \[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_3\}_2\text{(dppe)}\] is thermodynamically unstable with respect to \[\text{Mo(CO)}_6\] and \[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_3\}_2\text{(dppe)}\]. The kinetic stability of the trimetallic complex prevents complete conversion during the room temperature reaction, affording only a small quantity of \[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_3\}_2\text{(dppe)}\] after chromatographic work-up. \[\text{Pt}(\mu\text{-PPhH})_2\{\text{Mo(CO)}_3\}_2\text{(dppe)}\] has also been prepared from the direct thermolysis of \[\text{PtCl}_2\text{(dppe)}\] and \[\text{Mo(CO)}_6\text{(PPhH)}\] eliminating two molecules of HCl per molecule of bimetallic complex formed.
### 7.4 Preparation of Di- and Trimetallic Phosphido Bridged Complexes

#### 7.4.1 Reaction of \([\text{Mo(CO)}_5(\text{PPhH})]^-\) and \([\text{PtCl}_2(\text{PEt}_3)_2]\)

\([\text{Mo(CO)}_5(\text{PPhH})]^-\) undergoes nucleophilic substitution at \([\text{PtCl}_2(\text{dppe})]\) to afford the bis-substituted platinum(II) complex \([\text{Pt}(\mu-\text{PPhH})_2{\text{Mo(CO)}_5}_2(\text{dppe})]\), characterised by X-ray crystallography. The reaction of the same anionic ligand with either pure cis-\([\text{PtCl}_2(\text{PEt}_3)_2]\) or a mixture of the cis and trans-isomers was investigated and found to afford a range of products, both mono- and di-substituted, two of which are characterised by single-crystal X-ray crystallography.

\([\text{PtCl}_2(\text{PEt}_3)_2]\) was found to react with a 1:1 mixture of \([\text{Mo(CO)}_3(\text{PPhH}_2)]\) and DBU in tetrahydrofuran, evident from the shift of the carbonyl absorptions to lower frequency. Chromatographic work-up of the reaction mixture afforded three well-separated bands, all of which were extracted into dichloromethane and successfully crystallised from dichloromethane/ethanol mixtures to afford pale yellow crystalline solids.

The product isolated from the slowest moving band on the t.l.c. plate was characterised by elemental analysis. Elemental analytical data obtained on the crystalline sample (C, H, and Cl) were consistent with values calculated for several possible formulations, of which two were \([\text{Pt}(\mu-\text{PPhH})_2{\text{Mo(CO)}_5}_2(\text{PEt}_3)_2].\text{CH}_2\text{Cl}_2\) and \([\text{Pt}(\mu-\text{PPhH}){\text{Mo(CO)}_5}_2\text{Cl}(\text{PEt}_3)_2]\). The \(^{31}\text{P}\{^1\text{H}\}\text{n.m.r. spectrum consisted of two sets of well-separated resonances. The high-field resonance was assigned to the phosphido ligand by analogy with previous n.m.r. data correlations. Restoring proton coupling confirmed correct assignment of this resonance, and the extra doublet splitting was consistent with a single proton directly bonded to the phosphido bridge. The triplet splitting of the phosphido resonance \[^1J(\text{PP}) = 25.5\text{ Hz}\] was consistent with coupling to two equivalent PET$_3$ ligands and the small size of this coupling confirmed a trans arrangement of PET$_3$ ligands. The value of \(^1J(\text{PtPP})\) of 2078.0 Hz is much smaller than that coupling we would expect if the phosphorus donor was trans to a chloride (3500 Hz in cis-\([\text{PtCl}_2(\text{PEt}_3)_2])\). We have already observed that the \(^1J(\text{PtPP})\) for a phosphido bridge trans to a phosphine is much smaller than \(^1J(\text{PtP})\) for a phosphine trans to a phosphine. The \(^{31}\text{P}\{^1\text{H}\}\text{n.m.r. spectrum of }[\text{Pt}(\mu-\text{PPhH})_2{\text{Mo(CO)}_5}_2(\text{dppe})] contained
phosphido resonances with $^1J(^{195}\text{Pt}\mu) = 1450$ Hz, trans to dppe. The larger value of $^1J(^{195}\text{Pt}\mu)$ (2078 Hz) implies that a phosphido ligand trans to a chloride might be expected. That $^1J(^{195}\text{Pt}\mu)$ for this new complex is smaller than $^1J(^{195}\text{PtP})$ for cis-[PtCl$_2$(PEt$_3$)$_2$] does not exclude the possibility of the phosphido being trans to a chloride ligand and the product therefore being the mono-substituted platinum(II) complex. If the Pt-P phosphido bond does not contain as much s orbital character as the Pt-P phosphine bond, we expect intuitively the coupling constant to be smaller. Thus the magnitude of $^1J(^{195}\text{Pt}\mu)$ indicates that the complex contains phosphido trans to a chloride. The PEt$_3$ resonance was broad at room-temperature with $^1J(^{195}\text{PtP})$ in the range expected for trans phosphines. Approximate integral ratios for phosphido : phosphine indicates the presence of two of each type of ligand in the complex, in direct contradiction with the proposal based on platinum-phosphorus coupling constants.

Because of the ambiguity regarding the nature of the phosphido complex we decided to undertake a single-crystal X-ray structure determination. The structure was solved at University College London by Professor A. J. Deeming.

7.4.2 Crystal Structure of [Pt(μ-PPhH)(Mo(CO)$_3$)Cl(PEt$_3$)$_2$]

Suitable crystals for single-crystal X-ray structure determination were grown by slow evaporation of a dichloromethane/ethanol solution of the complex. The complex crystallises in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 11.159(4)$ Å, $b = 24.570(1)$ Å, $c = 11.897(4)$ Å, $\beta = 106.61(3)$ ° with four molecules per unit cell. The structure was refined to $R = 0.0458$ and $R_w = 0.0500$. Important bond lengths and angles are given in Table 7.2 and views of the complex are shown in Figures 7.21 and 7.22.

Immediately apparent is the presence of a chloride ligand trans to a phosphido confirming that only a single chloride ligand has been substituted. The geometry about the platinum centre is essentially planar [Cl-Pt-P(1) 177.5(1) ° and P(3)-Pt-P(2) 169.9(1) °]. The larger angles P(2)-Pt-P(1) 95.6(1) ° and P(1)-Pt-P(3) 93.8(1) ° compared to P(2)-Pt-Cl 83.3(1) ° and P(3)-Pt-Cl 87.4 ° are reflective of the larger steric requirements of the phosphido ligands. Two ethyl groups on P(2) and P(3) nearest to the phosphido ligand are directed away from the metal centre whereas the remaining ethyl groups are orientated towards the platinum centre. The Mo-P(1)-Pt bond angle 120.9(1) ° is very
Figure 7.21 Structure of [Pt(µ-PPhH)\{Mo(CO)$_3$\}Cl(PEt)$_3$]$_2$
Figure 7.22 Structure of \( \{\text{Pt(\mu-PPhH)\{Mo(CO)\}_3Cl(PEt)_3}\} \)
Table 7.2 Selected bond lengths and angles for [Pt(μ-PPhH)(Mo(CO)₅)Cl(PEt₃)₂]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
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<th>Bond angles (deg.)</th>
<th></th>
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</thead>
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<td>Pt-P(1)</td>
<td>2.288(3)</td>
<td>P(1)-Pt-P(2)</td>
<td>95.6(1)</td>
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<td>Pt-P(2)</td>
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<td>P(1)-Pt-P(3)</td>
<td>93.8(1)</td>
</tr>
<tr>
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<td>2.325(4)</td>
<td>P(2)-Pt-P(3)</td>
<td>169.9(1)</td>
</tr>
<tr>
<td>Pt-Cl</td>
<td>2.384(4)</td>
<td>P(1)-Pt-Cl</td>
<td>177.5(1)</td>
</tr>
<tr>
<td>Mo-P(1)</td>
<td>2.601(3)</td>
<td>P(2)-Pt-Cl</td>
<td>83.3(1)</td>
</tr>
<tr>
<td>Mo-C(1)</td>
<td>1.972(16)</td>
<td>P(3)-Pt-Cl</td>
<td>87.4(1)</td>
</tr>
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<td>2.052(15)</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>2.053(11)</td>
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</tr>
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</tr>
<tr>
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<td>Mo-c(5)-O(5)</td>
<td>178.4(14)</td>
</tr>
</tbody>
</table>
close to those found in the trimetallic complex [Pt(μ-PPhH)₂{Mo(CO)₅}(dppe)] (Pt-P(1)-Mo(1) 123.5(1) ° and Pt-P(2)-Mo(2) 122.1(1) °). The Mo-Pt distance [Pt-Mo 4.255(2) Å] is asymmetrically bridged by the phosphido ligand [Pt-P(1) 2.288(3) Å and Mo-P(1) 2.601(3) Å] consistent with previous observations. The platinum-phosphido bond-length, Pt-P(1), of 2.288(3) Å is much shorter than the two Pt-Phosphido bond-lengths in [Pt(μ-PPhH)₂{Mo(CO)₅}(dppe)] (Pt-P(1) 2.361(3) Å and Pt-P(2) 2.363(2) Å).

