THE SYNTHESIS AND REACTIVITY OF FOUR- AND FIVE-MEMBERED METALLACYCLES OF PLATINUM AND PALLADIUM

Thesis submitted for the Degree of
Doctor of Philosophy

by

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in the
Faculty of Science

of the
Department of Chemistry

at the
University of Leicester

APRIL 1991
For my Parents
THE SYNTHESIS AND REACTIVITY OF FOUR- AND FIVE-MEMBERED METTALLACYCLES OF PLATINUM AND PALLADIUM

by

SIMON MASON

ABSTRACT

Chapter 1 reviews the literature concerning the synthesis and reactivity of oxodimethyl-enedemethane metal complexes and their applications in organic synthesis. The preparation of metal-ureylene complexes and amino acid complexes of platinum are also discussed.

Chapter 2 describes the synthesis of metallaphosphetane-3-oxide complexes of platinum and palladium, \([\text{M(}\text{CH(R)P(O)(Ph)}\text{HR})\text{L}_2]\). Crystallographic and n.m.r. evidence for benzoyl substituted complexes, indicates that the four-membered rings are puckered, with the phosphoryl oxygen adopting an equatorial environment. The ligand substitution reactions of platinum analogues are also discussed.

The preparation of new platina-2,4,3-diazaphosphetidine-3-oxide complexes, \([\text{Pt} \{\text{N(R)P(O)(Ph)NR}\} \text{L}_2]\) is presented in Chapter 3. An X-ray crystal structure determination on an \(\text{N,N'-diphenyl derivative}\) indicates that the four-membered metallacyclic ring is almost planar, the nitrogen atoms of which show sp² hybrid character. An investigation into the insertion reactions of the \(\text{N,N'-dihydrogen derivatives with dimethyl acetylenedicarboxylate resulted in the isolation of six-membered platinaecyclic products, characterised by n.m.r. and i.r. spectroscopy. Attempts to prepare a similar insertion product using hexafluorobut-2-ylene, led only to the formation of an organic polymeric material. The formation of a novel four-membered ring species containing a phosphin-imine functionality \([\text{Pt}\{\text{SP(=NPh)(Ph)NPh}\}\text{L}_2]\) is also described in Chapter 3. The phosphinimine group was shown to have Lewis base capabilities and also underwent Wittig-type reactions with C=O and C=S containing molecules to form \([\text{Pt}\{\text{SP(O)(Ph)NPh}\} \text{L}_2]\) and \([\text{Pt}\{\text{SP(S)(Ph)S}\} \text{L}_2]\) ring systems respectively.

The formation and characterisation of phosphonato, phosphato and arsonato complexes of platinum(II) are described in Chapter 4. The molecular structure of a bis(phosphine)phosphonato complex establishes the presence of a slightly puckered four-membered ring with the phosphoryl oxygen adopting an equatorial position. The decomposition in solution of a bis(benzylidiphenylphosphine) analogue led to the formation of the di-orthometallated product cis-\([\text{Pt}\{\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\} \text{L}_2]\), as shown by X-ray crystallography.

Chapter 5 describes the synthesis of five-membered platinacycles containing amino acid derivatives, \([\text{Pt}\{\text{N(R^2)-CH(R^1)-C(O)O}\} \text{L}_2]\). An X-ray crystal structure determination on an \(\text{N-acetylglycinato(2-)-N,O}\) complex, indicated the presence of an almost planar five-membered ring that contains substantial electron delocalisation within the carboxylate and amide functionalities. The reaction of these complexes in ethanol with carbon monoxide or sulphur dioxide led to the formation of bis(ethoxycarbonyl) or bis(ethylsulphonato) metal complexes respectively.

The final Chapter investigates the syntheses of several new five-membered metallacyclic species which contain metal bonds to carbon, nitrogen, oxygen or sulphur. The isolation of the metallaoxacyclopentenone ring system \([\text{Pt}\{\text{CH-C(NHCOMe)C(O)O}\} \text{L}_2]\), formed via the rearrangement of an initially produced \([\text{Pt}\{\text{N(COMe)C(=CH}_2\text{)C(O)O}\} \text{L}_2]\) species, was confirmed by a single crystal X-ray diffraction study. The natures of the other complexes were examined using n.m.r. and i.r. spectroscopy.
ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. R. D. W. Kemmitt, for all the help, guidance and encouragement he has given me over the last three years.

I am indebted to Dr. D. R. Russell, Dr. J. Fawcett, and Mrs. L. J. S. Prouse, who carried out the X-ray crystal structure determinations. Similarly, my thanks are extended to Dr. G. A. Griffith for the high-field n.m.r. spectra. I would also like to thank Dr. J. V. Martin for substructure searches conducted in the Chemical Abstracts Registry File.

For the stimulating environment in the Chemistry Department, I wish to thank my fellow workers.

I would also like to thank Mrs. C. A. Crane and Miss V. Orson-Wright for their preparation of the diagrams and typescript respectively.

Finally, acknowledgement is made to the S.E.R.C. for funding this research, and to Johnson Matthey p.l.c. for the generous loan of platinum metal salts.
STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy entitled "The Synthesis and Reactivity of Four- and Five-Membered Metalla-cycles of Platinum and Palladium" is based on work conducted by the author in the Department of Chemistry of the University of Leicester between the period October 1987 and September 1990.

The work has not been, and is not concurrently being presented for any other degree.

Signed: ................ Date: /

Date: 28th June 1991
ABBREVIATIONS AND SYMBOLS

General and Physical:

Å = Angström unit
atm = Atmospheres (pressure)
br = Broad
°C = Centigrade
cm⁻¹ = Wave number
cm³ = Cubic centimetres
d = Doublet
δ = Chemical Shift
(°) = Degrees
g = Gramme
h = Hour
Hz = Hertz
i.r. = Infrared
K = Kelvin
m = Multiplet (n.m.r.)
MHz = Megahertz
min = Minute
mmol = Millimole
m.p. = Melting point
n.m.r. = Nuclear magnetic resonance
p.p.m. = Parts per million
{¹H} = Proton decoupled
q = Quartet
s = Singlet (n.m.r.); Strong (i.r.)
t = Triplet
w = Weak
ABBREVIATIONS AND SYMBOLS (Continued) ....

Chemical:

Ac = Acetyl
acac = Anion of pentane-2,4-dione
AlaH = d/-Alanine
Ala = Mono-anion of d/-alanine
Ar = Aryl
bipy = 2,2'-Bipyridine
Bu^n = n-Butyl
Bu^t = t-Butyl
Bz = Benzyl
cod = cis, cis-Cyclo-octadiene
Cp = Cyclopentadienyl anion
dba = Dibenzylideneacetone
dmad = Dimethyl acetylenedicarboxylate
DMF = N,N-Dimethylformamide
DMSO = Dimethyl sulfoxide
dppm = Bis(diphenylphosphino)methane
dppe = 1,2-Bis(diphenylphosphino)ethane
dppp = 1,3-Bis(diphenylphosphino)propane
dppb = 1,4-Bis(diphenylphosphino)butane
Et = Ethyl
GlyH = Glycine
Gly = Mono-anion of glycine
GlyglyH = Glycylglycine
Glygly = Mono-anion of glycylglycine
Me = Methyl
Ph = Phenyl
Phen = 1,10-Phenanthroline
Pr = n-Propyl
Pr^i = i-Propyl
Py = Pyridine
THF = Tetrahydrofuran
tosyl = Toluenesulphonyl
Val = Mono-anion of d/-valine
# LIST OF CONTENTS

## CHAPTER 1 - METAL COMPLEXES INVOLVING OXODIMETHYLENE-METHANE, UREYLENE OR AMINO ACID LIGANDS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 - Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 - Synthesis of Oxodimethylenemethane Metal Complexes</td>
<td>3</td>
</tr>
<tr>
<td>1.3 - Reactions of Oxodimethylenemethane Metal Complexes</td>
<td>8</td>
</tr>
<tr>
<td>1.4 - The Rôle of Oxodimethylenemethane in Organic Synthesis</td>
<td>9</td>
</tr>
<tr>
<td>1.5 - Ureylene Complexes of Transition Metals</td>
<td>14</td>
</tr>
<tr>
<td>1.6 - Amino Acid Complexes of Platinum</td>
<td>19</td>
</tr>
</tbody>
</table>

## CHAPTER 2 - THE SYNTHESIS AND REACTIVITY OF METALLAPHOSPHETANE-3-OXIDE COMPLEXES OF PLATINUM AND PALLADIUM

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 - Introduction</td>
<td>32</td>
</tr>
<tr>
<td>2.2 - Synthesis of Metallaphosphetane-3-oxide Complexes</td>
<td>35</td>
</tr>
<tr>
<td>2.3 - Structural Properties of Platinaphosphetane-3-oxide Complexes</td>
<td>36</td>
</tr>
<tr>
<td>2.4 - N.M.R. Spectra of Metallaphosphetane-3-oxide Complexes</td>
<td>41</td>
</tr>
<tr>
<td>2.4.1 - $^1$H N.m.r. Spectra</td>
<td>41</td>
</tr>
<tr>
<td>2.4.2 - $^{13}$C-$^1$H N.m.r. Spectra</td>
<td>45</td>
</tr>
<tr>
<td>2.4.3 - $^{31}$P-$^1$H N.m.r. Spectra</td>
<td>46</td>
</tr>
<tr>
<td>2.5 - I.R. Spectra of Metallaphosphetane-3-oxide Complexes</td>
<td>47</td>
</tr>
<tr>
<td>2.6 - Reactions of Platinaphosphetane-3-oxides</td>
<td>47</td>
</tr>
<tr>
<td>2.6.1 - Ligand Substitution Reactions</td>
<td>47</td>
</tr>
<tr>
<td>2.6.2 - Attempted Reactions of the Phosphoryl Group</td>
<td>49</td>
</tr>
<tr>
<td>2.6.3 - Miscellaneous Reactions of Platinaphosphetane-3-oxides</td>
<td>51</td>
</tr>
<tr>
<td>2.7 - Conclusion</td>
<td>51</td>
</tr>
<tr>
<td>2.8 - Experimental</td>
<td>52</td>
</tr>
</tbody>
</table>

## CHAPTER 3 - THE SYNTHESIS AND REACTIVITY OF 1-PLATINA-2,4,3-DIAZAPHOSPHETIDINE-3-OXIDE AND PLATINACYCLOPHOSPHINIMINE COMPLEXES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 - Introduction</td>
<td>66</td>
</tr>
<tr>
<td>3.2 - Synthesis of 1-Platina-2,4,3-diazaphosphetidine-3-oxide and Platinacyclopophosphinimine Complexes</td>
<td>67</td>
</tr>
<tr>
<td>3.3 - Structural Properties of 1-Platina-2,3,4-triphenyl-2,4,3-diazaphosphetidine-3-oxide Complexes</td>
<td>71</td>
</tr>
</tbody>
</table>
LIST OF CONTENTS (Continued)  ..... 

3.4 - N.M.R. Spectra of 1-Platina-2,4,3-Diazaphosphetidine-3-oxide and Platinacyclophosphinimine Complexes 75
  3.4.1 - ^H N.m.r. Spectra 75
  3.4.2 - ^13C-{^1H} N.m.r. Spectra 75
  3.4.3 - ^31P-{^1H} N.m.r. Spectra 76

3.5 - I.R. Spectra of 1-Platina-2,4,3-Diazaphosphetidine-3-oxide and Platinacyclophosphinimine Complexes 77

3.6 - Reactions of 1-Platina-2,4,3-Diazaphosphetidine-3-oxide Complexes 77
  3.6.1 - General Properties 77
  3.6.2 - Ligand substitution reactions 78
  3.6.3 - Reactions with methyl iodide 78
  3.6.4 - Reactions with multiple bonded species 78
  3.6.5 - Reaction with t-butyl isocyanide 84

3.7 - Reactions of Platinacyclophosphinimine Complexes 85

3.8 - Conclusion 90

3.9 - Experimental 92

CHAPTER 4 - THE SYNTHESIS AND REACTIVITY OF PLATINA-
PHOSPHONATO, PHOSPHATO AND ARSONATO METAL COMPLEXES

4.1 - Introduction 114

4.2 - Synthesis of Platinaphosphonato, Phosphato and Arsonato Metal Complexes 116

4.3 - Structural Properties of Platinaphosphonato Complexes 117

4.4 - Comparison of the Crystal Structures of Platinaphosphetane, Phosphetidine and Phosphonato Metal Complexes 122

4.5 - N.M.R. Spectra of Platinaphosphonato, Phosphato and Arsonato Metal Complexes 123

4.6 - I.R. Spectra of Platinaphosphonato, Phosphato and Arsonato Metal Complexes 124

4.7 - Reactions of Platinaphosphonato Complexes 124
  4.7.1 - Decomposition of [Pt{OP(O)(Ph)O}(PBzPh)2] (I81).H2O 124
  4.7.2 - Reaction with carbon monoxide 128
  4.7.3 - Reaction with tin(II) chloride 130

4.8 - Conclusion 131

4.9 - Experimental 132
LIST OF CONTENTS  (Continued) ......

CHAPTER 5 - THE SYNTHESIS AND REACTIVITY OF [AMINO ACID(2-)-N,O]PLATINUM(II) COMPLEXES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 - Introduction</td>
<td>145</td>
</tr>
<tr>
<td>5.2 - Synthesis of [Amino Acid(2-)-N,O]bis(ligand)platinum(II) Complexes</td>
<td>145</td>
</tr>
<tr>
<td>5.3 - Structural Properties of [N-Acetylglycinato(2-)-N,O]bis(ligand)-platinum(II) Complexes</td>
<td>147</td>
</tr>
<tr>
<td>5.4 - N.M.R. Spectra of [Amino Acid(2-)-N,O]bis(ligand)platinum(II) Complexes</td>
<td>152</td>
</tr>
<tr>
<td>5.4.1 - $^1$H N.m.r. Spectra</td>
<td>152</td>
</tr>
<tr>
<td>5.4.2 - $^{13}$C-{$^1$H} N.m.r. Spectra</td>
<td>155</td>
</tr>
<tr>
<td>5.4.3 - $^{31}$P-{$^1$H} and $^{19}$F-{$^1$H} N.m.r. Spectra</td>
<td>156</td>
</tr>
<tr>
<td>5.5 - I.R. Spectra of [Amino Acid(2-)-N,O]bis(ligand)platinum(II) Complexes</td>
<td>157</td>
</tr>
<tr>
<td>5.6 - Reactions of [Amino Acid(2-)-N,O]bis(ligand)platinum(II) Complexes</td>
<td>158</td>
</tr>
<tr>
<td>5.6.1 - Ligand Substitution Reactions</td>
<td>158</td>
</tr>
<tr>
<td>5.6.2 - Reactions with Ethanol</td>
<td>159</td>
</tr>
<tr>
<td>5.6.3 - Reactions with Sulphur Dioxide</td>
<td>160</td>
</tr>
<tr>
<td>5.6.4 - Reactions with Carbon Monoxide</td>
<td>161</td>
</tr>
<tr>
<td>5.6.5 - Attempted Insertion Reactions</td>
<td>162</td>
</tr>
<tr>
<td>5.7 - Conclusion</td>
<td>163</td>
</tr>
<tr>
<td>5.8 - Experimental</td>
<td>164</td>
</tr>
</tbody>
</table>

CHAPTER 6 - THE SYNTHESIS OF FURTHER METALLACYCLIC COMPLEXES OF PLATINUM AND PALLADIUM USING SILVER(I) OXIDE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 - Introduction</td>
<td>187</td>
</tr>
<tr>
<td>6.2 - Synthesis of Metallacyclic Complexes of Platinum and Palladium</td>
<td>187</td>
</tr>
<tr>
<td>6.3 - Structural Properties of Platinaoxacyclopentenone Complexes</td>
<td>192</td>
</tr>
<tr>
<td>6.4 - N.M.R. Spectra of Metallacyclic Complexes of Platinum and Palladium</td>
<td>196</td>
</tr>
<tr>
<td>6.4.1 - $^1$H N.m.r. Spectra</td>
<td>196</td>
</tr>
<tr>
<td>6.4.2 - $^{13}$C-{$^1$H} N.m.r. Spectra</td>
<td>198</td>
</tr>
<tr>
<td>6.4.3 - $^{31}$P-{$^1$H} N.m.r. Spectra</td>
<td>199</td>
</tr>
<tr>
<td>6.5 - I.R. Spectra of Metallacyclic Complexes of Platinum and Palladium</td>
<td>200</td>
</tr>
<tr>
<td>6.6 - Conclusion</td>
<td>202</td>
</tr>
<tr>
<td>6.7 - Experimental</td>
<td>202</td>
</tr>
</tbody>
</table>

REFERENCES                                                  215
CHAPTER 1

Metal Complexes involving
Oxodimethylenemethane, Ureylene
or Amino Acid Ligands
1.1 INTRODUCTION

Intermediates containing transition metals play an increasingly significant rôle in both catalytic and stoichiometric organic syntheses. It is therefore important to understand the mechanisms and bonding in such reactions and to investigate the properties of the species involved. Metal mediated cycloadditions, as shown in Scheme 1, are one such example, for which metallacyclobutan-3-one complexes (1a), Figure 1, are seen as being important intermediates.\(^1\) These complexes may be referred to as \(\eta^3\)-oxodimethylenemethane metal species (1b), as a consequence of crystallographic evidence for related counterparts, indicating a delocalised structure.\(^2,3\)

![Scheme 1](image)

Metal-ureylene complexes have been proposed in key stages of metal catalysed conversions of organic nitrogen compounds.\(^4\) Monometallic (2a) and bimetallic (2b) species are known with a number of different metal centres.

Modification of the basic framework of oxodimethylenemethane and ureylene metal complexes, has led to the formation of several related species including metallathietane-3-oxide (3a), metallathietane-3,3-dioxide (3b), and metallathia-2,4-diazetidine-3,3-dioxide (4) complexes. The chemistry of these derived systems is reviewed in Chapters 2 and 3 respectively, and is used as a comparison to that of new analogous phosphoryl containing species, the syntheses of which are described in those chapters.

Complexes of amino acids with transition metals are well known and studied. The rôle of transition metal ions in biological systems is extensively documented and is a large area of current research, mainly with the first row metals.\(^5,6\) Platinum complexes of amino acids,
due to their relative inertness, are of interest to investigate the coordination of peptides and proteins to metal ions, and a varied range of compounds have been synthesised.

This chapter summarises the literature concerning the preparation and reactivity of metal-oxodimethylene complexes and their use in organic synthesis. Metal-ureylene complexes and the formation of amino acid complexes of platinum are also reviewed.
1.2 SYNTHESIS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

The reaction of the dimethyl or diethyl ester of 3-oxopentanedioic acid with the zero valent metal species [ML₄] (M = Pd or Pt) in aerated benzene, yielded the first examples of the transition metal oxodimethylenemethane complexes (5, R = CO₂Me, CO₂Et, L = PPh₃ or AsPh₃) and (6, R = CO₂Me, L = PPh₃, PMePh₂, PMe₂Ph, AsPh₃; R = CO₂Et, L = PPh₃ or AsPh₃), Scheme 2.²,⁷,⁸

\[
[ML₄] + RCH₂COCH₂R \xrightarrow{\text{Benzene Air}} L₂M\overset{O}{\overset{\text{R}}{\text{R}}} \\
(5, M=\text{Pd}) \quad (6, M=\text{Pt})
\]

The complex (6, R = CO₂Me, L = PPh₃) can also be synthesised from the corresponding ester and [Pt(trans-stilbene)(PPh₃)₂] under similar conditions.² The treatment of [Pd₂(dba)₃].CHCl₃ with the dialkyl esters of 3-oxopentanedioic acid and excess of the appropriate donor ligand in diethyl ether under oxygen, provided high yield syntheses of the complexes (5, R = CO₂Me, L = PPh₃, PMePh₂, PMe₂Ph, AsPh₃ or L₂ = bipy; R = CO₂Et, L = PPh₃, AsPh₃ or L₂ = bipy; R = CO₂Pr¹, L₂ = bipy).⁹ The reaction is thought to proceed via a dioxygen complex of the metal, since treatment of [Pd(O₂)(PPh₃)₂] with the dimethyl ester of 3-oxopentanedioic acid in oxygenated benzene gave (5, R = CO₂Me, L = PPh₃).⁹ Analogous treatment of [Pt(O₂)(PPh₃)₂] yielded (7), which, on further treatment with triphenylphosphine and dimethyl-3-oxopentanедioate, gave complex (6, R = CO₂Me, L = PPh₃).² Further evidence to support the pathway via the dioxygen complex is given by the fact that these species cannot be formed from [ML₄] (M = Pd or Pt) in the absence of oxygen.²
The X-ray crystal structure of (6, R = CO₂Me, L = PPh₃) confirms a significant η²-allylic description of the complex.² An interesting feature of the complex is that the central oxygen atom of the fragment is tipped out of the CCC plane towards the metal.²

The platinum carbonate complexes [Pt(CO₂)L₂] (L = PPh₃ or AsPh₃) have been used successfully with the dialkyl esters of 3-oxopentanedioic acid in ethanol to give the corresponding complexes (6, R = CO₂Me, L = PPh₃, AsPh₃; R = CO₂Et, L = PPh₃ or AsPh₃).¹⁰ Complexes (6, R = COMe, L = PPh₃, AsPh₃) may be made in a similar fashion, using heptane-2,4,6-trione as the source of the coordinating fragment.¹⁰

The reaction of Na₂[PdCl₄] with the dimethyl ester of 3-oxopentanedioic acid in water at room temperature gives (8), which on treatment with triphenylphosphine yields (5, R = CO₂Me, L = PPh₃).⁸

The treatment of [PdCl₂] or [PdCl₄]²⁻ in water with heptane-2,4,6-trione yields the acetylacetonato palladium complex (9), which on treatment with 2,2'-bipyridine gives (5, R = COMe, L₂ = bipy).⁸

Complex (6, R = CO₂Me, L = PPh₃) may also be obtained by the action of either silver(I) oxide² or triethylamine⁸ on dimethyl-3-oxopentanedioate in the presence of cis-[PtCl₂(PPh₃)₂].
Phenyl substituted derivatives (10) can be obtained from the reaction of the 1,3 dianion of dibenzylketone in THF with the metal complexes cis-[PtCl₂L₂] (L = PPh₃, AsPh₃ or L₂ = cod) or trans-[PdCl₂L₂] (L = PPh₃ or PEt₃), Scheme 3.¹¹

Interestingly, the phenyl groups both occupy equatorial positions and do not show the trans-disubstitution pattern as in (6, R = CO₂Me, L = PPh₃). The cod ligand in (10, M = Pt, L₂ = cod) can be displaced by tertiary phosphines to yield the corresponding phosphine analogues.¹¹

Palladium and platinum complexes in which the oxodimethylenemethane fragment is monosubstituted are also known. [PdCl₂] reacts with β-diketones to produce 2-hydroxyallyl dimer complexes (11). These react with bidentate nitrogen donors to give chloro-σ-alkyls (12), which can be converted into the oxodimethylenemethane complexes (13, R = Me or OEt) by treatment with thallium(I) acetylacetonate, Scheme 4.¹²
Bidentate phosphines can displace bipy or phen from \((\text{13}, R = \text{Me or OEt})\) to produce a new range of such complexes.\(^{13,14}\)

\([\text{Pt(acac)}]_2\), when treated with tri-\(p\)-chlorophenylphosphine in chloroform, yielded a new platinum complex \((\text{14}, L = \{p-\text{ClC}_6\text{H}_4\}_3\text{P}\) of a monosubstituted oxodimethylenemethane moiety.\(^{15}\)

\[
\begin{align*}
\text{L}_2\text{Pt} &-\text{COMe} \\
\text{(14)}
\end{align*}
\]

More recently, the complex \([\text{Pt(acac)}(\text{PPh}_3)_2](\text{acac})\) was prepared from \([\text{Pt(acac)}]_2\) and triphenylphosphine in hot methanol.\(^{16}\) When the mixture was maintained at 60°C for more than four hours, \((\text{14}, L = \text{PPh}_3\) was obtained along with the bimetallic species \((\text{15})\) which could be isolated as either its \(\text{PF}_6^-\) or \((\text{acac})^-\) salts.\(^{16}\)

\[
\begin{align*}
\left[\begin{array}{c}
\text{Ph}_3\text{P} \\
\text{Pt} \\
\text{Ph}_3\text{P}
\end{array}\right] &\phantom{=} \quad \left[\begin{array}{c}
\text{O} \\
\text{Pt} \\
\text{PPh}_3 \\
\text{PPh}_3
\end{array}\right] \\
\text{(15)}
\end{align*}
\]

Unsubstituted complexes can also be prepared. When the complex \([\text{IrL}_4]\text{Cl} (L = \text{PMe}_3, \text{AsMe}_3)\) was treated with the enolate salt of acetone, complexes \((\text{16}, L = \text{PMe}_3 \text{ or AsMe}_3)\) were formed via the oxidative addition of a distal C–H bond.\(^{17}\)

\[
\begin{align*}
\text{L}_3(\text{H})\text{Ir} &\phantom{=} \quad \text{O} \\
\text{(16)}
\end{align*}
\]

An improved route to unsubstituted oxodimethylenemethane complexes utilises the silyl
enol ether (17). The formation of osmium (18), iridium (19) and platinum (20) complexes using this reagent is outlined in Scheme 5. Complex (20) may also be obtained by the action of sodium amalgam on cis-[PtCl(CH\_2COCH\_2Cl)(PPh\_3\_2)] in THF. A diruthenium complex, (21), which contains an $\eta^4$-oxodimethylenemethane ligand has been reported by Holmgren et al., an X-ray structure determination confirming the coordination mode.
Recently, Frey et al. isolated and characterised the first example of an iron oxodimethylenemethane complex. The reaction of [Fe₂(CO)₉] with the silyl enol ether (17) followed by treatment with silver tetrafluoroborate in pyridine yielded the dimeric complex (22), whose structure was elucidated by X-ray techniques.²⁰

\[
\begin{array}{c}
\text{Fe(CO)}_3 \\
\text{(OC)₃Fe-O-} \\
\end{array}
\]

\[(22)\]

### 1.3 REACTIONS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

Oxodimethylenemethane complexes of platinum are extremely susceptible to electrophilic attack. Thus treatment of (6, \( R = \text{CO}_2\text{Me}, L = \text{PPh}_3 \)) with hydrogen chloride, iodine or trifluoroacetic acid yields the complexes cis-[PtCl₂(PPh₃)₂], cis-[PtI₂(PPh₃)₂] and cis-[Pt(O₂CCF₃)₂(PPh₃)₂] respectively.⁸,²¹ The reaction of (6, \( R = \text{CO}_2\text{Me}, L = \text{PMePh}_2 \)) with excess hexafluoroacetone led to the formation of complex (23).⁷

\[
\begin{array}{c}
\text{MePh₂P} \\
\text{MePh₂P} \\
\text{Pt} \\
\text{CO}_2\text{Me} \\
\text{CF}_3 \\
\text{HO} \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3 \\
\end{array}
\]

\[(23)\]

Ligand substitution at platinum or palladium oxodimethylenemethane complexes occurs easily. Triphenylarsine can be displaced from (5, \( R = \text{CO}_2\text{Me}, L = \text{AsPh}_3 \)) or (6, \( R = \text{CO}_2\text{Me}, L = \text{AsPh}_3 \)) by tertiary phosphines in refluxing dichloromethane.²² One mole equivalent of t-butyl isocyanide can displace a phosphine or arsine ligand from the complexes (5, \( R = \text{CO}_2\text{Me}, L = \text{PPh}_3 \) or \( \text{AsPh}_3 \)) and (6, \( R = \text{CO}_2\text{Me}, L = \text{PPh}_3 \) or \( \text{AsPh}_3 \)) to give a series of monosubstituted complexes. Treatment of (6, \( R = \text{CO}_2\text{Me}, L = \text{PPh}_3 \) or
AsPh$_3$) with an excess of t-butyl isocyanide produces the zwitterionic complex (24) via ligand displacement and insertion of an isocyanide moiety into a platinum carbon bond.$^{22}$

![Chemical structure of complex (24)](image)

The palladium complex (13, $R = \text{Me}$) has been shown to act as a donor ligand towards other metals, forming ligand bridged species (25).$^{13,14}$

$$
\begin{align*}
\begin{array}{c}
\text{L}_2\text{Pd} \\
\text{[M]} \\
\text{[CIO}_4\text{]_2}
\end{array}
\end{align*}
$$

n=1 \quad [M] = \text{PdL}_2, \text{PtL}_2 \\
n=2 \quad [M] = \text{Mg, Ni}

(25)

1.4 THE RÔLE OF OXODIMETHYLENEMETHANE IN ORGANIC SYNTHESIS

There has been enormous interest in the cycloaddition of the oxodimethylenemethane fragment to alkenes and dienes, to produce five- and seven-membered rings respectively.$^{23}$ The reaction of $[\text{Fe}_2(\text{CO})_3]$ with the 1,3-dibromoketone (26) in the presence of furan results in a [3 + 4] cyclocoupling to give the bridged ketone (27).$^{24}$ In the absence of substrates, intramolecular cycloaddition occurs to give the product (28), as shown in Scheme 6.$^{24,25}$
Following the isolation of osmium and iridium oxodimethylenemethane complexes, these iron-mediated cycloadditions were suggested to proceed via an oxodimethylenemethane complex of iron, perhaps of the nature of (29).^26

In addition to this, the recent isolation of the iron dimer (22) indicates such an intermediate as (29) may be possible.

Acyclic dienes react similarly to furan, to give 4-cycloheptanones.\textsuperscript{27} Interestingly, the yield of these reactions was increased when diene-irontricarbonyl complexes were used instead of the free diene with the metal carbonyl.\textsuperscript{27}

Aryl substituted alkenes react with 1,3-dibromoketones in the presence of [Fe\textsubscript{2}(CO)\textsubscript{9}] in a [3 + 2] manner to yield 3-arylcylopentanones (30), although in a limited number of cases, 2-alkylidenetetrahydrofurans (31) may be formed via cycloaddition through the oxygen and carbon atoms of the oxodimethylenemethane fragment, Scheme 7.\textsuperscript{28-30}

Isobutylene\textsuperscript{31} and enamines\textsuperscript{32} have also been used as olefinic components in these
Scheme 7

The main drawback of these reactions is that they require a stoichiometric amount of $[\text{Fe}_2(\text{CO})_9]$ with regard to the 1,3-dibromoketone, and this led to the investigation of other suitable systems. $\text{Zn/Cu}$, $\text{Zn/Ag}$, and $\text{Cu/NaI}$ couples have all been employed in the dehalogenation and subsequent cycloadditions of 1,3-dibromoketones with furans, pyrroles and cyclopentadienes, as shown in Scheme 8.

Scheme 8

The yields of these reactions are not as great as when $[\text{Fe}_2(\text{CO})_9]$ was used, but they can be improved with the use of ultrasound. These couples can be used to provide alternative products to those obtained in an $[\text{Fe}_2(\text{CO})_9]$ mediated cycloaddition. The reaction of $N,N$-dimethylcarboxamides (32) with a 1,3-dibromoketone in the presence of $[\text{Fe}_2(\text{CO})_9]$ yields 3(2H)-furanones (33), via a [3 + 2] cycloaddition and then subsequent loss of dimethylamine. In contrast, when a $\text{Zn/Cu}$ couple was employed, cyclocoupling through carbon and oxygen was observed, to give (34) as the major product, Scheme 9.
Zinc dichloride has been used, in conjunction with silyl enol ethers \((35)\), to provide a catalytic route to five- and seven-membered rings,\(^{41}\) for example Scheme 10.

\[
\begin{align*}
\text{(35)} & \quad \text{OSiMe}_3 \\
\text{+ } \text{Cl} & \quad \text{ZnCl}_2 \\
\Longrightarrow & \quad \text{O} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

Recently, work on palladium(0) catalysed reactions involving substrates with strained double bonds has been published.\(^{42}\) The cyclopropanations of norbornene, norbornadiene and dicyclopentadiene using 1-acetoxy-3-trimethylsilyl-2-propanone \((36)\) were carried out in the presence of \([\text{Pd(PPh}_3)_4]\), Scheme 11. It was noted that electron deficient and non-strained alkenes did not react.
The mechanism was formulated to proceed via the addition to a strained double bond of an unsubstituted palladium oxodimethylenemethane complex (37), which is generated \textit{in situ} in the reaction mixture. A subsequent 1,3-proton shift followed by reductive elimination yielded the observed products.\textsuperscript{42}
1.5 UREYLENE COMPLEXES OF TRANSITION METALS

The reaction of \([\text{Fe}_3(\text{CO})_{12}]\) with either phenyl isocyanate or phenyl azide was found, after crystallographic studies, to have produced the first known example of a bimetallic-ureylene bridged complex (38, \(R = \text{Ph}\)).\(^{43,44}\)

\[
\begin{array}{c}
\text{O} \\
\text{(OC)}_3\text{Fe} \quad \text{Fe}(\text{CO})_3 \\
\end{array}
\]

(38)

This product was also isolated from the treatment of \([\text{Fe}_2(\text{CO})_9]\) with phenyl azide at room temperature in benzene.\(^{45}\) Methyl derivatives have also been studied, \((38, R = \text{Me})\) was obtained from the reaction of \([\text{Fe}_2(\text{CO})_9]\) with either methyl isocyanate, methyl azide or nitromethane.\(^{46}\) Ethyl,\(^{47,48}\) n-propyl\(^{49}\) and tert-butyl\(^{49}\) derivatives \((38, R = \text{Et}, \text{Pr}^n \text{ or Bu}^t)\) were synthesised from the corresponding nitroalkane and diiron-nonacarbonyl in benzene at room temperature. Compounds of this type have been suggested as intermediates in metal carbonyl mediated transformations of aryl azides into aryl substituted ureas in the presence of acetic acid.\(^4\)

Vinyl substituted derivatives can be produced in a similar manner. Thus treatment of \([\text{Fe}_2(\text{CO})_9]\) with vinyl isocyanate in benzene at 40°C gives the complex \((39, R = \text{H})\).\(^{50}\)

\[
\begin{array}{c}
\text{O} \\
\text{(OC)}_3\text{Fe} \quad \text{Fe}(\text{CO})_3 \\
\end{array}
\]

(39)

The reaction of \([\text{Fe}_2(\text{CO})_9]\) with 1-phenylvinyl azide at 50°C\(^{51}\) or photolysis of the same compound in the presence of \([\text{Fe}(\text{CO})_5]\) in hexane,\(^{50}\) gives the complex \((39, R = \text{Ph})\). Analogous compounds can be synthesised by the use of azirines as the nitrogen source. Reaction in benzene of \([\text{Fe}_2(\text{CO})_9]\) with (40) led to the isolation of complexes \((41)-(45)\).\(^{50,51}\)
A bimetallic cobalt ureylene complex (46) has also been isolated, from the reaction of [Co(Cp)(CO)$_2$] and N-t-butylsulphurdiimide. An X-ray crystal structure verified the bridged nature of the product.$^{52-54}$

Complexes which contain a single metal atom with a chelating ureylene fragment are also known. The action of tosyl azide on the metal complexes [M(NO)(CO)(PPh$_3$)$_2$] (M = Rh or Ir), yields (47, R = p-MeC$_6$H$_4$SO$_2$).$^{55}$ This same product may be obtained by the reaction of tosyl isocyanate with [M(NO)(PPh$_3$)$_3$] (M = Rh or Ir) in dry benzene, Scheme 12.$^{55}$
Platinum and palladium analogues can be formed in a similar manner. Thus, treatment of $[\text{Pd(CO)(PPh}_3\text{)}_3]$ with tosyl azide or the reaction of $[\text{M(PPh}_3\text{)}_4]$ ($\text{M} = \text{Pt or Pd}$) with tosyl isocyanate, led to the formation of $\text{(48, R = p-MeC}_6\text{H}_4\text{SO}_2)$, as shown in Scheme 13.$^{55}$

$p$-Toluenesulphonyl isocyanate in dry benzene also reacts with the metal complex $[\text{RhCl(PPh}_3\text{)}_3]$ to give the product $\text{(49, R = p-MeC}_6\text{H}_4\text{SO}_2)$. The related product $\text{(49, R = P(O)(OPh)_2)}$ may be obtained by the action of diphenylphosphoryl azide on $\text{trans-[RhCl(CO)(PPh}_3\text{)}_2]$ for fourteen days in dry benzene.$^{56}$
p-Toluenesulphonyl azide and isocyanate may also be used to prepare ruthenium and osmium ureylene derivatives. Thus, treatment of [Ru(CO)\(_3\)(PPh\(_3\))] with either the azide or isocyanate gives (50, M = Ru, R = p-MeC\(_6\)H\(_4\)SO\(_2\)),\(^5\) whilst reaction of [MH\(_2\)(CO)(PPh\(_3\))] (M = Ru or Os) with tosyl isocyanate in refluxing toluene yields (50, M = Ru or Os, R = p-MeC\(_6\)H\(_4\)SO\(_2\)), Scheme 14.\(^{58}\)

![Scheme 14](image)

The oxidative addition of N,N'-di-p-toluenesulphonyl urea to the metal complexes [Pt(PPh\(_3\)]\(_4\)], [RhCl(PPh\(_3\))] or [Ru(CO)\(_2\)(PPh\(_3\))] gives (48, M = Pt, R = p-MeC\(_6\)H\(_4\)SO\(_2\)), (49, R = p-MeC\(_6\)H\(_4\)SO\(_2\)) or (50, M = Ru, R = p-MeC\(_6\)H\(_4\)SO\(_2\)) respectively.\(^{55,57}\)

Ureylene ligands also form complexes of the early transition metal titanium. When a large excess of phenyl isocyanate was added to [Ti(Cp)\(_2\)(CO)] at room temperature, the trimetallic species (51) was formed, whereas a 1:1 ratio heated to 60°C yields the bimetallic bridged species (52).\(^5\) When a toluene solution of (51) was heated, the monometallic ureylene chelated compound (53) was formed, along with the toluene solvate of (52). (53) can also be prepared from (51) by the action of phenanthrene-9,10-quinone which complexes the central Ti(Cp)\(_2\) unit. A further route to (52) is then provided by the reaction of (53) with [Ti(Cp)\(_2\)(CO)]\(_2\)], which sees a loss of carbon monoxide, Scheme 15.

Crystal structure determinations were carried out on (51) and on the toluene solvate of (52), and these indicated that the diphenyl-ureylene moiety is acting as a delocalised ligand as shown in Scheme 15 rather than as in complex (38, R = Ph).\(^5\)

Reaction of [Ti(Cp)\(_2\)(CO)]\(_2\)] with diphenylidiazomethane in toluene yields (54) which is
Scheme 15

i, excess PhNCO
ii, 1 mole eq PhNCO, Δ
iii, Δ, toluene
iv, phenanthrene-9,10-quinone
v, (53)
analogous to compound (51). Similarly, treatment of (54) with phenanthrene-9,10-quinone gave the bidentate ureylene complex (55).

\[
\begin{align*}
\text{(Cp)}_2\text{Ti} & \quad \text{N} \quad \text{CPh}_2 \\
\text{N} \quad \text{CPh}_2 & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

(54)

\[
\begin{align*}
\text{(Cp)}_2\text{Ti} & \quad \text{N} \quad \text{CPh}_2 \\
\text{N} \quad \text{CPh}_2 & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

(55)

1.6 AMINO ACID COMPLEXES OF PLATINUM

In 1912, Ley and Ficken described the reaction between glycine and \( \text{K}_2[\text{PtCl}_4] \) in aqueous solution and formulated the product as \([\text{Pt}(@\text{Gly})_2]\). In 1935 Pinkard et al. expanded on this and were able to separate and identify the cis and trans isomers of \([\text{Pt}(@\text{Gly})_2] \), (56) and (57) respectively.

\[
\begin{align*}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} & \begin{array}{c}
\text{C} \quad \text{CH}_2 \\
\text{O} \\
\text{Pt} \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{C} \quad \text{CH}_2 \\
\end{array}
\end{align*}
\]

(56)

\[
\begin{align*}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} & \begin{array}{c}
\text{C} \quad \text{CH}_2 \\
\text{O} \\
\text{Pt} \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{C} \quad \text{CH}_2 \\
\end{array}
\end{align*}
\]

(57)

An improved route to the isomers was provided by Grinberg et al. who heated an aqueous solution of \( \text{K}_2[\text{PtCl}_4] \), glycine and potassium hydroxide in a 1:4:4 ratio, to obtain the tetraglycine salt (58), which contains four glycinate anions bonded to the platinum through the amino groups. Acidification with two mole equivalents of dilute HCl yielded
\[ \text{H}_2\text{[Pt(Gly)}]_4 \ (59) \text{, which on heating gave cis-[Pt(Gly)}]_2 \text{, via the ring closure of two cis ligands.} \text{ Acidification of (58) with excess concentrated HCl followed by heating in} \]

\[ \text{aqueous solution yielded (60) which on treatment with alkali gave trans-[Pt(Gly)}]_2 \text{, Scheme 16.} \text{ Tris(glycine) platinum(II) compounds are also known. Treatment of (59) with one} \]

\[ \text{equivalent of potassium hydroxide gave complex (61), which contains one bidentate and} \]

\[ \text{two monodentate glycine ligands.} \text{ The reactions of cis and trans-[Pt(Gly)}]_2 \text{ with a number of reagents have been studied. When (56) is heated with dilute HCl or HBr, one glycine ring opens to give the complexes} \]

\[ (62, \ X = \text{Cl or Br}) \text{, whereas treatment with excess concentrated HCl opens both the} \]

\[ \text{rings to yield (63).} \text{ (62, X = Cl or Br) and (63) may be converted back into (56) by} \]

\[ \text{titration with the appropriate amount of alkali.} \text{ Complex (64) may be obtained by the} \]

\[ \text{treatment of hot concentrated ammonia solution on either (56) or (63).} \text{ The action of} \]

\[ \]
Scheme 17
cold concentrated HCl on this product yields (65), which when heated with the same reagent, gives the mono glycine compound (66) due to Jörgensen splitting. (67) or (68) may be prepared from (66) by the action of aqueous alkali or thiourea respectively. Scheme 17. Cis-[Pt(Gly)₂] may also be converted directly into the trans isomer by either U.V. photolysis or by prolonged boiling with excess glycine.  

Trans-[Pt(Gly)₂] reacts in a similar manner to the cis isomer and compounds (63), (64) and (65) all have their trans analogues. However, the reaction of trans-[Pt(NH₃)₂(GlyH)₂]Cl₂ with concentrated HCl does not give an analogue of (66) but instead yields trans-[PtCl₂(NH₃)₂]. Differences also occur in the reaction of cis and trans-[PtCl₂(GlyH)₂] with excess thiourea. The cis isomer yields (69) whereas the trans isomer retains its coordinated acids and forms (70).  

\[
\text{[Pt}\{S=C(NH₂)₂\}_4]\text{Cl}_2
\]

(69)

Along with (66), various other mono glycine compounds have been synthesised. The addition of 3 equivalents of K₂[PtCl₄] to a solution of (58) and subsequent heating yielded complex (71). Treatment of (71) with warm concentrated ammonia solution gave the complex salt (72).  

If Zeise’s salt in ethanol is treated with glycine in potassium hydroxide solution, the mono-olefin complex (73, L = C₂H₄) is formed.
If the chloride bridged dimer \([(\text{PtCl}_2\text{P(Bu)}_3)_2]\) is treated with neutralised glycine in methanol, the monomeric complex (73, \(L = \text{P(Bu)}_3\)) is formed.\(^7\) The \(\alpha\)-CH\(_2\) of this complex can be functionalised by the action of a base and a suitable substrate. Thus, complexes (75, \(R = \text{Me or Ph}\)) can be formed by the treatment of the anion (74) with either acetaldehyde or benzaldehyde and the complexes (76, \(R = \text{Me or CH}_2\text{Ph}\)) with either methyl or benzyl iodide respectively, Scheme 18.\(^7\)

\[
\begin{align*}
\text{(73)}
\end{align*}
\]

\[
\begin{align*}
\text{(74)}
\end{align*}
\]

\[
\begin{align*}
\text{(75)}
\end{align*}
\]

\[
\begin{align*}
\text{(76)}
\end{align*}
\]

Scheme 18
Schiff base formation of chelating glycine ligands has also been achieved, using an amide acetal. Complexes (77), (78) and (79) have all been made using the corresponding glycine complex with N,N-dimethylformamide-dimethyl acetal in DMF.\textsuperscript{76} The structure of complex (78) was confirmed by crystallographic studies.\textsuperscript{76}

\[
\begin{array}{c}
\text{(77)} \\
\text{(78)} \\
\text{(79)}
\end{array}
\]

Most of the other simple, acyclic amino acids containing a hydrocarbon side chain have been used to prepare complexes similar to some of those mentioned for glycine.\textsuperscript{77-82} The tendency of proline to form metal adducts with platinum is somewhat less than that of other simple amino acids, conditions of formation of such compounds being generally more harsh.\textsuperscript{83,84}

Mixed amino acid complexes in which two different acids are bonded to the platinum can also be prepared. If K[PtCl\textsubscript{2}(Ala)] is treated with either excess glycine or valine, then the compounds \textit{trans}-[Pt(Ala)(Gly)] (80) and \textit{trans}-[Pt(Ala)(Val)] (81) are formed.\textsuperscript{85} These react similarly to the \textit{trans}-bis(glycine) platinum complex (57) and thus the chelate rings can be opened with either concentrated HCl or concentrated ammonia solution.\textsuperscript{85}

\[
\begin{array}{c}
\text{(80)} \\
\text{(81)}
\end{array}
\]
Complexes (82) and (83) of the basic amino acid histidine have been prepared using histidinium hydrochloride with potassium hydroxide and either $K_2[PtCl_4]$ or $cis-[PtCl_2(NH_3)_2]$ respectively.$^{86,87}$ Coordination of the acid occurs through the amino group and tertiary nitrogen atom of the imidazole ring. The cis or trans nature of (82) was not determined.

![Diagram](image)

Amino acids which contain sulphur coordinate differently to glycine due to the presence of its lone pairs. When a 1:1 mixture of methionine and $K_2[PtCl_4]$ was heated in water, chelation through nitrogen and sulphur occurred to yield (84).$^{88}$ Addition of another equivalent of methionine to (84) yielded complex (85) which contains two chelating rings in a trans orientation. If (84) is treated with cold aqueous ammonia, displacement of one chlorine atom occurs together with deprotonation of the acid group to give complex (86).$^{88}$ If the mixture is heated, both chlorines are displaced and the complex salt (87) is formed, Scheme 19.$^{89}$ Ethionine and S-methylcysteine have also been used to prepare analogues of compound (84).$^{90}$

$Trans-[PtCl_2(NH_3)_2]$ reacts with two mole equivalents of methionine to give the non-chelated product (88).$^{91}$ Conversely, $cis-[PtCl_2(NH_3)_2]$ reacts with two equivalents of methionine to yield the novel complex salt (89) in which one methionine is chelating to the platinum and the other is bound via its sulphur atom only.$^{91}$
Scheme 19
Oxidation of platinum(II) amino acid compounds provides a simple preparative route into their platinum(IV) chemistry. Thus the treatment of (56) or (57) with hydrogen peroxide yielded the octahedral compounds (90) or (91) respectively.\(^2\)

Reaction of trans-[Pt(Gly)\(_2\)(NH\(_3\))\(_2\)] with excess hydrogen peroxide similarly yielded the octahedral complex (92), which on treatment with HCl, dehydrated to form (93).\(^2\) (93) may be prepared directly by the oxidation of (94), as shown in Scheme 20.\(^2\)

The chemistry of the cis complexes is analogous, with the formation of cis-(amino acid) platinum(IV) complexes.\(^2\)

Chlorine and phosphorus pentachloride have also been used to oxidise platinum(II) amino acid complexes. When trans-[Pt(NH\(_3\))\(_2\)(AlaH)\(_2\)]Cl\(_2\) was treated with chlorine in
concentrated HCl, compound (95) was precipitated. Treatment of (95) with excess sodium hydroxide solution deprotonated the acid groups and exchanged a chlorine atom for a hydroxyl group to give complex (96). Ring closure of one alanine ligand can then occur, by reaction with dilute nitric acid to give the salt (97). (97) can be converted back into (95) by treatment with concentrated HCl, as can complex (96), Scheme 21.

Treatment of the methionine chelate (84) with PCl$_5$ gave the tetra-chloro complex (98). In this reaction, the free carboxylic acid group was converted into an acyl chloride, as well as oxidation of the platinum.
\[ \text{K}_2[\text{PtCl}_4] + 4\text{GlyglyH} + 4\text{KOH} \xrightarrow{\text{H}_2\text{O}} \text{K}_2[\text{Pt(Glygly)}_4] \]

(99)

\[ \text{R.T. conc.HCl} \]

\[ \text{H}_2\rightleftharpoons \text{NCH}_2\text{CONHCH}_2\text{CO}_2\text{H} \]

(100)

\[ \Delta/\text{KOH} \]

\[ \left[ \begin{array}{c}
\text{O}_2\text{CCH}_2
\text{N} \\
\text{NH}_2
\text{Pt}
\text{NH}
\text{H}_2\text{N}
\text{C} \text{CH}_2\text{CO}_2
\end{array} \right] \]

(101)

Scheme 22
Dipeptide complexes of platinum(II) can be made in a similar fashion to the corresponding glycine complexes. Thus (99) may be obtained by treating K₂[PtCl₄] with glycylglycine and potassium hydroxide in water. Room temperature treatment of this salt with concentrated HCl yields (100) whereas heating with this reagent also severs the peptide bonds to give complex (60). When (100) is heated with aqueous alkali, trans-[Pt(Glygly)₂] (101) is formed, Scheme 22.

_Cis_-complexes may be obtained by the reaction of the dipeptide ester-hydrochloride with K₂[PtCl₄] in water. The X-ray crystal structure of (102) confirmed the stereochemistry around the platinum.

\[
\begin{array}{c}
\text{Cl} \\
\text{H₂} \quad \text{NCH₂CONHCH₂CO₂Et} \\
\text{Pt} \\
\text{Cl} \quad \text{NCH₂CONHCH₂CO₂Et} \\
\text{H₂}
\end{array}
\]

(102)

This thesis describes the syntheses and reactions of new four-membered ring systems containing the atom frameworks \( \text{M–C–P–C} \) (M = Pt or Pd), \( \text{Pt–N–P–N} \) and \( \text{Pt–O–P–O} \). New five-membered cyclic complexes of platinum containing amino acid derivatives are investigated in Chapter 5 and Chapter 6 is concerned with the syntheses of further five-membered rings containing platinum or palladium.
CHAPTER 2

The Synthesis and Reactivity of Metallaphosphetane-3-oxide Complexes of Platinum and Palladium
2.1 INTRODUCTION

The formation of oxodimethylenemethane metal complexes may be achieved by using a range of synthetic pathways as described in Chapter 1, but these methods do not generally provide routes to complexes containing a heteroatom functionality in the central position of the fragment. However, the use of silver(I) oxide to synthesise ($6$, $R = CO_2 Me$, $L = PPh_3$) was extended by Henderson et al. to prepare metallathietane-3,3-dioxide complexes of the type ($103$) in high yield. Thus treatment of cis or trans-[MCl$_2$L$_2$] ($M = Pt$ or $Pd$) with the corresponding sulphone and excess silver(I) oxide in refluxing dichloromethane yielded complexes ($103$, $M = Pt$ or $Pd$, $R = COPh$, $L = PPh_3$, PMePh$_2$, PMe$_2$Ph, PEt$_3$; $R = CO_2 Me$, $L = PPh_3$), Scheme 23.

\[
\text{cis or trans-[MCl}_2\text{L}_2\text{]} + \text{RCH}_2\text{S(O)}_2\text{CH}_2\text{R} \xrightarrow{\text{Ag}_2\text{O}} \text{L}_2\text{M} \quad (103)
\]

Scheme 23

Corresponding phenyl derivatives ($103$, $M = Pt$, $R = Ph$, $L = PPh_3$, AsPh$_3$, SEt$_2$; $M = Pd$, $R = Ph$, $L = PPh_3$, PEt$_3$; $M = Ni$, $R = Ph$, $L = PMe_3$ or $L_2 = dppe$) were obtained via the treatment of either cis or trans-[MCl$_2$L$_2$] complexes with one mole equivalent of Li$_2$[PhCHS(O)$_2$CHPh] in THF at low temperature. Crystal structure determinations showed that unlike oxodimethylenemethane metal complexes, metallathietane-3,3-dioxides contain only a small $\eta$-allylic contribution to the structure. The complexes do contain puckered rings and exist in a trans-disubstituted form with one $R$ group being pseudo-axial and the other pseudo-equatorial, as indicated in Scheme 23.

Ligand displacement in these complexes occurs easily; trimethylphosphite and triphenylphosphite readily displace both diethylsulphide ligands in ($103$, $M = Pt$, $R = Ph$, $L = $ SEt$_2$) whereas carbon monoxide replaces just one. One equivalent of either t-butyl or n-butyl isocyanide replaces a triphenylphosphine ligand in complex ($103$, $M = Pt$, $R = COPh$, $L = PPh_3$), and bis(isocyanide) complexes were obtained by the reaction of ($103$, ...
M = Pt, R = Ph, L = AsPh₃) with an excess of either t-butyl or n-butyl isocyanide in refluxing dichloromethane.¹⁰¹ Ring insertions can also occur, leading to the formation of zwitterionic products. Thus treatment of (103, M = Pt, R = COPh, L = PPh₃ or PMePh₂) with excess t-butyl isocyanide gave compounds (104, L = PPh₃ or PMePh₂) in good yield.¹⁰²

![Diagram](image)

(104)

The analogous platinathietane-3-oxide ring system (105) which contains a central sulphoxide moiety, can also be prepared using silver(I) oxide in conjunction with diphenacylsulphoxide and cis-[PtCl₂L₂] (L = PPh₃, PMePh₂, PMe₂Ph) in refluxing dichloromethane.⁹⁸,¹⁰³

![Diagram](image)

(105)

Crystal structure data of (105, L = PPh₃) shows that the ring is puckered to a greater extent than the corresponding sulphone complexes, but again only a small trans-annular interaction is indicated.⁹⁸,¹⁰³ The sulphoxide oxygen atom occupies an equatorial position on the ring, the benzoyl substituents of which lie in a trans-disubstituted manner.⁹⁸,¹⁰³

The basicity of the sulphur lone pair in complexes (105) is shown in the formation of
chelate complexes of rhodium and palladium. Reaction of [RhCl₂(CO)₄] or [PdCl₂(cod)]
with (105, L = PPh₃) in dichloromethane gave (106, M = Rh, X = CO) or (106, M = Pd, X =
Cl) respectively, via displacement of the appropriate ligands.⁹⁸,¹⁰⁴

![Diagram](image)

The ability of silver(I) oxide to react with activated C–H protons and metal dichlorides
to produce metal-carbon bonds has also been noted in the reaction of cis-[PtCl₂(PEt₃)₂] with
either acetone or nitromethane in the presence of this reagent, Scheme 24.¹⁰⁵

\[
cis-[PtCl₂(PEt₃)₂] + RH ∆_{Ag₂O} cis-[PtCl(R)(PEt₃)₂]
\]

R=CH₂C(O)CH₃ or CH₂NO₂

Scheme 24

The β,β'-diketophosphine oxide (107),¹⁰⁶ contains activated methylene protons, and its
reaction with metal dichlorides in the presence of silver(I) oxide to form
metallaphosphetane-3-oxide complexes (108, M = Pt or Pd, R = COPh) is described in this
Chapter.

![Diagram](image)
The structural properties of the metallaphosphetane-3-oxide ring are discussed and compared to those of organic analogues and the metallathietane oxide rings mentioned above. The ligand displacement reactions of platinum derivatives \( (108, M = \text{Pt}, R = \text{COPh}) \) are studied, as is the attempted synthesis of the phenyl substituted metallacycle \( (108, M = \text{Pt}, R = \text{Ph}) \).

### 2.2 SYNTHESIS OF METALLAPHOSPHETANE-3-OXIDE COMPLEXES

Treatment of complexes \( \text{cis-[PtCl}_2\text{L}_2] \) (\( L = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{Bu}^t\text{NC}; \text{L}_2 = \text{dppe, dppp or dppb} \)) (prepared \textit{in situ} by the reaction of \( \text{[PtCl}_2\text{(cod)}] \)) with either two molar equivalents of \( L \) or one equivalent of \( \text{L}_2 \) with one equivalent of the phosphine oxide \( (107) \) in refluxing dichloromethane in the presence of excess silver(II) oxide gave the complexes \( (109)-(115) \) in high yield. Similarly, complex \( (116) \) may be obtained by the reaction of \( \text{[PtCl}_2\text{(cod)}] \)) with \( (107) \) in the presence of silver(I) oxide, Scheme 25.

\[
cis-[\text{PtCl}_2\text{L}_2] + \text{PhC(O)CH}_2\text{P(O)(Ph)CH}_2\text{C(O)Ph} \quad (107)
\]

\[
\begin{align*}
\text{cis-[PtCl}_2\text{L}_2] & \quad \text{refluxing CH}_2\text{Cl}_2 \quad \text{excess Ag}_2\text{O} \\
& \quad \text{PhC(O)CH}_2\text{P(O)(Ph)CH}_2\text{C(O)Ph}
\end{align*}
\]

\[
(109), \text{L} = \text{PPh}_3 \\
(110), \text{L} = \text{PMePh}_2 \\
(111), \text{L} = \text{PMe}_2\text{Ph} \\
(112), \text{L}_2 = \text{dppe} \\
(113), \text{L}_2 = \text{dppp} \\
(114), \text{L}_2 = \text{dppb} \\
(115), \text{L} = \text{Bu}^t\text{NC} \\
(116), \text{L}_2 = \text{cod}
\]

\textbf{Scheme 25}

The reaction of complexes \( \text{cis-[PtCl}_2\text{L}_2] \) (\( \text{L}_2 = \text{dppe, dppp or dppb} \)) with one equivalent of \( (107) \) and excess potassium hydroxide in refluxing THF gave compounds \( (112)-(114) \) in moderate yield.

Treatment of \( \text{cis-[PdCl}_2\text{(dppp)}] \)) with one equivalent of \( (107) \) in the presence of excess silver(I) oxide in refluxing dichloromethane, led to the formation of complex \( (117) \).
Analogous treatment of complexes \( \text{cis-}[\text{PdCl}_2L_2] \) (\( L_2 = \text{dppe} \) or \( \text{dppb} \)) led to the production of the corresponding metallaphosphetane-3-oxides although these products were contaminated with several impurities which could not be removed without decomposition of the product. Attempts to synthesise palladaphosphetane-3-oxide rings using \( \text{(107)} \) with potassium hydroxide in THF did not lead to the formation of the desired products.

The attempted synthesis of complex \( \text{(118)} \) from \( \text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] \) and dibenzylphenylphosphine oxide \( \text{(119)} \) either with silver(I) oxide in dichloromethane or potassium hydroxide in THF failed, with the recovery of starting materials only.

However, treatment of \( \text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] \) with one mole equivalent of the lithium salt \( \text{Li}_2[\text{PhCHP(O)(Ph)CHPh}] \) (formed by the treatment of dibenzylphenylphosphine oxide with two equivalents of \( n \)-butyl lithium in THF at low temperature) in THF yielded complex \( \text{(118)} \) in moderate yield.

All the complexes \( \text{(109)-(118)} \) were isolated as white to pale yellow, air-stable, microcrystalline solids.

2.3 STRUCTURAL PROPERTIES OF PLATINAPHOSPHETANE-3-OXIDE COMPLEXES

An X-ray crystal structure determination of the triphenylphosphine complex \( \text{(109)} \) was carried out to investigate its molecular conformation for comparison with organic
phosphetane oxides and the four-membered metallathietane oxide rings. Of particular interest were the degree of puckering of the metallacycle and the competing conformational preferences of the phosphoryl oxygen and phenyl ring. Figure 2 shows the molecular geometry of the complex with the crystallographic numbering system and Table 1 shows important bond lengths and angles. Some structural data for a number of 1-phenylphosphetane-1-oxide ring systems together with selected data for complex (109) for comparison, are presented in Table 2.

Figure 2 clearly shows the framework of the metallaphosphetane-3-oxide ring, which contains a fold angle between planes C(1)-Pt-C(2) and C(1)-P(l)-C(2) of 31.05°. The phosphoryl oxygen occupies an equatorial position and the coordination about the platinum is essentially square planar, the twist angle between the planes C(1)-Pt-C(2) and P(2)-Pt-P(3) being 5.32°.

The puckering angle is slightly less than that in the platinathietane-3-oxide complex (105, L = PPh₃) (fold angle = 36.7°), but is greater than those of the platinathietane-3,3-dioxides (103, M = Pt, R = COPh, L = PPh₃) and (103, M = Pt, R = Ph, L = AsPh₃) (fold angles 15.3° and 24.6°), and organic 1-phenylphosphetane-1-oxides (fold angles in the range 16.7-29.8°). The trans-annular Pt----P(1) distance of 2.821(2)Å indicates no significant Pt----P(1) interaction and there is no lengthening of the phosphoryl bond [1.486(6)Å] as compared to those in phosphetane-1-oxides, which occur in the range 1.47-1.51Å. This information indicates that an η²-allylic contribution to this structure is minimal, as was found for the metallathietane oxide complexes.

The equatorial preference of the phosphoryl oxygen forces the sterically larger phenyl ring into an axial position. This conformation is also adopted in organic 1-phenylphosphetane-1-oxides, unless there is a cis-3-methyl-1-phenyl interaction, in which case, the oxygen occupies an axial position. In complex (105, L = PPh₃), the sulfoxide group also adopts an equatorial position, which again reflects the behaviour of its organic analogues. In the case of this complex, Henderson et al. explained the conformation by suggesting that the axial lone pair on sulphur causes less steric strain between that axial
TABLE 1a

Selected Bond Lengths and Angles for
[Pt{(CH(COPh)P(O)(Ph)CH(COPh)}(PPh3)2} (109).CHCl3

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–P(2)</td>
<td>2.283 (2)</td>
<td>P(2)–Pt–P(3)</td>
<td>98.3 (1)</td>
</tr>
<tr>
<td>Pt–P(3)</td>
<td>2.301 (2)</td>
<td>P(2)–Pt–C(1)</td>
<td>92.9 (2)</td>
</tr>
<tr>
<td>Pt–C(1)</td>
<td>2.137 (7)</td>
<td>P(3)–Pt–C(2)</td>
<td>93.7 (2)</td>
</tr>
<tr>
<td>Pt–C(2)</td>
<td>2.162 (7)</td>
<td>C(1)–Pt–C(2)</td>
<td>74.9 (2)</td>
</tr>
<tr>
<td>Pt–P(1)</td>
<td>2.821 (2)</td>
<td>Pt–C(1)–P(1)</td>
<td>91.4 (3)</td>
</tr>
<tr>
<td>C(1)–P(1)</td>
<td>1.790 (8)</td>
<td>Pt–C(2)–P(1)</td>
<td>90.8 (3)</td>
</tr>
<tr>
<td>C(2)–P(1)</td>
<td>1.782 (8)</td>
<td>C(1)–P(1)–C(2)</td>
<td>94.0 (3)</td>
</tr>
<tr>
<td>P(1)–O(3)</td>
<td>1.486 (6)</td>
<td>C(1)–P(1)–O(3)</td>
<td>119.2 (3)</td>
</tr>
<tr>
<td>P(1)–C(31)</td>
<td>1.810 (5)</td>
<td>C(2)–P(1)–O(3)</td>
<td>117.4 (4)</td>
</tr>
<tr>
<td>C(1)–C(3)</td>
<td>1.493 (10)</td>
<td>O(3)–P(1)–C(31)</td>
<td>109.3 (3)</td>
</tr>
<tr>
<td>C(2)–C(4)</td>
<td>1.483 (10)</td>
<td>Twistb</td>
<td>5.32</td>
</tr>
<tr>
<td>C(3)–O(1)</td>
<td>1.217 (10)</td>
<td>Foldc</td>
<td>31.05</td>
</tr>
<tr>
<td>C(4)–O(2)</td>
<td>1.197 (9)</td>
<td>P(2)–Pt–C(1)–H(1) Torsion</td>
<td>-34.98</td>
</tr>
<tr>
<td>Pt–H(32)</td>
<td>2.578</td>
<td>P(3)–Pt–C(2)–H(2) Torsion</td>
<td>-61.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)–P(1)–C(1)–H(1) Torsion</td>
<td>83.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)–P(1)–C(2)–H(2) Torsion</td>
<td>29.44</td>
</tr>
</tbody>
</table>

a See Figure 2 for crystallographic numbering system;
b < C(1)–Pt–C(2) / P(2)–Pt–P(3);
c < C(1)–Pt–C(2) / C(2)–P(1)–C(2).
Figure 2
Molecular structure of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(PPh₃)₂] (109) with triphenylphosphine carbon atoms other than those bonded to phosphorus, the benzoyl phenyl carbon atoms other than C(11) and C(21), and all phenyl hydrogen atoms being omitted.
TABLE 2
Selected structural data for 1-phenylphosphetane-1-oxide and platinaphosphetane-3-oxide ring systems.

<table>
<thead>
<tr>
<th>Ring</th>
<th>Fold Angle (°)</th>
<th>C–P–C (°)</th>
<th>Mean Bond Distance (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P–C</td>
<td>P=O</td>
</tr>
<tr>
<td>Ph</td>
<td>25.8</td>
<td>80.4 (1)</td>
<td>1.822 (3)</td>
<td>1.482 (2)</td>
</tr>
<tr>
<td>Ph</td>
<td>16.7</td>
<td>79.4 (2)</td>
<td>1.812 (5)</td>
<td>1.472 (3)</td>
</tr>
<tr>
<td>Ph</td>
<td>29.8</td>
<td>80.8 (2)</td>
<td>1.820 (5)</td>
<td>1.477 (4)</td>
</tr>
<tr>
<td>Ph</td>
<td>23.8</td>
<td>81.3 (2)</td>
<td>1.835 (4)</td>
<td>1.494 (2)</td>
</tr>
<tr>
<td>Ph</td>
<td>23.4</td>
<td>81.9 (6)</td>
<td>1.87 (1)</td>
<td>1.48 (1)</td>
</tr>
<tr>
<td>Ph</td>
<td>31.05</td>
<td>94.0 (3)</td>
<td>1.786 (8)</td>
<td>1.486 (6)</td>
</tr>
</tbody>
</table>

*< C–C–C / C–P–C*
position and the bis(triphenylphosphine)platinum group, since lone pairs occupy less space and are more deformable than oxygen atoms.\textsuperscript{103} This reasoning cannot be applied to explain the preferences in complex (109) as an axial phenyl group increases any steric strain between that axial environment and the bis(phosphine)platinum group compared with an oxygen atom, due to its larger size. This is highlighted by the presence of a reasonably close non-bonded contact between the hydrogen atom attached to C(32) and the platinum of 2.578\AA. Thus the equatorial preference of O(3) in complex (109) must be due to other factors such as electronic or crystal packing considerations and not steric effects.

The P(1)–C(1) and P(1)–C(2) bonds [1.790(8) and 1.782(8)\AA] are shorter than those in organic analogues (average P–C ca. 1.84\AA) and the C(1)–P(1)–C(2) ring angle of 94.0(3)° is somewhat larger (average < C–P–C ca. 80.9°),\textsuperscript{107–110} which indicates that the introduction of a platinum atom into the 3-position of a ring, significantly reduces ring strain. A similar effect was also noted in the metallathietane oxide rings.\textsuperscript{99,101,103}

Complex (109) exists as the trans-disubstituted isomer with respect to the benzoyl substituents which again, mimics the structural properties of the metallathietane oxide systems.\textsuperscript{99,101,103}

Complex (109) crystallises with chloroform molecules incorporated into the lattice, although there are no short intermolecular contacts between the solvent and the metal complex.

2.4 NMR SPECTRA OF METALLAPHOSPHETANE-3-OXIDE COMPLEXES

2.4.1 $^1$H N.m.r. Spectra

The room temperature $^1$H n.m.r. spectra for the platinum-phosphine complexes (109–114) are consistent with the static structure shown in Figure 3.

Two distinct resonances can be seen for the equatorial H(1) and axial H(2) ring hydrogens as illustrated in Figure 4 for complex (109). Shielding of H(1) by the axial phenyl group and deshielding of H(2) by the phosphoryl oxygen causes the shifts of H(1) and H(2) to be significantly separated [$\Delta \delta = 0.92$ p.p.m. for (109)]. Both signals show coupling to the ring phosphorus P(1); the magnitude of which is determined by the dihedral
angle made by the C–H bond to the P=O group.$^{111}$ Thus the signal due to the axial proton H(2) shows a coupling to P(1) of 17 Hz [the H(2)–C(2)–P(1)–C(3) torsion angle is 29.44°] whilst the equatorial proton H(1) shows a coupling of only 7 Hz [the H(1)–C(1)–P(1)–O(3) torsion angle is 83.89°].

The size of the coupling of H(1) and H(2) to their respective cis-phosphine ligand is also under dihedral angle control, as in the Karplus relationships for vicinal proton couplings in organic molecules.$^{112}$ Thus the higher field resonance due to H(1) shows coupling to both the cis-phosphorus atom [the P(2)–Pt–C(1)–H(1) torsion angle is 34.98°] and the trans-phosphorus, giving rise to an overlapping doublet of doublet of doublets. It must be noted that in complexes (111) and (112), the coupling to the cis-phosphorus-31 nucleus is not seen and the signal for H(1) appears as a doublet of doublets. The lower field resonance due to axial H(2) shows coupling to its trans-phosphorus atom only to give a doublet of doublets [the P(3)–Pt–C(2)–H(2) torsion angle is 61.63°]. As can be seen from Figure 4, both H(1) and H(2) show coupling to platinum-195.

The chiral nature of the ring carbon atoms is demonstrated by the proton n.m.r. spectrum of the dimethylphenylphosphine complex (111), in which the two methyl groups bonded to each phosphorus become chemically non-equivalent. This results in two pairs of diastereotopic methyl groups and is shown in the spectrum by four separate signals in the methyl region.

For complexes (115) and (116) which contain no phoshpine ligands, the ring protons H(1) and H(2) appear as doublets with corresponding platinum-195 satellites.
Figure 4

Room temperature $^1$H n.m.r. spectrum at 300MHz for the Pt-CH protons of the complex $[\text{Pt(CH(COPh)P(O)Ph)CH(COPh)}](\text{PPh}_3)_2$ (109). CHCl$_3$. 

- 43 -
The room temperature $^1$H n.m.r. spectrum for the palladium complex (117) again confirms a static puckered structure, as for its platinum counterparts. The two ring protons appear as two sharp, distinct resonances at $\delta$ 3.38 and 4.40 p.p.m., although unlike its platinum analogues, the signals are complex and coupling constants cannot be assigned.

In the $^1$H n.m.r. spectrum of the diphenyl substituted platinum complex (118), only one resonance is observed for both ring protons. If the substitution of the phenyl groups on the ring is trans (as for the di-benzoyl complexes), these protons can never be chemically equivalent, even if the ring flips, since one proton will always be aligned closer to the phosphoryl group than the phenyl ring and vice versa. Therefore, the only way that one resonance may be observed is if the two signals overlap. This is unlikely in this case, as the proton closer to the phosphoryl group will experience deshielding and the one close to the phenyl group of the phosphorus will be shielded, and so a significant difference in the chemical shift of the signals would be expected. However, if the substitution of the phenyl groups on the ring is cis, the two ring protons would be chemically equivalent in any ring conformation and would therefore appear as a single resonance. The chemical shift of the signal ($\delta$ 3.06 p.p.m.) indicates the hydrogens are aligned close to the phenyl group of the ring phosphorus and therefore the structures in Figure 5 show the possible conformations, although (A) is the more likely with the sterically larger phenyl rings in equatorial positions, even though the phosphoryl group is axial.

![Figure 5](image)

The crystal structure study of a diphenyl substituted metallathietane-3,3-dioxide complex
showed that in these systems, the phenyl groups were trans. However, an X-ray study of the diphenyl substituted oxodimethylenemethane complex (10, L = AsPh₃) showed the phenyl rings in a cis orientation, occupying the equatorial positions of the fragment as shown.