This shorter bond-length is consistent with the larger value of ^1(^{195}PtP) observed in the ^31P{^1H} n.m.r. spectrum. The shorter bond length is a consequence of the smaller trans-influence of the chloride ligand compared to that of the chelating dppe ligand. Although this Pt-phosphido bond length appears short, it is much longer than a Pt-phosphine bond lengths trans to a chloride ligand (2.258(4) Å in cis-[PtCl₂(PPh₃)₂]).²⁹¹ The platinum-chlorine bond-length of 2.384(4) Å is much longer than the platinum-chlorine bond-lengths in trans-[PtCl₂(PPh₃)₂] (2.294(4) Å)²⁰¹,²⁹² where chloride is trans to chloride. It is also somewhat longer than in cis-[PtCl₂(PPh₃)₂] where the Pt-Cl bond-length trans to PPh₃ has increased to 2.361(5) Å.²⁹¹ This lengthening of the Pt-Cl bond is an indication of the magnitude of the trans effect of the phosphido ligand.

### 7.4.3 ^31P{^1H} N.M.R Studies of [Pt{μ-PPhH}(Mo(CO)₅)Cl(PPh₃)₂]

The room-temperature ^31P{^1H} n.m.r. spectrum of [Pt(μ-PPhH)(Mo(CO)₅)Cl(PPh₃)₂] has been reported to contain a sharp triplet resonance [δ -66.4, ^1J(^{195}PtP) = 2078 Hz] assigned to the phosphido ligand and a broad doublet (δ +10.5) due to PPh₃. Variable-temperature ^31P{^1H} n.m.r. studies indicated that there were several isomers in solution and that they were undergoing rapid exchange at room-temperature. Figure 7.23 shows the variable-temperature ^31P{^1H} n.m.r. spectra of [Pt(μ-PPhH)(Mo(CO)₅)Cl(PPh₃)₂].

At low temperature (-75 °C, CD₂Cl₂) the high-field resonance was split into a doublet of doublets [δ -66.5, ^1J(PP) = 17.3 Hz and ^2J(PP) = 9.6 Hz]. The small values of ^2J(PP) indicates coupling of the phosphido phosphorus to magnetically non-equivalent PPh₃ ligands. At low temperature the PPh₃ ligands are no longer magnetically equivalent and appear as an AB quartet [δ +9.0 (B₁), and +14.1 (A₁)]. These diastereotopic phosphorus nuclei couple to the phosphido phosphorus with widely different coupling constants [^1J(PP) = 17.3 Hz(B₁), 9.6 Hz(A₁)], and this difference is
Figure 7.23 Variable temperature $^{31}$P($^1$H) n.m.r. spectra of the $\text{PEt}_3$ region of the complex \([\text{Pt}(\mu-\text{PPhH})\{\text{Mo(CO)}_5\}\text{Cl(PEt}_3\)\text{]}}\)
Figure 7.24  Low temperature (-75 °C) $^3P('H)$ n.m.r spectrum of [Pt(μ-
PPhH)(Mo(CO)$_3$)Cl(PEt$_3$)$_2$]

$J(\text{PtA}) \neq J(\text{PtB})$
most apparent in the separate branches of the AB quartet. Both PE₃ ligands couple to platinum but with slightly different values \(^1J(^{195}\text{PtPA}_1) = 2413.0 \) Hz and \(^1J(^{195}\text{PtPB}_1) = 2526.4 \) Hz. These values are in the range expected for trans PE₃ ligands, for example, trans-[PtCl₂(PEt₃)] has \(^1J(^{195}\text{PtP}) = 2400 \) Hz. It appears that \(^1J(^{195}\text{PtP}) \) depends only weakly on the nature of the cis ligand. An order of decreasing cis influence (as measured by \(^1J(^{195}\text{PtP}) \) for [Pt(C₂F₆)X(PEt₃)]), (X = halide or pseudohalide) has been established. The changes in \(^1J(^{195}\text{PtP}) \) from 2012Hz (X = CO) to 2603Hz (X = NO₂) are less pronounced than those observed from changing the trans ligands.\(^{284}\) The trans \(^2J(\text{PP}) \) of 366 Hz is much greater than the trans \(^3P-\text{^3P} \) coupling in [Pt(μ-PPhH₂)[Mo(CO)₅]₂(dppe)] \(^1J(\text{PP}) = 213.0 \) Hz).

After assignment of the AB quartet due to the major isomer and its corresponding platinum satellites several unassigned resonances remained, which belong to minor products accounting for only 3-5% of the total sample. Careful examination of the low temperature \(^{31}\text{P}[^1\text{H}] \) n.m.r. spectrum revealed that each minor species consisted of an AB quartet resonance [δ +8.60 (B₂), +13.75 (A₂) and +8.44 (B₃), +13.60 (A₃)], and that separate branches of the AB quartets consisted of smaller couplings of vastly different size \(^2J(\text{PPA}_n) = 9.0 \) Hz, \(^2J(\text{PPB}_n) = 15.0 \) Hz and \(^2J(\text{PPA}_n) = 9.6 \) Hz, \(^2J(\text{PPB}_n) = 15.4 \) Hz] similar to the values found for the major species. Figure 7.24 shows an expansion of the low temperature \(^{31}\text{P}[^1\text{H}] \) n.m.r. spectrum to clarify the situation. Raising the temperature of the n.m.r. solvent lead to exchange of the minor

![Figure 7.25](image-url)
isomers with the major isomer and to exchange of the PEt₃ environments. Each of the resonances in the low temperature n.m.r. spectrum has been assigned to one of three conformational isomers with an ABX spin system. Figure 7.25 shows each of the three possible conformational isomers. The isomer found in the crystal is the sterically least hindered conformer, (A), and has been assigned to the major species in the low temperature ³¹P{¹H} n.m.r. spectrum (A₁ and B₁, Figure 7.4). Rotamers (B) and (C) are some what less populated as a result of unfavourable steric interactions with both bulky substituents on the same side of the PtP₃ plane. Rapid rotation about the M-Phosphido bond averages the environments of P^A and P^B leading to the exchange of phosphines at high temperature, as well as exchange of the rotamers. At the high temperature limit we expect a simple doublet pattern for the PEt₃ resonance.

7.4.4 Characterisation of cis- and trans-[Pt(μ-PPhH)₂(Mo(CO)₅)₂(PEt₃)₂]

There are two possible geometrical isomers resulting from the substitution of both chloride ligands in [PtCl₂(PEt₃)₂]; these are the cis and trans-[Pt(μ-PPhH)₂(Mo(CO)₅)₂(PEt₃)₂] (Figure 7.26). Both these isomers have been identified from the reaction of [PtCl₂(PEt₃)₂] with [Mo(CO)₅(PPhH)]⁺ and the formation of these products seems to be independent of whether pure cis or a mixture of cis- and trans-[PtCl₂(PEt₃)₂] was used.
The *cis* isomer occurred as the minor product from the reaction and has been identified from its characteristic $^{31}$P{$^1$H} n.m.r. spectrum (Figure 7.27). A large value of $^3$P-$^3$P coupling confirmed the *cis* geometry at platinum, although the observed *trans* $^2$J(PPμ) of 200 Hz is much smaller than the coupling between *trans* PEt$_3$ ligands (compare $^2$J(PP) of 366 Hz in *trans*-\{Pt(μ-PPhH)(Mo(CO)$_5$)$_2$Cl(PEt$_3$)]). This reduced value of $^2$J(PP) confirms the presence of PEt$_3$ *trans* to {PPhH(Mo(CO)$_5$)} (compare $^2$J(PPμ) = 213.0 Hz and $^2$J(PPμ) = 222.0 Hz for \{Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_2$(dppe)] and \{Pt(μ-PPhH)$_2$(Mo(CO)$_5$)}(dppe) respectively). The high-field resonance (δ +5.7, $^2$J(PPμ) = 200 Hz) was assigned to the singly-bridging phosphido ligand consistent with previous literature correlations.$^2$ We have successfully simulated the second order coupling observed in the $^3$P{$^1$H} n.m.r. spectrum of *cis*-\{Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_2$(PEt$_3$)$_2$\}. Figure 7.28 shows the close agreement between the simulated and observed spectra. We were required to employ *cis* and *trans* couplings of opposite sign to enable correct simulation; *cis* $^2$J(PP) = -15 Hz and *trans* $^2$J(PP) = +200 Hz were used and gave simulated spectra with both weaker lines of the multiplet pattern on the outside of the large doublet resonance. Couplings of the same sign afforded significant discrepancies in the pattern of the simulated spectra. The use of *cis* and *trans* coupling constants of opposite sign in spin simulations of $^3$P{$^1$H} n.m.r. spectra has been a characteristic feature of spin systems containing four phosphines coplanar.

Finally, the *trans*-\{Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_2$(PEt$_3$)$_2$\} isomer was isolated from the reaction mixture as a pale yellow crystalline material from a dichloromethane/ethanol mixture. The $^3$P{$^1$H} n.m.r. spectrum of this isomer contained two sets of resonances each consisting of a high-field (phosphido) and a low-field (PEt$_3$) counterpart. The high-field chemical shift of the phosphido resonance is consistent with the absence of a metal-metal bond.$^{274}$ The chemical shift is close to those found in the $^3$P{$^1$H} n.m.r. spectra of \{PtMn$_2$(H)(μ-PPh$_2$)$_3$(CO)$_8$\} (δ -84, μ-PPh$_2$ bridging a non-bonded metal pair) and \{CpMoPt(H)(μ-PPh$_2$)$_2$(CO)$_8$\} (δ -130.8) and significant shifts of the phosphido resonance to low-field occur upon Pt-Mo and Pt-Mn bond formation (δ +124.0 and δ +152.8 in \{PtMn$_2$(H)(μ-PPh$_2$)$_3$(CO)$_8$\} and \{CpMoPt(H)(μ-PPh$_2$)$_2$(CO)$_8$\} respectively). The two phosphido resonances appear as triplets [δ -72.2 (t) and -68.5 (t)] and are recognised as the two possible diastereomeric forms: the SS/RR enantiomeric pair and the *meso* stereoisomer. The small triplet coupling $^2$J(PP) = 13.6 Hz and 12.7 Hz is consistent with the *trans* arrangement of PEt$_3$ ligands. The PEt$_3$ resonances appeared as
Figure 7.27 $^{31}\text{P}^{1}\text{H}$ n.m.r. spectrum of the complex $\text{cis-}[\text{Pt}(\mu-\text{PPhH})_2(\text{PET}_3)_2]$
Figure 7.28: Simulated, (a), and Observed, (b), $^{1}P(H)$ n.m.r. spectra of cis-[Pt(μ-
PPhH)₂(Mo(CO)₅)₂(PE₃)₂]₂.
a broad singlet (δ -1.0) and a triplet (δ -1.8). The similarity between the spectra of trans-[Pt(μ-PPhH)(Mo(CO)₃)Cl(PEt₃)] and trans-[Pt(μ-PPhH)₂(Mo(CO)₃)₂(PEt₃)], both containing a sharp phosphido resonance and a broad PEt₃ resonance, implies that the low temperature ³¹P{¹H} n.m.r. spectrum should consist of several rotameric forms in slow exchange on the n.m.r. time-scale. Before further ³¹P{¹H} n.m.r. studies were performed, we decided to undertake a single-crystal X-ray structure determination.

7.4.5 Crystal structure of trans-[Pt(μ-PPhH)₂(Mo(CO)₃)₂(PEt₃)]

Crystals suitable for structure determination were grown by layering a dichloromethane solution of the complex with ethanol and allowing them to diffuse slowly. The structure was solved at University College London by B. Cockerton. The complex crystallises in the monoclinic space group P2₁/a with unit cell dimensions a = 20.027(9) Å, b = 10.465(4) Å, c = 20.774(9) Å, β = 103.00(3) °. The structure was refined to R = 0.085 and Rₓ = 0.068. Important bond lengths and angles are given in Table 7.3 and views of one of the two independent molecules are shown in Figures 7.29 and 7.30.

The unit cell of [Pt(μ-PPhH)₂(Mo(CO)₃)₂(PEt₃)] contains two crystallographically independent but practically identical molecules, which are located at two independent inversion centres so that the asymmetric unit consists of two half molecules. Each of the independent molecules has C₁ molecular symmetry. Only one half of the molecule is unique, the other coordinates have been generated by crystal symmetry.

Mo(1), Mo(1a), Mo(2) and Mo(2a) retain approximate octahedral symmetry and Pt(1) and Pt(2) are planar with P(1)-Pt-P(1a), P(2)-Pt-P(2a), P(3)-Pt-P(3a) and P(4)-Pt-P(4a) bond angles of 180 ° as required by the crystal symmetry. The Pt-Mo distances [Pt(1)-Mo(1) 4.504(2) Å, Pt(2)-Mo(2) 4.573(2) Å] are asymmetrically bridged by the two phosphido ligands [Pt(1)-P(1) 2.407(5) Å, Pt(2)-P(3) 2.397(4) Å and Mo(1)-P(1) 2.644(5) Å, Mo(2)-P(3) 2.648(5) Å]. This asymmetrically bridging mode has been observed in several other molybdenum-platinum complexes. For example, those prepared by Braunstein and co-workers [(Cp)MoPtH(μ-PPh₂)₂(CO)₄]²⁺ and [Cp₂Mo₂Pt(μ-PPh₂)₂(CO)₃]²⁻ typically have Mo-phosphido bond lengths of 2.429 (4) Å and Pt-phosphido lengths of 2.254 (4) Å. Figure 7.31 shows the crystal structure of [CpMoPtH(μ-PPh₂)₂(CO)₄]₂ and [(CO)₄Mn(μ-PPh₂)PtH(μ-PPh₂)₂Mn(CO)₄]²⁻ determined...
Figure 7.29  Structure of $\text{trans-[Pt(\mu-\text{PPh})_2(Mo(CO)_5)_2(P\text{Et}_3)_2]}$
Figure 7.30 Structure of trans-[Pt(μ-PPH₂)(Mo(CO)₅)(PET₃)]
Table 7.3 Selected bond lengths and angles for [Pt(μ-PPhH)₂(Mo(CO)₅)₂(PEt₃)₂]

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by Braunstein. These complexes contain phosphido ligands bridging both metal-metal bonding and non-bonding distances ($\delta +154.5$ and $\delta +124.0$ for the phosphido ligand bridging the metal-metal bonds of $[\text{CpMoPtH}(\mu-\text{PPh}_2)\text{CO}]_2$ and $[(\text{CO})_2\text{Mn}(\mu-\text{PPh}_2)\text{PtH}(\mu-\text{PPh}_2)\text{Mn}(\text{CO})_4]$ respectively and $\delta -130.8$ and $\delta -84.0$ for the phosphido ligands bridging the non bonding metal-metal interactions in the same two compounds).

This provides a good example of the chemical shift differences we might expect in the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum for the different bonding types. The $\text{Pt-P(\mu)-}$

**Figure 7.31**

(a) $[\text{CpMoPtH}(\mu-\text{PPh}_2)\text{CO}]_2$  
(b) $[(\text{CO})_2\text{Mn}(\mu-\text{PPh}_2)\text{PtH}(\mu-\text{PPh}_2)\text{Mn}(\text{CO})_4]$  

Mo bond angles $[\text{Mo(1)-P(1)-Pt(1)} 126.1(2) ^{\circ}$ and $\text{Mo(2)-P(3)-Pt(2)} 130.0(2) ^{\circ}$] are similar to those already observed in the related complexes $[\text{Pt}(\mu-\text{PPhH})_2(\text{Mo(CO)})_3]_2(\text{dppe})$ $[120.9(1) ^{\circ}$ and $123.5(1) ^{\circ}$] and $\text{trans-[Pt}(\mu-\text{PPhH})(\text{Mo(CO)})_3\text{Cl}(\text{PEt}_3)_2]$ $[122.1(1) ^{\circ}$]. The $\text{Pt-P-Mo}$ bond angles are clearly longer than those in $[\text{Pt}(\mu-\text{PPhH})_2(\text{Mo(CO)})_3]_2(\text{dppe})$ and $[\text{Pt}(\mu-\text{PPhH})(\text{Mo(CO)})_3\text{Cl}(\text{PEt}_3)_2]$ and can be associated with the longer $\text{Pt-Mo}$ distances as well as the longer $\text{Pt-phosphido}$ bond lengths. The platinum-phosphido bond-lengths are much longer $[\text{Pt(1)-P(1), Pt(1)-P(1a)} 2.407 \AA$ and $\text{Pt(2)-P(3), Pt(2)-P(3a)} 2.397(4) \AA$] than those in $[\text{Pt}(\mu-\text{PPhH})_2(\text{Mo(CO)})_3]_2(\text{dppe})$ and $\text{trans-[Pt}(\mu-\text{PPhH})(\text{Mo(CO)})_3\text{Cl}(\text{PEt}_3)_2]$ $[\text{Pt-P(1)} 2.361(3) \AA, \text{Pt-P(2)} 2.363(2) \AA$ and $\text{Pt-P(1)} 2.288(3) \AA$ respectively]. These longer bond lengths are consistent with the smaller values of $^{1}J(^{195}\text{PtP}) (1110.0 \text{ Hz})$ found in the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum. The longer bond lengths are not due to steric interactions alone (as evident from the shorter $\text{Pt-Phosphido}$ bond-lengths in $[\text{Pt}(\mu-\text{PPhH})_2(\text{Mo(CO)})_3]_2(\text{dppe})$) but are a consequence of the strong $\text{trans}$ influence exerted
by the phosphido ligand (apparent from the long Pt-Cl distances in trans-[Pt(μ-
PPhH)(Mo(CO)₅)Cl(PEt₃)]). These long Pt-P(μ) distances are reflected in the slightly
greater Pt-P(μ)-Mo bond angles than those observed in [Pt(μ-PPh)₂{(Mo(CO)₅)₂(dppe)}]
and trans-[Pt(μ-PPhH)(Mo(CO)₅)Cl(PEt₃)] and consequently in the longer Pt-Mo non-
bonding distances. The trans PEt₃ ligands contain one ethyl substituent
directed away from the platinum centre (that substituent nearest to the Mo(CO)₅ and
phenyl group of the cis phosphido ligand) whilst the other two ethyl groups are directed
towards the metal centre where there are no bulky substituents.