![Chemical structure](image)

(10, L=AsPh₃)

Hence the cis-disubstituted form proposed for complex (118) has precedent, although for confirmation of the structure, an X-ray study would be needed.

### 2.4.2 ¹³C-{¹H} N.m.r. Spectra

The ¹³C-{¹H} n.m.r. spectra for the platinum complexes (109-114) show two distinct resonances for the Pt-C ring carbons, although on the basis of current data, the assignment of these two signals to C(1) or C(2) cannot be made unambiguously. Both signals show a large one bond coupling to the adjacent ring phosphorus atom and a two bond coupling to the trans-phosphine phosphorus atom, the values of which cannot be assigned in all cases due to their similarity. In the case of complexes (109), (110), (111) and (114) some two bond coupling also occurs to the cis-phosphine ligand, although this is small, less than 5 Hz in each case. For complexes (115) and (116), the ring carbons appear as doublets due to the one bond coupling of the ring phosphorus. For all the complexes, coupling to platinum-195 was not discernible.

The carbonyl carbons of the benzoyl substituents appear as two weak signals in the range δ 194.72–202.38 p.p.m. For complexes (109-114) they appear either as an unresolved multiplet or as a doublet of doublets due to coupling to the ring phosphorus and to the trans-phosphine ligand. For (115) and (116), they appear as doublets with 2J[P(1)C] in the
range 4-6 Hz. The signals of complex (113) are sufficiently well resolved to show platinum-195 satellites, $^2J(\text{PtC})$ being 26 and 41 Hz.

The chiral nature of the ring carbons was demonstrated again by the $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum of complex (111) which contains four sets of methyl resonances.

The $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum for the palladium derivative (117) shows two distinct resonances for the ring carbons and also two signals for the carbonyl groups, data which is consistent with the proposed structure.

### 2.4.3 $^{31}\text{P}-\{^1\text{H}\}$ N.m.r. Spectra

The $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectra of compounds (109)-(114) indicate the presence of three non-equivalent phosphorus nuclei and coupling between them is observed for each pair. Therefore, the spectra exhibit a doublet of doublets for each nucleus with corresponding platinum-195 satellites, the two bond coupling constant $^2J(\text{PtP(1)})$ lying in the range 538–589 Hz. The $^{31}\text{P}-\{^1\text{H}\}$ spectra of complexes (115) and (116) consist of a singlet with accompanying platinum-195 satellites, the value of $^2J(\text{PtP(1)})$ being 593 and 588 Hz respectively.

The room temperature $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectrum of the palladium complex (117) shows the presence of three non-equivalent phosphorus nuclei. However, coupling is not seen between the two phosphorus nuclei of the dppp ligand, hence the spectrum shows only doublets for these nuclei, due to 3-bond coupling with the third phosphorus atom, which itself appears as a doublet of doublets.

The $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectrum of the diphenyl substituted platinacycle (118) is consistent with the cis-structures proposed in the discussion of the $^1\text{H}$ n.m.r. spectra. Thus, the two ligand phosphorus-31 nuclei are chemically equivalent and appear as a singlet with platinum-195 satellites [$^1J(\text{PtP}) 2419$ Hz], as does the ring phosphorus [$^2J(\text{PtP}) 564$ Hz]. No 3-bond phosphorus-phosphorus coupling is observed in the spectrum.
2.5 I.R. SPECTRA OF METALLAPHOSPHETANE-3-OXIDE COMPLEXES

The infra-red spectra of compounds (109-116) show clearly the characteristic bands due to the phosphoryl and carbonyl stretches. The phosphoryl bands occur within the range 1180-1190 cm\(^{-1}\) and are easily distinguished. This range agrees well with that of phosphetane-1-oxides whose P=O stretch generally occurs in the region 1170-1230 cm\(^{-1}\).\(^{113,114}\) This may be expected from comparison of the P=O bond lengths which are very similar.\(^{107-110}\) The expected increase in frequency of the phosphoryl stretch in going from (107) to (109-116), i.e. acyclic to cyclic phosphine oxide,\(^{115}\) does not occur, the value for (107) being 1180 cm\(^{-1}\).

However, there is a significant decrease in the carbonyl stretching frequencies of about 30-40 cm\(^{-1}\) in comparing the metal complexes to (107). In the spectra of compounds (109-116), the two carbonyl bands overlap giving one relatively broad band whose peak lies within the range 1630-1640 cm\(^{-1}\), whereas for (107) two bands can be seen at 1665 and 1680 cm\(^{-1}\) respectively.

The i.r. spectrum of complex (115) has, in addition, two peaks at 2200 and 2225 cm\(^{-1}\) assigned to the isocyanide stretches.

The spectrum of the palladium compound (117) hardly differs from those of its platinum analogues, bands at 1180 and 1630 cm\(^{-1}\) assigned to the phosphoryl and combined carbonyl stretches respectively.

The i.r. spectrum of compound (118) shows its phosphoryl stretching frequency at 1180 cm\(^{-1}\), which is almost identical to that of dibenzylphenylphosphine oxide, which occurs at 1183 cm\(^{-1}\).\(^{116}\)

2.6 REACTIONS OF PLATINAPHOSPHETANE-3-OXIDES

2.6.1 Ligand Substitution Reactions

The cycloocta-1,5-diene complex (116) undergoes simple ligand displacement reactions with mono or bidentate tertiary phosphines or t-butyl isocyanide to yield the corresponding phospine or isocyanide complexes. Thus treatment of (116) with two equivalents of triphenylphosphine or methylidiphenylphosphine in dichloromethane, afforded the complexes
respectively, whereas treatment of (116) with one equivalent of dppp yielded complex (113). Two mole equivalents of t-butyl isocyanide readily displaces the cod ligand of (116) to yield (115), as shown by $^1$H n.m.r. and i.r. spectroscopy.

The ligand substitution and insertion reactions of alkyl isocyanides with oxodi-methylenemethane and metallathietane-3,3-dioxide complexes have been discussed in the literature and are mentioned in Chapter 1 and in Section 2.1 of this Chapter.\textsuperscript{23,102} This led to an investigation of the chemistry of the metallaphosphetane-3-oxide ring system with t-butyl isocyanide in order to compare the reactivity of these different systems. Thus, treatment of the platinum complex (109) with one equivalent of t-butyl isocyanide in dichloromethane afforded the monosubstituted metallaphosphetane-3-oxide complex (120) in high yield.

The i.r. spectrum of this compound exhibits a phosphoryl stretch at 1190 cm\(^{-1}\), overlapping carbonyl stretches at 1640 cm\(^{-1}\) and an intense band at 2220 cm\(^{-1}\) which is characteristic of a terminal isocyanide ligand bound to a metal. Its $^{31}$P-$^1$H n.m.r. spectrum shows two resonances with corresponding platinum-195 satellites [$^1$J(PtP) 2708 and $^2$J(PtP) 569 Hz]. The stereochemistry of the complex can be determined from its $^1$H n.m.r. spectrum by a consideration of the coupling constants between the ring protons and the terminal phosphine ligand. Thus, the lower field signal due to the axial proton retains its coupling to the $trans$-phosphine ligand and is observed as a triplet (due to an overlapping doublet of doublets) with platinum-195 satellites, whereas the signal due to the equatorial proton loses its coupling to the $trans$-phosphine ligand but retains a small coupling to the $cis$ ligand and therefore is also split into a doublet of doublets. This information indicates that
the isocyanide ligand lies opposite to the carbon bearing the equatorial ring proton, as shown for (120).

The treatment of complex (109) with an excess of t-butyl isocyanide in refluxing dichloromethane did not result in the formation of a zwitterionic five-membered ring, as did similar reactions with platinathietane-3,3-dioxide and metal-oxodimethylenemethane complexes.\(^{23,102}\) \(^{31}\)P-\(\{^1\)H\} n.m.r. spectra of the reaction mixture indicated the formation of a number of products, none of which could be easily isolated. The reaction of the monosubstituted complex (120) or of the di-isocyanide complex (115) with an excess of t-butyl isocyanide also led to the formation of a number of products, even when the reactions were attempted at room temperature. The reason for the failure of these reactions is not apparent and indicates a significant difference in the reactivity of the four-membered ring species.

2.6.2 Attempted Reactions of the Phosphoryl Group

The reduction of phosphetane-1-oxides to phosphetanes has been achieved in high yield using a number of silicon reagents.\(^{117,118}\) The reduction of the metallaphosphetane-3-oxide ring system was thus attempted with several of these reagents in order to try and specifically reduce the ring phosphorus atom to a phosphine. The reaction of complex (109) with either trichlorosilane/triethylamine or hexachlorodisilane in toluene resulted in the formation of cis-[PtCl\(_2\)(PPh\(_3\))\(_2\)] as the only platinum and phosphorus containing product, as shown by \(^{31}\)P-\(\{^1\)H\} n.m.r. spectroscopy. The reaction of complex (109) with phenylsilane in toluene resulted in decomposition of the complex, platinum metal being deposited in the reaction flask and triphenylphosphine being the only observable signal in the \(^{31}\)P-\(\{^1\)H\} n.m.r. spectrum. Thus, the presence of a platinum(II) moiety in a phosphetane-1-oxide ring, makes it much more difficult to reduce the phosphoryl group without destruction of the ring.

Coordination compounds of boron halides with phosphine oxides are well known and can be prepared by direct combination in a suitable solvent.\(^{119}\) Thus the coordinating ability of the phosphoryl group of the metallaphosphetane-3-oxides was examined using
boron trifluoride as a Lewis acid. The reaction of the dppp complex \((113)\) with boron trifluoride in dichloromethane yielded a complex which can be provisionally given the structure shown in Figure 6 by consideration of its i.r., \(^{31}\text{P}-\{^1\text{H}\}\) and \(^{19}\text{F}-\{^1\text{H}\}\) n.m.r. spectra.

![Figure 6](image)

A number of unidentified minor products were also formed in this reaction. The \(^{19}\text{F}-\{^1\text{H}\}\) n.m.r. spectrum shows a broad signal at 149.79 p.p.m. and the \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectrum shows a shift of ca. 18 p.p.m. to low field of the ring phosphorus on coordination of the \(\text{BF}_3\). The i.r. spectrum shows the disappearance of the phosphoryl stretch at 1180 cm\(^{-1}\) and the appearance of strong bands in the region 1040–1160 cm\(^{-1}\) which can be tentatively assigned to B–F stretching modes by comparison with spectra of known boron trifluoride adducts of phosphine oxides.\(^{120}\)

Phosphetane-1-oxides have been shown to catalyse the formation of carbodiimides from isocyanates, \textit{via} the formation of a phosphetane-imide, Scheme 26.\(^{121}\)

\[
\begin{align*}
\text{Ph} & \quad \text{P} \equiv \text{O} \quad + \quad \text{RNCO} \quad \rightarrow \quad \text{Ph} \quad \text{P} \equiv \text{N} \equiv \text{R} \quad \text{RNCO} \\
\text{Ph} & \quad \text{Ph} \quad \text{Ph} & \quad \text{Ph} \quad \text{Ph} \quad \text{RNCNR}
\end{align*}
\]

\textbf{Scheme 26}

Attempts to prepare the corresponding imide from the metallaphosphetane-3-oxide complex \((109)\) using tosyl or phenyl isocyanate failed, with the recovery of the starting material. An investigation into the organic residue from these reactions showed, \textit{via} i.r. 
spectra, that the initial isocyanate was present and that no significant amount of carbodi-imide had been produced.

2.6.3 Miscellaneous Reactions of Platinaphosphetane-3-oxides

The oxidative addition of gaseous hydrogen chloride to complex (109) in dichloromethane, afforded cis-[PtCl$_2$(PPh$_3$)$_2$] in quantitative yield, along with (107).

Examination of the residues from the reactions of complex (109) with carbon monoxide or sulphur dioxide in dichloromethane, showed in both cases, the recovery of starting material.

The attempted oxidative addition of methyl iodide to complex (109) in refluxing dichloromethane, again yielded only unreacted starting material.

2.7 CONCLUSION

The preparation of new metallaphosphetane-3-oxide complexes of platinum(II) and palladium(II) may be achieved in high yield via the treatment of cis-[MCl$_2$L$_2$] (M = Pt or Pd; L = donor ligand) with diphenacylphenylphosphine oxide (107) and silver(I) oxide in refluxing dichloromethane. The platinum complexes (where L$_2$ = chelating phosphine) may also be synthesised using potassium hydroxide instead of silver(I) oxide. N.m.r. studies, together with a single crystal X-ray diffraction study, indicate that the four-membered metallacycle is puckered, both in solution and in the solid state, with the phosphoryl group adopting an equatorial environment and the benzoyl substituents showing trans-axial-equatorial substitution. A diphenyl substituted metallacycle was prepared by the action of Li$_2$[PhCHP(0)(Ph)CHPh] on cis-[PtCl$_2$(PPh$_3$)$_2$] at low temperatures in THF, the n.m.r. study of which indicates that the phenyl groups occupy cis-positions on the ring.

Simple ligand displacement reactions of some of these complexes have been investigated, along with their behaviour with a range of reagents.
2.8 EXPERIMENTAL

Microanalyses were carried out by C.H.N. Analysis Ltd., Alpha House, Countesthorpe Road, South Wigston, Leicester, LE8 2PJ, and by Butterworth Laboratories Ltd., 54-56, Waldegrave Road, Teddington, Middlesex, TW11 8LG. M.p.'s were recorded on a Reichert hot-stage apparatus, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer as KBr discs unless otherwise stated. The $^1$H n.m.r. spectra were recorded at room temperature in $^{[2]}$H$_2$]-chloroform, unless otherwise stated, on a Bruker AM 300 spectrometer operating at 300.13 MHz, or on a Varian EM 390 spectrometer operating at 90 MHz, with SiMe$_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field). Coupling constants J are in Hz. The $^{13}$C-$^1$H n.m.r. spectra were recorded in $^{[2]}$H$_2$]-chloroform at room temperature on a Bruker AM 300 spectrometer operating at 75.47 MHz, with SiMe$_4$ (0.0 p.p.m.) as internal reference. The $^{13}$C-$^1$H n.m.r. data for the aromatic region between δ 140 and 125 p.p.m. have been omitted for clarity. The $^{31}$P-$^1$H n.m.r. spectra were recorded in dichloromethane unless otherwise stated, on either a JEOL JNM FX90Q spectrometer operating at 36.24 MHz with [P(OH)$_4$]$^+$ 122 in $^{[2]}$H$_2$]-water (0.0 p.p.m.) as external reference, or on a Bruker AM 300 spectrometer operating at 121.50 MHz with H$_3$PO$_4$ as external reference, with positive values to high frequency (low field). The $^{19}$F-$^1$H n.m.r. spectra were recorded in dichloromethane on a JEOL JNM FX90Q spectrometer, operating at 84.3 MHz, relative to external reference fluorotrichloromethane (0.0 p.p.m.). Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use, from the following drying agents: dichloromethane (calcium hydride); diethyl ether, tetrahydrofuran (sodium/benzophenone); toluene, light petroleum (sodium). Light petroleum refers to the fraction boiling in the range 40–60°C. The platina- and palladaphosphetane-3-oxide complexes were recrystallised in air. The compounds triphenylphosphine, methylidiphenylphosphine, dimethylphenylphosphine, dppe, dppp, dpb, n-butyl lithium (1.8 mol dm$^{-3}$), trichlorosilane, hexachlorodisilane, $p$-tosyl isocyanate, phenyl isocyanate, methyl iodide (Aldrich), potassium hydroxide, hydrogen chloride,
sulphur dioxide (BDH), silver(I) oxide (Fisons), t-butyl isocyanide (Fluka), boron trifluoride (Fluorochem) and phenylsilane (Ventron) were used as supplied from commercial sources. Triethylamine was dried and distilled under nitrogen from calcium hydride prior to use. The compounds [PtCl$_2$(cod)],$^{123}$ cis-[PtCl$_2$(PPh$_3$)$_2$],$^{124}$ [PdCl$_2$(cod)],$^{125}$ diphenacylphenylphosphine oxide ($^{107}$),$^{106}$ and dibenzylphenylphosphine oxide$^{116}$ were prepared as described in the literature. The platinum metal salts were obtained on loan from Johnson Matthey p.l.c.
Preparation of metallaphosphetane-3-oxide complexes using silver(I) oxide; general method

Two equivalents of tertiary phosphine or $t$-butyl isocyanide, or one equivalent of chelating tertiary phosphine, followed by one equivalent of diphenacylphenylphosphine oxide (107), and an excess of silver(I) oxide were added in succession to a stirred solution of $[\text{MCl}_2\text{(cod)}]$ (M = Pt or Pd) in dichloromethane (ca. 40 cm$^3$), and the mixture was refluxed for 15 h. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish-brown oil. Dissolution of the oil in dichloromethane (ca. 5 cm$^3$) followed by addition of light petroleum afforded, on standing, a white to pale yellow microcrystalline solid, which was recrystallised from dichloromethane - light petroleum, and dried in vacuo.

(i) $[\text{Pt(CH(COPh)}P(O)(\text{Ph})\text{CH(COPh)}]}(\text{PPh}_3)_2]$ (109).CH$_2$Cl$_2$

The complex $[\text{PtCl}_2\text{(cod)}]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and diphenacylphenylphosphine oxide (107) (0.10g, 0.28 mmol) gave white microcrystals of (109).CH$_2$Cl$_2$ (0.29g, 93%). (Found: C, 61.5; H, 4.3. C$_{59}$H$_{49}$O$_2$P$_2$Pt.CH$_2$Cl$_2$ requires C, 61.6; H, 4.3%), m.p. 188°C; $\nu_{\text{C=O}}$ at 1635s(br) cm$^{-1}$; $\nu_{\text{P=O}}$ at 1180s cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz), $\delta$ 8.35-6.89 (m, 45H, Ph), 5.25 (s, 2H, CH$_2$Cl$_2$), 4.56 (dd, 1H, H(2), 2$J[P(1)H(2)]$ 17, 3$J[P(2)H(2)]$ 9, 2$J[PtH(2)]$ 67) and 3.62 p.p.m. (ddd, 1H, H(1), 2$J[P(1)H(1)]$ 7, 3$J[P(3)H(1)]$ 10, 3$J[P(2)H(1)]$ 3, 2$J[PtH(1)]$ 43); $^{13}$C-{*H), 202.38 (dd, CO, 2$J[PtC]$ not discernible), 200.56 [s, CO, 2$J[PtC]$ not discernible], 53.42 (s, CH$_2$Cl$_2$), 34.15 (ddd, Pt–C, 2$J[P \text{cis C}]$ 4, 2$J[P \text{trans C}]$ 43, 1$J[P(1)C]$ 66) and 35.90 p.p.m. (ddd, Pt–C, 2$J[P \text{cis C}]$ 4, 2$J[P \text{trans C}]$ 40, 1$J[P(1)C]$ 74); $^{31}$P-{*H) (36.2 MHz) $\delta$ 30.39 (dd, P(1), 3$J[P(2)P(1)]$, 3$J[P(3)P(1)]$ 12, 5, 2$J[PtP(1)]$ 562), 18.07 (dd, Pt–P, 2$J(PP)$ 12, 3$J[P(1)P]$ 5, 1$J(PtP)$ 2808) and 13.73 p.p.m. (dd, Pt–P, 2$J(PP)$ 12, 3$J[P(1)P]$ 12, 1$J(PtP)$ 2781). See Figure 3. X-ray quality crystals of (109).CHCl$_3$ were grown slowly from chloroform - light petroleum, in air.

(ii) $[\text{Pt(CH(COPh)}P(O)(\text{Ph})\text{CH(COPh)}]}(\text{PMePh}_2)_2]$ (110)

The complex $[\text{PtCl}_2\text{(cod)}]$ (0.10g, 0.27 mmol) with methylidiphosphane (0.11g, 0.55
mmol) and diphenacylphenylphosphine oxide \((107)\) (0.10g, 0.28 mmol) gave white microcrystals of \((110)\) (0.24g, 94%). (Found: C, 59.8; H, 4.5. \(\text{C}_{48}\text{H}_{45}\text{O}_{3}\text{P}_{3}\text{Pt}\) requires C, 60.3; H, 4.5%), m.p. 151°C; \(v_{\text{C-O}}\) at 1640s(br) cm\(^{-1}\); \(v_{\text{P=O}}\) at 1180s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 8.48-6.82 (m, 35H, Ph), 4.75 (ddd, 1H, H(2), \(^2\text{J}[\text{P}(1)\text{H}(2)]\) 20, \(^3\text{J}[\text{P}(2)\text{H}(2)]\) 8, \(^2\text{J}[\text{PtH}(2)]\) 57), 3.58 (ddd, 1H, H(1), \(^2\text{J}[\text{P}(1)\text{H}(1)]\) 5, \(^3\text{J}[\text{P}(3)\text{H}(1)]\) 9, \(^3\text{J}[\text{P}(2)\text{H}(1)]\) 1, \(^2\text{J}[\text{PtH}(1)]\) 49), 1.87 [d, 3H, Me, \(\text{PMe}_{2}\text{Ph}\)], \(^4\text{J}([\text{PH}]+4\text{J}([\text{PH}])\) 9, \(^3\text{J}([\text{PtH}])\) 31], and 1.58 [d, 3H, Me, \(\text{PMe}_{2}\text{Ph}\)], \(^2\text{J}([\text{PH}]+4\text{J}([\text{PH}])\) 8, \(^3\text{J}([\text{PtH}])\) 27]; \(^{13}\text{C}-([\text{H}])\), \(\delta\) 201.01 (m, CO, \(^2\text{J}([\text{PtC}])\) not discernible), 200.08 (dd, CO, \(^2\text{J}([\text{P}(1)\text{C}])\) 5, \(^3\text{J}([\text{PC}])\) 5, \(^2\text{J}([\text{PtC}])\) not discernible), 37.20 (ddd, Pt–C, \(^2\text{J}([\text{PtC}])\) 56, \(^1\text{J}([\text{PC}])\) 61), 14.78 [dd, 3H, Me, \(\text{PMe}_{2}\text{Ph}\)], \(^1\text{J}([\text{PC}])\) 34, \(^2\text{J}([\text{ PtC}])\) 31], 13.65 [d, Me, \(\text{PMe}_{2}\text{Ph}\)], \(^1\text{J}([\text{PC}])\) 34, \(^2\text{J}([\text{ PtC}])\) 28]; \(^{31}\text{P}-([\text{H}])\) (121.50 MHz) \(\delta\) 28.90 (dd, \(\text{P}(1), \(^3\text{J}([\text{P}(2)\text{P}(1)])\) 14, \(^5\text{J}([\text{PtP}(1)])\) 564), -5.48 (dd, Pt–P, \(^2\text{J}([\text{PP}])\) 14, \(^3\text{J}([\text{P}(1)\text{P}])\) 5, \(^1\text{J}([\text{PtP}])\) 2588) and -6.40 p.p.m. (dd, Pt–P, \(^2\text{J}([\text{PP}])\) 14, \(^3\text{J}([\text{P}(1)\text{P}])\) 14, \(^1\text{J}([\text{PtP}])\) 2898).

(iii) \([\text{Pt}([\text{CH}([\text{COPh}])\text{P}(0)\text{(Ph)}]([\text{CH}([\text{COPh}])])(\text{PMe}_2\text{Ph})_2])\) \((111).\text{CH}_2\text{Cl}_2\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dimethylphenylphosphine (0.08g, 0.58 mmol) and diphenacylphenylphosphine oxide \((107)\) (0.10g, 0.28 mmol) gave white microcrystals of \((111).\text{CH}_2\text{Cl}_2\) (0.22g, 90%). (Found: C, 51.4; H, 4.4. \(\text{C}_{38}\text{H}_{39}\text{O}_3\text{P}_3\text{Pt}.\text{CH}_2\text{Cl}_2\) requires C, 51.1; H, 4.5%), m.p. 93°C; \(v_{\text{C=O}}\) at 1640s(br) cm\(^{-1}\); \(v_{\text{P=O}}\) at 1180s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 8.41-7.14 (m, 25H, Ph), 5.26 (s, 2H, \(\text{CH}_2\text{Cl}_2\)), 4.41 (ddd, 1H, H(2), \(^2\text{J}[\text{P}(1)\text{H}(2)]\) 20, \(^3\text{J}[\text{P}(2)\text{H}(2)]\) 8, \(^3\text{J}[\text{P}(3)\text{H}(2)]\) 1, \(^2\text{J}[\text{PtH}(2)]\) 53), 3.87 (ddd, 1H, H(1), \(^2\text{J}[\text{P}(1)\text{H}(1)]\) 7, \(^3\text{J}[\text{P}(3)\text{H}(1)]\) 7, \(^2\text{J}[\text{PtH}(1)]\) 50), 1.46 (d, 3H, Me, \(\text{PMe}_2\text{Ph}\)), \(^4\text{J}([\text{PH}]+4\text{J}([\text{PH}])\) 10, \(^3\text{J}([\text{PtH}])\) 34), 1.35 [d, 3H, Me, \(\text{PMe}_2\text{Ph}\)], \(^3\text{J}([\text{PH}]+4\text{J}([\text{PH}])\) 10, \(^3\text{J}([\text{PtH}])\) 30], 1.14 [d, 3H, Me, \(\text{PMe}_2\text{Ph}\)], \(^2\text{J}([\text{PH}]+4\text{J}([\text{PH}])\) 10, \(^3\text{J}([\text{PtH}])\) 26]; \(^{13}\text{C}-([\text{H}])\), \(\delta\) 202.21 [s, CO, \(^2\text{J}([\text{PtC}])\) 29], 199.27 (dd, CO, \(^2\text{J}([\text{PtC}])\) 5, \(^3\text{J}([\text{PC}])\) 5, \(^2\text{J}([\text{PtC}])\) 22), 53.29 (s, \(\text{CH}_2\text{Cl}_2\)), 36.27 (dd, Pt–C, \(^2\text{J}([\text{PtC}])\) 57, \(^1\text{J}([\text{PC}])\) 57), 36.18 [ddd, Pt–C, \(^2\text{J}([\text{PtC}])\) 4, \(^2\text{J}([\text{PtC}])\) 39, \(^1\text{J}([\text{PC}])\) 75], 16.77 [d, Me, \(\text{PMe}_2\text{Ph}\)], \(^1\text{J}([\text{PC}])\) 36, \(^2\text{J}([\text{PC}])\) 37], 16.67 [d, Me, \(\text{PMe}_2\text{Ph}\)], \(^1\text{J}([\text{PC}])\) 35, \(^2\text{J}([\text{PC}])\) 28], 15.07 [d, Me, \(\text{PMe}_2\text{Ph}\)], \(^1\text{J}([\text{PC}])\) 33, \(^2\text{J}([\text{PC}])\) 34], 13.49 [d, Me, \(\text{PMe}_2\text{Ph}\)], \(^1\text{J}([\text{PC}])\) +
\(^{3}J\)(PC) 33, \(^{2}J\)(PtC) 31; \(^{31}P\)-\(^{1}H\) (36.2 MHz) \(\delta\) 30.32 (dd, P(1), \(^{3}J\)(P(2)P(1)), \(^{3}J\)(P(3)P(1))) 15, 7, \(^{2}J\)(PtP(1)) 545), -15.21 (dd, Pt–P, \(^{2}J\)(PP) 15, \(^{3}J\)(P(1)P) 15, \(^{1}J\)(PtP) 2927) and -17.36 p.p.m. (dd, Pt–P, \(^{2}J\)(PP) 15, \(^{3}J\)(P(1)P) 7, \(^{1}J\)(PtP) 2573).

(iv) \([Pt(CH(COPh)P(O)(Ph)CH(COPh))\text{dppe}]^{(112)}\text{H}_{2}O\)

The complex \([PtCl}_{2}(\text{cod})\) (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and diphenacylphenylphosphine oxide \((107)\) (0.10g, 0.28 mmol) gave white microcrystals of \((112)\text{H}_{2}O\) (0.25g, 96%). (Found: C, 59.0; H, 4.4. \(C_{48}H_{41}O_{3}P_{3}PtH_{2}O\) requires C, 59.3; H, 4.4%), m.p. 166°C; \(v_{C=O}\) at 1630s (br) cm\(^{-1}\); \(v_{P=O}\) at 1190s cm\(^{-1}\). N.m.r. spectra: \(^{1}H\) (300 MHz), \(\delta\) 7.92-6.53 (m, 35H, Ph), 4.97 (dd, 1H, H(2), \(^{2}J\)(P(1)H(2)) 15, \(^{3}J\)(P(2)H(2)) 10, \(^{2}J\)(PtH(2)) 66), 4.08 (dd, 1H, H(1), \(^{2}J\)(P(1)H(1)) 7, \(^{3}J\)(P(3)H(1)) 7, \(^{2}J\)(PtH(1)) 54), 2.58 (s, br, 2H, H(3)), 2.51-2.15 (m, 2H, dppe), 1.81-1.49 (m, 2H, dppe); \(^{13}C\)-\(^{1}H\), \(\delta\) 199.43 [s, CO, \(^{2}J\)(PtC) not discernible], 199.02 (dd, CO, \(^{2}J\)(P(1)C) 5, \(^{3}J\)(PC) 5, \(^{2}J\)(PtC) not discernible), 38.45 (dd, Pt–C, \(^{2}J\)(P\text{ trans} C) 51, \(^{1}J\)(P(1)C) 66), 34.66 (dd, Pt–C, \(^{2}J\)(P\text{ trans} C) 58, \(^{1}J\)(P(1)C) 58), 30.78 [dd, CH\(_2\), dppe, \(^{1}J\)(PC) 37, \(^{2}J\)(PC) 14], 29.16 [dd, CH\(_2\), dppe, \(^{1}J\)(PC) 36, \(^{2}J\)(PC) 11]; \(^{31}P\)-\(^{1}H\) (121.50 MHz) \(\delta\) 40.30 (dd, Pt–P, \(^{2}J\)(PP) 2, \(^{3}J\)(P(1)P) 15, \(^{1}J\)(PtP) 2858), 39.74 (dd, Pt–P, \(^{2}J\)(PP) 2, \(^{3}J\)(P(1)P) 8, \(^{1}J\)(PtP) 2665) and 25.66 p.p.m. (dd, P(1), \(^{3}J\)(P(2)P(1)), \(^{3}J\)(P(3)P(1)) 15, 8, \(^{2}J\)(PtP(1)) 538).

(v) \([Pt\{CH(COPh)P(O)(Ph)CH(COPh)\}\text{dppe}]^{(113)}\text{H}_{2}Cl_{2}\)

The complex \([PtCl}_{2}(\text{cod})\) (0.10g, 0.27 mmol) with dppe (0.12g, 0.29 mmol) and diphenacylphenylphosphine oxide \((107)\) (0.10g, 0.28 mmol) gave white microcrystals of \((113)\text{H}_{2}Cl_{2}\) (0.26g, 92%). (Found: C, 56.7; H, 4.3. \(C_{48}H_{41}O_{3}P_{3}Pt\text{CHCl}_{2}\) requires C, 57.0; H, 4.3%), m.p. 154°C; \(v_{C=O}\) at 1640s (br) cm\(^{-1}\); \(v_{P=O}\) at 1180s cm\(^{-1}\). N.m.r. spectra: \(^{1}H\) (300 MHz), \(\delta\) 8.10-6.67 (m, 35H, Ph), 5.21 (s, 2H, CH\(_2\)Cl\(_2\)), 4.71 (dd, 1H, H(2), \(^{2}J\)(P(1)H(2)) 19, \(^{3}J\)(P(2)H(2)) 9, \(^{2}J\)(PtH(2)) 61), 3.65 (ddd, 1H, H(1), \(^{2}J\)(P(1)H(1)) 5, \(^{3}J\)(P(3)H(1)) 7, \(^{3}J\)(P(2)H(1)) 2, \(^{2}J\)(PtH(1)) 47), 2.52-2.10 (m, 4H, CH\(_2\), dppe), 1.87-1.68 (m, 2H, CH\(_2\), dppe); \(^{13}C\)-\(^{1}H\), \(\delta\) 200.69 (dd, CO, \(^{2}J\)(P(1)C) 5, \(^{3}J\)(PC) 5, \(^{2}J\)(PtC) 41), 200.27 (dd, CO, \(^{2}J\)(P(1)C) 4, \(^{3}J\)(PC) 4, \(^{2}J\)(PtC) 26), 53.51 (s, CH\(_2\)Cl\(_2\)), 37.17 (dd, Pt–C, \(^{2}J\)(P\text{ trans}
C] 44, 1J(P(1)C] 70), 34.81 [dd, Pt–C, 2J(P trans C] 43, 1J(P(1)C] 66), 25.17 [dd, P–CH2, dppp, 1J(PC) 34, 3J(PC) 9], 23.55 [dd, P–CH2, dppp, 1J(PC) 33, 3J(PC) 9], 18.40 (s, CH2, dppp); 31P-{1H} (121.50 MHz) δ 27.43 {dd, P(1), 3J(P(2)P(1)) 15, 6, 2J(PtP(1)) 556}, -6.38 {dd, Pt–P, 2J(PP) 24, 3J(P(1)P] 15, 1J(PtP) 2753} and -7.27 p.p.m. {dd, Pt–P, 2J(PP) 24, 3J(P(1)P] 6, 1J(PtP) 2510).

(vi) [Pt(CH(COPh)P(O)(Ph)CH(COPh))(dppb)](II4)
The complex [PtCl2(cod)] (0.10g, 0.27 mmol) with dppb (0.12, 0.28 mmol) and diphenacylphenylphosphine oxide (107) (0.10g, 0.28 mmol) gave white microcrystals of (II4) (0.24g, 91%). (Found: C, 61.0; H, 4.8. C50H48O2P3Pt requires C, 61.2; H, 4.6%), m.p. above 220°C; νC=O at 1640s(br) cm⁻¹; νP=O at 1180s cm⁻¹. N.m.r. spectra: (300 MHz), 8 7.94-6.70 (m, 35H, Ph), 4.55 {dd, 1H, H(2), 2J(P(1)H(2)) 20, 3J(P(2)H(2)) 8, 2J(PtH(2)) 58}, 3.69 {ddd, 1H, H(1), 2J(P(1)H(1)) 5, 3J(P(3)H(1)) 9, 3J(P(2)H(1)) 4, 2J(PtH(1)) 40}, 2.64-2.26 (m, 4H, P–CH2, dppb), 2.04 (m, 1H, dppb), 1.70 (m, 2H, dppb), 1.46 (m, 1H, dppb); 13C-{1H}, δ 201.24 {ddd, CO, 2J(P(1)C] 2, 3J(PC) 2, 2J(PtC) not discernible}, 200.28 [m, CO, 2J(PtC) not discernible], 37.92 {ddd, Pt–C, 2J[P cis C] 1, 2J[P trans C] 39, 1J(P(1)C] 74}, 33.76 {ddd, Pt–C, 2J[P trans C] 49, 1J(P(1)C] 64}, 31.78 [d, P–CH2, dppb, 1J(PC) 31, 2J(PtC) 29], 29.20 [d, P–CH2, dppb, 1J(PC) 30, 2J(PtC) 36], 24.44 [d, CH2, dppb, 2J(PC) 2], 23.74 (s, CH2, dppb); 31P-{1H} (36.2 MHz) δ 32.34 {dd, P(1), 3J(P(2)P(1)), 3J(P(3)P(1)) 16, 5, 2J(PtP(1)) 569}, 13.33 {dd, Pt–P, 2J(PP) 16, 3J(P(1)P] 16, 1J(PtP) 2876} and 7.00 p.p.m. {dd, Pt–P, 2J(PP) 16, 3J(P(1)P] 5, 1J(PtP) 2515}.

(vii) [Pt(CH(COPh)P(O)(Ph)CH(COPh))(CNBu+)](II5)
The complex [PtCl2(cod)] (0.10g, 0.27 mmol) with t-butyl isocyanide (0.048, 0.57 mmol) and diphenacylphenylphosphine oxide (107) (0.10g, 0.28 mmol) gave pale yellow microcrystals of (II5) (0.17g, 88%). No analytical data available, m.p. above 220°C; νC=NN at 2225s and 2200s cm⁻¹; νC=O at 1640s(br) cm⁻¹; νP=O at 1190s cm⁻¹. N.m.r. spectra: 1H (300 MHz), δ 8.31-7.30 (m, 15H, Ph), 4.60 {d, 1H, H(2), 2J(P(1)H(2)) 14, 2J(PtH(2)) 68}, 4.18 {d, 1H, H(1), 2J(P(1)H(1)) 4, 2J(PtH(1)) 67}, 1.19 (s, 9H, Bu+), 1.10 (s, 9H, Bu+);
\(^{13}\)C-\(^{1}\)H, \(\delta\) 198.72 (d, CO, \(^{2}\)J(P(1)C) 5, \(^{2}\)J(PtC) not discernible), 197.41 (d, CO, \(^{2}\)J(P(1)C) 6, \(^{2}\)J(PtC) not discernible), 58.18 (s, C, Bu\(^{3}\)), 58.14 (s, C, Bu\(^{3}\)), 29.79 (d, Pt–C, \(^{1}\)J(P(1)C) 54), 29.69 (s, Me, Bu\(^{3}\)), 29.52 (2, Me, Bu\(^{3}\)), 27.73 (d, Pt–C, \(^{1}\)J(P(1)C) 63); \(^{31}\)P-\(^{1}\)H) (36.2 MHz) \(\delta\) 31.43 p.p.m. (s, P(1), \(^{2}\)J(PtP(1)) 588).

(viii) \([\text{Pt}\{\text{CH(COPh)}\text{P(O)(Ph)}\text{CH(COPh)}\}\text{(cod)}]\) (116).CH\(_{2}\)Cl\(_{2}\)

The complex \([\text{PtCl\(_{2}\)}\text{(cod)}]\) (0.10g, 0.27 mmol) with diphenacylphenylphosphine oxide (107) (0.10g, 0.28 mmol) gave pale yellow microcrystals of (116) (0.18g, 90%). (Found: C, 50.3; H, 4.0. \(\text{C}_{30}\text{H}_{29}\text{O}_{3}\text{PdPtCl\(_{2}\)}\) requires C, 49.8; H, 4.1%), m.p. 176\(^\circ\)C; \(\nu_{\text{C=O}}\) at 1640s(br) cm\(^{-1}\); \(\nu_{\text{P=O}}\) at 1190s cm\(^{-1}\). N.m.r. spectra: \(^{1}\)H (300 MHz), \(\delta\) 8.25-7.13 (m, 15H, Ph), 5.64-5.50 (m, 2H, C–H, cod), 5.12 (m, 1H, C–H, cod), 4.76 (d, 1H, H(2), \(^{2}\)J(P(1)H(2)) 17, \(^{2}\)J[PtH(2)] 79), 4.72 (m, 1H, C–H, cod), 4.39 (d, 1H, H(1), \(^{2}\)J(P(1)H(1)) 3, \(^{2}\)J[PtH(1)] 80), 2.77-1.83 (m, 8H, CH\(_{2}\), cod); \(^{13}\)C-\(^{1}\)H, \(\delta\) 198.75 (d, CO, \(^{2}\)J(PtC) not discernible), 194.72 (d, CO, \(^{2}\)J(P(1)C) 6, \(^{2}\)J(PtC) not discernible), 103.18 (s, CH, cod, \(^{1}\)(PtC) not discernible), 100.43 (s, CH, cod, \(^{1}\)(PtC) not discernible), 100.27 (s, CH, cod, \(^{1}\)(PtC) not discernible), 100.09 (s, CH, cod, \(^{1}\)(PtC) not discernible), 53.45 (s, CH\(_{2}\)Cl\(_{2}\)), 39.39 (d, Pt–C, \(^{1}\)J(P(1)C) 51), 35.88 (d, Pt–C, \(^{1}\)J(P(1)C) 62), 31.42 (s, CH\(_{2}\), cod), 31.22 (s, CH\(_{2}\), cod), 28.61 (s, 2 x CH\(_{2}\), cod); \(^{31}\)P-\(^{1}\)H) (36.2 MHz) \(\delta\) 31.77 p.p.m. (s, P(1), \(^{2}\)J(PtP(1)) 593).

(ix) \([\text{Pd}\{\text{CH(COPh)}\text{P(O)(Ph)}\text{CH(COPh)}\}\text{(dppp)}]\) (117)

The complex \([\text{PdCl\(_{2}\)}\text{(cod)}]\) (0.10g, 0.35 mmol) with dppp (0.15, 0.36 mmol) and diphenacylphenylphosphine oxide (107) (0.13g, 0.36 mmol) gave white microcrystals of (117) (0.24g, 94%). (Found: C, 66.5; H, 4.9. \(\text{C}_{49}\text{H}_{43}\text{O}_{3}\text{P}_{2}\text{Pd}\) requires C, 66.9; H, 4.9%), m.p. 193\(^\circ\)C; \(\nu_{\text{C=O}}\) at 1630s(br) cm\(^{-1}\); \(\nu_{\text{P=O}}\) at 1180s cm\(^{-1}\). N.m.r. spectra: \(^{1}\)H (300 MHz), \(\delta\) 8.16-6.81 (m, 35H, Ph), 4.40 (m, 1H, H(2)), 3.38 (m, 1H, H(1)), 2.23 (m, 4H, P–CH\(_{2}\), dppp), 1.93 (m, 1H, CH\(_{2}\), dppp), 1.63 (m, 1H, CH\(_{2}\), dppp); \(^{13}\)C-\(^{1}\)H, \(\delta\) 200.72 (s, CO), 200.43 (s, CO), 39.81 (m, Pd–CH), 35.27 (m, Pd–CH), 26.84 (d, P–CH\(_{2}\), dppp, \(^{1}\)(PC) 17, \(^{3}\)(PC) 17), 25.65 (d, P–CH\(_{2}\), dppp, \(^{1}\)(PC) 17, \(^{3}\)(PC) 15), 18.38 (s, CH\(_{2}\), dppp); \(^{31}\)P-\(^{1}\)H)
(121.50 MHz) δ 23.95 {dd (br), P(1), 3J[2P(1)] 13, 9}, 2.09 {d, P=P, 3J[P(1)P] 13} and 2.04 p.p.m. {d, P=P, 3J[P(1)P] 9}.

**Attempted syntheses of \([\text{Pd}\{(\text{CH COPh})\text{OP}((\text{Ph})\text{CH}((\text{COPh}))\text{dppe})\}]\) and \([\text{Pd}\{(\text{CH COPh})\text{OP}((\text{Ph})\text{CH}((\text{COPh}))\text{dppb})\}]\)**

The complex \([\text{PdCl}_2\text{cod}]\) (0.10g, 0.35 mmol) with either dppe (0.14g, 0.35 mmol) or dppb (0.15g, 0.35 mmol) and diphenacylphenylphosphine oxide (107) (0.13g, 0.36 mmol) gave, after evaporation of the filtrate, a pale brown oil, which was shown to contain several products by \(^{31}\text{P}\}-\text{H} \text{ n.m.r. spectroscopy.} \)

**Attempted synthesis of \([\text{Pt}\{(\text{CH COPh})\text{OP}((\text{Ph})\text{CH}((\text{COPh}))\text{PPh}_3)\_2\}]\)**

The complex cis-[\text{PtCl}_2\text{PPh}_3]_2 (0.21g, 0.27 mmol) with dibenzylphenylphosphine oxide (119) (0.09g, 0.29 mmol) gave, after evaporation of the filtrate, a white solid, which was shown to contain cis-[\text{PtCl}_2\text{PPh}_3]_2 and (119) by \(^{31}\text{P}\}-\text{H} \text{ n.m.r. spectroscopy.} \)

**Preparation of Platinaphosphetane-3-oxide complexes using potassium hydroxide**

To a stirred THF solution of cis-[\text{PtCl}_2L_2] (L = dppe, dppp or dppb) [prepared prior by the reaction in dichloromethane of \([\text{PtCl}_2\text{cod}]\) (0.10g, 0.27 mmol) with one mole equivalent of L_2 (0.27 mmol)] was added one equivalent of diphenacylphenylphosphine oxide (107) (0.10g, 0.28 mmol) and an excess of potassium hydroxide pellets, and the mixture was refluxed for 6h. The products were extracted and purified as for the preparations using silver(I) oxide.

(i) \(L_2 = \text{dppe.} \) White microcrystals (0.15g, 60%) were obtained and were identified as (112) by i.r. and \(^{31}\text{P}\}-\text{H} \text{ n.m.r. spectroscopy.} \)

(ii) \(L_2 = \text{dppp.} \) White microcrystals (0.18g, 70%) were obtained and were identified as (113) by \(^{31}\text{P}\}-\text{H} \text{ n.m.r. spectroscopy.} \)

(iii) \(L_2 = \text{dppb.} \) White microcrystals (0.16g, 61%) were obtained and were identified as (114) by \(^{31}\text{P}\}-\text{H} \text{ n.m.r. spectroscopy.} \)
 Attempted synthesis of $[\text{Pd(CH(COPh)P(O)(Ph)}]CH(COPh))(dppp)]$ (117)

To a stirred THF solution of $[\text{PdCl}_2(dppp)]$ (prepared prior by the reaction in dichloromethane of $[\text{PdCl}_2(\text{cod})]$ (0.10g, 0.35 mmol) with dppp (0.15g, 0.36 mmol)) was added diphenacylphenylphosphine oxide (107) (0.13g, 0.36 mmol) and an excess of potassium hydroxide pellets, and the mixture was refluxed for 6h. Evaporation of the reaction mixture filtrate yielded a brown oil which contained unreacted (107) as shown by $^{31}\text{P-}^1\text{H} \text{n.m.r. spectroscopy.}$

 Attempted synthesis of $[\text{Pt(CH(Ph)P(O)(Ph)}]CH(Ph))(\text{PPh}_3)_2)]$ (118)

To a stirred THF solution of cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ (prepared prior by the reaction in dichloromethane of $[\text{PtCl}_2(\text{cod})]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol)) was added dibenzylphenylphosphine oxide (119) (0.09g, 0.29 mmol) and an excess of potassium hydroxide pellets, and the mixture was refluxed for 8h. Evaporation under reduced pressure of the reaction mixture filtrate yielded a colourless oil, which contained cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ and unreacted (119) as shown by $^{31}\text{P-}^1\text{H} \text{n.m.r. spectroscopy.}$

 Preparation of $[\text{Pt(CH(Ph)P(O)(Ph)}]CH(Ph))(\text{PPh}_3)_2)] \cdot \text{CHCl}_3$ (118)

a) Dibenzylphenylphosphine oxide (119) (0.50g, 1.63 mmol) was dissolved in THF (ca. 50 cm$^3$) and the solution was cooled to -78°C. n-Butyl lithium (1.9 cm$^3$ of a 1.8 mol dm$^{-3}$ solution) was added slowly, under nitrogen, to the cooled solution which was stirred for 15 mins. at -78°C. The solution was allowed to warm to room temperature and then stirred overnight. The dark red solution was estimated for total base content by hydrolysis of a 5.0 cm$^3$ aliquot in water (ca. 20 cm$^3$), followed by titration of the liberated hydroxide with hydrochloric acid, using phenolphthalein indicator.

b) One mole equivalent of Li$_2$[PhCHP(O)(Ph)CHPh] was added dropwise to a stirred suspension of cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ (0.20g, 0.25 mmol) in THF (ca. 40 cm$^3$) at -78°C. The mixture was stirred for 15 mins. at -78°C and for a further 5h at room temperature, to give a clear, pale yellow solution. Evaporation to dryness under reduced pressure gave an oil, which was extracted into dichloromethane (20 cm$^3$) and the solution filtered. The volume
of the filtrate was reduced to ca. 5 cm$^3$ and addition of light petroleum afforded, on standing, a pale yellow microcrystalline solid, which on recrystallisation from chloroform - light petroleum yielded (118). CHCl$_3$ (0.18g, 62%). (Found: C, 59.7; H, 4.5. C$_{56}$H$_{47}$OP$_3$Pt. CHCl$_3$ requires C, 59.9; H, 4.2%), m.p. above 220°C; $v_{p=O}$ at 1180 cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz), $\delta$ 8.49-5.89 (m, 46H, Ph + CHCl$_3$), 3.05 (m, 2H, Pt–CH); $^{31}$P–{$^1$H} (36.2 MHz), $\delta$ 32.91 [s, P=O, $^1$J(PtP) 564] and 20.53 p.p.m. [s, PPh$_3$, $^1$J(PtP) 2419].

Reactions of Platinaphosphetane-3-oxide complexes

(i) Ligand substitution reactions of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(cod)] (116). CH$_2$Cl$_2$

(a) With triphenylphosphine
A solution of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(cod)] (116). CH$_2$Cl$_2$ (0.10g, 0.13 mmol) in dichloromethane (30 cm$^3$) with triphenylphosphine (0.08g, 0.30 mmol) was stirred for 30 mins. at room temperature. The mixture was evaporated to dryness under reduced pressure to afford a pale yellow oil which was crystallised from dichloromethane - light petroleum to afford white microcrystals of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(PPh$_3$)$_2$] (109) (0.14g, 97%), identified by $^{31}$P–{$^1$H} n.m.r. spectroscopy.

(b) With methyldiphenylphosphine
A solution of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(cod)] (116). CH$_2$Cl$_2$ (0.10g, 0.13 mmol) in dichloromethane (30 cm$^3$) with methyldiphenylphosphine (0.06g, 0.30 mmol) was stirred for 30 mins. at room temperature. Work-up as in (a) afforded white microcrystals of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(PMMePh$_2$)$_2$] (110) (0.11g, 89%), identified by $^{31}$P–{$^1$H} n.m.r. spectroscopy.

(c) With dppp
A solution of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(cod)] (116). CH$_2$Cl$_2$ (0.10g, 0.13 mmol) in dichloromethane (30 cm$^3$) with dppp (0.06g, 0.14 mmol) was stirred for 30 mins. at room temperature. Work-up as in (a) afforded white microcrystals of [Pt(CH(COPh)P(O)(Ph)CH(COPh))(dppp)] (113) (0.12g, 95%), identified by $^{31}$P–{$^1$H} n.m.r. spectroscopy.
(d) With t-butyl isocyanide
A solution of \([\text{Pt}(\text{CO})\text{P(O)(Ph)}\text{CH(Ph)(CO})]\)(\text{cod})\) (116).\text{CH}_2\text{Cl}_2 (0.10g, 0.13 mmol) in dichloromethane (30 cm\(^3\)) with t-butyl isocyanide (0.025g, 0.30 mmol) was stirred for 30 mins. at room temperature. Work-up as in (a) afforded white microcrystals of \([\text{Pt}(\text{CO})\text{P(O)(Ph)}\text{CH(Ph)(CO})]\)(\text{CNBu'})\) (115) (0.80g, 85%), identified by i.r. and \(^{31}\text{P}\)-{\(^1\text{H}\)} n.m.r. spectroscopy.

(ii) Reactions of Platinaphosphetane-3-oxide complexes with t-butyl isocyanide
(a) Preparation of \([\text{Pt}(\text{CO})\text{P(O)(Ph)}\text{CH(Ph)(CO})]\)(\text{CNBu'})\)(\text{PPh}_3)\) (120)
t-Butyl isocyanide (0.015g, 0.18 mmol) in dichloromethane (ca. 10 cm\(^3\)) was added dropwise to a stirred solution of \([\text{Pt}(\text{CO})\text{P(O)(Ph)}\text{CH(Ph)(CO})]\)(\text{PPh}_3)\) (109).\text{CH}_2\text{Cl}_2 (0.20g, 0.17 mmol) in dichloromethane (30 cm\(^3\)), and the mixture stirred for 4h at room temperature. Evaporation to dryness under reduced pressure afforded a colourless oil. Dissolution of the oil in dichloromethane (ca. 2 cm\(^3\)) followed by addition of light petroleum afforded white microcrystals of the title complex (120) (0.13g, 85%). (Found: C, 60.0; H, 4.3; N, 1.6. \text{C}_{45}\text{H}_{41}\text{NO}_3\text{P}_2\text{Pt} requires C, 60.0; H, 4.6; N, 1.6%), m.p. 184°C; \(\nu_{\text{C}==\text{N}}\) at 2220s cm\(^{-1}\); \(\nu_{\text{C}==\text{O}}\) at 1640s(br) cm\(^{-1}\); \(\nu_{\text{P}=\text{O}}\) at 1190s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 8.41-6.91 (m, 30H, Ph), 4.91 (dd, 1H, H(2), \(^2\)\[^1\text{J}(\text{P}(1)\text{H}(2))\] 11, \(^3\)\[^1\text{J}(\text{P}(2)\text{H}(2))\] 11, \(^2\)\[^1\text{J}(\text{PtH}(2))\] 67), 3.47 (dd, 1H, H(1), \(^2\)\[^1\text{J}(\text{P}(1)\text{H}(1))\] 4, \(^3\)\[^1\text{J}(\text{P}(3)\text{H}(1))\] 11, \(^2\)\[^1\text{J}(\text{PtH}(1))\] 51), 0.61 (s, 9H, Bu'); \(^{13}\text{C}\)_{\text{C}==\text{N}} (101.11 (d, \text{CO}, \(^2\)\[^1\text{J}(\text{P}(1)\text{C})\] 7, \(^2\)\[^1\text{J}(\text{PtC})\] not discernible), 198.41 [s, \text{CO}, \(^2\)\[^1\text{J}(\text{PtC})\] not discernible], 57.55 (s, C, Bu'), 33.84 (dd, Pt–CH, \(^1\)\[^1\text{J}(\text{P}(1)\text{C})\] 45, \(^2\)\[^1\text{J}(\text{P}(2)\text{C})\] 2), 31.76 (dd, Pt–CH, \(^1\)\[^1\text{J}(\text{P}(1)\text{C})\] 60, \(^2\)\[^1\text{J}(\text{P}(2)\text{C})\] 60), 28.78 (s, Me, Bu'); \(^{31}\text{P}\)_{\text{C}==\text{N}} (36.2 MHz) \(\delta\) 29.71 (d, P(1), \(^3\)\[^1\text{J}(\text{P}(2)\text{P}(1))\] 6, \(^2\)\[^1\text{J}(\text{PtP}(1))\] 569) and 13.60 p.p.m. (d, P(2), \(^3\)\[^1\text{J}(\text{P}(1)\text{P}(2))\] 6, \(^2\)\[^1\text{J}(\text{PtP}(2))\] 2708).

(b) Reaction of \([\text{Pt}(\text{CO})\text{P(O)(Ph)}\text{CH(Ph)(CO})]\)(\text{PPh}_3)\) (109).\text{CH}_2\text{Cl}_2 with excess t-butyl isocyanide
A solution of \([\text{Pt}(\text{CO})\text{P(O)(Ph)}\text{CH(Ph)(CO})]\)(\text{PPh}_3)\) (109).\text{CH}_2\text{Cl}_2 (0.20g, 0.17 mmol) in dichloromethane (40 cm\(^3\)) with t-butyl isocyanide (0.10g, 1.2 mmol) was refluxed for 3h. The mixture was evaporated to dryness under reduced pressure to afford a pale
yellow oil, which was shown to contain several unidentified products by $^{31}$P-$^1$H n.m.r. spectroscopy.

(c) **Reaction of $[\text{Pt}(\text{CH}(\text{CO})\text{P}(\text{O})(\text{Ph})\text{CH}(\text{CO})\text{P})(\text{CNBu})_2(\text{PPh})_3]$ (120) with excess t-butyl isocyanide**

A solution of $[\text{Pt}(\text{CH}(\text{CO})\text{P}(\text{O})(\text{Ph})\text{CH}(\text{CO})\text{P})(\text{CNBu})_2(\text{PPh})_3]$ (120) (0.10g, 0.11 mmol) in dichloromethane (30 cm$^3$) with t-butyl isocyanide (0.07g, 0.84 mmol) was stirred at room temperature for 2h. Work-up as in (b) afforded a pale yellow oil, which was shown to contain several products by $^{31}$P-$^1$H n.m.r. spectroscopy.

(d) **Reaction of $[\text{Pt}(\text{CH}(\text{CO})\text{P}(\text{O})(\text{Ph})\text{CH}(\text{CO})\text{P})(\text{CNBu})_2]$ (115) with excess t-butyl isocyanide**

A solution of $[\text{Pt}(\text{CH}(\text{CO})\text{P}(\text{O})(\text{Ph})\text{CH}(\text{CO})\text{P})(\text{CNBu})_2]$ (115) (0.20g, 0.28 mmol) in dichloromethane (30 cm$^3$) with t-butyl isocyanide (0.10g, 1.2 mmol) was stirred at room temperature for 2h. Work-up as in (b) afforded a pale yellow oil, which was shown to contain several products by $^1$H and $^{31}$P-$^1$H n.m.r. spectroscopy.

(iii) **Attempted reduction of the phosphoryl group**

(a) **With trichlorosilane/triethylamine**

Trichlorosilane (0.023g, 0.17 mmol) in toluene (10 cm$^3$) was added slowly to a stirred solution of triethylamine (0.02g, 0.20 mmol) and $[\text{Pt}(\text{CH}(\text{CO})\text{P}(\text{O})(\text{Ph})\text{CH}(\text{CO})\text{P})(\text{PPh})_3]$ (109).CH$_2$Cl$_2$ (0.2g, 0.17 mmol) in toluene (30 cm$^3$) at 0°C. After 30 mins., 5M potassium hydroxide solution (10 cm$^3$) was added dropwise. The organic layer was then washed with water, and the solvent was removed under reduced pressure to afford a pale brown oil. $^{31}$P-$^1$H n.m.r. spectroscopy showed that the only platinum and phosphorus containing product present in the oil was cis-$[\text{PtCl}_2(\text{PPh})_3]$.

(b) **With hexachlorodisilane**

Hexachlorodisilane (0.045g, 0.17 mmol) in toluene (10 cm$^3$) was added slowly to a stirred solution of $[\text{Pt}(\text{CH}(\text{CO})\text{P}(\text{O})(\text{Ph})\text{CH}(\text{CO})\text{P})(\text{PPh})_3]$ (109).CH$_2$Cl$_2$ (0.2g, 0.17 mmol) in toluene (30 cm$^3$) at 0°C. The solution was stirred for 1h and work-up as in (a) afforded a
colourless oil. $^{31}$P-$^1$H n.m.r. spectroscopy showed the main constituent of the oil to be cis-$\text{[PtCl}_2\text{(PPh}_3)_2$].

(c) **With phenylsilane**

Phenylsilane (0.018g, 0.17 mmol) in toluene (10 cm$^3$) was added slowly to a stirred solution of $\text{[Pt}(\text{CH(COPh)}\text{P(O)}\text{(Ph)})\text{(CH(COPh))}{\text{PPh}_3}_2$] (109).CH$_2$Cl$_2$ (0.2g, 0.17 mmol) in toluene (30 cm$^3$) at 0°C. The solution was stirred for 1h, during which a black suspension formed. Evaporation of the solution under reduced pressure afforded a dark oil. $^{31}$P-$^1$H n.m.r. spectroscopy showing the presence of only triphenylphosphine in the residue.

(iv) **Reaction with boron trifluoride**

Boron trifluoride (ca. 0.10g, 1.5 mmol) was condensed onto a frozen dichloromethane solution of $\text{[Pt}(\text{CH(COPh)}\text{P(O)}\text{(Ph)})\text{CH(COPh))}(\text{dppp})]$ (109).CH$_2$Cl$_2$ (0.2g, 0.19 mmol) at -196°C. The reaction vessel was then allowed to warm to room temperature and the solution was stirred for 2h. Evaporation of the solution under reduced pressure afforded a pale brown solid, tentatively assigned as $\text{[Pt}(\text{CH(COPh)}\text{P(O)}\text{(ObF}_3)\text{CH(COPh))}(\text{dppp})]$ (0.17g, 86%). No analytical data available, m.p. 133°C; v$_{B.F}$ at 1160–1040s cm$^{-1}$. N.m.r. spectra: $^{31}$P-$^1$H (36.2 MHz), δ 45.57 {m, br, P(1), $^2$J[PtP(1)] 210}, -1.95 {dd, Pt–P, $^2$J(PP) 32, $^3$J[P(1)P] 17, $^1$J(PtP) 2512} and -9.09 p.p.m. {dd, Pt–P, $^2$J(PP) 32, $^3$J[P(1)P] 22, $^1$J(PtP) not discernible}.

(v) **Attempted reactions with isocyanates**

Phenyl isocyanate (0.02g, 0.17 mmol) or p-tosyl isocyanate (0.035g, 0.18 mmol) in dichloromethane (10 cm$^3$) was added slowly to a solution of $\text{[Pt}(\text{CH(COPh)}\text{P(O)}\text{(Ph)})\text{CH(COPh))}(\text{PPh}_3)_2$] (109).CH$_2$Cl$_2$ (0.2g, 0.17 mmol) in dichloromethane (30 cm$^3$), and the mixture stirred for 5h. No gas evolution was seen. Removal of the solvent under reduced pressure afforded a colourless oil, whose i.r. spectrum indicated the presence of unreacted (109) and respective isocyanate. $^{31}$P-$^1$H n.m.r. spectroscopy confirmed the presence of unreacted (109) by comparison of the spectrum to that of an authentic sample.
(vi) **Miscellaneous reactions of Platinaphosphetane-3-oxide complexes**

(a) **With hydrogen chloride**

A slow stream of gaseous hydrogen chloride was passed through a solution of \((109)\).\(\text{CH}_2\text{Cl}_2\) (0.10g) in dichloromethane for 3 mins. Evaporation to dryness under reduced pressure afforded white microcrystals, which were identified as \(\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]\) by comparison of their \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectrum with that of an authentic sample.

(b) **With sulphur dioxide**

A slow stream of gaseous sulphur dioxide was passed through a solution of \((109)\).\(\text{CH}_2\text{Cl}_2\) (0.10g) in dichloromethane for 30 mins. Evaporation to dryness under reduced pressure afforded a colourless oil, which was identified as unreacted \((109)\) by its \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectrum.

(c) **With carbon monoxide**

A slow stream of carbon monoxide was bubbled through a solution of \((109)\).\(\text{CH}_2\text{Cl}_2\) (0.10g) in dichloromethane for 5h. Evaporation to dryness under reduced pressure afforded a colourless oil, which was identified as unreacted \((109)\) by its \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectrum.

(d) **With methyl iodide**

A solution of \((109)\).\(\text{CH}_2\text{Cl}_2\) (0.10g) in dichloromethane (30 cm\(^3\)) with methyl iodide (3 cm\(^3\)) was refluxed for 6h. The resulting colourless solution was evaporated to dryness under reduced pressure to afford an oily solid, which was identified as containing unreacted \((109)\) by its \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectrum.
CHAPTER 3

The Synthesis and Reactivity of 1-Platina-2,4,3-diazaphosphetidine-3-oxide and Platinacyclophosphinimine Complexes
3.1 INTRODUCTION

The use of organic azides and isocyanates together with respective metal species to yield metal-ureylene complexes was described in Chapter 1. However, modifications of this procedure to prepare complexes in which the central carbonyl group has been replaced by an alternative functionality have not appeared in the literature. Nevertheless, mono-metallic complexes containing an M-NR-SO$_2$-NR fragment have been prepared by the action of a base on either sulphamide or its N,N'-diphenyl derivative in the presence of bis(phosphine)platinum dichloride complexes. Hence, Woollins et al. took sulphamide in liquid ammonia with cis-[PtCl$_2$L$_2$] to produce the complexes (I21, R = H, L = PPh$_3$, PMePh$_2$, PMe$_2$Ph or PEt$_3$), Scheme 27.$^{126}$

\[
(H_2N)_2SO_2 + cis-[PtCl_2L_2] \rightarrow L_2Pt\begin{array}{c} R \\ N \end{array}\begin{array}{c} N \\ R \end{array}SO_2
\]

Scheme 27

Complexes (I21, R = H, L = PPh$_3$, PMePh$_2$ or L$_2$ = dppe; R = Ph, L = PPh$_3$, PMePh$_2$, or L$_2$ = dppe, cod) may be synthesised by the action of silver(I) oxide on sulphamide or N,N'-diphenylsulphamide with cis-[PtCl$_2$L$_2$] in refluxing dichloromethane.$^{127}$ X-ray crystal structure determinations of complexes (I21, R = H, L = PMePh$_2$)$^{128}$ and (I21, R = Ph, L$_2$ = cod)$^{128}$ showed the metallacyclic rings to be planar, with both molecules showing two-fold rotational symmetry.

The action of dimethyl acetylenedicarboxylate on (I21, R = H, L = PMePh$_2$) at room temperature afforded the novel insertion product (I22) which contains a six-membered metallacyclic ring. An X-ray crystal structure determination confirmed the nature of the product, which adopted a pseudo-boat conformation.$^{127}$

The related compounds (I23, R = H or Ph) may be envisaged from the introduction of a phenylphosphoryl group to replace the SO$_2$ group in complexes (I21, R = H or Ph).

Accordingly, the preparation of complexes (I23, R = H or Ph) using silver(I) oxide with
The structural properties of an N,N'-diphenyl substituted complex (I23, R = Ph) are discussed, as are the reactions of the various metallacycles including ligand displacement, acetylene insertion and the properties of the phosphinimine group in complexes (I26).

3.2 SYNTHESIS OF 1-PLATINA-2,4,3-DIAZAPHOSPHETIDINE-3-OXIDE AND PLATINACYCLOPHOSPHINIMINE COMPLEXES

Treatment of the complexes cis-[PtCl₂L₂] (L = PPh₃, PMePh₂, PMe₂Ph; L₂ = dppm, dppe, dppp or dppb) (prepared in situ by the reaction of [PtCl₂(cod)] with either 2 mole
equivalents of L or 1 mole equivalent of L₂ with one equivalent of N,N',P-triphenylphosphonic diamide (I24, R = Ph) and an excess of silver(I) oxide in refluxing dichloromethane gave complexes (I27)-(I33) in high yield, whilst analogous treatment of [PtCl₂(cod)] yielded complex (I34), also in high yield, Scheme 28. Treatment of the bromide bridged dimeric complex [(PtBr₂(PPr₃))₂] with one equivalent of triphenylarsine and one equivalent of (I24, R = Ph) per platinum, in the presence of excess silver(I) oxide in refluxing dichloromethane, afforded the mixed ligand complex (I35) in quantitative yield. Treatment of cis-[PtCl₂(PPh₃)₂] with one equivalent of (I24, R = p-nitrophenyl) and an excess of silver(I) oxide in refluxing dichloromethane gave complex (I36) in good yield.

\[
cis-[PtCl_2L_2] + PhP(O)(NHPh)_2
\]

refluxing \[ CH_2Cl_2 \] excess \[ Ag_2O \]

(127), L=PPPh₃
(128), L=PMcPh₂
(129), L=PMc₂Ph
(130), L₂=dppm
(131), L₂=dppe
(132), L₂=dppp
(133), L₂=dppb
(134), L₂=cod

Scheme 28
The complexes (127)-(136) were isolated as golden yellow to pale green, air stable, microcrystalline solids, most of which showed thermochromic properties.

Using a similar methodology, complexes (137)-(141) were prepared using phenylphosphonic diamide (124, R = H), and complex (142) using phenyl phosphorodiamidate (143).^{132}

\[
\begin{align*}
(137), \ L = & \text{PPh}_3 \\
(138), \ L = & \text{PMePh}_2 \\
(139), \ L_2 = & \text{dppe} \\
(140), \ L_2 = & \text{dppp} \\
(141), \ L_2 = & \text{dppb}
\end{align*}
\]

Complexes (137)-(142) were isolated as white, air-stable, microcrystalline or powdery solids.

Treatment of cis-[PtCl_2(PPh_3)_2] with one equivalent of N,N',P-triphenylphosphonothioic diamide (125, R = Ph) and an excess of silver(I) oxide in refluxing dichloromethane led to the formation of numerous products, as seen by \(^{31}\text{P}-\text{H}^{1}\text{H} \) n.m.r. spectroscopy. It was noted that analogous treatment of the same platinum dichloride complex with N,N'-diphenylthiourea yielded complex (144), presumably via redistribution of an anionic charge onto sulphur.^{128}

\[
(144)
\]

The failure to produce a complex of the type (126) using silver(I) oxide may be due to the oxygenating potential of this reagent which could allow it to react with a P=S or P=NPh group to form a P=O moiety, thus complicating the reaction. Consequently, the reaction was repeated using potassium hydroxide as a non-oxygenating base. Thus, treatment of the
complexes $\text{cis-}[\text{PtCl}_2 L_2]$ ($L = \text{PPh}_3$; $L_2 = \text{dppe, dppp or dppb}$) with one equivalent of $(125, R = \text{Ph})$ and an excess of potassium hydroxide pellets in refluxing THF, gave complexes $(145)-(148)$ in high yield.

$$
\begin{align*}
\text{L}_2 \text{Pt} & \quad \text{NPh} \\
& \quad \text{P} \equiv \text{NPh} \quad (145), \text{L}=\text{PPh}_3 \\
& \quad \text{Ph} \\
\end{align*}
$$

Complexes $(145)-(148)$ were isolated as yellow, air stable, microcrystalline solids.

The suitability of n-butyl lithium as a base in this reaction was also considered. Preparation of the dianion $\text{Li}_2[\text{PhNP(S)(Ph)NPh}]$ $(149)$ was accomplished by treating $(125, R = \text{Ph})$ with two mole equivalents of n-butyl lithium in THF at low temperature. Subsequent treatment of $\text{cis-}[\text{PtCl}_2 (\text{PPh}_3)_2]$ with the dianion $(149)$ in THF at low temperature afforded complex $(145)$ in moderate yield.

Attempts to obtain the bimetallic rhodium species $(150)$ using the dianion $(149)$ with $[(\text{RhCl(CO)}(\text{dppm})_2)_2$ in THF at low temperature, led to the formation of the sulphur bridged system $(151)$,133 as confirmed by $^{31}\text{P-}{^1}\text{H}$ n.m.r. and i.r. spectroscopy, in good yield. The reaction probably proceeds through attack of the sulphur anion on rhodium. Whether a complex of the type $(150)$ is then formed which eliminates $\text{PhP(NPh)}_2$ to yield the product or whether complex $(151)$ is formed directly was not established.

$$
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{Rh} \quad \text{CO} \quad \text{CO} \\
\text{PhN} & \quad \text{S} \quad \text{P} \quad \text{Ph} \quad \text{PPh}_2 \\
\text{Ph} & \quad \text{PPh}_2 \quad \text{Ph} \\
\end{align*}
$$

Interestingly, the reaction of $\text{cis-}[\text{PtCl}_2 (\text{PPh}_3)_2]$ with one equivalent of phenylphosphonothioic diamide $(125, R = \text{H})$ in refluxing dichloromethane in the presence of excess silver(I) oxide, led to the formation of $(137)$ as the only phosphorus containing product, in high
yield. This suggests that the silver(I) oxide first oxygenates the phosphorus of \((125, R = H)\) to give phenylphosphonic diamide \((124, R = H)\), and then acts as a base to form the metal complex \((137)\) as described earlier, Scheme 29.

\[
\begin{align*}
\text{S} & \quad \text{Ag}_2\text{O} \\
\text{PhP(NH}_2\text{)}_2 & \quad \text{PhP(NH}_2\text{)}_2 \\
(125, R=H) & \quad (124, R=H) \\
\text{oxygenation} & \quad \text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] \\
\end{align*}
\]

Scheme 29

As no other products were spectroscopically observed in the crude reaction mixture, oxidation must be fast compared to the second stage of the reaction, otherwise products where the platinum is bonded to sulphur would have been expected. Treatment of \textit{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] with one equivalent of \((125, R = H)\) in refluxing THF in the presence of excess potassium hydroxide, resulted only in the recovery of unreacted platinum starting material.

### 3.3 STRUCTURAL PROPERTIES OF 1-PLATINA-2,3,4-TRIPHENYL-2,4,3-DIAZAPHOSPHETIDINE-3-OXIDE COMPLEXES

An X-ray crystal structure determination of the triphenylphosphine complex \((127)\) was carried out to investigate its molecular conformation. Important bond lengths and angles are presented in Table 3 whilst the molecular structure is illustrated in Figure 7 along with the crystallographic numbering system for the non-hydrogen atoms.