The configuration of the complex found in the crystal has been determined as
(P1R,J1S)-[Pt(μ-PPhH)₂{(Mo(CO)₅)₂(PEt₃)}] and this molecule is clearly the meso
form.

7.4.6 ³¹P{¹H} N.M.R. Studies of trans-[Pt(μ-PPhH)₂{(Mo(CO)₅)₂(PEt₃)}]

By analogy with the variable-temperature ³¹P{¹H} n.m.r. spectrum of trans-
[Pt(μ-PPhH)(Mo(CO)₅)Cl(PEt₃)], we expect the room-temperature spectrum of [Pt(μ-
PPhH)₂{(Mo(CO)₅)₂(PEt₃)}] to be the result of several rotamers in exchange. The variable-
temperature ³¹P{¹H} n.m.r. study of the title complex is shown in Figure 7.32 and an
expansion of the low-temperature spectrum corresponding to the PEt₃ resonances is
shown in Figure 7.33. The low temperature spectrum consists of at least three sets of
resonances, evident from the phosphido signals, and therefore three conformational
isomers. The meso stereoisomer found in the crystal was seen to contain pairs of trans
phosphines staggered, assuming that only staggered conformations are possible the six
rotamers expected are shown in Figure 7.34. The resonance at δ -72.2 remained sharp
throughout the whole temperature range examined, as did its PEt₃ counterpart at δ -
1.8 (t), and these resonances have been assigned to a totally symmetrical conformer
(A₂X₂). The phosphido resonance [δ -68.5 (t)] separated into a triplet and a non first-
order multiplet at -75 °C, whilst its corresponding PEt₃ resonances appeared as an AB
quartet and a triplet, i.e an ABXY and an A₂X₂ spin system at low temperature.

The six staggered conformational isomers in Figure 7.34 do not account for the
isomers present in the low-temperature ³¹P{¹H} n.m.r. spectrum. Only one of the
rotamers in Figure 7.34 contains pairs of trans phosphines magnetically equivalent yet
the low-temperature ³¹P{¹H} n.m.r. spectrum contains two conformers with two pairs
of magnetically equivalent nuclei. The conformer found in the crystal should contribute

-367-
Figure 7.32  Variable temperature $^{31}$P{'H} n.m.r. spectra of the PEt$_3$ region of the complex $^{trans}$-[Pt(μ-PPh)$_2$(Mo(CO)$_3$)$_2$(PEt)$_3$]
Figure 7.33  Low temperature $^{31}$P($^1$H) n.m.r. spectra of the PEt$_3$ region of the complex $\text{trans-}[\text{Pt(μ-PPhH)}_2\{\text{Mo(CO)}_5\}_2(\text{PEt}_3)_2]$
Figure 7.34

(A) 

(B) 

(C) 

(D) 

(E) 

(F)
an $A_2X_2$ spin system to the low-temperature n.m.r. spectrum and we have assigned this to the triplet resonances at $\delta$ -1.8 and $\delta$ - 67.8. This rotamer was established as the meso stereoisomer (A). This implies that the AB quartet resonance ($\delta$ -2.4 and +5.8) must correspond to a conformer of the meso stereoisomer because these undergo exchange as the temperature of the n.m.r. solvent is raised and eventually coalesce. Both remaining meso conformers are expected to contribute ABXY coupling patterns and the $^{31}P\{^1H\}$ n.m.r. spectrum is consistent with either of these conformational isomers.

The minor non-fluxional rotamer must therefore belong to an SS/RR stereoisomer but the remaining $A_2X_2$ resonance to be assigned is not consistent with any of the rotamers (D), (E) or (F) in the staggered conformation. In an eclipsed conformation this stereoisomer can exist in a totally symmetrical form (G) (Figure 7.35) with pairs of trans phosphine magnetically equivalent, related by a $C_2$ axis. The existence of eclipsed conformational isomers of complexes containing four phosphines coplanar has been observed for several compound characterised crystallographically, [IrCl$_2$(PMePh)$_4$][ClO$_4$], [IrCl$_2$(PMe$_3$)$_2$(PMe$_3$Ph)]ClO$_4$, [IrCl$_2$(PMe$_3$)$_3$(PPh$_2$H)]ClO$_4$ and for the related complex [Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_3$(dppe)].

The AB quartet coupling pattern observed for the unsymmetrical conformer of the meso stereoisomer has cis $^2J(PP)$ coupling constants of widely disparate values ($\delta$ +5.8 $^2J(PP) = 8.8$ Hz and $\delta$ -2.4 $^2J(PP) = 16.6$ Hz). Different couplings of a phosphido
phosphorus nucleus to magnetically non-equivalent \( \text{cis} \) PEt\(_3\) ligands has been observed in the low-temperature \(^{31}\text{P}(^1\text{H})\) n.m.r. spectrum of \([\text{Pt}(\mu-\text{PPPhH})(\text{Mo}(\text{CO})_3\text{Cl})(\text{PEt}_3)_2]\) \(^{1}J(\text{PP}) = 17.3\text{ Hz and 9.6 Hz.}\)

7.4.7 Correlation of \(^{1}J(^{195}\text{PtP})\) and Pt-P bond distances

The possibility of a correlation between \(^{1}J(^{195}\text{PtP}))\) and Pt-P bond distances in platinum(II) phosphine complexes has been the subject of several investigations.\(^{283-285}\) Both parameters are expected to be sensitive to the s orbital character of the bond.\(^{282}\) Powell has recently reported a good correlation for \(^{1}J(^{195}\text{PtP}_\mu)/\text{Pt-P bond length data for the PtP}_3\) fragments in some closely related complexes \([\text{Cp(NO)}\text{Re}((\mu-\text{PR}_2)(\mu-\text{H})\text{Pt}(\text{PPh}_3)_2]^{+}\) \(\text{R} = \text{Ph, Cy}\) and \([\text{Cp(NO)}\text{HRe}((\mu-\text{PCy}_2)\text{Pt}(\text{PPh}_3)_2]^{+}\). Particularly noteworthy was that for comparable bond lengths (Pt-PR\(_3\) and Pt-P\(_\mu\)), \(^{1}J(^{195}\text{PtP}_\mu)\) was less than 50% of that for \(^{1}J(^{195}\text{PtPR}_3)\), suggesting a lower phosphorus s-orbital contribution to the Pt-P\(_\mu\) bond.

We have found that in the platinum-molybdenum phosphido complexes Pt-P\(_\mu\) bond lengths correlate well with \(^{1}J(^{195}\text{PtP})\), with longer bonds being associated with decreasing \(J\) values (Figure 7.36). In the complex \([\text{Pt}(\mu-\text{PPPhH})(\text{Mo}(\text{CO})_3\text{Cl})(\text{PEt}_3)_2]\) the Pt-P\(_\mu\) bond length (2.288(3) Å) is shorter than the Pt-P\(_\mu\) \text{trans} to PEt\(_3\) or dppe consistent with it being \text{trans} to chloride. The small value of \(^{1}J(^{195}\text{PtP}_\mu)\) (2135 Hz) for a phosphorus \text{trans} to a chloride is reflected in the length of the Pt-P\(_\mu\) bond compared to Pt-P bonds of tertiary phosphines \text{trans} to chloride ligands. For example, \text{cis}-\([\text{PtCl}_2(\text{PEt}_3)_2]\) contains Pt-P (2.258(4) (\text{trans} to chloride) for which \(^{1}J(^{195}\text{PtP})\) is approximately 3500 Hz. The Pt-Cl bond distance (2.384(4) Å) in \([\text{Pt}(\mu-\text{PPPhH})(\text{Mo}(\text{CO})_3\text{Cl})(\text{PEt}_3)_2]\) is unusually long compared with the sum of the covalent radii and with the Pt-Cl bond length of other platinum(II) complexes. For example, \text{trans}-\([\text{PtCl}_2(\text{PEt}_3)_2]\) contains a Pt-Cl bond-length of 2.301(4) Å, but even in \text{cis}-\([\text{PtCl}_2(\text{PEt}_3)_2]\), with a chloride ligand \text{trans} to a ligand exerting a strong \text{trans}-influence, the Pt-Cl bond-length is only 2.361(5) Å, putting the anionic phosphido ligand above PEt\(_3\) in the \text{trans}-influence series.

Lower values of \(^{1}J(^{195}\text{PtP}_\mu)\) compared to \(^{1}J(^{195}\text{PtP})\) for similar bond lengths were observed indicating a decreased s-orbital contribution to the Pt-P\(_\mu\) bond.
Figure 7.36 Plot of Pt-P distance vs $^{1}J(^{195}Pt,^{31}P)$ for
(a) $[\text{Pt}(\mu-\text{PhH})_2\text{Mo(CO)}_5]_2(\text{dppe})$, (b) $[\text{Pt}(\mu-\text{PhH})(\text{Mo(CO)}_5)\text{Cl}(\text{PEt}_3)_2]$ and (c) $[\text{Pt}(\mu-\text{PhH})_2\text{Mo(CO)}_5]_2(\text{PEt}_3)_2$
7.5 Conclusions

[Mo(CO)$_5$(PPhR)]$^-$ (R = Ph, H) has been established as a highly reactive nucleophilic centre. It was found to react with simple organic and metallic electrophiles such as Me$^+$, [Au(PPh$_3$)]$^+$ and [HgEt]$^+$. Reaction with [Au(PPh$_3$)$_2$Cl] afforded the bimetallic complex [Mo(CO)$_5$(μ-PPhR)(AuPPh$_3$)] and there was no evidence for the symmetrisation of this complex in solution.