The structure consists of a 4-membered platinacyclic ring containing two metal-nitrogen and two phosphorus-nitrogen single bonds with two coordinating triphenylphosphine ligands giving the metal a distorted square planar environment. The platinum lies in the least squares plane defined by itself and its four nearest neighbours, however the twist angle between planes \(P(1)-\text{Pt}-P(2)\) and \(N(1)-\text{Pt}-N(2)\) is quite large, at \(16.1(3)^{\circ}\). The reason for this significant deviation from planar geometry may be due to steric interactions between the phosphine ligands and the phenyl groups attached to \(N(1)\) and \(N(2)\). This can be seen in
TABLE 3 a

Selected Bond Lengths and Angles for

\[ \text{[Pt(N(Ph)P(O)(Ph)N(Ph)(PPh)\textsubscript{2}] (127).H}_2\text{O.CH}_2\text{Cl}_2. \]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – P(1)</td>
<td>2.279 (2)</td>
<td>P(1) – Pt – P(2)</td>
<td>100.7 (1)</td>
</tr>
<tr>
<td>Pt – P(2)</td>
<td>2.284 (2)</td>
<td>N(1) – Pt – N(2)</td>
<td>70.2 (2)</td>
</tr>
<tr>
<td>Pt – N(1)</td>
<td>2.085 (7)</td>
<td>P(1) – Pt – N(1)</td>
<td>96.5 (1)</td>
</tr>
<tr>
<td>Pt – N(2)</td>
<td>2.077 (6)</td>
<td>P(2) – Pt – N(2)</td>
<td>94.6 (2)</td>
</tr>
<tr>
<td>N(1) – P(3)</td>
<td>1.648 (6)</td>
<td>Pt – N(1) – P(3)</td>
<td>98.5 (2)</td>
</tr>
<tr>
<td>N(2) – P(3)</td>
<td>1.662 (7)</td>
<td>Pt – N(2) – P(3)</td>
<td>98.4 (2)</td>
</tr>
<tr>
<td>P(3) – O(1)</td>
<td>1.478 (9)</td>
<td>N(1) – P(3) – N(2)</td>
<td>92.6 (3)</td>
</tr>
<tr>
<td>P(3) – C(31)</td>
<td>1.826 (7)</td>
<td>O(1) – P(3) – C(31)</td>
<td>106.6 (4)</td>
</tr>
<tr>
<td>N(1) – C(51)</td>
<td>1.431 (6)</td>
<td>C(51) – N(1) – Pt</td>
<td>137.0 (5)</td>
</tr>
<tr>
<td>N(2) – C(61)</td>
<td>1.411 (6)</td>
<td>C(51) – N(1) – P(3)</td>
<td>121.2 (5)</td>
</tr>
<tr>
<td>Pt ----- P(3)</td>
<td>2.843 (2)</td>
<td>C(61) – N(2) – Pt</td>
<td>137.1 (5)</td>
</tr>
<tr>
<td>O(1) ----- O(2)</td>
<td>2.745</td>
<td>C(61) – N(2) – P(3)</td>
<td>123.7 (5)</td>
</tr>
</tbody>
</table>

   Twist b
   Fold c
   C(32) – C(31) – P(3) – O(1) Torsion 16.5 (5)
   C(56) – C(51) – N(1) – Pt Torsion -34.3 (12)
   C(62) – C(61) – N(2) – Pt Torsion -36.1 (10)

a See Figure 7 for crystallographic numbering system
b < P(1) – Pt – P(2) / N(1) – Pt – N(2)
c < N(1) – Pt – N(2) / N(1) – P(3) – N(2)
Figure 7

Molecular structure of [Pt(N(Ph)P(O)(Ph)NPh)(PPh$_3$)$_2$] (127).H$_2$O.CH$_2$Cl$_2$ with all hydrogen atoms and CH$_2$Cl$_2$ being omitted.
Figure 7, especially for the C(61) phenyl ring and the P(2) phosphine ligand.

The four-membered ring itself is almost planar, the fold angle between planes N(1)–Pt–N(2) and N(1)–P(3)–N(2) being just 6.2(4)°, with the oxygen atom O(1) adopting the pseudo equatorial site. The X-ray crystal structure of complex (127, R = Ph, L₂ = cod) showed the metallacyclic ring to be exactly planar with no puckering whatsoever. The origin of the slight fold-angle in complex (127) is not obvious, although it may arise from the asymmetry of the phenylphosphoryl group opposite the metal. A consequence of the near planarity of the ring is that the trans-annular Pt–P(3) distance of 2.843(2) Å is well outside the sum of the covalent radii of the two atoms, thus indicating no significant interaction between them.

An interesting feature of the structure of (127) is that the nitrogen atoms N(1) and N(2) are in an almost planar environment with respect to their nearest neighbours. N(1) lies 0.170 Å out of the plane defined by the atoms Pt, P(3) and C(51), whereas N(2) lies only 0.083 Å out of a similar plane defined by Pt, P(3) and C(61). The expected displacement of nitrogen for pseudo-tetrahedral coordination to three carbon atoms a distance of 1.45 Å away is about 0.50 Å. The bond angles around N(1) and N(2) sum to 356.7° and 359.2° respectively, and are very close to the value of 360.0° expected for a planar environment and very much larger than the 328.5° expected for pure sp³ hybridisation. The lone pair on the nitrogens must therefore reside mainly in a 2p orbital lying perpendicular to the coordination plane. Similar geometry about the nitrogen atoms was observed in the structure of (127, R = Ph, L₂ = cod), however in (127, R = H, L = PMePh₂) the two nitrogens adopted a definite pyramidal arrangement. The phenyl rings attached to N(1) and N(2) are each rotated out of the N(1)–Pt–N(2) plane by about 35°, therefore disallowing any overlap between the π-system of the aromatic rings and the lone pair on the adjacent nitrogens.

Apart from the planar hybridisation of N(1) and N(2), the magnitudes of the bond lengths and angles in complex (127) are generally as expected. The complex crystallises with one molecule of both water and dichloromethane per molecule of (127). There are no short
intermolecular contacts between the dichloromethane molecule and the metal complex, however, the water molecule containing O(2), (the hydrogens were not found), is hydrogen bonded to the phosphoryl group as indicated in Figure 7. The water molecule probably originates from the synthesis stage of the metallacycle, and other complexes formed using silver(I) oxide have been shown to contain water molecules in their unit cell. 

3.4 N.M.R. SPECTRA OF 1-PLATINA-2,4,3-PHOSPHETIDINE-3-OXIDE AND PLATINACYCLOPHOSPHINIMINE COMPLEXES

3.4.1 $^1$H N.m.r. Spectra

The room temperature $^1$H n.m.r. spectra of complexes (127)-(136) are consistent with the static structures shown in section 3.2. In complex (130), the dppm methylene protons are inequivalent, since they are either cis or trans to the phosphoryl group in the opposing ring. They each appear as a doublet of triplets owing to coupling between each other and to the adjacent equivalent phosphorus nuclei. The spectrum for complex (134) shows only two sets of signals for the cyclo-octa-1,5-diene olefinic protons, which indicates the presence of a mirror plane through the middle of the molecule, passing through the platinum, phosphorus and oxygen atoms.

The room temperature $^1$H n.m.r. spectra for complexes (137)-(142) are also consistent with the structures shown in section 3.2. The N-H protons appear as multiplets between $\delta$ 1.0 and 2.0 p.p.m. although the assignment of coupling constants within the signals was not attempted. Complex (139) readily decomposes in solution and no representative spectrum for this compound could be obtained.

Where solubility allows, the $^1$H n.m.r. spectra for complexes (145)-(148) are compatible with the predicted structures.

3.4.2 $^{13}$C-$^1$H N.m.r. Spectra

The room temperature $^{13}$C-$^1$H n.m.r. spectra, where appropriate, for complexes (127)-(142) and (145)-(148) are consistent with the structures shown in section 3.2. Spectra for compounds (138) and (139) were not recorded owing to the decomposition of the complexes in solution.
3.4.3 $^{31}$P-{$^1$H} N.m.r. Spectra

The room temperature $^{31}$P-{$^1$H} n.m.r. spectra of complexes (127)-(133), (135) and (136) are highly distinctive, the donor ligand phosphorus nuclei appearing as a singlet with $^1$J(PtP) in the range 2800-3440 Hz, and the phosphorus of the four-membered metallacyclic ring, also appearing as a singlet but with a 2-bond coupling to platinum-195 in the range 132-186 Hz. No 3-bond phosphorus-phosphorus coupling is observed in any of the spectra. In the bis(phosphine) complexes, this information, along with the fact that the signals integrate to a ratio of 2:1, provides an instant recognition of the respective compound. As the phosphorus donor nuclei are equivalent by n.m.r. spectroscopy, the structure in solution of at least complex (127) must be different to that in the solid state as the X-ray crystal structure of (127) showed them to be inequivalent. However, only minor adjustments would be required to the solid state structure to give it a plane of symmetry, and such modifications in solution are not unreasonable. The spectrum of complex (134), which contains no phosphine donor ligands, comprises of a singlet with $^2$J(PtP) 149 Hz.

The $^{31}$P-{$^1$H} n.m.r. spectra of complexes (137)-(142) are unsurprisingly very similar to those of their phenyl substituted analogues. The only major difference arises from the magnitude of $^2$J(PtP), which is significantly larger for these complexes, lying in the range 220-240 Hz. Again, no 3-bond phosphorus-phosphorus coupling was observed.

The room temperature $^{31}$P-{$^1$H} n.m.r. spectra for complexes (145), (147) and (148) are consistent with the basic structures indicated in Figure 8. Complex (146) was too insoluble for n.m.r. studies. The spectra indicate 3 non-equivalent phosphorus sites, coupling between each site is observed, as is coupling to platinum-195 for each signal. The main signal to low field in each of the spectra was accredited to the phosphinimine phosphorus P(3), a signal which shows a 2-bond coupling to platinum-195 of between 181 and 186 Hz.

\[ \text{Figure 8} \]
Of the other two signals, the one to high field was assigned to the phosphorus P(1) \textit{trans} to nitrogen, on the basis of chemical shift comparisons, whereas the central signal was ascribed to P(2), which is \textit{trans} to sulphur, again on the basis of chemical shift.

3.5 I.R. SPECTRA OF 1-PLATINA-2,4,3-PHOSPHETIDINE-3-OXIDE AND PLATINACYCLOPHOSPHINIMINE COMPLEXES

The i.r. spectra of compounds (127)-(136) clearly show the characteristic band of the phosphoryl stretch between 1250 and 1280 cm\textsuperscript{-1}. For such a group, these values are quite high, one probable reason being the fact that the phosphorus forms part of a strained ring. Increases in the frequency of phosphoryl stretches when the phosphorus atom is involved in a cyclic structure have been previously noted.\textsuperscript{115} The spectrum of complex (136), in addition, shows two strong bands at 1490 and 1350 cm\textsuperscript{-1} corresponding to the asymmetric and symmetric stretching respectively of the nitro groups.\textsuperscript{112}

The i.r. spectra of complexes (137)-(142) all show a strong band in the region 1180-1220 cm\textsuperscript{-1}, assigned to the phosphoryl stretch. The reason for the lower frequencies compared to compounds (127)-(136) is unclear, but the effect of hydrogen bonding between the N-H and P=O groups cannot be discounted. The N-H stretch itself comes within the range 3380-3420 cm\textsuperscript{-1} and is observed as a fairly weak band.

The phosphinimine complexes (145)-(148) all show a strong band between 1310 and 1320 cm\textsuperscript{-1} in their i.r. spectra, attributed to the stretching vibration of the P=NPh group. These values come easily within a general range quoted in the literature,\textsuperscript{115} and compare with a value of 1344 cm\textsuperscript{-1} for Ph\textsubscript{3}P=NPh.\textsuperscript{134}

3.6 REACTIONS OF 1-PLATINA-2,4,3-PHOSPHETIDINE-3-OXIDE COMPLEXES

3.6.1 General Properties

Complexes (138) and (139) were found to be quite unstable in solution, even under a nitrogen atmosphere. This hindered attempts to obtain analytically pure samples and n.m.r. spectroscopic data were also subject to impurities. Complexes (140) and (141) were also found to be unstable in solution but not to the same extent as the former compounds. The
decomposition products of (138) and (139) were numerous as seen by $^{31}\text{P-}{^1\text{H}}$ n.m.r.
spectroscopy, but none were isolated or identified.

### 3.6.2 Ligand substitution reactions

The cycloocta-1,5-diene complex (134) readily undergoes simple ligand displacement reactions with mono or bidentate tertiary phosphines to yield the corresponding phosphine complexes. Thus treatment of (134) with two mole equivalents of triphenylphosphine in dichloromethane at room temperature afforded complex (127), whereas similar treatment of (134) with one equivalent of either dppe or dppp gave complexes (131) and (132) respectively, in good yield.

### 3.6.3 Reactions with methyl iodide

The nucleophilicity of the nitrogen lone pairs on complexes (127) and (137) were compared by their attempted quaternisation using methyl iodide. Both complexes were treated with excess methyl iodide in dichloromethane at room temperature. With the N,N'-diphenyl substituted metallacycle, there was no visible reaction even after several hours, and a $^{31}\text{P-}{^1\text{H}}$ n.m.r. spectrum taken after this time showed mainly starting material, with other only very minor peaks also present. In contrast, complex (137) reacted completely with methyl iodide within a few minutes, giving a bright yellow precipitate of cis-[PtL$_2$(PPh$_3$)$_2$]. The other product from this reaction was identified by $^{31}\text{P-}{^1\text{H}}$ and $^1\text{H}$ n.m.r. spectroscopy as PhP(O)(NHMe)$_2$.$^{135}$

Hence, it can be concluded that the nitrogen lone pairs on complex (137) have a much greater nucleophilicity than those on the N,N'-diphenyl substituted complex (127), and this result should be apparent in comparing the relative reactivities of the two compounds towards electrophiles.

### 3.6.4 Reactions with multiple bonded species

(a) **With a carbon-carbon multiple bond**

Recent work by Bergman et al.$^{136}$ and Cenini et al.$^{137,138}$ described the insertion of small, unsaturated organic molecules such as isocyanates and carbon disulphide into Ir–N
and Pt–N bonds respectively. These results led Moore\textsuperscript{128} to examine the reactions of complex \((121, \text{R} = \text{H}, \text{L} = \text{PMePh}_2)\) with similar reagents, and he was able to isolate and characterise the dimethyl acetylenedicarboxylate insertion product \((122).\textsuperscript{127}\) The similarity between complex \((121, \text{R} = \text{H}, \text{L} = \text{PMePh}_2)\) and complexes \((137)-(142)\) led to an investigation of the possible insertion reactions of the latter compounds and also their N,N’-diphenyl substituted analogues.

Treatment of complex \((127)\) with either diphenylacetylene, benzylidenemalononitrile or dimethyl acetylenedicarboxylate in dichloromethane at room temperature resulted in the recovery of the starting complex only. Treatment of complex \((137)\) with diphenylacetylene under similar conditions also resulted in the recovery of starting material, though its reaction with benzylidenemalononitrile yielded the dicyano complex \([\text{Pt(CN)}_2(\text{PPh}_3)_2]\).\textsuperscript{139}\n
However, the reaction of an excess of dimethyl acetylenedicarboxylate with complexes \((137), (138)\) and \((140)-(142)\) at room temperature led to the isolation of compounds \((152)-(156)\) in high yield.

\[
\begin{align*}
\text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\
\text{C} & & \text{C} \\
\text{L}_2\text{Pt} & & \text{NH} \\
\text{N} & & \text{P} \quad \text{O} \\
\text{H} & & \text{Ph}
\end{align*}
\]

\((152), \text{L} = \text{PPh}_3\)

\[
\begin{align*}
\text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\
\text{C} & & \text{C} \\
\text{L}_2\text{Pt} & & \text{NH} \\
\text{N} & & \text{P} \quad \text{O} \\
\text{H} & & \text{Ph}
\end{align*}
\]

\((153), \text{L} = \text{PMePh}_2\)

\[
\begin{align*}
\text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\
\text{C} & & \text{C} \\
\text{L}_2\text{Pt} & & \text{NH} \\
\text{N} & & \text{P} \quad \text{O} \\
\text{H} & & \text{Ph}
\end{align*}
\]

\((154), \text{L}_2 = \text{dppe}\)

\[
\begin{align*}
\text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\
\text{C} & & \text{C} \\
\text{L}_2\text{Pt} & & \text{NH} \\
\text{N} & & \text{P} \quad \text{O} \\
\text{H} & & \text{Ph}
\end{align*}
\]

\((155), \text{L}_2 = \text{dppb}\)

\[
\begin{align*}
\text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\
\text{C} & & \text{C} \\
\text{L}_2\text{Pt} & & \text{NH} \\
\text{N} & & \text{P} \quad \text{O} \\
\text{H} & & \text{Ph}
\end{align*}
\]

\((156)\)

Complexes \((152)-(156)\) were characterised on the basis of n.m.r. and i.r. spectroscopic data and by the comparison of such data with that for complex \((122).\textsuperscript{128}\)

The proton n.m.r. spectra of complexes \((152)-(156)\) show two sharp singlets for the inequivalent methyl ester groups and also two signals for the N–H protons, the one to higher field being assigned to the group adjoining platinum. This signal is observed as a multiplet, whereas the other N–H proton is generally observed as a doublet between \(\delta 4.79\) and \(5.02\) p.p.m. with a 2-bond coupling to phosphorus of \(6\) Hz.

The \(^{13}\text{C}-\{^1\text{H}\}\) n.m.r. spectra show two carbonyl resonances, a lower field singlet and a
doublet of doublets. However, the signals cannot be assigned to a particular carbonyl group with confidence. The ester methyl groups appear as two singlets, but the signals for the alkene carbon atoms of the six-membered ring were not discernible, either because of phosphorus-31 coupling diminishing the signals or because the signals are positioned within the complicated aromatic region.

The $^{31}\text{P}-\text{H}$ n.m.r. spectra for complexes (152)-(156) all show the presence of three non-equivalent phosphorus environments with coupling observed only between the two phosphine donor nuclei. The phosphorus atom in the six-membered ring is observed as a singlet, and uniquely in complex (156), this signal has platinum-195 satellites, with $^{2}J(\text{PtP})$ 78 Hz.

The i.r. spectra of these complexes show, as expected, bands due to the N–H, carbonyl and phosphoryl stretching vibrations in the ranges 3380-3390 cm$^{-1}$, 1690-1730 cm$^{-1}$ and 1190-1220 cm$^{-1}$ respectively.

Interestingly, complexes (152)-(156) may be formed directly from cis-[PtCl$_2$L$_2$] by the addition of excess dmad into the starting mixtures for the preparation of compounds (137), (138) and (140)-(142). The formation of stable insertion products proved to be the easiest way to properly characterise complexes (138), (140) and (141) due to the ease of their decomposition in solution.

Two mechanisms were suggested for the formation of complex (122). Firstly, nucleophilic attack of a nitrogen lone pair on one of the carbon atoms of the electron-deficient triple bond, followed by attack of the thus formed carbanion on platinum to yield the product. Alternatively, initial coordination of the acetylene to the metal may occur, followed by direct insertion into one of the platinum-nitrogen bonds. Scheme 30 shows the effect of these mechanisms on complex (137). Attempts to observe intermediates via n.m.r. spectroscopy were unsuccessful.

Although no mechanistic studies were undertaken, mechanism A seems the most likely route, as it not only describes the formation of complexes (152)-(156) but also explains the other reactions with multiple bonded species. The nitrogen lone pairs in the diphenyl
Scheme 30

Scheme 31
substituted complex (127) have been shown to be poorly nucleophilic and so initial attack on an electrophile would be unlikely. The reason diphenylacetylene is unreactive towards complex (137) may lie in the fact that it is not sufficiently electrophilic for the nitrogen lone pair to attack. A possible explanation for the formation of [Pt(CN)₂(PPh₃)₂] from complex (137) with benzylidenemalononitrile is shown in Scheme 31. Instead of the formation of a carbanion, a cyanide group is ejected which itself attacks the platinum forming a stable platinum-carbon bond. A similar mechanism can be envisaged to introduce the other cyanide group to the platinum, which leads to the observed product. Attempts to determine the fate of the ejected phosphorus fragment were unsuccessful.

Hence, for insertion to occur into a complex such as (137), the organic substrate must contain: (a) a multiple bond in which one or both ends are highly electrophilic; and (b) no potential leaving groups.

These criteria led to the investigation of hexafluorobut-2-yne as a possible candidate for insertion. Hence, a THF solution of complex (137) was treated with liquid hexafluorobut-2-yne at -78°C. On warming, an orange gel-like substance solidified the solution. The gel was dessicated and washed to yield a pale brown rubbery powder which was highly insoluble and shown to contain no hydrogen or nitrogen by elemental analysis. As this was obviously not a monomeric insertion product, it was tentatively assigned as a polymer of hexafluorobut-2-yne, mainly on the basis of elemental analysis and its physical appearance and properties. A possible mechanism for the formation of the polymer is outlined in Scheme 32.

Assuming a first step as in mechanism A, Scheme 30, then instead of the carbanion attacking the platinum, it attacks another molecule of acetylene to form a short 2-unit chain. This step can then be repeated until a sufficient length is reached and the chain 'breaks off' to give the free polymer. If this reasoning is correct, then it is unclear why the initially formed carbanion does not attack the platinum. However, once the chain is 2 or 3 units long, attack at the metal is less likely, due to the distance away of the negative charge, and therefore the chain continues to increase in length.
(b) With cumulated double bond species

The reaction of complex \((137)\) with either phenyl isocyanate or phenyl isothiocyanate in dichloromethane at room temperature resulted in the formation of a number of products as shown by \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectroscopy. Similar treatment of \((137)\) with carbon disulphide also resulted in the formation of several products, although a main component was visible in the \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectrum at \(\delta 17.34\) p.p.m. with \(^1\text{J}(\text{PtP})\) 3135 Hz. The attempted isolation of this component was unsuccessful. Treatment of \((137)\) with carbon dioxide in dichloromethane led to the quantitative formation of \([\text{Pt}(\text{CO}_2)(\text{PPh}_3)_2]\) \((157)\) as shown by \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectroscopy.\(^{138}\) Whether the formation of this complex was initiated by the insertion of \(\text{CO}_2\) into a platinum-nitrogen bond was not determined and evidence for possible intermediates was not seen. Complex \((127)\) did not react with either phenyl isocyanate or carbon dioxide when treated at room temperature in dichloromethane.
3.6.5 Reaction with t-butyl isocyanide

The product of the reaction of t-butyl isocyanide with complex (121, R = H, L₂ = cod) was tentatively assigned as the double insertion product (158) on the basis of n.m.r. and i.r. spectroscopic data.¹²⁸

![Chemical Structure](image)

In order to try and effect an analogous reaction, complex (137) in dichloromethane (20 cm³) was stirred with excess t-butyl isocyanide for 3h. A single product was obtained and tentatively assigned the structure (159) on the basis of n.m.r. and i.r. spectroscopic data. The ¹H n.m.r. spectrum of the product showed the presence of two inequivalent t-butyl groups and also two inequivalent N–H protons. The ¹³C-{¹H} n.m.r. spectrum confirmed the presence of two non-equal t-butyl groups. The ³¹P-{¹H} n.m.r. spectrum of the reaction mixture indicated that a triphenylphosphine ligand had been displaced from the metal presumably replaced directly by a t-butyl isocyanide group. The coupling of platinum-195 to the remaining phosphine was only 1665 Hz, a sharp reduction from that of the starting material. The spectrum also showed that the ring phosphorus had moved downfield by 35 p.p.m. and had an increased coupling to platinum-195 of 344 Hz. A large phosphorus-phosphorus coupling was also seen. The i.r. spectrum showed two bands attributed to N–H stretching and a single strong band at 2170 cm⁻¹, indicative of a terminal isocyanide moiety bound to a metal. There were a number of bands in the phosphoryl region of the spectrum, making assignment in this region difficult.

This data obviously signifies the presence of two isocyanide moieties in the molecule, one being terminal and the other presumably being inserted into a Pt–N bond. The
relatively unusual $^{31}$P-{$^1$H} n.m.r. data, especially for the phosphoryl group, suggests probable delocalisation within the ring, however such an increase in $^3J$($PP$), $^2J$(PtP) and chemical shift is difficult to explain.

### 3.7 REACTIONS OF PLATINACYCLOPHOSPHINIMINE COMPLEXES

The reactivity of phosphinimines is derived from the polarity of the P–N bond and the resulting basicity of the nitrogen atom, i.e. Figure 9.\(^{140,141}\)

\[
R_3P=NR \leftrightarrow R_3P^+ \rightarrow NR
\]

Figure 9

The chemical properties of phosphinimines are often analogous to those of phosphorus-carbon ylides and the reactions of complexes (145) and (147) with a number of reagents were studied, in order to compare their reactivity with known, purely organic phosphinimines and to see if the presence of a metal atom would in any way modify the results.

(a) **With Lewis acids**

Phosphinimines react with Lewis acids, although sometimes only under harsh conditions, to give coordination compounds of varying stoichiometry. Adducts formed with boron trifluoride,\(^{142}\) cobalt or nickel chloride,\(^{143}\) vanadium hexacarbonyl\(^{144}\) and cadmium iodide\(^{145}\) are just a few examples. Thus, addition of excess cadmium(II) iodide to a stirred THF solution of complex (147), led to the formation of a complex tentatively assigned the structure (160) on the basis of a large downfield shift of the signal for P(3), Figure 8, of over 23 p.p.m. in the $^{31}$P-{$^1$H} n.m.r. spectrum.
The i.r. spectrum of the product showed the absence of the P=NPh band as seen for the starting complex (147), although its new position could not be determined with confidence.

(b) With Methyl Iodide

Phosphinimines react with alkyl halides to yield amino-phosphonium salts, as shown in Scheme 33.\(^{146}\)

\[
R^1_3P=NR^2 + R^3X \rightarrow [R^1_3P — NR^2R^3]X
\]  
Scheme 33

Accordingly, the addition of an excess of methyl iodide to a dichloromethane solution of complex (147) at room temperature, led to the formation of (161) in good yield.

\[
\begin{array}{c}
\text{(dppp)Pt} \\
\text{Ph} \\
\text{Ph}
\end{array}
\begin{array}{c}
S \\
N \\
Ph
\end{array}
\begin{array}{c}
+ \\
\text{N} \\
\text{Me}
\end{array}
\text{Ph}
\text{I}^-
\]

(161)

The product was characterised mainly using n.m.r. spectroscopy. In both the \(^1H\) and \(^{13}C-{1H}\) n.m.r. spectra of (161), the methyl group on nitrogen appeared as a doublet, due to coupling to P(3). In the \(^{31}P-{1H}\) n.m.r. spectrum, P(3) was, as expected, shifted downfield by 37 p.p.m. on addition of the methyl iodide, due to the formation of a formal positive charge on this phosphorus. The signals for the dppp phosphorus nuclei were almost unaffected by the reaction.

(c) With double bonds to oxygen or sulphur

Phosphinimines undergo Wittig-type reactions with aldehydes and isocyanates and other compounds containing polarisable double bonds to oxygen or sulphur.\(^{141,147}\) The driving force for the reaction is the formation of the thermodynamically stable P=O or P=S bond, and the suggested mechanism for these reactions is shown in Scheme 34.\(^{141}\)

Thus, both the metallacyclic complexes (145) and (147) were treated with a range of
The metal-containing products (162) and (163) were identified by n.m.r. and i.r. spectroscopy and elemental analysis. The $^{31}$P-$^1$H n.m.r. spectra of compounds (162) and (163) showed that P(3) had been shifted downfield by over 12 p.p.m. on the formation of the phosphoryl group, whereas the signals for the phosphine donor ligands remained virtually unchanged. Interestingly, $^2J[PtP(3)]$ increased by over 35 Hz in going from P(3) = NPh to P(3) = O. The i.r. spectra of complexes (162) and (163) showed bands due to the phosphoryl stretch at 1240 and 1250 cm$^{-1}$ respectively.

The most interesting reactions in which (162) and (163) were formed, were reactions 6 and 7 which involved silver(I) carbonate. The action of this reagent on phosphinimines has seemingly not been covered in the literature, and the reaction is interesting both mechanistically and in the fact that the organic product was a diimide and not the isocyanate. The reaction probably proceeds via nucleophilic attack of an oxygen of the carbonate group on phosphorus rather than nucleophilic attack of nitrogen on the carbonate group. However both possible mechanisms result in the supposed formation of the organic product phenyl isocyanate, yet, an i.r. spectrum of the reaction mixture indicated only the presence of diphenylcarbodiimide.$^{148}$ Thus, once formed, the phenyl isocyanate must immediately react with another molecule of phosphinimine as indicated in reaction 1, Scheme 35, to produce the diimide. Even in the presence of excess silver(I) carbonate, no
isocyanate was observed and therefore the reaction of phosphinimines with silver(I) carbonate must be much slower than the reaction with phenyl isocyanate.

Interestingly, the reaction mentioned in section 3.2 of cis-[PtCl₂(PPPh₃)₂] with (125, R = Ph) in the presence of silver(I) oxide was repeated using silver(I) carbonate as the base. N.m.r. and i.r. spectroscopy showed the only phosphorus containing product of the reaction to be complex (162), formed in high yield. The presence of diphenylcarbodiimide was also observed. Undoubtedly, during the course of the reaction, the phosphinimine complex
(145) is formed, which is then oxygenated by silver(I) carbonate and phenyl isocyanate.

Also shown in Scheme 35 are the reactions of complexes (145) and (147) with phenyl isothiocyanate and carbon disulphide. The formation of complexes (164) and (165) was confirmed by n.m.r. and i.r. spectroscopy and they presumably arise due to the affinity of platinum to bond to sulphur in preference to nitrogen. Scheme 36 shows a probable mechanism for the reaction, which involves a 1,3 shift of platinum from nitrogen to sulphur.

Compounds containing a Pt-S-P(S)-S ring system have been previously prepared and data for complexes (164) and (165) compare well to that of the known compounds. Attempts to isolate one of the intermediates (166) or (167) were only partially successful. Treatment of (147) with one equivalent of phenyl isothiocyanate led to the formation of a mixture of (165), starting material and a complex presumed to be (166, L₂ = dppp), due to the fact that P(3) appeared as a doublet of doublets, indicating that the two phosphine nuclei were inequivalent, and its downfield shift of 60 p.p.m. indicated the presence of a P=S rather than a P=NPh group. Attempts to separate this product from the mixture were unsuccessful.

(d) With electron deficient acetylenes

Phosphinimines have been shown to react with dimethyl acetylenedicarboxylate, via a similar mechanism to that shown in Scheme 34 to produce compounds of the type (168).
Thus, complex (147) was treated with dmad in dichloromethane at room temperature. However, after 2h, the reaction mixture was shown to contain a number of products by $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectroscopy. This difference in reactivity is almost certainly due to the presence of both the platinum, which can form strong $\pi$-complexes with this acetylene, and sulphur, whose lone pairs could attack the electron deficient sites in this reagent.

The formation and general properties of the metallacycrophosphinimine complexes are summarised in Scheme 37.

3.8 CONCLUSION

The preparation of new platina-2,4,3-diazaphosphetidine-3-oxide complexes may be achieved in high yield via the treatment of cis-[PtCl$_2$L$_2$] ($L =$ donor ligand) with either N,N',P-triphenylphosphonic diamide (124, R = Ph) or phenylphosphonic diamide (124, R = H), and silver(I) oxide in refluxing dichloromethane. The treatment of cis-[PtCl$_2$L$_2$] with N,N',P-triphenylphosphonothioic diamide (125, R = Ph) and potassium hydroxide led to the formation of the novel 4-membered ring system (126) which contains a phosphinimine functionality. A single crystal X-ray diffraction study on the N,N'-diphenyl substituted complex (127) showed the metallacyclic ring to have only a small fold angle, the nitrogen atoms of which adopted almost planar hybridisation.

The nucleophilic properties and insertion reactions of some of the new complexes were investigated with a number of reagents. In particular, the reaction of dimethyl acetylene-dicarboxylate with complexes (137), (138) and (140)-(142) led to the isolation of 6-membered metallacyclic insertion products in good yield. A polymer-type substance was obtained from the reaction of hexafluorobut-2-yne with complex (137). The properties of the metallaphosphinimine complexes were investigated with a number of reagents. The phosphinimine group was shown to have Lewis base capabilities and also underwent
cis-[PtCl₂L₂] + PhP(NHPh)₂ → [

\[
\text{S} \quad \text{L₂Pt} < S \quad \text{P=O} \quad \text{Ph}
\]

KOH or n-BuLi

THF

L₂Pt < S < N < Ph

PhNCO or CO₂ or

O₂N-CHO or

Ph₂C=O or

Ag₂CO₃

CS₂ or PhNC₂

MeI

L₂Pt < S < P=O < Ph

Scheme 37
Wittig-type reactions with C=O and C=S containing molecules, the latter reagents leading to the formation of 1-platina-2,4,3-dithiophosphetane-3-sulphide complexes.

3.9 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. Tables 4 and 5 show m.p.’s, microanalytical results and i.r. spectroscopic data for compounds (127)-(142) and (145)-(148). The $^{13}$C-$\{^1$H$\}$ n.m.r. data for the aromatic region between $\delta$ 140 and 120 p.p.m. are omitted for clarity. All $^{31}$P-$\{^1$H$\}$ n.m.r. spectra were recorded on a JEOL JNM FX90Q spectrometer, operating at 36.24 MHz. The compounds triphenylarsine, dppm, n-butyl lithium (1.8 mol dm$^{-3}$), silver(I) carbonate, methyl iodide, diphenylacetylene, phenyl isocyanate, phenyl isothiocyanate, benzylidenemalononitrile, dimad, cadmium(II) iodide, $p$-nitrobenzaldehyde (Aldrich), potassium hydroxide, carbon disulphide (BDH), silver(I) oxide (Fisons), $t$-butyl isocyanide (Fluka), hexafluorobut-2-yne (Fluorochem) and carbon dioxide (BOC) were used as supplied from commercial sources. The compounds [PtCl$_2$(cod)],$^{123}$ [[PtBr$_2$(PPr$_3$)$_2$],$^{153}$ cis-[PtCl$_2$(PPh$_3$)$_2$],$^{124}$ [[RhCl(CO)(dppm)]$_2$],$^{154}$ N,N',P-triphenylphosphonic diamide (124, R = Ph),$^{130}$ phenylphosphonic diamide (124, R = H),$^{129}$ phenyl phosphorodiamidate (143),$^{132}$ N,N'-di-p-nitrophenyl-P-phenylphosphonic diamide (124, R = p-nitrophenyl),$^{130}$ N,N',P-triphenylphosphonothioic diamide (125, R = Ph),$^{131}$ phenylphosphonothioic diamide (125, R = H),$^{129}$ and diphenyl ketene$^{155}$ were prepared as described in the literature.

Preparation of 1-Platina-2,4,3-diazaphosphetidine-3-oxide complexes; general method

Two equivalents of tertiary phosphine or one equivalent of chelating tertiary phosphine, followed by one equivalent of respective diamide, and an excess of silver(I) oxide were added in succession to a stirred solution of [PtCl$_2$(cod)] in dichloromethane (ca. 45 cm$^3$), and the mixture was refluxed for 15h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish brown oil. Dissolution of the oil in dichloromethane (ca. 5 cm$^3$) followed by addition of light petroleum afforded, on standing, a white to greeny yellow microcrystalline solid,
which was recrystallised from dichloromethane - light petroleum, and dried in vacuo.

(i) $[\text{Pt}\{\text{N}(\text{Ph})\text{P}(\text{O})(\text{Ph})\text{NPh}\}\{\text{PPh}_3\}_2] \cdot \text{H}_2\text{O}$

The complex $[\text{PtCl}_2(\text{cod})]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and $N,N',P$-triphenylphosphonic diamide ($I24$, $R = \text{Ph}$) (0.09g, 0.29 mmol) gave greeny-yellow microcrystals of ($I27$).H$_2$O (0.27g, 96%). N.m.r. spectra: $^1\text{H}$ (90 MHz), $\delta$ 8.2-6.1 (m, 45H, Ph), 2.1 (s, br, 2H, H$_2$O); $^{31}\text{P}$-$\{^1\text{H}\}$, $\delta$ 46.51 [s, P=O, $^2\text{J}(\text{PtP})$ 151], and 9.15 p.p.m. [s, PPh$_3$, $^1\text{J}(\text{PtP})$ 3401]. X-ray quality crystals of ($I27$).H$_2$O.CH$_2$Cl$_2$ were grown slowly from dichloromethane - light petroleum, in air.

(ii) $[\text{Pt}\{\text{N}(\text{Ph})\text{P}(\text{O})(\text{Ph})\text{NPh}\}\{\text{PMePh}_2\}_2] \cdot \text{H}_2\text{O}$

The complex $[\text{PtCl}_2(\text{cod})]$ (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and $N,N',P$-triphenylphosphonic diamide ($I24$, $R = \text{Ph}$) (0.09g, 0.29 mmol) gave greeny-yellow microcrystals of ($I28$).H$_2$O (0.23g, 93%). N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 8.08-6.48 (m, 35H, Ph), 2.37 (s, br, 2H, H$_2$O), 1.57 [d, 6H, Me, PMePh$_2$, $^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})$ 10]; $^{13}\text{C}$-$\{^1\text{H}\}$, $\delta$ 15.08 [d, Me, PMePh$_2$, $^1\text{J}(\text{PC}) + ^3\text{J}(\text{PC})$ 42]; $^{31}\text{P}$-$\{^1\text{H}\}$, $\delta$ 43.48 [s, P=O, $^2\text{J}(\text{PtP})$ 152], and -7.20 p.p.m. [s, PMePh$_2$, $^1\text{J}(\text{PtP})$ 3308].

(iii) $[\text{Pt}\{\text{N}(\text{Ph})\text{P}(\text{O})(\text{Ph})\text{NPh}\}\{\text{PMePh}_2\}_2]$ ($I29$)

The complex $[\text{PtCl}_2(\text{cod})]$ (0.10g, 0.27 mmol) with dimethylphenylphosphine (0.08g, 0.58 mmol) and $N,N',P$-triphenylphosphonic diamide (0.09g, 0.29 mmol) gave greeny-yellow microcrystals of ($I29$) (0.29g, 95%). N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 8.03-6.66 (m, 25H, Ph), 1.14 (m, 12H, Me, PMe$_2$Ph); $^{13}\text{C}$-$\{^1\text{H}\}$, $\delta$ 13.77 (m, Me, PMe$_2$Ph); $^{31}\text{P}$-$\{^1\text{H}\}$, $\delta$ 40.72 [s, P=O, $^2\text{J}(\text{PtP})$ 156], and -23.69 p.p.m. [s, PMe$_2$Ph, $^1\text{J}(\text{PtP})$ 3241].

(iv) $[\text{Pt}\{\text{N}(\text{Ph})\text{P}(\text{O})(\text{Ph})\text{NPh}\}\{\text{dppm}\}]$ ($I30$)

The complex $[\text{PtCl}_2(\text{cod})]$ (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and $N,N',P$-triphenylphosphonic diamide (0.09g, 0.29 mmol) gave pale green microcrystals of ($I30$) (0.22g, 92%). N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 8.20-6.32 (m, 35H, Ph), 4.54 [dt, 1H, CH$_2$, dppm, $^2\text{J}(\text{HH})$ 16, $^2\text{J}(\text{PH})$ 11], 4.38 [dt, 1H, CH$_2$, dppm, $^2\text{J}(\text{HH})$ 16, $^2\text{J}(\text{PH})$ 11];
\( ^{13}\text{C}-\{^1\text{H}\}, \delta 49.94 [t, \text{CH}_2, \text{dppm}, ^1\text{J}(\text{PC}) 34]; ^{31}\text{P}-\{^1\text{H}\}, \delta 38.91 [s, \text{P}=\text{O}, ^2\text{J}(\text{PtP}) 186], \text{and} -57.62 \text{ p.p.m. [s, dppm, } ^1\text{J}(\text{PtP}) 2803] .

(v) \[\text{Pt}(\text{N(Ph)P(0)(Ph)NPh})(\text{dppe})\] \((131)\)

The complex \([\text{PtCl}_2(\text{cod})]\) \((0.10 \text{g}, 0.27 \text{ mmol})\) with dppe \((0.11 \text{g}, 0.28 \text{ mmol})\) and \(\text{N,N',p-triphenylphosphonic diamide (0.09g, 0.29 mmol)}\) gave greeny-yellow microcrystals of \((131)\) \((0.23 \text{g}, 95\%)\). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 8.16-6.37 \text{ (m, 35H, Ph), 2.20-1.98 (m, 4H, CH}_2, \text{dppe); } ^{13}\text{C}-\{^1\text{H}\}, \delta 30.29 \text{ [dd, CH}_2, \text{dppe, } ^1\text{J}(\text{PC}) 45, ^2\text{J}(\text{PC}) 8]; ^{31}\text{P}-\{^1\text{H}\}, \delta 39.53 [s, \text{P} = \text{O}, ^2\text{J}(\text{PtP}) 142], \text{and} -38.12 \text{ p.p.m. [s, dppe, } ^1\text{J}(\text{PtP}) 3291] .

(vi) \[\text{Pt}(\text{N(Ph)P(0)(Ph)NPh})(\text{dppp})\] \((132).\text{H}_2\text{O}\)

The complex \([\text{PtCl}_2(\text{cod})]\) \((0.10 \text{g}, 0.27 \text{ mmol})\) with dppp \((0.12 \text{g}, 0.29 \text{ mmol})\) and \(\text{N,N',p-triphenylphosphonic diamide (0.09g, 0.29 mmol)}\) gave greeny-yellow microcrystals of \((132).\text{H}_2\text{O}\) \((0.24 \text{g}, 95\%)\). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 8.08-6.34 \text{ (m, 35H, Ph), 2.32 (m, 4H, P–CH}_2, \text{dppp), 2.01 (s, br, 2H, H}_2\text{O), 1.74 (m, 2H, CH}_2, \text{dppp); } ^{13}\text{C}-\{^1\text{H}\}, \delta 41.46 [s, \text{P} = \text{O}, ^2\text{J}(\text{PtP}) 142], \text{and} -7.20 \text{ p.p.m. [s, dppp, } ^1\text{J}(\text{PtP}) 3157] .

(vii) \[\text{Pt}(\text{N(Ph)P(0)(Ph)NPh})(\text{dppb})\] \((133).\text{CH}_2\text{Cl}_2\)

The complex \([\text{PtCl}_2(\text{cod})]\) \((0.10 \text{g}, 0.27 \text{ mmol})\) with dppb \((0.12 \text{g}, 0.28 \text{ mmol})\) and \(\text{N,N',p-triphenylphosphonic diamide (0.09g, 0.29 mmol)}\) gave pale green microcrystals of \((133).\text{CH}_2\text{Cl}_2\) \((0.25 \text{g}, 91\%)\). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 8.00-6.32 \text{ (m, 35H, Ph), 5.22 (s, 2H, CH}_2\text{Cl}_2), 2.48 \text{ (m, 4H, P–CH}_2, \text{dppb), 1.52 (m, 4H, CH}_2, \text{dppb); } ^{13}\text{C}-\{^1\text{H}\}, \delta 53.11 \text{ (s, CH}_2\text{Cl}_2), 32.81 \text{ (m, P–CH}_2, \text{dppb), 23.53 (s, CH}_2, \text{dppb); } ^{31}\text{P}-\{^1\text{H}\}, \delta 43.75 [s, \text{P} = \text{O}, ^2\text{J}(\text{PtP}) 154], \text{and} -7.07 \text{ p.p.m. [s, dppb, } ^1\text{J}(\text{PtP}) 3256] .

(viii) \[\text{Pt}(\text{N(Ph)P(0)(Ph)NPh})(\text{cod})\] \((134).\text{CHCl}_3\)

The complex \([\text{PtCl}_2(\text{cod})]\) \((0.10 \text{g}, 0.27 \text{ mmol})\) with \(\text{N,N',p-triphenylphosphonic diamide (0.09g, 0.29 mmol)}\) gave greeny-yellow microcrystals which were recrystallised from a saturated chloroform solution to give greeny-yellow crystals of \((134).\text{CHCl}_3\) \((0.18 \text{g}, 92\%)\). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 8.08-6.84 \text{ (m, 16H, Ph + CHCl}_3), \delta 4.97 \text{ [m, 2H, CH, cod,}
The complex \([\text{PtBr}_2(P\text{Pr}_3)]_2\) (0.20g, 0.19 mmol) with triphenylarsine (0.12g, 0.39 mmol) and N,N',P-triphenylphosphoric diamide (0.12g, 0.39 mmol) gave yellow microcrystals of \((J 3 5) \cdot H_2O\) (0.36g, 96%). N.m.r. spectra: \(^1H\) (300 MHz), \(\delta\) 8.05-6.24 (m, 30H, Ph), 2.41 (s, br, 2H, H\_2O), 1.36 (m, 6H, \(P-\chi\_2, P\text{Pr}_3\)), 1.13 (m, 6H, CH\_2, P\text{Pr}_3), 0.74 [t, 9H, CH\_3, P\text{Pr}_3, \(3^1(J(HH))\) 7]; \(^{13}C\)\{-\(1^H\), 26.07 [d, \(P-\chi\_2, P\text{Pr}_3, \(1^J(PC)\) 34], 17.94 (s, CH\_2, P\text{Pr}_3), 15.45 [d, CH\_3, P\text{Pr}_3, \(3^1(PC)\) 15]; \(^{31}P\)\{-\(1^H\), \(\delta\) 44.37 [s, \(P=O, 2^J(PtP)\) 166], and -12.91 p.p.m. [s, P\text{Pr}_3, \(1^J(PtP)\) 3174].

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N,N'-di-p-nitrophenyl-P-phenylphosphonic diamide \((I 2 4, R = p\text{-nitrophenyl})\) (0.11g, 0.28 mmol) gave golden yellow microcrystals of \((I 3 6) \cdot H_2O\) (0.29g, 95%). I.r. spectra: \(\nu\text{NO}_2\) at 1490 (asym) and 1350 (sym) cm\(^{-1}\). N.m.r. spectra: \(^1H\) (90 MHz), \(\delta\) 8.2-6.4 (m, 43H, Ph), 1.9 (s, br, 2H, H\_2O); \(^{31}P\)\{-\(1^H\), \(\delta\) 43.41 [s, \(P=O, 2^J(PtP)\) 132], and 7.67 p.p.m. [s, P\text{Ph}_3, \(1^J(PtP)\) 3440].

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and phenylphosphonic diamide \((I 2 4, R = H)\) (0.045g, 0.29 mmol) gave white microcrystals of \((I 3 7) \cdot H_2O\) (0.22g, 91%). N.m.r. spectra: \(^1H\) (90 MHz), \(\delta\) 8.2-6.4 (m, 35H, Ph), 2.9 (s, br, 2H, H\_2O), 1.4 (m, 2H, N\text{-H}); \(^{31}P\)\{-\(1^H\), \(\delta\) 38.52 [s, \(P=O, 2^J(PtP)\) 220], and 13.51 p.p.m. [s, P\text{Ph}_3, \(1^J(PtP)\) 3300].
(xii) \([\text{Pt}\{\text{NHP(O)}(\text{Ph})\text{NH}\}\{\text{PMelPh}_{2}\}] (138)\cdot \text{H}_{2}\text{O}\)

The complex \([\text{PtCl}_{2}(\text{cod})]\) (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and phenylphosphonic diamide (124, R = H) (0.045g, 0.29 mmol) gave the white powdery solid (138).H_{2}O (0.18g, 87%). N.m.r. spectra: {\textsuperscript{1}H} (300 MHz), δ 8.11-7.03 (m, 25H, Ph), 3.15 (s, br, 2H, H_{2}O), 1.85 [d, 6H, Me, PMePh_{2}, \{J(PH) + ^{4}J(PH)\} 10, \{J(Pt)\} 33], 1.21 (m, 2H, N–H); {\textsuperscript{13}C}-{\textsuperscript{1}H}, δ 12.61 [dd, Me, PMePh_{2}, \{J(PC)\} 39, \{J(PC)\} 5]; \{^{31}P-{\textsuperscript{1}H}\}, δ 40.54 [s, P=O, \{J(Pt)\} 225], and -5.65 p.p.m. [s, PMePh_{2}, \{J(Pt)\} 3228].

(xiii) \([\text{Pt}\{\text{NHP(O)}(\text{Ph})\text{NH}\}\{\text{dppe}\}] (139)\)

The complex \([\text{PtCl}_{2}(\text{cod})]\) (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and phenylphosphonic diamide (0.045g, 0.29 mmol) gave the white powdery solid (139) (0.18g, 89%). N.m.r. spectra: No \{\textsuperscript{1}H\} or \{\textsuperscript{13}C-{\textsuperscript{1}H}\} n.m.r. data for complex (139) could be collected due to its decomposition in solution; \{^{31}P-{\textsuperscript{1}H}\}, δ 44.97 [s, P=O, \{J(Pt)\} 239], and 37.92 p.p.m. [s, dppe, \{J(Pt)\} 3208].

(xiv) \([\text{Pt}\{\text{NHP(O)}(\text{Ph})\text{NH}\}\{\text{dppp}\}] (140)\cdot \text{H}_{2}\text{O}\)

The complex \([\text{PtCl}_{2}(\text{cod})]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and phenylphosphonic diamide (0.045g, 0.29 mmol) gave white microcrystals of (140).H_{2}O (0.19g, 90%). N.m.r. spectra: \{\textsuperscript{1}H\} (300 MHz), δ 8.12-6.75 (m, 25H, Ph), 3.24 (s, br, 2H, H_{2}O), 2.62-2.33 (m, 4H, P–CH_{2}, dppp), 2.02 (m, 2H, CH_{2}, dppp), 1.45 (m, 2H, N–H), on a D_{2}O shake, the peaks at 3.24 and 1.45 p.p.m. disappeared, HOD at 4.73 p.p.m.; \{\textsuperscript{13}C-{\textsuperscript{1}H}\}, δ 24.58 (m, P–CH_{2}, dppp), 19.61 (s, CH_{2}, dppp); \{^{31}P-{\textsuperscript{1}H}\}, δ 40.52 [s, P=O, \{J(Pt)\} 225], and -7.00 p.p.m. [s, dppp, \{J(Pt)\} 3054].

(xv) \([\text{Pt}\{\text{NHP(O)}(\text{Ph})\text{NH}\}\{\text{dppb}\}] (141)\)

The complex \([\text{PtCl}_{2}(\text{cod})]\) (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and phenylphosphonic diamide (0.045g, 0.29 mmol) gave the white powdery solid (141) (0.19g, 91%). N.m.r. spectra: \{\textsuperscript{1}H\} (300 MHz), δ 7.96-6.81 (m, 25H, Ph), 2.62 (m, 4H, P–CH_{2}, dppb), 1.91 (m, 4H, CH_{2}, dppb), 1.18 (m, 2H, N–H); No \{\textsuperscript{13}C-{\textsuperscript{1}H}\} n.m.r. data for complex (141) could be collected due to its decomposition in solution; \{^{31}P-{\textsuperscript{1}H}\}, δ 39.78 [s, P=O,
\[ ^2J(\text{PtP}) \text{ 222}, \text{ and 7.27 p.p.m. } [\text{s, dppb, } ^1J(\text{PtP}) \text{ 3181}]. \]

(xvi) \[ \text{[Pt[NHP(O)(OPh)NH](PPh}_{3}\text{)]_2}(I42).\text{H}_2\text{O} \]

The complex \[ \text{[PtCl}_2(\text{cod})] \text{ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and phenyl phosphorodiamidate (I43) (0.05g, 0.29 mmol) gave white microcrystals of (I42).H}_2\text{O} \text{ (0.24g, 98%). N.m.r. spectra: } ^1\text{H} \text{ (300 MHz), } \delta 7.68-6.74 \text{ (m, 35H, Ph), 2.67 (s, br, 2H, } \text{H}_2\text{O), 1.14 (m, 2H, N–H); } ^3\text{P}–[^1\text{H}], \delta 39.91 \text{ [s, P=O, } ^2J(\text{PtP}) \text{ 229], and 12.86 p.p.m. [s, PPh}_3, ^1J(\text{PtP}) \text{ 3367}.} \]

(xvii) The reaction of cis-[PtCl}_2(PPh}_{3}\text{)] \text{ with N,N'P-triphenylphosphonothioic diamide (I25, } \text{R = Ph) in the presence of silver(I) oxide}

The complex \[ \text{[PtCl}_2(\text{cod})] \text{ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N,N',P-triphenylphosphonothioic diamide (I25, } \text{R = Ph) (0.09g, 0.28 mmol) gave, after evaporation of the filtrate, a brown oil, which was shown to contain several products by } ^3\text{P}–[^1\text{H}] \text{ n.m.r. spectroscopy.} \]

(xviii) The reaction of cis-[PtCl}_2(PPh}_{3}\text{)] \text{ with phenylphosphonothioic diamide (I25, } \text{R = H) in the presence of silver(I) oxide}

The complex \[ \text{[PtCl}_2(\text{cod})] \text{ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and phenylphosphonothioic diamide (I25, } \text{R = H) (0.05g, 0.29 mmol) gave white microcrystals of complex (I37) (0.21g, 89%) as shown by } ^1\text{H} \text{ and } ^3\text{P}–[^1\text{H}] \text{ n.m.r. spectroscopy.} \]

Preparation of Platinacyclophosphinimine complexes; general method

To a stirred THF solution of \[ \text{cis-[PtCl}_2L}_2\text{]} \text{(L = PPh}_3; \text{ } \text{L}_2 \text{ = dppe, dppp or dppb) \text{[prepared prior, by the reaction in dichloromethane of [PtCl}_2(\text{cod})] \text{ (0.10g, 0.27 mmol) with two mole equivalents of triphenylphosphine (0.15g, 0.57 mmol) or one mole equivalent of either dppe (0.11g, 0.28 mmol), dppp (0.12g, 0.29 mmol) or dppb (0.12g, 0.28 mmol)) was added one equivalent of respective diamide and an excess of potassium hydroxide pellets, and the mixture was refluxed for 5h. The products were extracted and purified as for the preparations using silver(I) oxide.} \]
(i) $\left[\text{Pt}\{\text{SP}=\text{NPh}\}\{\text{Ph}\}\text{NPh}\}{\text{PPPh}_3}_2\right]_2 (145).\text{H}_2\text{O}$

The complex cis-$[\text{PtCl}_2(\text{Ph})_2]$ (0.27 mmol) with N,N',P-triphenylphosphonothioic diamide (125, R = Ph) (0.09g, 0.28 mmol) gave yellow microcrystals of $(145).\text{H}_2\text{O}$ (0.27g, 94%). N.m.r. spectra: $^1\text{H}$ (90 MHz), $\delta$ 8.1-6.2 (m, 45H, Ph), 2.0 (s, br, 2H, $\text{H}_2\text{O}$); $^{31}\text{P}-[^1\text{H}]$, $\delta$ 35.61 (dd, $^3\text{J}[\text{P}(1)\text{P}(3)]$ 24, $^3\text{J}[\text{P}(2)\text{P}(3)]$ 24, $^3\text{J}[\text{PtP}(3)]$ 10, $^2\text{J}[\text{PtP}(3)]$ 186), 17.04 (dd, P(2), $^2\text{J}[\text{P}(1)\text{P}(2)]$ 24, $^3\text{J}[\text{P}(3)\text{P}(2)]$ 10, $^1\text{J}[\text{PtP}(2)]$ 3472), and 8.47 p.p.m. (dd, P(1), $^2\text{J}[\text{P}(2)\text{P}(1)]$ 24, $^3\text{J}[\text{P}(3)\text{P}(1)]$ 24, $^1\text{J}[\text{PtP}(1)]$ 3184).

(ii) $\left[\text{Pt}\{\text{SP}=\text{NPh}\}\{\text{Ph}\}\text{NPh}\}{\text{dppe}}_2\right] (146).\text{H}_2\text{O}$

The complex [PtCl$_2$(dppe)] (0.27 mmol) with N,N',P-triphenylphosphonothioic diamide (125, R = Ph) (0.09g, 0.28 mmol) gave yellow microcrystals of $(146).\text{H}_2\text{O}$ (0.24g, 95%). Complex $(146).\text{H}_2\text{O}$ was too insoluble for n.m.r. spectroscopy.

(iii) $\left[\text{Pt}\{\text{SP}=\text{NPh}\}\{\text{Ph}\}\text{NPh}\}{\text{dppp}}_2\right] (147).\text{H}_2\text{O}$

The complex [PtCl$_2$(dppp)] (0.27 mmol) with N,N',P-triphenylphosphonothioic diamide (125, R = Ph) (0.09g, 0.28 mmol) gave yellow microcrystals of $(147).\text{H}_2\text{O}$ (0.25g, 98%). N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 8.12-6.17 (m, 35H, Ph), 2.35 (m, 4H, P–CH$_2$, dppp), 2.08 (s, br, 2H, $\text{H}_2\text{O}$), 1.88 (m, 2H, CH$_2$, dppp); $^{13}\text{C}-[^1\text{H}]$, $\delta$ 28.90 (m, P–CH$_2$, dppp), 24.66 (m, P–CH$_2$, dppp), 18.80 (s, CH$_2$, dppp); $^{31}\text{P}-[^1\text{H}]$, $\delta$ 35.70 (dd, P(3), $^3\text{J}[\text{P}(1)\text{P}(3)]$ 24, $^3\text{J}[\text{P}(2)\text{P}(3)]$ 7, $^2\text{J}[\text{PtP}(3)]$ 183), -1.51 (dd, P(2), $^2\text{J}[\text{P}(1)\text{P}(2)]$ 34, $^3\text{J}[\text{P}(3)\text{P}(2)]$ 7, $^1\text{J}[\text{PtP}(2)]$ 3225), and -11.58 p.p.m. (dd, P(1), $^2\text{J}[\text{P}(2)\text{P}(1)]$ 34, $^3\text{J}[\text{P}(3)\text{P}(1)]$ 24, $^1\text{J}[\text{PtP}(1)]$ 2908).

(iv) $\left[\text{Pt}\{\text{SP}=\text{NPh}\}\{\text{Ph}\}\text{NPh}\}{\text{dppb}}_2\right] (148).\text{CH}_2\text{Cl}_2$

The complex [PtCl$_2$(dppb)] (0.27 mmol) with N,N',P-triphenylphosphonothioic diamide (125, R = Ph) (0.09g, 0.28 mmol) gave yellow microcrystals of $(148).\text{CH}_2\text{Cl}_2$ (0.26g, 94%). N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 7.98-6.25 (m, 35H, Ph), 5.28 (s, 2H, CH$_2$Cl$_2$), 2.62-2.37 (m, 4H, P–CH$_2$, dppb), 2.04 (m, 2H, CH$_2$, dppb), 1.56 (m, 2H, CH$_2$, dppb); $^{13}\text{C}-[^1\text{H}]$, too insoluble; $^{31}\text{P}-[^1\text{H}]$, $\delta$ 36.21 (dd, P(3), $^3\text{J}[\text{P}(1)\text{P}(3)]$ 22, $^3\text{J}[\text{P}(2)\text{P}(3)]$ 10, $^2\text{J}[\text{PtP}(3)]$ 181), 16.60 (dd, P(2), $^2\text{J}[\text{P}(1)\text{P}(2)]$ 27, $^3\text{J}[\text{P}(3)\text{P}(2)]$ 10, $^1\text{J}[\text{PtP}(2)]$ 3384), and 0.00 p.p.m. (dd, P(1), $^2\text{J}[\text{P}(2)\text{P}(1)]$ 27, $^3\text{J}[\text{P}(3)\text{P}(1)]$ 22, $^1\text{J}[\text{PtP}(1)]$ 3001).
(v) Attempted preparation of $[\text{Pt}^{\{\text{SP}(=\text{NH})(\text{Ph})\text{NH}\}}(\text{PPh}_3)_2]$

The complex cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ with phenylphosphonothioic diamide (125, $R = \text{H}$) (0.05g, 0.29 mmol) gave, after evaporation of the filtrate, a colourless oil, which was shown to contain cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ by $^{31}\text{P}-{^1\text{H}}$ n.m.r. spectroscopy.

**Preparation of Li$_2$[PhNP(S)(Ph)NPh] (149)**

$N,N',P$-triphenylphosphonothioic diamide (125, $R = \text{Ph}$) (0.50g, 1.54 mmol) was dissolved in THF (ca. 45 cm$^3$) and the solution was cooled to -78$^\circ$C. n-Butyl lithium (1.8 cm$^3$ of a 1.8 mol dm$^{-3}$ solution) was added slowly, under nitrogen, to the cooled solution which was then stirred for 15 mins at -78$^\circ$C. The solution was allowed to warm to room temperature and then stirred overnight. The dark red solution was estimated for total base content by hydrolysis of a 5.0 cm$^3$ aliquot in water (ca. 20 cm$^3$), followed by titration of the liberated hydroxide with hydrochloric acid, using phenolphthalein indicator.

**Reaction of cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ with Li$_2$[PhNP(S)(Ph)NPh] (149)**

One mole equivalent of Li$_2$[PhNP(S)(Ph)NPh] (149) was added dropwise to a stirred suspension of cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ (0.20g, 0.25 mmol) in THF (ca. 40 cm$^3$) at -78$^\circ$C. The mixture was stirred for 15 mins at -78$^\circ$C and for a further 5h at room temperature, to give a pale yellow solution. Evaporation to dryness under reduced pressure gave an oil, which was extracted into dichloromethane (20 cm$^3$) and the solution filtered. The volume of the filtrate was reduced to ca. 5 cm$^3$ and the addition of light petroleum afforded yellow microcrystals of (145) (0.19g, 73%) identified by comparison of i.r. and $^{31}\text{P}-{^1\text{H}}$ n.m.r. spectra with those of an authentic sample.

**Reaction of [(RhCl(CO)(dpmm))]$_2$ with Li$_2$[PhNP(S)(Ph)NPh] (149)**

One mole equivalent of Li$_2$[PhNP(S)(Ph)NPh] (149) was added dropwise to a stirred suspension of [(RhCl(CO)(dpmm))]$_2$ (0.30g, 0.27 mmol) in THF at -78$^\circ$C. The mixture was stirred for 15 mins at -78$^\circ$C and for a further 15h at room temperature, to give an orange solution. Evaporation to dryness under reduced pressure gave an orange solid, which was
extracted into dichloromethane and the solution filtered. The volume of the filtrate was reduced and the addition of light petroleum afforded the orange powder [Rh₂(μ-S)(CO)₂(dppe)₂] (151) (0.20 g, 70%) identified by comparison of i.r. and ³¹P-{¹H} n.m.r. spectra with those of an authentic sample.¹³³

Reactions of 1-Platina-2,4,3-diazaphosphetidine-3-oxide Complexes

(i) Ligand substitution reactions of [Pt{N(Ph)P(O)(Ph)NPh}(cod)] (134).CHCl₃

(a) With triphenylphosphine

A solution of [Pt{N(Ph)P(O)(Ph)NPh}(cod)] (0.10 g, 0.14 mmol) in dichloromethane (30 cm³) with triphenylphosphine (0.08 g, 0.30 mmol) was stirred for 30 mins at room temperature. The mixture was evaporated to dryness under reduced pressure to afford an oil which was crystallised from dichloromethane - light petroleum to afford greeny-yellow microcrystals of [Pt{N(Ph)P(O)(Ph)NPh}(PPh₃)₂] (127) (0.14 g, 98%), identified by ³¹P-{¹H} n.m.r. spectroscopy.

(b) With dppe

A solution of (134).CHCl₃ (0.10 g, 0.14 mmol) in dichloromethane (30 cm³) with dppe (0.06 g, 0.15 mmol) was stirred for 30 mins at room temperature. Work-up as in (a) afforded greeny-yellow microcrystals of [Pt{N(Ph)P(O)(Ph)NPh}(PPh₃)₂] (131) (0.12 g, 95%), identified by ³¹P-{¹H} n.m.r. spectroscopy.

(c) With dppp

A solution of (134).CHCl₃ (0.10 g, 0.14 mmol) in dichloromethane (30 cm³) with dppp (0.06 g, 0.15 mmol) was stirred for 30 mins at room temperature. Work-up as in (a) afforded greeny-yellow microcrystals of [Pt{N(Ph)P(O)(Ph)NPh}(dppp)] (132) (0.12 g, 94%), identified by ³¹P-{¹H} n.m.r. spectroscopy.

(ii) Reactions with methyl iodide

(a) A solution of [Pt{N(Ph)P(O)(Ph)NPh}(PPh₃)₂] (127).H₂O (0.10 g, 0.10 mmol) in dichloromethane (25 cm³) with methyl iodide (1.5 cm³) was stirred for 4 h at room temperature. Evaporation to dryness under reduced pressure afforded a green oil which was
shown to contain mainly unreacted (I27) by $^{31}$P-$^{1}$H n.m.r. spectroscopy.

(b) A solution of $\text{[Pt(NH_{2}P(Ph)NH)(PPh_{3})_{2}]}$ (I37).H$_{2}$O (0.10g, 0.11 mmol) in dichloromethane (20 cm$^{3}$) with methyl iodide (1.5 cm$^{3}$) was stirred for 15 min at room temperature. A bright yellow precipitate was observed, which was filtered, dried in vacuo, and identified as cis-[Pt$_{2}$(PPh$_{3}$)$_{2}$] via i.r. spectroscopy. The filtrate was evaporated to dryness under reduced pressure to afford a white solid, which was identified as PhP(O)(NHMe)$_{2}$ by comparison of its $^{1}$H and $^{31}$P-$^{1}$H n.m.r. spectra with those of an authentic sample.

(iii) Reactions with carbon-carbon multiple bonds

(a) Reactions of $\text{[Pt(N(Ph)P(O)(Ph)NH)(PPh_{3})_{2}]}$ (I27).H$_{2}$O

A solution of $\text{[Pt(N(Ph)P(O)(Ph)NH)(PPh_{3})_{2}]}$ (I27).H$_{2}$O (0.10g, 0.10 mmol) in dichloromethane (25 cm$^{3}$) was treated with either diphenylacetylene (0.10g, 0.56 mmol), benzylidenemalononitrile (0.10g, 0.65 mmol) or dmad (0.10g, 0.70 mmol) and stirred for 8h at room temperature. Evaporation to dryness under reduced pressure afforded an oil which was shown to contain unreacted (I27) as the only visible signal in the $^{31}$P-$^{1}$H n.m.r. spectra.

(b) Reaction of $\text{[Pt(NH_{2}P(Ph)NH)(PPh_{3})_{2}]}$ (I37).H$_{2}$O with diphenylacetylene

A solution of (I37).H$_{2}$O (0.10g, 0.11mmol) in dichloromethane (20 cm$^{3}$) with diphenylacetylene (0.10g, 0.56 mmol) was stirred for 12h at room temperature. Evaporation to dryness under reduced pressure afforded a colourless oil which was shown to contain unreacted (I37) by $^{31}$P-$^{1}$H n.m.r. spectroscopy.

(c) Reaction of $\text{[Pt(NH_{2}P(Ph)NH)(PPh_{3})_{2}]}$ (I37).H$_{2}$O with benzylidenemalononitrile

A solution of (I37).H$_{2}$O (0.10g, 0.11 mmol) in dichloromethane (20 cm$^{3}$) with benzylidenemalononitrile (0.10g, 0.65 mmol) was stirred for 12h at room temperature. Evaporation to dryness under reduced pressure afforded an oil which was shown not to contain unreacted (I37) by $^{31}$P-$^{1}$H n.m.r. spectroscopy. Crystallisation of the oil from dichloromethane - light petroleum afforded a white powdery solid, shown to be $\text{[Pt(CN)_{2}]}$
(PPh₃)₂] by comparison of i.r. data with that of an authentic sample.

(d) **Reaction of complexes (137), (138), (140), (141) and (142) with dimethyl acetylenedicarboxylate; general method**

A solution of the metallacyclic complex in dichloromethane (ca. 25 cm³) with excess dmad, was stirred for 5h at room temperature. Evaporation to dryness under reduced pressure afforded a pale yellow oil. Dissolution of the oil in dichloromethane (ca. 5 cm³) followed by addition of light petroleum afforded, on standing, pale yellow microcrystals which were filtered off, washed with light petroleum and dried in vacuo.

(i) [{Pt(C(CO₂Me)=C(CO₂Me)NHP(O)(Ph)NH}(PPh₃)₂]}(152).H₂O.CHCl₃

The complex [{Pt{NHP(O)(Ph)NH}(PPh₃)₂}] (137).H₂O (0.10g, 0.11 mmol) with dmad (0.08g, 0.56 mmol) gave, after recrystallisation from chloroform - light petroleum, pale yellow microcrystals of (152).H₂O.CHCl₃ (0.12g, 95%). (Found: C, 51.1; H, 3.9; N, 2.3.
C₄₈H₄₃N₂O₅P₃Pt.H₂O.CHCl₃ requires C, 51.0; H, 4.0; N, 2.4%), m.p. 142°C; νᵣH at 3380 cm⁻¹; νC=O at 1720 and 1700 cm⁻¹; νPtO at 1190 cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.77-7.09 (m, 36H, Ph + CHCl₃), 5.00 {d, 1H, H(1), ²J[P(3)H(1)] 6}, 3.34 (s, 3H, CH₃), 3.06 (s, 3H, CH₃), 2.69 (s, br, 2H, H₂O), 0.97 [m, 1H, H(2)]; ¹³C-{¹H}, δ 173.55 (s, CO), 164.08 [dd, CO, J(PC) 4, 10], 77.20 (s, CHCl₃), 51.67 (s, CH₃), 50.22 (s, CH₃); ³¹P-{¹H}, δ 18.98 {d, P(2), ²J[P(1)P(2)] 20, ¹J[PtP(2)] 2097), 11.47 {d, P(1), ²J[P(2)P(1)] 20, ¹J[PtP(1)] 3481}, and 8.28 p.p.m. [s, P(3)]. See Figure 10.

![Figure 10](image-url)
The complex $[\text{Pt}(\text{NHP}(\text{Ph})\text{NH})(\text{PMePh}_2)_2]$ (153)·$\text{H}_2\text{O}$ gave pale yellow microcrystals of (153)·$\text{H}_2\text{O}$ (0.11 g, 93%). (Found: C, 50.2; H, 4.7; N, 2.7. $C_{38}H_{39}N_2O_5P_3\text{Pt}·\text{H}_2\text{O}$ requires C, 50.1; H, 4.5; N, 3.1%), m.p. 118°C; $\nu_{\text{N-H}}$ at 3380 cm$^{-1}$; $\nu_{\text{C=O}}$ at 1720 and 1700 cm$^{-1}$; $\nu_{\text{P-O}}$ at 1200 cm$^{-1}$. N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 7.79-6.36 (m, 25H, Ph), 4.87 (d, 1H, H(1), $^2J(\text{P}(3)\text{H}(1))$ 6), 3.42 (s, 3H, CH$_3$), 3.01 (s, 3H, CH$_3$), 2.97 (s, br, 2H, H$_2$O), 2.18 [d, 3H, Me, PMePh$_2$, $^1J(\text{PH}) + 2J(\text{PH})$ 59, $^3J(\text{PtH})$ 39], 1.46 [d, 3H, Me, PMePh$_2$, $^2J(\text{PH}) + 3J(\text{PH})$ 9, $^4J(\text{PtH})$ 19], 0.55 [d, Me, 3J(Ph) 300 MHz], $\delta$ 7.89-7.12 (m, 25H, Ph), 4.79 (d, 1H, H(1), $^2J(\text{P}(3)\text{H}(1))$ 6), 3.28 (s, 3H, CH$_3$), 2.98 (s, br, 2H, H$_2$O), 2.51-1.66 (m, 6H, CH$_2$, dppp), 1.00 [m, 1H, H(2)]; $^{13}\text{C}-^1\text{H}$, $\delta$ 173.75 (s, CO), 163.85 [dd, CO, $J(\text{PC})$ 4, 10], 51.78 (s, CH$_3$), 50.26 (s, CH$_3$), 18.00 [d, Me, PMePh$_2$, $^1J(\text{PC}) + 2J(\text{PC})$ 43, $^3J(\text{PtC})$ 53], 11.04 [d, Me, PMePh$_2$, $^1J(\text{PC}) + 3J(\text{PC})$ 33, $^4J(\text{PtC})$ 26]; $^{31}\text{P}-^1\text{H}$, $\delta$ 8.35 [s, P(3)], 1.95 [d, P(2), $^2J(\text{P}(1)\text{P}(2))$ 19, $^3J(\text{PtP}(2))$ 2082], and 0.47 p.p.m. [d, P(1), $^2J(\text{P}(2)\text{P}(1))$ 19, $^3J(\text{PtP}(1))$ 3376].