[Mo(CO)$_5$(μ-PPh$_2$)(AuPPh$_3$)] was observed to undergo a fluxional process in solution, which was rapid enough on the n.m.r. time scale to lose the $^{31}$P-$^{31}$P coupling. In comparison no exchange was seen for the analogous cluster [Os$_5$(μ-H)(μ-PPhAuPMe$_2$Ph)(CO)$_{10}$] even on raising the temperature of the n.m.r. solvent.

[Mo(CO)$_3$(PPhH)]$^-$ underwent nucleophilic attack at the platinum(II) complexes [PtCl$_2$(dppe)] and [PtCl$_2$(PEt$_3$)$_2$] to give a range of substituted products. Rather than nucleophilic attack at platinum(II) the synthesis of heterometallic complexes bridged by phosphido ligands has been described as a "bridge assisted reaction" involving ligand displacement (Cl$^-$ from [PtCl$_2$((dppe))] induced by a ligand on a second metal complex ([Mo(CO)$_5$(PPhH)]$^-$).

Reaction with [PtCl$_2$(dppe)] afforded two major products, the SS/RR and the meso stereoisomers of [Pt(μ-PPhH)$_2$(Mo(CO)$_5$)(dppe)] and a minor product characterised as [Mo(μ-PPhH)$_2$(Mo(CO)$_5$)(dppe)]. Variable-temperature $^{31}$P-$^1$H n.m.r. studies revealed the presence of several conformational isomers in exchange, which were interconverting rapidly on the n.m.r. time-scale at room-temperature. The single-crystal X-ray structure of the complex revealed it to be the P$_3$S-$P_3$S stereoisomer. The Pt-Mo distances were found to be non-bonding [Pt-Mo(1) 4.349(2) Å, Pt-Mo(2) 4.320(2) Å] and as a consequence the Pt-P-Mo bond angles are extremely large [Pt-P(1)-Mo(1) 123.5(1) °, Pt-P(2)-Mo(2) 122.1(1) °].

Reaction of [Mo(CO)$_5$(PPhH)]$^-$ with [PtCl$_2$(PEt$_3$)$_2$] afforded three major products two of which have been identified crystallographically. A minor product cis-[Pt(μ-PPhH)$_2$(Mo(CO)$_5$)(PEt$_3$)$_2$] was identified from its $^{31}$P-$^1$H n.m.r. spectrum, which exhibited a significantly reduced trans $^3$J(PP) (200 Hz) confirming the presence of a phosphido trans to a phosphine.

The two major products trans-[Pt(μ-PPhH)$_2$(Mo(CO)$_5$)Cl(PEt$_3$)$_2$] and trans-[Pt(μ-PPhH)$_2$(Mo(CO)$_5$)$_2$(PEt$_3$)$_2$] have been crystallographically characterised. Trans-[Pt(μ-
PPhH){Mo(CO)₅}Cl(PEt₃)₂ was found to contain PEt₃ ligands trans as evidenced from the $^{31}$P{¹H} n.m.r. spectrum. A particularly long Pt-Cl (2.384(4) Å) length has established the phosphido ligand as having a strong trans influence (greater than that of PEt₃). The large Pt-P-Mo bond angle (120.9(1) °) was consistent with a long Pt-Mo distance (4.255(2) Å). The low-temperature $^{31}$P{¹H} n.m.r. spectrum revealed the presence of three conformational isomers in solution each containing magnetically non-equivalent PEt₃ ligands.

Finally the single-crystal X-ray structure of trans-[Pt(μ-PPhH)₂{Mo(CO)₅}₂(PEt₃)₂] established the trans geometry of the PEt₃ ligands, as expected from the small value of $^2$J(PP) in the $^{31}$P{¹H} n.m.r. spectrum. The platinum-molybdenum [Pt(1)-Mo(1) 4.504(2) Å, Pt(2)-Mo(2) 4.573(2) Å] and platinum-phosphido-molybdenum [Pt(1)-P(1)-Mo(1) 126.1(1) °, Pt(2)-P(3)-Mo(2) 130.0(1) °] bond lengths and angles in this structure are similar to those in the related complexes [Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)] and trans-[Pt(μ-PPhH){Mo(CO)₅}Cl(PEt₃)]₂. The room-temperature $^{31}$P{¹H} n.m.r. spectrum confirmed the presence of two diastereoisomers, the result of the presence of two chiral phosphido bridges in the complex. The room-temperature $^{31}$P{¹H} n.m.r. spectrum showed several similarities to that of trans-[Pt(μ-PPhH){Mo(CO)₅}Cl(PEt₃)] and as a consequence the low-temperature spectrum was recorded. It revealed the presence of several rotamers in exchange although unambiguous assignment of the resonances to their conformational isomers was not possible.

Each of these related complexes exhibited reduced trans $^2$J(PP) coupling constants for phosphines trans to phosphido ligands (200 Hz) compared to trans phosphines (350 Hz). Values of $^1$J(¹⁹⁵PtP) proved useful in structure elucidation, these coupling constants being extremely sensitive to the nature of the phosphorus containing ligand and to that of the ligand occupying the trans coordination site. $^1$J(¹⁹⁵PtP) for a phosphine trans to a phosphido (2323 Hz) is less than that for a phosphine trans to a phosphine (2512 Hz). Even greater variations were found for $^1$J(¹⁹⁵PtP) for a phosphido trans to a phosphido [$^1$J(¹⁹⁵PtP) 1110.0 Hz].
7.6 Experimental

[PtCl₂(dppe)]²⁻ [PtCl₂(PEt₃)₂],²⁸⁶ [Mo(CO)₅(C₅H₅N₂)₂]²⁻ and [PtCl₂(dpae)]²⁻ were prepared by literature methods. MeLi and DBU (Aldrich) were purchased and used as received without further purification. Tetrahydrofuran was dried over sodium and distilled from potassium/benzophenone under nitrogen before use.

7.6.1 Synthesis of [Mo(CO)₅(PPhH₂)]

A modified procedure similar to that previously described was used. A solution of Mo(CO)₆ (1.599 g, 6.0 mmol) in n-octane (200 cm³) was heated under reflux with phenylphosphine (0.617 cm³, 5.6 mmol) for 30 minutes during which time the colour changed to brown. The solvent was removed under reduced pressure and the product extracted into n-hexane. The product was purified by column chromatography [neutral alumina; eluant: petroleum spirit (b.p. 30-40°C)] to give one major fast moving band. Removal of the solvent from this band followed by crystallisation from n-hexane (-20 °C 4 hours) and vacuum drying afforded colourless crystals of the title compound (0.900 g, 49%). [Found: C, 38.26; H, 1.94; P, 8.67. C₁₁H₂MoO₅P requires C, 38.19; H, 2.04; P, 8.95%].

7.6.2 Synthesis of [Mo(CO)₅(PPhH₂)₂]

Phenylphosphine (0.61 cm³, 5.5 mmol) was added to a solution of the piperidine complex [Mo(CO)₅(C₅H₅N)₂] (1.04 g, 2.8 mmol) in dichloromethane at ambient temperature. The mixture was brought to reflux and heated for ca. 15 minutes under nitrogen during which time the solution changed to pale yellow in colour. Volatile materials were removed under vacuum and the oily residue remaining was purified by column chromatography [neutral alumina; eluant: petroleum spirit (b.p. 30-40 °C)] to yield 2 major bands. The fast moving band was identified as [Mo(CO)₅(PPhH₂)] (0.450 g) by comparison of its spectroscopic data with that of the pure compound. The slower moving colourless band was identified as the title complex (0.433 g, 40%) and gave colourless crystals on cooling an n-hexane solution to -20°C overnight.
7.6.3 Synthesis of [Mo(CO)$_5$(PPh$_2$H)]

A procedure similar to that above was followed with diphenylphosphine (0.775 g, 4.17 mmol) and molybdenum hexacarbonyl (1.10 g, 4.17 mmol) in n-octane (100 cm$^3$). Work up as before and purification by column chromatography [neutral alumina: eluant; petroleum spirit (b.p. 30-40 °C)] gave a single major band identified as [Mo(CO)$_5$(PPh$_2$H)] (0.950 g, 54%). Removal of the solvent from this band followed by crystallisation from n-hexane gave colourless crystals. [Found: C, 48.21; H, 2.42; P, 7.17. C$_{17}$H$_{11}$MoO$_5$P requires C, 48.38; H, 2.63; P, 7.35%].