The complex $[\text{Pt}(\text{NHP}(\text{Ph})\text{NH})(\text{dppp})]$ (140)·$\text{H}_2\text{O}$ (0.10 g, 0.13 mmol) gave pale yellow microcrystals of (140)·$\text{H}_2\text{O}$ (0.11 g, 92%). (Found: C, 50.5; H, 4.3; N, 2.7. $C_{39}H_{39}N_2O_3P_3\text{Pt}·\text{H}_2\text{O}$ requires C, 50.6; H, 4.4; N, 3.0%), m.p. 132°C; $\nu_{\text{N-H}}$ at 3380 cm$^{-1}$; $\nu_{\text{C=O}}$ at 1720 and 1690 cm$^{-1}$; $\nu_{\text{P-O}}$ at 1200 cm$^{-1}$. N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 7.89-7.12 (m, 25H, Ph), 4.79 (d, 1H, H(1), $^2J(\text{P}(3)\text{H}(1))$ 6), 3.28 (s, 3H, CH$_3$), 2.98 (s, br, 2H, H$_2$O), 2.51-1.66 (m, 6H, CH$_2$, dppp), 1.00 [m, 1H, H(2)]; $^{13}\text{C}-^1\text{H}$, $\delta$ 174.12 (s, CO), 163.88 [dd, CO, $J(\text{PC})$ 4, 10], 51.50 (s, CH$_3$), 49.97 (s, CH$_3$), 26.85 [dd, P--CH$_2$, dppp, $^1J(\text{PC})$ 41, $^3J(\text{PC})$ 12], 21.64 [dd, P--CH$_2$, dppp, $^1J(\text{PC})$ 32, $^3J(\text{PC})$ 7], 18.27 (s, CH$_2$, dppp); $^{31}\text{P}-^1\text{H}$, $\delta$ 8.35 [s, P(3)], -1.95 [d, P(2), $^2J(\text{P}(1)\text{P}(2))$ 29, $^3J(\text{PtP}(2))$ 1956], and -4.03 p.p.m. [d, P(1), $^2J(\text{P}(2)\text{P}(1))$ 29, $^3J(\text{PtP}(1))$ 3274].

The complex $[\text{Pt}(\text{NHP}(\text{Ph})\text{NH})(\text{dppb})]$ (141) (0.10 g, 0.13 mmol) gave pale yellow microcrystals of (141) (0.11 g, 92%). For analytical data, see direct synthesis from $[\text{PtCl}_2(\text{cod})]$. M.p. 124°C; $\nu_{\text{N-H}}$ at 3380 cm$^{-1}$; $\nu_{\text{C=O}}$ at 1730 and 1690
cm⁻¹; νₚ=ₒ at 1200 cm⁻¹. N.m.r. spectra: \(^1\)H (300 MHz), δ 7.87-7.16 (m, 25H, Ph), 4.89 [d, 1H, H(1), \(^2\)J(P(3)H(1)) 6], 3.38 (s, 3H, CH₃), 3.11 (s, 3H, CH₃), 2.64-2.33 (m, 4H, P–CH₂, dppb), 2.03-1.80 (m, 4H, CH₂, dppb), 1.26 [m, 1H, H(2)]; \(^13\)C–[\(^1\)H], δ 174.04 (s, CO), 164.84 [dd, CO, J(PC) 5, 10], 51.74 (s, CH₃), 50.42 (s, CH₃), 29.40 [d, P–CH₂, dppb, \(^1\)J(PC) 38], 27.15 [d, P–CH₂, dppb, \(^1\)J(PC) 29], 24.05 (s, 2x CH₂, dppb); \(^31\)P–[\(^1\)H], δ 10.33 [d, P(2), \(^2\)J(P(1)P(2)) 22, \(^1\)J(PtP(2)) 2007], 9.59 [d, P(1), \(^2\)J(P(2)P(1)) 22, \(^1\)J(PtP(1)) 3415], and 8.41 p.p.m. [s, P(3)].

\[\text{v} (\text{v}) \{\text{Pt\{C(COMe)₂}=C(COMe)NHP(O)(OPh)NH\}(PPh₃)₂\}] (I56)

The complex \([\text{Pt\{NHP(O)(OPh)NH\}(PPh₃)₂}], (I42)\)·H₂O (0.10g, 0.11 mmol) with dmad (0.08g, 0.56 mmol) gave pale yellow microcrystals of (I56) (0.11g, 97%). (Found: C, 55.7; H, 4.4; N, 2.6. C₄₈H₄₃N₂O₆P₃Pt requires C, 55.9; H, 4.2; N, 2.7%), m.p. 184°C; νₚ=ₒ at 3380 cm⁻¹; νₚ=ᵦ at 1730 and 1700 cm⁻¹; νₚ=ₒ at 1220 cm⁻¹. N.m.r. spectra: \(^1\)H (300 MHz), δ 7.62-6.81 (m, 35H, Ph), 5.02 [m, 1H, H(1)], 3.35 (s, 3H, CH₃), 2.97 (s, 3H, CH₃), 0.90 [m, 1H, H(2)]; \(^13\)C–[\(^1\)H], δ 172.85 (s, CO), 163.50 [dd, CO, J(PC) 5, 10], 51.58 (s, CH₃), 50.15 (s, CH₃); \(^31\)P–[\(^1\)H], δ 18.75 [d, P(2), \(^2\)J(P(1)P(2)) 20, \(^1\)J(PtP(2)) 2105], 11.30 [d, P(1), \(^2\)J(P(2)P(1)) 20, \(^1\)J(PtP(1)) 3541], and 6.45 p.p.m. [s, P(3), \(^2\)J(PtP(3)) 78].

(e) *Direct Synthesis of Complexes (I52)-(I56) from [PtCl₂(cod)]*

This may be achieved by adding excess dmad directly into the starting mixtures for the preparations of complexes (I37), (I38) and (I40)-(I42). A similar work-up procedure gives the pale yellow microcrystalline product in >90% yield. An example preparation is given for complex (I55).

The chelating phosphine dppb (0.12g, 0.28 mmol) followed by phenylphosphonic diamide (I24, R = H) (0.045g, 0.29 mmol), dmad (0.20g, 1.41 mmol), and an excess of silver(I) oxide were added in succession to a stirred solution of [PtCl₂(cod)] (0.10g, 0.27 mmol) in dichloromethane (ca. 45 cm³), and the mixture was refluxed for 15h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (ca. 5 cm³) followed
by addition of light petroleum afforded, on standing, a pale yellow microcrystalline solid, which was identified as \[\text{Pt(} \text{C(CO}_2\text{Me)} = \text{C(CO}_2\text{Me)}\text{NHP(O)(Ph)}\text{NH)}(\text{dpbb})\] (155).\text{H}_2\text{O} (0.24g, 95%) by $^1\text{H}$ and $^{31}\text{P-}^{1\text{H}}$ n.m.r. spectroscopy. (Found: C, 51.1; H, 4.5; N, 2.9. \(\text{C}_{40}\text{H}_{44}\text{N}_2\text{O}_5\text{Pt.H}_2\text{O}\) requires C, 51.2; H, 4.6; N, 3.0%).

(f) Reaction of \[\text{Pt(NHP(O)(Ph)NH)}(\text{PPhi})_7\] (137)\text{H}_2\text{O} with hexafluorobut-2-ylene

Hexafluorobut-2-ylene (ca. 1.00g, 6.17 mmol) was condensed onto a THF solution of (137).\text{H}_2\text{O} (0.10g, 0.11 mmol) at -78°C. The stirred solution was allowed to warm to room temperature in which time the mixture was solidified by the formation of an orange gel. Desiccation of the gel under vacuum yielded a pale brown powder which was washed well with dichloromethane and dried at room temperature. The product (0.60g) was insoluble in all common organic solvents and showed no melting point below 220°C. [Found: C, 29.3; F, 66.1. (\text{C}_4\text{F}_6)_n \text{requires C, 29.6; F, 70.4%}.] However, the analysis laboratory stated that the fluorine level exceeded the limit of their methodology and a standard sample of polytetrafluoroethylene showed a similar deficit in its fluorine level when analysed using the same method, [Found: C, 22.8; F, 72.3. (\text{C}_2\text{F}_4)_n \text{requires C, 24.0; F, 76.0%}]. I.r. data: \(\nu_{\text{C-F}}\) between 1150 and 1300(br) cm\(^{-1}\).

(iv) Reactions with Cumulated Double Bond Systems

(a) Reaction of \[\text{Pt(NHP(O)(Ph)NH)}(\text{PPhi})_7\] (137)\text{H}_2\text{O} with phenyl isocyanate and phenyl isothiocyanate

A solution of (137).\text{H}_2\text{O} (0.10g, 0.11 mmol) in dichloromethane (25 cm\(^3\)) was treated with either phenyl isocyanate (0.04g, 0.34 mmol) or phenyl isothiocyanate (0.05g, 0.37 mmol) and stirred for 4h at room temperature. Evaporation to dryness under reduced pressure afforded an oil, which was shown, in both cases, to contain several products by $^{31}\text{P-}^{1\text{H}}$ n.m.r. spectroscopy.

(b) Reaction of \[\text{Pt(NHP(O)(Ph)NH)}(\text{PPhi})_7\] (137)\text{H}_2\text{O} with carbon disulphide

A solution of (137).\text{H}_2\text{O} (0.10g, 0.11 mmol) in dichloromethane (25 cm\(^3\)) was treated with carbon disulphide (0.03g, 0.39 mmol) and stirred for 4h at room temperature. Work-up as in (a) afforded a pale brown oil which was shown to contain several products.
by $^{31}$P-$^1$H n.m.r. spectroscopy, though there was a main component, which however, could not be isolated. $^{31}$P-$^1$H n.m.r. spectrum of main component, $\delta$ 17.34 p.p.m. [s, $^1$J(PtP) 3135].

(c) Reaction of $[^{127}$Pt$($NHP$(O)(Ph)NH$)$2(PPh$_3$)$_2$] $\cdot$ $\text{H}_2\text{O}$ with carbon dioxide

A slow stream of carbon dioxide was bubbled through a dichloromethane solution of $\text{(137)}$ $\cdot$ $\text{H}_2\text{O}$ (0.10g, 0.11 mmol) for 4h at room temperature. Work-up as in (a) afforded a colourless oil, shown to contain the complex $[^{127}$Pt$(\text{CO}_3)(\text{PPh}_3)_2]$ (157) by $^{31}$P-$^1$H n.m.r. spectroscopy. Dissolution of the oil in dichloromethane (ca. 5 cm$^3$), followed by filtration, and addition to the filtrate of light petroleum afforded on standing, the white microcrystalline solid (157) (0.08g, 93%); the purity of which was checked by $^{31}$P-$^1$H n.m.r. and i.r. spectroscopy.

(d) Reaction of $[^{127}$Pt$($N(Ph)P(0)(Ph)NPh$)$]$2(PPh$_3$)$_2$] $\cdot$ $\text{H}_2\text{O}$ with phenyl isocyanate and carbon dioxide

The complex (127) $\cdot$ $\text{H}_2\text{O}$ (0.10g, 0.10 mmol) was treated with either phenyl isocyanate (0.04g, 0.34 mmol) or carbon dioxide as described for complex (137) $\cdot$ $\text{H}_2\text{O}$ in (a) and (c) above. Work-up as in (a) afforded, in both cases, a pale green oil which was shown to contain unreacted (127) by $^{31}$P-$^1$H n.m.r. spectroscopy.

(v) Reaction of $[^{127}$Pt$($NHP$(O)(Ph)NH$)$]$2(PPh$_3$)$_2$] $\cdot$ $\text{H}_2\text{O}$ with t-butyl isocyanide

To a stirred solution of complex (137) $\cdot$ $\text{H}_2\text{O}$ (0.10g, 0.11 mmol) was added excess t-butyl isocyanide (0.05g, 0.60 mmol) and the mixture was stirred at room temperature for 3h. Evaporation to dryness under reduced pressure yielded a pale brown oil which resisted crystallisation. The oil was washed well with light petroleum to remove excess t-butyl isocyanide, to leave the product (159) (0.05g, 59%) as a pale brown oil. I.r. data: $\nu_{\text{N-H}}$ at 3470 and 3380 cm$^{-1}$; $\nu_{\text{CON}}$ at 2170 cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz), $\delta$ 7.87-7.03 (m, 20H, Ph), 4.99 (m, 1H, N=H), 2.07 (m, 1H, N=H), 1.42 (s, 9H, Bu$^i$), 1.15 (s, 9H, Bu$^i$); $^{13}$C-$^1$H, $\delta$ 53.31 (s, C, Bu$^i$), 53.17 (s, C, Bu$^i$), 29.56 (s, Me, Bu$^i$), 29.05 (s, Me, Bu$^i$); $^{31}$P-$^1$H, $\delta$ 70.13 [d, P=O, $^3$J(PP) 54, $^2$J(PtP) 344], and 16.35 p.p.m. [d, PPh$_3$, $^3$J(PP) 54,
Reactions of Platinacyclopophosphinimine Complexes

(i) Reaction with cadmium(II) iodide

A solution of \([\text{Pt} \{\text{SP(=NPh)(Ph)NPh}\}\text{dppp}\}] (I47)\cdot\text{H}_2\text{O} (0.12\text{g}, 0.13 \text{mmol})\) in THF (30 cm\(^3\)) with cadmium(II) iodide (0.10g, 0.27 mmol) was stirred for 4h at room temperature. The solution was filtered and evaporation of the filtrate to dryness under reduced pressure afforded a pale brown solid. The product was recrystallised from dichloromethane - light petroleum to afford the pale brown powdery solid \([\text{Pt} \{\text{SP(=NPhCdI}_2\)(Ph)NPh}\}\text{dppp}\}] (I60) (0.14g, 83%). N.m.r. spectra: \(^{31}\text{P}\)\(-\{^1\text{H}\}\), \(\delta\ 59.00 \ [\text{dd, P=NPh, } ^{29}\text{J}(\text{PP}) 12, 29, ^{21}\text{J}(\text{PtP}) 250]\), -1.54 \ [dd, \text{dppp, } ^{21}\text{J}(\text{PP}) 34, ^{23}\text{J}(\text{PP}) 12, ^{1}\text{J}(\text{PtP}) 3360]\), and -12.58 p.p.m. \ [dd, \text{dppp,} ^{21}\text{J}(\text{PP}) 34, ^{3}\text{J}(\text{PP}) 29, ^{1}\text{J}(\text{PtP}) 3005]\).

(ii) Reaction with Methyl Iodide

A solution of \([\text{Pt} \{\text{SP(=NPh)(Ph)NMe}\}\text{dppp}\}] (I47)\cdot\text{H}_2\text{O} (0.12\text{g}, 0.13 \text{mmol})\) in dichloromethane (25 cm\(^3\)) with methyl iodide (0.07g, 0.49 mmol) was stirred for 6h at room temperature. Evaporation to dryness under reduced pressure afforded a pale yellow oil. Dissolution of the oil in dichloromethane (ca. 3 cm\(^3\)) followed by the addition of light petroleum gave, on standing, pale yellow microcrystals of \([\text{Pt} \{\text{SP(NMePh)(Ph)NPh}\}\text{dppp}\}] (I61)\cdot\text{H}_2\text{O} (0.12g, 85%).\) (Found: C, 50.9; H, 4.4; N, 2.4. \(\text{C}_{46}\text{H}_{44}\text{IN}_2\text{P}_{3}\text{PtS.H}_2\text{O}\) requires C, 50.6; H, 4.2; N, 2.6%); m.p. 141°C. N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\ 8.04-6.06\) (m, 35H, Ph), 3.13 \ [d, 3H, Me, ^{3}\text{J}(\text{PH}) 11], 2.85-1.68 \ (m, \text{br, 8H, CH}_2, \text{dppp + H}_2\text{O}); ^{13}\text{C}-\{^1\text{H}\}, \(\delta\ 39.14 \ [d, \text{Me, } ^{2}\text{J}(\text{PC}) 5], 27.75 \ [dd, \text{P–CH}_2, \text{dppp, } ^{1}\text{J}(\text{PC}) 42, ^{3}\text{J}(\text{PC}) 5], 23.92 \ [dd, \text{P–CH}_2, \text{dppp, } ^{1}\text{J}(\text{PC}) 35, ^{3}\text{J}(\text{PC}) 3], 18.81 \ (s, \text{CH}_2, \text{dppp}); ^{31}\text{P}-\{^1\text{H}\}, \(\delta\ 72.58 \ [dd, \text{P–NMePh, } ^{3}\text{J}(\text{PP}) 10, 27, ^{2}\text{J}(\text{PtP}) 249], -1.55 \ [dd, \text{dppp, } ^{2}\text{J}(\text{PP}) 34, ^{3}\text{J}(\text{PP}) 10, ^{1}\text{J}(\text{PtP}) 3357]\), and -12.73 p.p.m. \ [dd, \text{dppp,} ^{2}\text{J}(\text{PP}) 34, ^{3}\text{J}(\text{PP}) 27, ^{1}\text{J}(\text{PtP}) 2991]\).

(iii) Reactions with double bonds to oxygen or sulphur; general method

A solution of the metallacyclic complex in dichloromethane (25 cm\(^3\)) with excess of the respective substrate was stirred overnight at room temperature. The solution was then
filtered and evaporation of the filtrate to dryness under reduced pressure afforded a pale yellow to pale brown oil. Dissolution of the oil in dichloromethane (ca. 3 cm$^3$) followed by the addition of light petroleum gave, on standing, pale yellow microcrystals which were dried in vacuo.

(a) $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$ with phenyl isocyanate

The complex $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$ (0.15g, 0.14 mmol) with phenyl isocyanate (0.03g, 0.25 mmol) gave pale yellow microcrystals of $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$ (0.13g, 94%).

(b) $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{dppp})]$ with phenyl isocyanate

The complex $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{dppp})]$ (0.15g, 0.16 mmol) with phenyl isocyanate (0.04g, 0.34 mmol) gave pale yellow microcrystals of $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{dppp})] \cdot \text{H}_2\text{O}$ (0.13g, 93%).

(c) $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$ with carbon dioxide

A slow stream of carbon dioxide was bubbled through a dichloromethane solution of $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$ (0.15g, 0.14 mmol) for 5h at room temperature. Work-up as above gave pale yellow microcrystals of $[\text{Pt} \{ \text{SP}(=\text{NPh})(\text{Ph})\text{NPh}\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$ (0.13g, 94%) identified by $^{31}$P-$^1$H n.m.r. and i.r. spectroscopy.
(d) [(Pt{SP(=NPh)NPh(dppp)}) (147)].H₂O with carbon dioxide

A slow stream of carbon dioxide was bubbled through a dichloromethane solution of (147).H₂O (0.15g, 0.16 mmol) for 5h at room temperature. Work-up as above gave pale yellow microcrystals of (163).H₂O (0.13g, 93%) identified by ³¹P-{¹H} n.m.r. and i.r. spectroscopy.

(e) [(Pt{SP(=NPh)NPh(dppp)}) (147)].H₂O with p-nitrobenzaldehyde

The complex (147).H₂O (0.15g, 0.16 mmol) with p-nitrobenzaldehyde (0.05g, 0.33 mmol) gave pale yellow microcrystals of (163).H₂O (0.13g, 93%) identified by ³¹P-{¹H} n.m.r. and i.r. spectroscopy.

(f) [(Pt{SP(=NPh)NPh(dppp)}) (147)].H₂O with diphenyl ketene

The complex (147).H₂O (0.15g, 0.16 mmol) with diphenyl ketene (0.06g, 0.31 mmol) gave pale yellow microcrystals of (163).H₂O (0.13g, 93%) identified by ³¹P-{¹H} n.m.r. and i.r. spectroscopy.

(g) [(Pt{SP(=NPh)NPh(PPh₃)₂}) (145)].H₂O with silver(I) carbonate

The complex (145).H₂O (0.15g, 0.14 mmol) with silver(I) carbonate (0.08g, 0.29 mmol) gave pale yellow microcrystals of (162).H₂O (0.13g, 94%) identified by ³¹P-{¹H} n.m.r. and i.r. spectroscopy.

(h) [(Pt{SP(=NPh)NPh(dppp)}) (147)].H₂O with silver(I) carbonate

The complex (147).H₂O (0.15g, 0.16 mmol) with silver(I) carbonate (0.09g, 0.33 mmol) gave pale yellow microcrystals of (163).H₂O (0.13g, 93%) identified by ³¹P-{¹H} n.m.r. and i.r. spectroscopy.

(i) [(Pt{SP(=NPh)NPh(PPh₃)₂}) (145)].H₂O with phenyl isothiocyanate

The complex (145).H₂O (0.15g, 0.14 mmol) with phenyl isothiocyanate (0.08g, 0.60 mmol) gave yellow microcrystals of [(Pt{SP(S)(Ph)S}(PPh₃)₂} (164) (0.12g, 93%). I.r. data: νₚ=ₛ at 680 cm⁻¹. N.m.r. spectra: ³¹P-{¹H}, δ 88.04 [s, P=ₛ, ᵃJ(PtP) 225], and 18.64 p.p.m. [s, PPh₃, ᵃJ(PtP) 3262].
(j) \( [\text{Pt(SP(=NPh)(Ph)NPh)(dppp)}] (147),\text{H}_2\text{O} \) with phenyl isothiocyanate

The complex \( (147),\text{H}_2\text{O} \) (0.15g, 0.16 mmol) with phenyl isothiocyanate (0.09g, 0.67 mmol) gave yellow microcrystals of \( [\text{Pt(SP(Ph)S)(dppp)}] (165) \) (0.12g, 92%). I.r. data: \( \nu_{\text{P=S}} \) at 670 cm\(^{-1}\). N.m.r. spectra: \( ^{31}\text{P}-\{^1\text{H}\}, \delta 92.68 [s, \text{P=S}, ^{2}\text{J}({\text{PtP}}) 220] \), and -3.63 p.p.m. [s, dppp, \( ^{1}\text{J}({\text{PtP}}) 2996 \)].

(k) \( [\text{Pt(SP(=NPh)(Ph)NPh)(dppp)}] (147),\text{H}_2\text{O} \) with one equivalent of phenyl isothiocyanate

The complex \( (147),\text{H}_2\text{O} \) (0.15g, 0.16 mmol) with phenyl isothiocyanate (0.022g, 0.16 mmol) gave, after evaporation of the filtrate, a pale brown oil shown to contain starting material \( (147),\text{H}_2\text{O}, [\text{Pt(SP(Ph)S)(dppp)}] (165) \), and \([\text{Pt(SP(Ph)NPh)(dppp)}] (166, L_2 = \text{dppp}) \) by \( ^{31}\text{P}-\{^1\text{H}\} \) n.m.r. spectroscopy. N.m.r. spectra for \( (166, L_2 = \text{dppp}) \):
\( ^{31}\text{P}-\{^1\text{H}\}, \delta 95.95 [dd, \text{P=S}, ^{3}\text{J}({\text{PP}}) 10, 25, ^{2}\text{J}({\text{PtP}}) 225] \), -1.75 [dd, dppp, \( ^{2}\text{J}({\text{PP}}) 34, ^{3}\text{J}({\text{PP}}) 25, ^{1}\text{J}({\text{PtP}}) 3208 \)], and -11.04 p.p.m. [dd, dppp, \( ^{2}\text{J}({\text{PP}}) 34, ^{3}\text{J}({\text{PP}}) 25, ^{1}\text{J}({\text{PtP}}) 2891 \)].

(l) \( [\text{Pt(SP(=NPh)(Ph)NPh)(PPh_3)_2]} (145),\text{H}_2\text{O} \) with carbon disulphide

The complex \( (145),\text{H}_2\text{O} \) (0.15g, 0.14 mmol) with carbon disulphide (0.02g, 0.26 mmol) gave yellow microcrystals of \([\text{Pt(SP(Ph)S)(PPh_3)_2]} (164) \) (0.12g, 93%), identified by \( ^{31}\text{P}-\{^1\text{H}\} \) n.m.r. and i.r. spectroscopy.

(m) \( [\text{Pt(SP(=NPh)(Ph)NPh)(dppp)}] (147),\text{H}_2\text{O} \) with carbon disulphide

The complex \( (147),\text{H}_2\text{O} \) (0.15g, 0.16 mmol) with carbon disulphide (0.03g, 0.39 mmol) gave yellow microcrystals of \([\text{Pt(SP(Ph)S)(dppp)}] (165) \) (0.12g, 92%), identified by \( ^{31}\text{P}-\{^1\text{H}\} \) n.m.r. and i.r. spectroscopy.

(n) Formation of \( [\text{Pt(SP(O)(Ph)NPh)(PPh_3)_2]} (162),\text{H}_2\text{O} \) from \( \text{cis-[PtCl}_2(PPh_3)_2] \) using silver(I) carbonate with \( N,N',P\)-triphenylphosphonothioic diamide

\( N,N',P\)-triphenylphosphonothioic diamide (125, R = Ph) (0.085g, 0.26 mmol) and excess silver(I) carbonate were added in succession to a stirred solution of \( \text{cis-[PtCl}_2(PPh_3)_2] \) (0.20g, 0.25 mmol) in dichloromethane (ca. 45 cm\(^3\)), and the mixture was refluxed for 15h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under
reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (ca. 5 cm$^3$) followed by the addition of light petroleum afforded, on standing, pale yellow microcrystals of [Pt(\text{SP}(0)(\text{Ph})\text{NPh})(\text{PPh}_3)_2] \text{H}_2\text{O} (0.24\text{g}, 97\%), identified by $^{31}\text{P}$-$^1\text{H}$ n.m.r. and i.r. spectroscopy.

(iv) Reaction with dimethyl acetylenedicarboxylate

A solution of [Pt(\text{SP}(-N\text{Ph})(\text{Ph})\text{NPh})(\text{dppp})] \text{H}_2\text{O} (0.12\text{g}, 0.13 \text{mmol}) in dichloromethane (25 cm$^3$) with dmad (0.04g, 0.28 mmol) was stirred for 2h at room temperature. Evaporation to dryness under reduced pressure afforded a pale brown oil which was shown to contain several products by $^{31}\text{P}$-$^1\text{H}$ n.m.r. spectroscopy.
TABLE 4
M.p.'s, analytical\(^a\) and selected i.r.\(^b\) data for 1-platina-2,3,4-triphenyl-2,4,3-diazaphosphetidine-3-oxide complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Elemental Analysis (%)</th>
<th>(v_{\text{P=O}}) (cm(^{-1}))(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(127).H(_2)O</td>
<td>126</td>
<td>61.5 (62.1) 4.5 (4.5) 2.6 (2.7)</td>
<td>1250</td>
</tr>
<tr>
<td>(128).H(_2)O</td>
<td>&gt;220</td>
<td>57.8 (57.5) 4.6 (4.7) 3.3 (3.1)</td>
<td>1260</td>
</tr>
<tr>
<td>(129)</td>
<td>116</td>
<td>52.3 (52.5) 4.9 (4.8) 3.6 (3.6)</td>
<td>1260</td>
</tr>
<tr>
<td>(130)</td>
<td>&gt;220</td>
<td>58.1 (58.2) 4.0 (4.2) 3.1 (3.2)</td>
<td>1270</td>
</tr>
<tr>
<td>(131)</td>
<td>123</td>
<td>58.4 (58.7) 4.4 (4.3) 3.1 (3.1)</td>
<td>1280</td>
</tr>
<tr>
<td>(132).H(_2)O</td>
<td>&gt;220</td>
<td>58.0 (58.0) 4.5 (4.6) 3.1 (3.0)</td>
<td>1270</td>
</tr>
<tr>
<td>(133).CH(_2)Cl(_2)</td>
<td>127</td>
<td>56.1 (55.7) 4.6 (4.5) 2.9 (2.8)</td>
<td>1260</td>
</tr>
<tr>
<td>(134).CHCl(_3)</td>
<td>205</td>
<td>44.8 (44.5) 3.7 (3.8) 3.9 (3.8)</td>
<td>1270</td>
</tr>
<tr>
<td>(135).H(_2)O</td>
<td>97</td>
<td>54.9 (54.8) 5.4 (5.4) 3.4 (2.9)</td>
<td>1260</td>
</tr>
<tr>
<td>(136).H(_2)O</td>
<td>160</td>
<td>56.9 (57.2) 3.9 (4.0) 4.9 (4.9)</td>
<td>1260</td>
</tr>
</tbody>
</table>

\(^a\) Calculated values given in parentheses;
\(^b\) Recorded as KBr discs;
\(^c\) All bands s.
TABLE 5
M.p.'s, analytical$^a$ and selected i.r.$^b$ data for complexes (137).H$_2$O - (142).H$_2$O and (145).H$_2$O - (148).CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Elemental Analysis (%)</th>
<th>$v_{P=O}$ or $v_{P=NPh}$$^c$ (cm$^{-1}$)</th>
<th>$v_{N-H}$ (cm$^{-1}$)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(137).H$_2$O</td>
<td>&gt;220</td>
<td>56.3 (56.6) 4.4 (4.4) 2.6 (3.1)</td>
<td>1210</td>
<td>3410</td>
</tr>
<tr>
<td>(138)</td>
<td>110</td>
<td>—</td>
<td>—</td>
<td>1190</td>
</tr>
<tr>
<td>(139)</td>
<td>155</td>
<td>—</td>
<td>—</td>
<td>1220</td>
</tr>
<tr>
<td>(140).H$_2$O</td>
<td>154</td>
<td>50.4 (50.8) 4.7 (4.5) 3.9 (3.6)</td>
<td>1190</td>
<td>3390</td>
</tr>
<tr>
<td>(141)</td>
<td>188</td>
<td>—</td>
<td>—</td>
<td>1180</td>
</tr>
<tr>
<td>(142).H$_2$O</td>
<td>220</td>
<td>55.2 (55.6) 4.6 (4.3) 3.0 (3.1)</td>
<td>1220</td>
<td>3420</td>
</tr>
<tr>
<td>(145).H$_2$O</td>
<td>188</td>
<td>60.6 (61.2) 4.3 (4.4) 2.7 (2.6)</td>
<td>1320*</td>
<td>–</td>
</tr>
<tr>
<td>(146).H$_2$O</td>
<td>&gt;220</td>
<td>56.9 (56.6) 4.1 (4.4) 3.0 (3.0)</td>
<td>1310*</td>
<td>–</td>
</tr>
<tr>
<td>(147).H$_2$O</td>
<td>129</td>
<td>57.0 (57.0) 4.4 (4.5) 2.8 (3.0)</td>
<td>1320*</td>
<td>–</td>
</tr>
<tr>
<td>(148).CH$_2$Cl$_2$</td>
<td>140</td>
<td>55.2 (54.9) 4.8 (4.4) 2.4 (2.7)</td>
<td>1320*</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Calculated values given in parentheses;
$^b$ Recorded as KBr discs;
$^c$ All bands s;
$^d$ All bands w.
CHAPTER 4

The Synthesis and Reactivity of Platinaphosphonato, Phosphato and Arsonato Metal Complexes
4.1 INTRODUCTION

Chapters 2 and 3 described the syntheses and reactions of complexes of the type (169, \( X = \text{CH(COPh)}, \text{NPh or NH} \)) which were derived from \( \text{cis-}[\text{PtCl}_2L_2] \) and (170) using silver (I) oxide as a base and halide abstracting agent. These results prompted an investigation into the synthesis of complexes of the type (169, \( X = \text{O} \)) in order to compare their structure and reactivity with those of the previously prepared complexes.

Other four-membered platinacycles containing two metal-oxygen bonds include the carbonato (157) and sulphato (171) complexes, both initially prepared from \([\text{Pt(O}_2)(\text{PPh}_3)_2]\) by reaction with either carbon dioxide and triphenylphosphine or sulphur dioxide respectively, Scheme 38.

\[
\begin{align*}
\text{(157)} & \quad \text{CO}_2 / \text{Ph}_3\text{P} & \quad \text{(Ph}_3\text{P})_2\text{Pt}(\text{O}_2) \\
\text{(171)} & \quad \text{SO}_2 & \quad \text{(Ph}_3\text{P})_2\text{Pt}(\text{S}_2\text{O})
\end{align*}
\]

Scheme 38

It is difficult to envisage a similar methodology for the preparation of complexes (169, \( X = \text{O} \)) due to the unavailability of PhPO or PhPO\(_2\) species. However, complexes (157) and (171) may also be prepared from \( \text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] \) with silver(I) carbonate or silver(I) sulphate respectively,\(^{158}\) which gives precedent to the use of silver(I) oxide with a substituted phosphonic acid to synthesise complexes (169, \( X = \text{O} \)).

Four-membered platinacycles containing two metal-sulphur (172) or metal-selenium...
Scheme 39

[Pt(C₂H₄)(PPh₃)₂] + \( \text{MeO} \) \( \begin{array}{c} \text{S} \\ \text{S} \end{array} \) \( \begin{array}{c} \text{P} \\ \text{S} \end{array} \) \( \begin{array}{c} \text{OMe} \end{array} \) → THF \( 1\text{h} \) (Ph₃P)₂Pt \( \begin{array}{c} \text{S} \\ \text{P} \\ \text{S} \end{array} \) \( \begin{array}{c} \text{OMe} \end{array} \) (172)

[PtCl₂(dppe)] + \( \begin{array}{c} \text{Se} \\ \text{Se} \end{array} \) \( \begin{array}{c} \text{P} \\ \text{Se} \end{array} \) \( \begin{array}{c} \text{Ph} \\ \text{Se} \\ \text{Ph} \end{array} \) → THF \( 2.75\text{h} \) (dppe)Pt \( \begin{array}{c} \text{Se} \\ \text{P} \\ \text{Se} \end{array} \) \( \begin{array}{c} \text{Ph} \\ \text{Se} \\ \text{Ph} \end{array} \) (173)
(173) bonds have been prepared, as shown in Scheme 39.\textsuperscript{150,159} Crystal structure determinations indicated that both ring systems are puckered with the P = S or P = Se group occupying an equatorial position.

Hence, the preparation of metallacyclic complexes of the type (174, R = Ph, Me, OPh) from the respective dibasic acid (175), (176) or (177) in the presence of silver(I) oxide is described in this Chapter, as are the syntheses of complexes (178) using phenylarsonic acid.

\[
\begin{align*}
\text{(174)} & \quad \begin{array}{c}
\text{L}_2\text{Pt} \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{R}
\end{array} \\
\text{(175)}, \text{R}=\text{Ph} & \quad \begin{array}{c}
\text{O} \\
\text{R} \text{P(OH)}_2
\end{array} \\
\text{(176)}, \text{R}=\text{Me} & \quad \begin{array}{c}
\text{L}_2\text{Pt} \\
\text{O} \\
\text{As} \\
\text{Ph}
\end{array} \\
\text{(177)}, \text{R}=\text{OPh}
\end{align*}
\]

The structural properties of the platinaphosphonato complexes are discussed and compared to those of the sulphur and selenium analogues (172) and (173), and also to the platinaphosphetane (109).\textsubscript{CHCl}\textsubscript{3} and platinaphosphetidine (127).\textsubscript{H\textsubscript{2}O.CH\textsubscript{2}Cl\textsubscript{2}} complexes. Various reactions of the new ring systems are studied as is the crystal structure of the di-orthometallated decomposition product of a benzyldiphenylphosphine adduct.