7.6.4 Synthesis of [Mo(CO)$_5$(PPhHMe)]

To a solution of [Mo(CO)$_5$(PPhH$_2$)] (0.238 g, 6.88 mmol) in dry tetrahydrofuran (40 cm$^3$) at -40 °C was added methyllithium (0.43 cm$^3$ of a 1.6 M solution in ether, 6.88 mmol) with stirring. A continuous flow of argon was maintained during the preparation. On addition of the MeLi there was an immediate colour change from colourless to deep yellow. After stirring for 30 minutes, methyl iodide (0.043 cm$^3$, 6.88 mmol) was added and the reaction mixture was left to stand for several hours. The solvent was removed under reduced pressure to give a deep yellow-orange oily residue which was chromatographed [t.l.c., SiO$_2$; eluant: petroleum spirit (b.p. 30-40 °C)/dichloromethane, (6:1 v/v)] to yield two bands. The fast moving band was identified as starting material by comparison of spectroscopic data. Removal of the solvent from the second band and crystallisation from n-hexane at -20 °C and vacuum drying for several hours afforded air-stable colourless microcrystals of the title complex (0.147 g, 54.9%).

7.6.5 Synthesis of [Mo(CO)$_5$(PPh$_2$AuPPh$_3$)]

A solution of [Mo(CO)$_5$(PPh$_2$H)] (0.1368 g, 0.32 mmol) in dry tetrahydrofuran (40 cm$^3$) was treated with the base DBU (0.046 cm$^3$, 0.32 mmol). There was an immediate colour change to deep yellow and the solution was stirred for a further 30 minutes under an atmosphere of argon. [Au(PPh$_3$)Cl] (0.158 g, 0.31 mmol) in tetrahydrofuran (5 cm$^3$) was added and the i.r. spectrum monitored until there was no further change. After 20 minutes all volatile material was removed under vacuum and the oily residue that remained was chromatographed [t.l.c., SiO$_2$; eluant: petroleum spirit (b.p. 30-40 °C)/dichloromethane, (3:1 v/v)] to give two major bands. The first was

-377-
identified as starting material (0.043 g) and the other [Mo(CO)₅(PPh₂AuPPh₃)] (0.188 g, 66%). [Found: C, 47.71; H, 2.26; P, 7.14. C₅₅H₃₂AuMoO₅P₂ requires C, 47.83; H, 2.87; P, 7.05%].

7.6.6 Synthesis of [Mo(CO)₅(PPhH₂AuPMe₂Ph)]

To a solution of [Mo(CO)₅(PPhH₂)] (0.0823 g, 0.23 mmol) in dry tetrahydrofuran (50 cm³) was added the base DBU (0.036 cm³, 0.23 mmol). After stirring under argon for 30 minutes [Au(PMe₂Ph)Cl] (0.102 g, 0.27 mmol) was added and the solution stirred for a further 30 minutes during which time the colour changed to yellow-orange. Removal of the solvent under vacuum left an oily residue which, on chromatography [t.l.c., SiO₂; eluant: petroleum spirit (b.p. 30-40 °C)/ dichloromethane, (3:1 v/v)] gave two colourless bands the first identified as starting material (0.023 g) and the slower band, after crystallisation at -20 °C from n-hexane, gave a colourless air stable crystalline material [Mo(CO)₅(PPhH₂AuPMe₂Ph)] (0.081 g, 70%), identified spectroscopically as the same product as that from the previous synthesis.

7.6.7 Synthesis of [Mo(CO)₅(PPh₂HgC₂H₅)]

A procedure similar to the above was followed with [Mo(CO)₅(PPh₂H)] (0.0542 g, 0.13 mmol) and the base DBU (0.021 cm³, 0.14 mmol) in dry tetrahydrofuran. [HgBrC₂H₅] (0.040 g, 0.13 mmol) was added and the reaction mixture was left stirring for 20 minutes. Removal of the solvent under reduced pressure and chromatographic work up [t.l.c., SiO₂; eluant: petroleum spirit (b.p. 30-40 °C)/dichloromethane, (3:1 v/v)] gave the title compound. Removal of the solvent from this band under reduced pressure and crystallisation from n-hexane (-20 °C overnight) and vacuum drying for 6 hours afforded air-stable colourless crystals (0.049 g, 61%). [Found: C, 35.79; H, 2.08; P, 4.93. C₁₉H₁₅HgMoO₅P requires C, 35.13; H, 2.31; P, 4.78%].

7.6.8 Synthesis of [{Mo(CO)₅(μ-PPhH)}₂Pt(dppe)]

To a solution of [Mo(CO)₅(PPhH₂)] (0.0875 g, 0.25 mmol) in dry tetrahydrofuran (50 cm³) was added an excess of base DBU (0.096 cm³, 0.63 mmol). There was an instantaneous colour change to deep yellow. The reaction mixture was stirred under an atmosphere of argon for 10 minutes before adding [PtCl₂(dppe)] (0.085 g, 0.13 mmol). After being stirred for a further 2 hours the yellow-orange solution was reduced to a
brown-orange oil by rotary evaporation. The oily residue was chromatographed [t.l.c., SiO₂; eluant: petroleum spirit (b.p. 30-40 °C)/dichloromethane, (3:2 v/v)] to give two bands. The fast moving minor band has been identified spectroscopically as [Mo(CO)₄(μ-PPhH₂)₂Pt(dppe)] (0.0151 g). The slower moving band contained [(Mo(CO)₅(μ-PPhH))₂Pt(dppe)]. Removal of the solvent under reduced pressure and crystallisation from dichloromethane/ethanol and vacuum drying for 6 hours afforded air-stable pale yellow crystals of the title complex (0.037 g, 22%). [Found: C, 44.66; H, 2.63; P, 9.91. C₄₈H₃₆Mo₂O₁₀P₄Pt requires C, 44.92; H, 2.83; P, 9.65%].

7.6.9 Synthesis of [(Mo(CO)₅(μ-PPhH))₂Pt(Ph₂PC₂H₂PPh₂)]

A similar procedure was followed with [Mo(CO)₅(PPhH₂)] (0.0747 g, 0.22 mmol) and base DBU (0.072 cm³, 0.47 mmol). This solution was treated with [PtCl₂(Ph₂PC₂H₂PPh₂)] (0.070 g, 0.11 mmol) and the reaction mixture was left to stand under nitrogen for 2 hours. The resultant solution was reduced to an orange oil by rotary evaporation and the residue chromatographed [t.l.c., SiO₂; eluant: petroleum spirit (b.p. 30-40°C)/dichloromethane, (3:2 v/v)]. The major band was collected and the solvent removed followed by crystallisation from dichloromethane/ethanol and vacuum drying for several hours to give the title complex as an air-stable pale yellow crystalline material (0.034 g, 25%). [Found: C, 44.69; H, 2.67. C₄₈H₃₆As₂Mo₂O₁₀P₄Pt requires C, 44.97; H, 2.83%].

7.6.10 Synthesis of [(Mo(CO)₅(μ-PPhH))₂Pt(dpae)]

Following the method above with [Mo(CO)₅(PPhH₂)] (0.137 g, 0.4 mmol) and DBU (0.12 cm³, 0.79 mmol) and [PtCl₂(dpae)] (0.1485 g, 0.2 mmol) gave an orange-yellow solution. Removal of the solvent under reduced pressure and a similar chromatographic procedure gave one major band. The solvent was removed by rotary evaporation to give a yellow oil. Crystallisation from dichloromethane/ethanol and vacuum drying for 1 day afforded air-stable pale yellow microcrystals (0.051 g, 19%). [Found: C, 40.65; H, 2.94; P, 4.64. C₄₈H₃₆As₂Mo₂O₁₀P₂Pt requires C, 42.0; H, 2.65; P, 4.53%].

7.6.11 Reaction of [Mo(CO)₅(PPhH)]²⁻ with [PtCl₂(PEt₃)₂]

A solution of [Mo(CO)₅(PPhH₂)] (0.1264 g, 0.36 mmol) in dry tetrahydrofuran
(50 cm³) was treated with the base DBU (0.160 cm³, 1.1 mmol). After being stirred for 10 minutes under nitrogen a solution of [PtCl₂(PEt₃)₂] (0.18 mmol) in dry THF (5 cm³) was added and the resultant mixture was left for a further 20 minutes. Removal of the solvent under reduced pressure left a brown-orange oil which was chromatographed [t.l.c., SiO₂; eluant: petroleum spirit (b.p. 30-40 °C)/dichloromethane, (3:2 v/v)] to give three bands. The fastest moving colourless band was identified as trans- [{Mo(CO)₅(µ-PPhH)}₂Pt(PEt₃)₂] (0.015 g). [Found: C, 33.63; H, 4.29; P, 11.77. C₃₆H₄₂Mo₂O₁₀P₄Pt requires C, 36.3; H, 3.75; P, 11.06%].

The second minor band was identified spectroscopically as cis- [{Mo(CO)₅(µ-PPhH)}₂Pt(PEt₃)₂] (0.009 g). Extraction of the slowest moving band into dichloromethane afforded a colourless solution. The solvent was removed under reduced pressure and the product crystallised from dichloromethane/ethanol to afford a colourless air-stable crystalline material. After several hours of vacuum drying the sample analysed correctly as the mono-substituted product trans- [PtCl(PET₃)₂{Mo(CO)₅(PPhH)}] (0.017 g). [Found: C, 34.01; H, 4.43; Cl, 5.24. C₂₃H₂₆ClMoO₅P₃Pt requires C, 33.69; H, 3.93; Cl, 4.37%].

7.6.12 Synthesis of [{Mo(CO)₄(µ-PPhH)₂}Pt(dppe)]

A tetrahydrofuran solution of [Mo(CO)₄(PPhH)₂] (0.102 g, 0.24 mmol) was treated with methyllithium (0.298 cm³ of a 1.6 moldm⁻³ solution in ether, 0.48 mmol) at -40 °C. The solution was allowed to stir under argon for 20 minutes to generate [Li₂][Mo(CO)₅(PPhH)₂] in situ. To this solution was added [PtCl₂(dppe)] (0.158 g, 0.23 mmol) in dry tetrahydrofuran (5 cm³) and the resultant orange-yellow solution was allowed to stir for 2 hours when most of the starting material had been consumed. The reaction mixture was allowed to warm up to room temperature and then volatile materials were removed under vacuum to leave a deep orange oil. The residue was chromatographed [t.l.c., SiO₂; eluant: petroleum spirit (b.p. 30-40 °C)/dichloromethane, (2:3 v/v)] to yield a single major yellow band. Removal of the solvent from this band followed by crystallisation from dichloromethane/ethanol and vacuum drying afforded the product as an orange-yellow solid (0.073 g, 30%).
7.7 Spectroscopic data for the complexes

Table 7.4 $^1$H n.m.r. data for molybdenum carbonyl phosphine and phosphido complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift ($\delta$)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(CO)$_5$(PPhH$_2$)]$^b$</td>
<td>5.40 (d)</td>
<td>P-H$_2$Ph (2H)</td>
<td>$^1$J(PH)=312.0</td>
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<td></td>
<td>7.56 (ddd)</td>
<td>PPhH (2H)</td>
<td>$^3$J(PH)=12.9, $^3$J(HH)=7.0, $^4$J(HH)=1.2</td>
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<tr>
<td></td>
<td>7.40 (m)</td>
<td>PPhH (3H)</td>
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</tr>
<tr>
<td>[Mo(CO)$_4$(PPhH$_2$)$_2$]$^b$</td>
<td>5.35 (dm)$^c$</td>
<td>PPh$_2$H (4H)</td>
<td>$^1$J(PH)=326.0</td>
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<tr>
<td></td>
<td>7.50 (m)</td>
<td>phenyl (3H)</td>
<td>$^4$J(HH)=20.0, $^3$J(PH)=7.0</td>
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<tr>
<td></td>
<td>7.40 (ddd)</td>
<td>phenyl (2H)</td>
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<tr>
<td>[Mo(CO)$_5$(PPh$_2$H)]$^b$</td>
<td>6.46 (d)</td>
<td>PPh$_2$H (1H)</td>
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<td></td>
<td>7.40 (m)</td>
<td>PPh$_2$H (6H)</td>
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<td></td>
<td>7.60 (m)</td>
<td>PPh$_2$H (4H)</td>
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<tr>
<td>[Mo(CO)$_5$(PPhHMe)]$^b$</td>
<td>1.90 (t)</td>
<td>PPhHMe (3H)</td>
<td>$^3$J(HH)=6.7, $^2$J(PH)=6.7</td>
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<td></td>
<td>5.60 (dq)</td>
<td>PPhHMe (1H)</td>
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<td>7.4-7.7 (m)</td>
<td>PPhHMe (5H)</td>
<td>$^1$J(PH)=328.0, $^3$J(HH)=6.7</td>
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<td>[Mo(CO)$_5$(PPhHAuPM$_2$Ph)]$^b$</td>
<td>2.06 (d)$^d$</td>
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<td>$^2$J(PH)=8.9, $^1$J(PH)=300.0</td>
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<td>5.30 (d)</td>
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<td>7.20 (m)</td>
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<td>7.50 (m)</td>
<td>PPhH (2H)</td>
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Table 7.4 continues overleaf .........
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<th>Compound</th>
<th>Chemical shift (δ)</th>
<th>Coupling constant (Hz)</th>
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<tbody>
<tr>
<td>[(CO)₃Mo(PPPh₂)(HgE)]</td>
<td>1.38 (dt), 1.75 (m), 7.3-7.6 (m)</td>
<td>3J(HH)=8.0</td>
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<tr>
<td>CH₃CH₂ (3H)</td>
<td>2.2 (m), 4.80 (m), 6.8 (m), 7.2-7.5 (m)</td>
<td>3J(HH)=33.0</td>
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<td>CH₂CH₂ (2H)</td>
<td>2.1 (m), 4.81 (dm), 7.0-7.6 (m)</td>
<td>3J(HH)=29.5</td>
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* Spectra recorded in CDCl₃ and referenced internally to the solvent.
* Non-first order multiplet, with coupling constants obtained from spin simulations.
Table 7.5 $^{31}$P $^{1}$H n.m.r. data for molybdenum carbonyl phosphine and phosphido complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift ($\delta$)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
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<tbody>
<tr>
<td>[Mo(CO)$_5$(PPhH$_2$)]$^b$</td>
<td>-66.5 (s)</td>
<td>PPhH$_2$</td>
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<tr>
<td>[Mo(CO)$_5$(PPh$_2$H)$_2$]$^{bc}$</td>
<td>-66.5 (tt)</td>
<td>PPhH$_2$</td>
<td>$^1$J(PH)$=312.0$, $^3$J(PH)$=12.0$</td>
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<tr>
<td>[Mo(CO)$_4$(PPhH$_2$)$_2$]$^b$</td>
<td>-59.4 (s)</td>
<td>PPhH$_2$</td>
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<tr>
<td>[Mo(CO)$_4$(PPh$_2$H)$_2$]$^{bc}$</td>
<td>-59.4 (tm)</td>
<td>PPhH$_2$</td>
<td>$^1$J(PH)$=326.0$</td>
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<td>[Mo(CO)$_5$(PPh$_2$AuPM$_2$Ph)$_2$]$^b$</td>
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<td>PPhH$_2$ AuPM$_2$Ph</td>
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<tr>
<td>[Mo(CO)$_5$(PPh$_2$AuP$_2$Ph)$_3$]$^{bd}$</td>
<td>+22.0 (d) +43.0 (d)</td>
<td>PPh$_2$ AuP$_2$Ph</td>
<td>$^2$J(PPh)$=235.0$, $^2$J(PPh)$=235.0$</td>
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<td>[Mo(CO)$_5$(PPh$_2$AuPPh$_3$)$_3$]$^b$</td>
<td>+22.0 (s) +43.0 (s)</td>
<td>PPh$_2$ AuPPh$_3$</td>
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<tr>
<td>[Mo(CO)$_5$(PPh$_2$HgEt)$_3$]$^b$</td>
<td>+35.3 (s)</td>
<td>PPh$_2$</td>
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<tr>
<td>[Mo(CO)$_5$(PPhH)$_2$]$_2$Pt(dppe)$_2$</td>
<td>+44.8 (dbroad) -33.6 (dbroad)</td>
<td>(Ph$_2$PCH$_2$)$_2$ PPhH</td>
<td>$^2$J(PPh)$=213.0$, $^1$J($^{195}$PtP)$=2323.0$ $^2$J(PPh)$=213.0$, $^1$J($^{195}$PtP)$=1450.0$</td>
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<td>(major diastereoisomer)</td>
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<th>Coupling constant (Hz)</th>
<th>Assignment</th>
<th>Chemical shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2187.0, 3J(199H-P) = 2160.0</td>
<td>(PPh₃)₂</td>
<td>+46.0 (broad)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2526.4, 3J(199H-P) = 17.3</td>
<td>(PPh₃)₂</td>
<td>+9.0 (ABX)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2413.0, 3J(199H-P) = 17.3, 2J(199H-P) = 9.6</td>
<td>(PPh₃)₂</td>
<td>+14.1 (ABX)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2135.0, 3J(199H-P) = 9.6</td>
<td>(PPh₃)₂</td>
<td>-66.5 (broad)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2179.6, 3J(199H-P) = 15.0, 2J(199H-P) = 9.6</td>
<td>(PPh₃)₂</td>
<td>+13.60 (ABX)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2376.0, 3J(199H-P) = 15.4</td>
<td>(PPh₃)₂</td>
<td>-10.5 (broad)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 2465.2, 3J(199H-P) = 25.5</td>
<td>(PPh₃)₂</td>
<td>-66.4 (s)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 1730.0, 3J(199H-P) = 25.5</td>
<td>(PPh₃)₂</td>
<td>-30.0 (s)</td>
</tr>
<tr>
<td>[(Mo(CO)₅)(PPh₃)]₂[P(As(CH₂)₃)₂]</td>
<td>1J(199H-P) = 17230.0, 3J(199H-P) = 25.5</td>
<td>(PPh₃)₂</td>
<td>-43.1 (broad)</td>
</tr>
</tbody>
</table>

Table 7.5 continued...
Table 7.5 continued.....

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (δ)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[{Mo(CO)}₅(PPhH)]₂Pt(PEt₃)₂</td>
<td>+44.7 (AA/XX')</td>
<td>PEt₃</td>
<td>²J(PP)=200.0, ²J(PP)=−15.0, ¹J(¹⁹⁵PtP)=2277.7</td>
</tr>
<tr>
<td>cis isomer</td>
<td>+5.7 (AA/XX')</td>
<td>PPhH</td>
<td>²J(PP)=200.0, ²J(PP)=−15.0, ¹J(¹⁹⁵PtP)=1400.6</td>
</tr>
<tr>
<td>[{Mo(CO)}₅(PPhH)]₂Pt(PEt₃)₂</td>
<td>+0.7 (t)</td>
<td>PEt₃</td>
<td>¹J(¹⁹⁵PtP)=2512.0, ²J(PP)=13.6</td>
</tr>
<tr>
<td>minor trans diastereoisomer</td>
<td>-71.4 (t)</td>
<td>PPhH</td>
<td>¹J(¹⁹⁵PtP)=1110.0, ²J(PP)=13.6</td>
</tr>
<tr>
<td>[{Mo(CO)}₅(PPhH)]₂Pt(PEt₃)₂</td>
<td>+1.2 (s, broad)</td>
<td>PEt₃</td>
<td>¹J(¹⁹⁵PtP)=2512.0</td>
</tr>
<tr>
<td>major trans diastereoisomer</td>
<td>-68.0 (t)</td>
<td>PPhH</td>
<td>¹J(¹⁹⁵PtP)=1146.0, ²J(PP)=12.7</td>
</tr>
<tr>
<td>[{Mo(CO)}₅(PPhH)]₂Pt(PEt₃)₂</td>
<td>+11.8 (t)</td>
<td>PEt₃</td>
<td>¹J(¹⁹⁵PtP)=2458.0, ²J(PP)=16.4</td>
</tr>
<tr>
<td>rotamer A</td>
<td>-67.8 (t)</td>
<td>PPhH</td>
<td>¹J(¹⁹⁵PtP)=1155.0, ²J(PP)=16.4</td>
</tr>
<tr>
<td>[{Mo(CO)}₅(PPhH)]₂Pt(PEt₃)₂</td>
<td>+0.7 (t)</td>
<td>PEt₃</td>
<td>¹J(¹⁹⁵PtP)=2459.0, ²J(PP)=14.8</td>
</tr>
<tr>
<td>rotamer B</td>
<td>-69.5 (t)</td>
<td>PPhH</td>
<td>¹J(¹⁹⁵PtP)=1127.0, ²J(PP)=16.4</td>
</tr>
<tr>
<td>[{Mo(CO)}₅(PPhH)]₂Pt(PEt₃)₂</td>
<td>+5.8 (ABX)</td>
<td>PEt₃</td>
<td>¹J(¹⁹⁵PtP)=2401.0, ²J(PP)=16.6, ²J(PP)=340.0</td>
</tr>
<tr>
<td>rotamer C</td>
<td>-2.4 (ABX)</td>
<td>PEt₃</td>
<td>¹J(¹⁹⁵PtP)=2592.0, ²J(PP)=8.8, ²J(PP)=340</td>
</tr>
<tr>
<td></td>
<td>-72.0 (t)</td>
<td>PPhH</td>
<td>¹J(¹⁹⁵PtP)=1136.0, ²J(PP)=12.8</td>
</tr>
</tbody>
</table>

Table 7.5 continue overleaf .........
Table 7.5 continued ....

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (δ)</th>
<th>Assignment</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[{Mo(CO)₅(PPhH)}₂Pt(Ph₂PCH₂)]²⁺</td>
<td>+54.0 (d)</td>
<td>(Ph₂PCH₂)⁵⁻</td>
<td>¹J(PtP)=2307.1, ²J(PP)=221.0</td>
</tr>
<tr>
<td>major diastereoisomer</td>
<td>-33.0 (d, broad)</td>
<td>PPhH</td>
<td>¹J(PtP)=1423.6, ²J(PP)=221.0</td>
</tr>
<tr>
<td>[{Mo(CO)₅(PPhH)}₂Pt(Ph₂PCH₂)]²⁺</td>
<td>+56.5 (d, broad)</td>
<td>(Ph₂PCH₂)⁵⁻</td>
<td>¹J(PtP)=2307.0, ²J(PP)=206.0</td>
</tr>
<tr>
<td>minor diastereoisomer</td>
<td>-54.0 (broad)</td>
<td>PPhH</td>
<td></td>
</tr>
<tr>
<td>[{Mo(CO)₄(PPhH)₂Pt(dppe)]²⁺</td>
<td>+47.0 (AA''XX'')</td>
<td>(Ph₂PCH₂)⁵⁻</td>
<td>¹J(PtP)=2063.0, ²J(PP)=216.0, ³J(PP)=60</td>
</tr>
<tr>
<td>major diastereoisomer</td>
<td>-134.5 (AA''XX'')</td>
<td>PPhH</td>
<td>¹J(PtP)=1280.0, ²J(PP)=216.0, ³J(PP)=5.0</td>
</tr>
<tr>
<td>[{Mo(CO)₄(PPhH)₂Pt(dppe)]²⁺</td>
<td>+47.1 (AA''XX'')</td>
<td>(Ph₂PCH₂)⁵⁻</td>
<td>¹J(PtP)=2066.0, ²J(PP)=222.0, ³J(PP)=60</td>
</tr>
<tr>
<td>minor diastereoisomer</td>
<td>-141.8 (AA''XX'')</td>
<td>PPhH</td>
<td>¹J(PtP)=1304.0, ²J(PP)=222.0, ³J(PP)=5.0</td>
</tr>
</tbody>
</table>

a: Spectra recorded in CDCl₃ and chemical shifts are quoted relative to 85% H₃PO₄ with downfield chemical shifts reported as positive.
b: Spectra recorded at 162 MHz.
c: Spectra recorded proton coupled.
d: Spectra recorded in CD₂Cl₂ at -75 °C.
e: Spectra recorded at +45 °C.
Table 7.6 infrared data for the complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>v (CO) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(CO)₅(PPhH₂)]⁺</td>
<td>2074 w, 1945 s</td>
</tr>
<tr>
<td>[Mo(CO)₄(PPhH₂)₂]⁺</td>
<td>2026 w, 1916 s, 1896 sh</td>
</tr>
<tr>
<td>[Mo(CO)₅(PPhMe)]⁺</td>
<td>2071 w, 1943 s, 1931 sh</td>
</tr>
<tr>
<td>[Mo(CO)₅(μ-PPhH)(AuPMe₂Ph)]⁺</td>
<td>2057 w, 2030 s, 1907 sh</td>
</tr>
<tr>
<td>[Mo(CO)₅(μ-PPh₂)(AuPPh₃)]⁺</td>
<td>2059 w, 1931 s, 1908 sh</td>
</tr>
<tr>
<td>[Mo(CO)₅(μ-PPhH)(HgC₂H₅)]⁺</td>
<td>2055 w, 1925 s, 1905 sh</td>
</tr>
<tr>
<td>[Pt(μ-PPhH)₂{Mo(CO)₅}₂(dppe)]⁺</td>
<td>2058 w, 1933 s, 1906 sh</td>
</tr>
<tr>
<td>[Pt(μ-PPhH){Mo(CO)₅}Cl(PEt₃)₂]⁺</td>
<td>2061 w, 1938 s, 1924 sh</td>
</tr>
<tr>
<td>cis-[Pt(μ-PPhH){Mo(CO)₅}₂(PEt₃)₂]⁺</td>
<td>2063 w, 1935 s, 1920 sh</td>
</tr>
<tr>
<td>trans-[Pt(μ-PPhH)₂{Mo(CO)₅}₂(PEt₃)₂]⁺</td>
<td>2057 w, 1928 s, 1901 sh</td>
</tr>
<tr>
<td>major diastereoisomer</td>
<td></td>
</tr>
<tr>
<td>trans-[Pt(μ-PPhH)₂{Mo(CO)₅}₂(PEt₃)₂]⁺</td>
<td>2058 w, 1928 s, 1901 sh</td>
</tr>
<tr>
<td>minor diastereoisomer</td>
<td></td>
</tr>
<tr>
<td>[Pt(μ-PPhH)₂{Mo(CO)₅}₂(Ph₂AsCH₂CH₂AsPh₂)]⁺</td>
<td>2062 w, 1935 s, 1908 sh</td>
</tr>
<tr>
<td>major diastereoisomer</td>
<td></td>
</tr>
<tr>
<td>[Pt(μ-PPhH)₂{Mo(CO)₅}₂(Ph₂AsCH₂CH₂AsPh₂)]⁺</td>
<td>2058 w, 1935 s, 1908 sh</td>
</tr>
<tr>
<td>minor diastereoisomer</td>
<td></td>
</tr>
<tr>
<td>[Pt(μ-PPhH)₂{Mo(CO)₄}₁(Ph₂PCH=CHPPH₂)]⁺</td>
<td>2057 w, 1933 s, 1095 sh</td>
</tr>
<tr>
<td>[Pt(μ-PPhH)₂{Mo(CO)₄}(dppe)]⁺</td>
<td>1996 w, 1875 s, 1852 sh</td>
</tr>
</tbody>
</table>

* a: Spectra recorded in n-hexane
References
References.


57. A. Marinetti and F. Mathey, Organometallics, 1982, 1, 1448.

-391-
82. D. A. Roberts, G. R. Steinmetz, M. J. Breen, P. M. Shulman, E. D. Morrison,


-393-
169. C. J. Cardin, S. B. Colbran, B. F. G. Johnson, J. Lewis, P. R. Raithby, *J.C.S.*

-399-
271. Comprehensive Organometalic Chemistery.