\section{4.2 SYNTHESIS OF PLATINAPHOSPHONATO, PHOSPHATO AND ARSONATO METAL COMPLEXES}

Treatment of the complexes cis-[PtCl\textsubscript{2}L\textsubscript{2}] (L = PPh\textsubscript{3}, PMePh\textsubscript{2}, PBzPh\textsubscript{2}; L\textsubscript{2} = dppe, dppp or dppb) (prepared \textit{in situ} by the reaction of [PtCl\textsubscript{2}(cod)] with either 2 mole equivalents of L or 1 equivalent of L\textsubscript{2}) with one equivalent of phenylphosphonic acid (175) and an excess of silver(I) oxide in refluxing dichloromethane, gave the complexes (179)-(184) in high yield, whilst analogous treatment of cis-[PtCl\textsubscript{2}(AsPh\textsubscript{3})\textsubscript{2}] yielded complex (185), Scheme 40. Treatment of the bromide bridged dimeric complex [(PtBr\textsubscript{2}(PP\textsubscript{3}))\textsubscript{2}] with one equivalent of either triphenylphosphine or triphenylarsine and one equivalent of (175) per platinum, in the presence of silver(I) oxide afforded the mixed ligand complexes (186) and (187) respectively. Similar treatment of [(PtBr\textsubscript{2}(PE\textsubscript{3}))\textsubscript{2}] with triphenylarsine and (175) gave complex (188) in good yield.
Using a similar methodology, complexes (189)-(194) may be prepared using methylphosphonic acid (176), complexes (195)-(199) using phenyl dihydrogen phosphate (177), and complexes (200)-(203) using phenylarsonic acid, all products being obtained in good yield.

All the new complexes, (179)-(203) were isolated as white to pale yellow, air stable, microcrystalline solids.

### 4.3 STRUCTURAL PROPERTIES OF PLATINAPHOSPHONATO COMPLEXES

An X-ray crystal structure determination of the bis(phosphine)platinum phosphonato complex (180) was carried out to investigate its molecular conformation for comparison with those of the related sulphur and selenium metallacycles (172)$^{159}$ and (173)$^{159}$ and also
with those of complexes (109) and (127), which were described in Chapters 2 and 3. Important bond lengths and angles are presented in Table 6 whilst the molecular structure is illustrated in Figure 11 along with the crystallographic numbering system for the non-hydrogen atoms. Selected structural data for complexes (172),\textsuperscript{150} (173)\textsuperscript{159} and (180) along with that for phenylphosphonic acid (175)\textsuperscript{160} are presented in Table 7 for comparison.

The structure consists of a four-membered metallacyclic ring containing two metal-oxygen and two phosphorus-oxygen bonds, with two coordinating methyl diphenylphosphine ligands giving the metal a slightly distorted square planar environment. The twist angle between planes P(2)–Pt–P(3) and O(2)–Pt–O(3) is 3.81° and the fold angle between planes O(2)–Pt–O(3) and O(2)–P(1)–O(3) is 12.86° with the phosphoryl group adopting the pseudo-equatorial position. This latter behaviour compares well with the molecular structures of (172) and (173), which also have fold angles of a similar magnitude.\textsuperscript{150,159}

The metal-phosphate distances in complex (180) are noticeably shorter than those in complexes (172)\textsuperscript{150} and (173).\textsuperscript{159} By comparison with the Pt–P distances in the respective bis(phosphine)platinum dichloride complexes, \text{[PtCl}_2(dppe)], Pt–P 2.208(6) Å,\textsuperscript{161} [PtCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}], av. Pt–P 2.258(9) Å;\textsuperscript{162} and [PtCl\textsubscript{2}(PMePh\textsubscript{2})\textsubscript{2}], av. Pt–P 2.247(2) Å\textsuperscript{163}, the series Se > S > Cl > O becomes apparent, for the magnitude of the trans influence of the respective atoms with a platinum(II) centre.

The Pt–O(3) bond length is significantly longer by ca. 0.03 Å than Pt–O(2), however the expected trend of the bond lengths Pt–E, P–E and P = E increasing down the group as E = O → S → Se can be seen in Table 7. The P(1)–O(2) and P(1)–O(3) bonds are slightly longer than the respective bonds in the structure of phenylphosphonic acid,\textsuperscript{160} though the P(1) = O(1) double bond is slightly shorter.

The E–Pt–E angle also increases as E = O → S → Se, however no trend is discernible for the E–P–E angle. The O(2)–P(1)–O(3) angle in complex (180) is 101.3(2)° and compares well to that of the free acid, which at 106.9(2)° is only ca. 6° larger. The internal ring angles at E, i.e. <Pt–E–P, decrease as E = O → S → Se.

The longer P–O bonds and smaller O–P–O angle in complex (180), compared with the
### TABLE 6

Selected bond lengths and angles for [Pt{OP(O)(Ph)O}(PMePh$_2$)$_2$] (180)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – P(2)</td>
<td>2.231 (1)</td>
<td>P(2) – Pt – P(3)</td>
<td>98.7 (1)</td>
</tr>
<tr>
<td>Pt – P(3)</td>
<td>2.222 (1)</td>
<td>O(2) – Pt – O(3)</td>
<td>71.2 (2)</td>
</tr>
<tr>
<td>Pt – O(2)</td>
<td>2.070 (4)</td>
<td>P(2) – Pt – O(3)</td>
<td>96.5 (1)</td>
</tr>
<tr>
<td>Pt – O(3)</td>
<td>2.102 (4)</td>
<td>P(3) – Pt – O(2)</td>
<td>93.7 (1)</td>
</tr>
<tr>
<td>O(2) – P(1)</td>
<td>1.576 (5)</td>
<td>Pt – O(2) – P(1)</td>
<td>93.4 (2)</td>
</tr>
<tr>
<td>O(3) – P(1)</td>
<td>1.563 (4)</td>
<td>Pt – O(3) – P(1)</td>
<td>92.6 (2)</td>
</tr>
<tr>
<td>P(1) – O(1)</td>
<td>1.475 (5)</td>
<td>O(2) – P(1) – O(3)</td>
<td>101.3 (2)</td>
</tr>
<tr>
<td>P(1) – C(11)</td>
<td>1.801 (5)</td>
<td>O(1) – P(1) – C(11)</td>
<td>108.9 (3)</td>
</tr>
<tr>
<td>P(2) – C(1)</td>
<td>1.809 (5)</td>
<td>O(2) – P(1) – O(1)</td>
<td>116.3 (3)</td>
</tr>
<tr>
<td>P(2) – C(21)</td>
<td>1.811 (3)</td>
<td>O(3) – P(1) – O(1)</td>
<td>115.7 (3)</td>
</tr>
<tr>
<td>P(2) – C(31)</td>
<td>1.819 (4)</td>
<td>Twist $^b$</td>
<td>3.81</td>
</tr>
<tr>
<td>P(3) – C(2)</td>
<td>1.811 (7)</td>
<td>Fold $^c$</td>
<td>12.86</td>
</tr>
<tr>
<td>P(3) – C(41)</td>
<td>1.810 (4)</td>
<td>C(12) – C(11) – P(1) – O(1) Torsion</td>
<td>-1.93</td>
</tr>
<tr>
<td>P(3) – C(51)</td>
<td>1.814 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt – Pt</td>
<td>2.676 (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ See Figure 11 for crystallographic numbering system;

$^b$ $< P(2) – Pt – P(3) / O(2) – Pt – O(3)$;

$^c$ $< O(2) – Pt – O(3) / O(2) – P(1) – O(3)$.
Figure 11
Molecular structure of $[\text{Pt}\{\text{OP(O)(Ph)O}\}(\text{PMePh}_2)_2] (180)$ with all hydrogen atoms being omitted.
TABLE 7
Selected structural data for complexes (172), (173) and (180) and also phenylphosphonic acid (175).

<table>
<thead>
<tr>
<th>Bond Length (Å) or Angle (°)</th>
<th>E = Se, R = Ph, L₂ = dppe (173)</th>
<th>E = S, R = C₆H₄OMe, L = PPh₃ (172)</th>
<th>E = O, R = Ph, L = PMePh₂ (180)</th>
<th>PhP(O)(OH)₂ (175)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – P</td>
<td>2.253 (2)</td>
<td>2.293 (2)</td>
<td>2.231 (1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.249 (2)</td>
<td>2.291 (2)</td>
<td>2.222 (1)</td>
<td></td>
</tr>
<tr>
<td>Pt – E</td>
<td>2.471 (1)</td>
<td>2.369 (2)</td>
<td>2.102 (4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.465 (1)</td>
<td>2.351 (2)</td>
<td>2.070 (4)</td>
<td></td>
</tr>
<tr>
<td>P – E</td>
<td>2.239 (3)</td>
<td>2.065 (2)</td>
<td>1.576 (5)</td>
<td>1.550 (4)</td>
</tr>
<tr>
<td></td>
<td>2.215 (3)</td>
<td>2.063 (2)</td>
<td>1.563 (4)</td>
<td>1.539 (3)</td>
</tr>
<tr>
<td>P = E</td>
<td>2.104 (3)</td>
<td>1.945 (3)</td>
<td>1.475 (5)</td>
<td>1.496 (4)</td>
</tr>
<tr>
<td>E – Pt – E</td>
<td>85.3 (1)</td>
<td>81.7 (1)</td>
<td>71.2 (2)</td>
<td></td>
</tr>
<tr>
<td>E – P – E</td>
<td>97.3 (1)</td>
<td>96.8 (1)</td>
<td>101.3 (2)</td>
<td>106.9 (2)</td>
</tr>
<tr>
<td>Pt – E – P</td>
<td>88.3 (1)</td>
<td>89.3 (1)</td>
<td>93.4 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>87.6 (1)</td>
<td>88.9 (1)</td>
<td>92.6 (2)</td>
<td></td>
</tr>
<tr>
<td>Fold</td>
<td>13.2</td>
<td>19.4</td>
<td>12.86</td>
<td></td>
</tr>
<tr>
<td>P = E</td>
<td>equatorial</td>
<td>equatorial</td>
<td>equatorial</td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>159</td>
<td>150</td>
<td>This Work</td>
<td>160</td>
</tr>
</tbody>
</table>

* a < E – Pt – E / E – P – E
values for phenylphosphonic acid are indicative of a degree of ring strain in the complex.

As was observed for the P–S and P–Se distances in (172) and (173), the exocyclic P=O length in (180) is only ca. 0.1 Å shorter than the P–O bond distances in the ring. In the discussion of the structures of (172) and (173), the closeness of the P–E (E = S or Se) bond lengths to that of the P=E (E = S or Se) bond length was accounted for by suggesting significant electron delocalisation in the rings. To what extent this may occur in complex (180) is unclear, and comparisons with the structure of the free acid, in which electron delocalisation is clearly possible, are complicated by the presence of hydrogen bonding in the latter case.

Finally, there are no solvent molecules or short intermolecular contacts within the unit cell.

4.4 COMPARISON OF THE CRYSTAL STRUCTURES OF PLATINAPHOSPHETANE, PHOSPHETIDINE AND PHOSPHONATO METAL COMPLEXES

The X-ray crystal structures of complexes (109).CHCl₃, (127).H₂O.CH₂Cl₂ and (180) show several similarities with respect to the conformation of the metallacyclic ring framework, however both the hybridisations and groups (not shown in Figure 12) attached to atoms X affect the inherent geometry of the molecules.

![Figure 12](image_url)

The basic feature of all the rings is the fold angle about the X–X axis and the equatorial positioning of the phosphoryl group on the ring. In addition, the phenyl ring attached to the phosphoryl group is orientated such that its plane is almost coincidental with the P=O moiety.
The metal-phosphine distances are indicative of the \textit{trans} influences of the atoms X and thus decrease in the order X = C \rightarrow N \rightarrow O. However steric effects, especially for the platinaphosphetidine complex (127) also affect this distance and so a quantitative relationship based on bond lengths is meaningless. The distances Pt–X, P–X and P=O generally decrease as X = C \rightarrow N \rightarrow O.

The \textit{trans}-annular Pt----P distances are all outside the sum of the covalent radii of the two atoms, and indicate no significant interaction between the platinum and phosphorus. Interestingly, this distance is greater for the platinaphosphetidine complex (127) than for the platinaphosphetane complex (109), even though the bond distances in the ring are greater for the latter complex. The reason for the greater \textit{trans}-annular distance is that the internal ring angle at X averages only 91.1° for (109) as opposed to 98.5° for (127) which, in the latter case, forces the atoms apart. The increase in this angle is mainly due to the change in hybridisation of the ring atom X, the ring carbon atom in (109) being sp^3 whilst the nitrogen in (127) was shown to be virtually sp^2.

There are no apparent trends in the comparison of the bond angles of these complexes, however the increase in the ring angle X–P–X as X = N \rightarrow C \rightarrow O is a possible indication of decreasing ring strain along this series.

4.5 NMR SPECTRA OF PLATINAPHOSPHONATO, PHOSPHATO AND ARSONATO METAL COMPLEXES

The room temperature $^1H$ n.m.r. spectra for complexes (179)-(203) are consistent with the structures shown in Section 4.2. Thus for complexes (189)-(194), a doublet is seen between $\delta$ 1.37 and 1.47 p.p.m. for the methyl group attached to the phosphorus atom of the four-membered ring, with $^3J(\text{PH})$ 16 Hz for each complex.

Where solubility allows, the room temperature $^{13}C$-$^1H$ n.m.r. spectra for complexes (179)-(203) are also consistent with the structures shown in Section 4.2. The methyl group attached to the four-membered ring of complexes (189)-(194) is observed as a doublet, $^1J(\text{PC})$ 124 Hz, in the range $\delta$ 17.09-17.55 p.p.m.

The room temperature $^{31}P$-$^1H$ n.m.r. spectra of the bis(phosphine) complexes
(179)-(184), (189)-(193) and (195)-(198) show the presence of two inequivalent phosphorus environments. The signal due to the two equivalent donor ligand phosphorus nuclei shows a one-bond coupling to platinum-195 in excess of 3500 Hz, characteristic of phosphine ligands opposite oxygen, and for complexes (182)-(184), (189) and (192), they appear as a doublet due to 3-bond coupling to the phosphorus atom of the phosphonate ring. This atom therefore appears as either a singlet or a triplet, with a 2-bond coupling to platinum-195 in the range 107-147 Hz. The equivalence of the phoshpine ligands in solution is despite the X-ray structure determination of (180), which showed them to be inequivalent in the solid state. A similar effect was also noted for complexes (172) and (173). The spectra of the triphenylarsine complexes (185), (194) and (199) show a singlet with corresponding platinum-195 satellites, with \(^J(PtP)\) in the range 147-181 Hz. The \(^{31}P\)-(\(^1\)H) n.m.r. spectra of the mixed ligand complexes (186)-(188) are consistent with the structures shown in Section 4.2, and the spectra for the phenylarsonato complexes (200)-(203) show the expected singlet with satellites.

4.6 I.R. SPECTRA OF PLATINAPHOSPHONATO, PHOSPHATO AND ARSONATO METAL COMPLEXES

The i.r. spectra of complexes (179)-(199) all show a band corresponding to the stretching mode of the phosphoryl group. For complexes (179)-(194), the absorption appears in the region 1190-1235 cm\(^{-1}\), whilst for complexes (195)-(199), the band appears in the slightly higher range 1240-1260 cm\(^{-1}\), as expected due to the presence of the more electronegative phenoxy substituent on the phosphorus atom.\(^{115}\)

The i.r. spectra for complexes (200)-(203) all show a band in the region 900-930 cm\(^{-1}\) which can be assigned to the As=O stretching frequency on the basis of literature values for such a group.\(^{164,165}\)

4.7 REACTIONS OF PLATINAPHOSPHONATO COMPLEXES

4.7.1 Decomposition of \([Pt\{OP(O)(Ph)\}(PBzPh\textsubscript{2})\textsubscript{2}](181)\textsubscript{\textsuperscript{2-}}\textsubscript{2}H\textsubscript{2}O\)

All the new complexes are air stable in the solid phase, however during n.m.r. studies, the benzylidiphenylphosphine complex (181) was found to decompose in either chloroform...
or dichloromethane solution. $^{31}$P-$^1$H n.m.r. studies showed the decomposition products to be numerous, even though some of the other complexes were stable in solution for several weeks. Attempts to isolate any of the decomposition products resulted in the collection of colourless crystals in ca. 17% yield. An X-ray crystal structure determination was carried out in order to confirm the identity of the product in the hope that it may provide an insight into the cause of decomposition. Important bond lengths and angles are presented in Table 8, whilst the molecular structure is illustrated in Figure 13 along with the crystallographic numbering system for the non-hydrogen atoms.

It should be noted that the molecule has a two-fold rotational symmetry axis passing through the platinum such that P(1) maps onto P(2), C(1) maps onto C(2) and C(11) maps onto C(41), etc. This also defines that the bond lengths on one side of the molecule are equal to their counterparts on the other.

The structure consists of 2 cis-metallated benzyldiphenylphosphine ligands bound to a platinum(n) centre, so as to give the metal a distorted square planar geometry. The phosphines thus act as chelating ligands, each forming a five-membered ring. The twist angle about the platinum between planes P(1)-Pt-C(11) and P(2)-Pt-C(41) is large at 16.4(1)° and the four valence angles around the metal are considerably displaced from 90°, presumably to accommodate the 2 five-membered rings. These two rings show an 'envelope'-type conformation: the Pt and C atoms lie in the plane whilst the P atom deviates from it. This behaviour was also shown in the structure of complex (204, R = Bz) which, interestingly, did not possess a 2-fold rotation axis.$^{166}$

\[
\text{cis-}[\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{PR}_2)_2]
\]

(204)

The bond lengths and angles in complex (204, R = Ph) are, as would be expected, close to those of (204, R = Bz).$^{166}$

Due to the 'envelope' effect, the planes of the 2 orthometallated rings [the C(11) and C(41) phenyl rings] diverge at an angle of 55.2(2)°, such that in Figure 13, the C(11) phenyl
**TABLE 8**

Selected bond lengths and angles for cis-[Pt\(\text{C}_6\text{H}_4\text{CH}_2\text{C} \equiv \text{H} \cdots \text{C} \equiv \text{PPh}_3\)] (204, R = Ph)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – P(1)</td>
<td>2.282 (1)</td>
<td>C(1) – Pt – P(2)</td>
<td>105.4 (1)</td>
</tr>
<tr>
<td>Pt – C(11)</td>
<td>2.064 (4)</td>
<td>P(1) – Pt – C(11)</td>
<td>81.2 (1)</td>
</tr>
<tr>
<td>P(1) – C(1)</td>
<td>1.831 (4)</td>
<td>C(11) – Pt – C(41)</td>
<td>94.2 (2)</td>
</tr>
<tr>
<td>P(1) – C(21)</td>
<td>1.828 (2)</td>
<td>P(1) – P(1) – C(1)</td>
<td>101.4 (2)</td>
</tr>
<tr>
<td>P(1) – C(31)</td>
<td>1.822 (2)</td>
<td>P(1) – C(1) – C(12)</td>
<td>105.9 (3)</td>
</tr>
<tr>
<td>C(1) – C(12)</td>
<td>1.512 (6)</td>
<td>C(1) – C(12) – C(11)</td>
<td>118.5 (4)</td>
</tr>
<tr>
<td>C(11) – C(12)</td>
<td>1.410 (6)</td>
<td>C(12) – C(11) – Pt</td>
<td>119.9 (3)</td>
</tr>
<tr>
<td>C(12) – C(13)</td>
<td>1.389 (6)</td>
<td>C(11) – C(12) – C(13)</td>
<td>121.6 (4)</td>
</tr>
<tr>
<td>C(13) – C(14)</td>
<td>1.383 (7)</td>
<td>C(12) – C(13) – C(14)</td>
<td>120.1 (5)</td>
</tr>
<tr>
<td>C(14) – C(15)</td>
<td>1.388 (8)</td>
<td>C(13) – C(14) – C(15)</td>
<td>120.5 (5)</td>
</tr>
<tr>
<td>C(15) – C(16)</td>
<td>1.391 (7)</td>
<td>C(14) – C(15) – C(16)</td>
<td>118.9 (5)</td>
</tr>
<tr>
<td>C(11) – C(16)</td>
<td>1.406 (6)</td>
<td>C(15) – C(16) – C(11)</td>
<td>122.7 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(16) – C(11) – C(12)</td>
<td>116.2 (4)</td>
</tr>
<tr>
<td>Twist (^a)</td>
<td></td>
<td></td>
<td>16.4 (1)</td>
</tr>
</tbody>
</table>

\(^a\) See Figure 13 for crystallographic numbering system;
\(^b\) \(< \text{Pt} – \text{Pt} – \text{C}(11) / P(2) – \text{Pt} – \text{C}(41)\).
Figure 13

Molecular structure of cis-[Pt(C₆H₄CH₂PPh₂)₂] (204, R = Ph) with all hydrogen atoms being omitted.
ring is behind the C(41) ring and is sloping away into the paper. The bond lengths and angles in these two rings deviate somewhat from average values, however the deviations are relatively small and can be accounted for by the fact that one bond in each ring is also part of a five-membered ring. The X-ray crystal structure of (204, R = Bu³) also showed that the planes of the two orthometallated rings diverge, with a very similar angle of 57°.\(^\text{167}\)

The formation of complex (204, R = Ph) is satisfied by the equation shown in Scheme 41.

\[
\text{(BzPh}_2\text{P)}_2\text{Pt}^{\text{PPh}} \rightarrow \text{Ph}_2\text{P}\text{Pt} + \text{OPhP(OH)}_2
\]

\text{(204, R=Ph)}

\text{Scheme 41}

The driving force behind the decomposition of (181) may be the formation of a thermodynamically more stable product (204, R = Ph) or perhaps the relief of ring strain. The benzyl group on the phosphine possibly provides an energetically favourable route to decomposition, as the final product contains two relatively stress-free, five-membered rings. With phenyl substituted phosphines, any orthometallation would lead to a four-membered ring, which may be even less stable than the initial platinaphosphonato complex.

Complex (204, R = Ph) was originally prepared in >80% yield by the action of (\(\sigma\)-lithio-benzyl)diphenylphosphine on \([\text{PtCl}_2(\text{SEt})_2]\).\(^\text{168}\) Therefore, the decomposition of complex (181) under the stated conditions does not constitute a primary synthetic route to (204, R = Ph).

4.7.2 Reaction with carbon monoxide

Complex (179) reacts with carbon monoxide at room temperature in dichloromethane or THF, to give a bright orange solution. The \(^{31}\text{P}-\text{\textsuperscript{1}H}\) n.m.r. spectrum of the solution shows
a singlet at δ 23.15 p.p.m. with satellites that appear to be doublets. There is also a broad peak corresponding to free phenylphosphonic acid. The fact that the satellites appear as doublets may indicate that the central singlet is actually two overlapping signals, however even a high field spectrum failed to resolve the peak. The $^{31}$P-$\{^1$H$\}$ n.m.r. spectrum also indicated that the triphenylphosphine ligands were not displaced during the reaction, and the i.r. spectrum indicated there are at least 2 types of carbonyl group present in the compound. Attempts to isolate and purify a solid sample invariably resulted in the formation of a mixture including the starting complex (179) and phenylphosphonic acid. It was noted that if the solution was allowed to stand in air, quantitative reformation of the starting complex (179) occurred over a period of ca. 48h.

The probable identity of the orange complex (205) is a platinum/phosphine/carbonyl cluster compound which is stable in the presence of phenylphosphonic acid only when under a carbon monoxide atmosphere. When this is removed, the acid attacks the cluster and reforms the starting complex. Stable cluster compounds, which are generally red or orange in colour, involving 3 or 5 platinum atoms have been known for some time, however the spectral data for the unknown complex does not match that of the compounds in the literature.$^{169,170}$

Interestingly, complex (205) reacted with either diphenylacetylene or dmad in dichloromethane to give the bis(triphenylphosphine)platinum acetylene complex as the main product, and also reacted with HCl to give cis-[PtCl$_2$(PPh$_3$)$_2$] in quantitative yield. Similar orange complexes were also prepared from both complex (195) and the methyldiphenylphosphine complex (180).

The decomposition of complex (181) to give (204, R = Ph) indicated the lability of the phenylphosphonate ligand providing a suitable product can be formed. In this instance, carbon monoxide could act as either a monodentate or bridging ligand to form such a product. In addition, preliminary indications suggest that when complex (179) is treated with liquid ammonia, the phosphonate fragment is displaced, presumably by coordinating NH$_3$ ligands.
4.7.3 Reaction with tin(II) chloride

The insertion of tin(II) chloride into a platinum-chlorine bond to form a Pt–SnCl₃ group is well known, and complexes containing a Pt–Sn linkage have been of use as effective hydroformylation catalysts. It was noted that the phosphonate group of complex (179) was labile under certain conditions and therefore the insertion of a tin(II) chloride moiety into the platinum-oxygen bond was attempted. The treatment of complex (179) with excess SnCl₂ in dichloromethane led to the formation of several products, however ³¹P-{¹H} n.m.r. spectroscopy showed the presence of a dominant species. This main product was shown as a doublet and a triplet with corresponding platinum-195 satellites, which seemed to indicate the presence of three phosphine groups on the platinum. For this to occur, the product must have scavenged a triphenylphosphine from another complex, and hence the reaction was repeated with one equivalent of free triphenylphosphine also present. The resulting ³¹P-{¹H} n.m.r. spectrum showed the presence of the same metal complex in quantitative yield along with free phenylphosphonic acid. Interestingly, an identical spectrum was obtained when cis-[PtCl₂(PPh₃)₂] was treated with excess SnCl₂ and one equivalent of triphenylphosphine in dichloromethane. The ³¹P-{¹H} n.m.r. spectrum indicates that the complex must have a structure somewhat similar to (206) in order to account for the data.

![Diagram](image)

(206)

No such compound could be found in the literature, but 5-coordinate complexes such as [PtH(SnCl₃)(CO)(PPh₃)₂] have been prepared and used as hydroformylation catalysts. It was considered worthwhile to attempt a hydroformylation reaction using one of the platinaphosphonate complexes with tin(II) chloride in order to assess its catalytic potential. It has been shown that complexes with bidentate phosphines forming seven-membered chelate rings give the optimum results for hydroformylation. Hence, the dppb complex
(184) with excess tin(II) chloride was used in the attempted hydroformylation of styrene under a pressure of 100 atmospheres of synthesis gas. The catalytic hydroformylation of styrene is outlined in Scheme 42, and this substrate has been well studied due to its prochiral nature and the possibility of forming optically active products.\(^\text{175}\)

![Scheme 42](image)

After 24h, the \(^1\)H n.m.r. spectrum of the distilled reaction mixture showed that hydroformylation had occurred, however there was no apparent preference towards forming either the chain or branched product, and comparison with data for hydroformylation reactions using a [PtCl\(_2\)(dppb)]/SnCl\(_2\) system,\(^\text{174}\) indicates that possibly the same catalytic species was active in each case. Hence, it can be assumed that complex (184) was just a source of platinum and that its reaction with SnCl\(_2\) probably proceeds via chlorination to give [PtCl\(_2\)(dppb)] and then insertion to yield the catalyst.

4.8 CONCLUSION

The preparation of new phosphonato, phosphato and arsonato complexes of platinum(II) may be achieved in high yield via the treatment of cis-[PtCl\(_2\)L\(_2\)] (L = donor ligand) with either phenylphosphonic acid (175), methylphosphonic acid (176), phenyl dihydrogen phosphate (177) or phenylarsonic acid and silver(I) oxide in refluxing dichloromethane. A single crystal X-ray diffraction study of a phenylphosphonato derivative, showed the four-membered metallacycle to have a small puckering angle, and its general features compared well to those of the platinaphosphetane and platinaphosphetidine complexes discussed in Chapters 2 and 3.

The decomposition product of the benzyldiphenylphosphine adduct (181) was shown, via an X-ray crystal structure determination, to be the di-orthometallated product
cis-[\text{Pt}\{\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]_2. The reactions of the phosphonato complexes with carbon monoxide and tin(II) chloride were also discussed.

4.9 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. Tables 9 and 10 show m.p.'s, microanalytical results and i.r. spectroscopic data for compounds (179)-(203). The $^{13}\text{C}$-{\text{\textsuperscript{1}H}} n.m.r. data for the aromatic region between $\delta$ 145 and 120 p.p.m. are omitted for clarity. All $^{31}\text{P}$-{\text{\textsuperscript{1}H}} n.m.r. spectra were recorded on a JEOL JNM FX90Q spectrometer operating at 36.24 MHz. The compounds triphenylarsine, phenylphosphonic acid (175), methylphosphonic acid (176), phenylarsionic acid, diphenylacetylene, dmad, tin(II) chloride, styrene (Aldrich), carbon monoxide, synthesis gas, and ammonia (BOC) were used as supplied from commercial sources. The compounds [PtCl$_2$(cod)],$^{123}$ cis-[PtCl$_2$(PPh$_3$)$_2$],$^{124}$ cis-[PtCl$_2$(AsPh$_3$)$_2$],$^{176}$ [(PtBr$_2$(PP$_3$))$_2$],$^{153}$ [(PtBr$_2$(PE$_3$))$_2$],$^{153}$ benzylidiphenylphosphine,$^{177}$ and phenyl dihydrogen phosphate (177)$^{178}$ were prepared as described in the literature.

Preparation of phosphonato, phosphato and arsonato complexes of platinum(II):

General method

Two equivalents of tertiary phosphine or one equivalent of chelating tertiary phosphine, followed by one equivalent of the appropriate acid, and an excess of silver(I) oxide were added in succession to a stirred solution of [PtCl$_2$(cod)] in dichloromethane (ca. 45 cm$^3$), and the mixture was refluxed for 4h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish-brown oil. Dissolution of the oil in dichloromethane (ca. 10 cm$^3$) followed by addition of light petroleum afforded, on standing, a white to pale yellow microcrystalline solid, which was recrystallised from dichloromethane - light petroleum, and dried in vacuo.

(i) [Pt(OP(O)(Ph)O)(PPh$_3$)$_2$] (179)

The complex [PtCl$_2$(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and phenylphosphonic acid (175) (0.045g, 0.28 mmol) gave white microcrystals of
(179) (0.23g, 97%). N.m.r. spectra: \(^1H\) (90 MHz), \(\delta\) 8.0-7.0 (m, 35H, Ph); \(^{31}P\)-\(^1H\), \(\delta\) 35.50 [s, P(1), \(^2J(PtP(1))\) 127], and 7.26 p.p.m. [s, PPh\(_3\), \(^1J(PtP)\) 3877].

(ii) \([Pt(O\{O\}(Ph)\{O\}(PMePh\(_2\))\{2\}] (180)\)

The complex \([PtCl\(_2\)(cod)]\) (0.10g, 0.27 mmol) with methyldiphenylphospine (0.11g, 0.55 mmol) and phenylphosphonic acid (175) (0.045g, 0.28 mmol) gave white microcrystals of (180) (0.18g, 89%). N.m.r. spectra: \(^1H\) (300 MHz), \(\delta\) 7.98-6.86 (m, 25H, Ph), 1.78 [d, 6H, Me, PMePh\(_2\), \(^2J(PH)\) + \(^4J(PH)\) 11]; \(^{13}C\)-\(^1H\), \(\delta\) 14.33 (m, Me, PMePh\(_2\)); \(^{31}P\)-\(^1H\), \(\delta\) 36.50 [s, P(1), \(^2J(PtP(1))\) 122], and -7.26 p.p.m. [s, PMePh\(_2\), \(^1J(PtP)\) 3755]. X-ray quality crystals of (180) were grown slowly from dichloromethane - light petroleum in air.

(iii) \([Pt(O\{O\}(Ph)\{O\}(PBzPh\(_2\))\{2\}] (181).H\(_2\)O\)

The complex \([PtCl\(_2\)(cod)]\) (0.10g, 0.27 mmol) with benzyldiphenylphospine (0.16g, 0.58 mmol) and phenylphosphonic acid (175) (0.045g, 0.28 mmol) gave white microcrystals of (181).H\(_2\)O (0.22g, 90%). N.m.r. spectra: \(^1H\) (300 MHz), \(\delta\) 7.96-6.68 (m, 35H, Ph), 3.66 (m, 4H, CH\(_2\), PBzPh\(_2\)), 3.03 (s, br, 2H, H\(_2\)O); \(^{13}C\)-\(^1H\), \(\delta\) 33.65 (m, CH\(_2\), PBzPh\(_2\)); \(^{31}P\)-\(^1H\), \(\delta\) 36.82 (t, P(1), \(^2J(PtP(1))\) 117, \(^3J(PP(1))\) 7), and 3.93 p.p.m. [d, PBzPh\(_2\), \(^1J(PtP)\) 3865, \(^3J(PP(1))\) 7].

(iv) \([Pt(O\{O\}(Ph)\{O\}(dppe))\{2\}] (182).H\(_2\)O\)

The complex \([PtCl\(_2\)(cod)]\) (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and phenylphosphonic acid (175) (0.045g, 0.28 mmol) gave white microcrystals of (182).H\(_2\)O (0.20g, 97%). N.m.r. spectra: \(^1H\) (300 MHz), \(\delta\) 8.13-6.76 (m, 25H, Ph), 3.27 (s, br, 2H, H\(_2\)O), 2.89-2.00 (m, 4H, CH\(_2\), dppe); \(^{13}C\)-\(^1H\), too insoluble; \(^{31}P\)-\(^1H\), \(\delta\) 40.38 (t, P(1), \(^2J(PtP(1))\) 128, \(^3J(PP(1))\) 7), and 31.80 p.p.m. [d, dppe, \(^1J(PtP)\) 3709, \(^3J(PP(1))\) 7].

(v) \([Pt(O\{O\}(Ph)\{O\})(dppp))\{2\}] (183).CH\(_2\)Cl\(_2\)\)

The complex \([PtCl\(_2\)(cod)]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and phenylphosphonic acid (175) (0.045g, 0.28 mmol) gave white microcrystals of (183).CH\(_2\)Cl\(_2\) (0.22g, 96%). N.m.r. spectra: \(^1H\) (300 MHz), \(\delta\) 7.84-7.16 (m, 25H, Ph), 5.26
(s, 2H, CH₂Cl₂), 2.35 (m, 4H, P–CH₂, dppp), 2.06 (m, 2H, CH₂, dppp); 13C-{¹H}, δ 53.48
(s, CH₂Cl₂), 23.72 [d, P–CH₂, dppp, 1J(PCS) 49], 19.41 (s, CH₂, dppp); 31P-{¹H}, δ 37.42 {t, P(1), 2J(PtP(1)) 124, 3J(PP(1)) 5}, and -11.71 p.p.m. {d, dppp, 1J(PtP) 3556, 3J(P(1)P) 5}.

(vi) [Pt(OP(O)(Ph)O)(dppb)] (I84)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and phenylphosphonic acid (I75) (0.045g, 0.28 mmol) gave white microcrystals of (I84) (0.20g, 95%). N.m.r. spectra: ¹H (300 MHz), δ 7.78-7.15 (m, 25H, Ph), 2.43 (m, 4H, P–CH₂, dppb), 1.84 (m, 4H, CH₂, dppb); 13C-{¹H}, δ 24.99 [d, P–CH₂, dppb, 1J(PCS) 40], 22.47 (s, CH₂, dppb); 31P-{¹H}, δ 37.92 {t, P(1), 2J(PtP(1)) 117, 3J(PP(1)) 10}, and 2.82 p.p.m. {d, dppb, 1J(PtP) 3701, 3J(P(1)P) 10}.

(vii) [Pt(OP(O)(Ph)O)(AsPh₃)]₂ (I85).H₂O

The complex cis-[PtCl₂(AsPh₃)₂] (0.30g, 0.34 mmol) with phenylphosphonic acid (I75) (0.055g, 0.35 mmol) gave pale yellow microcrystals of (I85).H₂O (0.31g, 93%). N.m.r. spectra: ¹H (90 MHz), δ 8.2-6.9 (m, 35H, Ph), 3.1 (s, br, 2H, H₂O); 31P-{¹H}, δ 40.94 {s, P(1), 2J(PtP(1)) 147}.

(viii) [Pt(OP(O)(Ph)O)(PPr₃)(PPh₃)] (I86)

The complex [{PtBr₂(PPr₃)₂}] (0.20g, 0.19 mmol) with triphenylphosphine (0.11g, 0.42 mmol) and phenylphosphonic acid (I75) (0.06g, 0.38 mmol) gave white microcrystals of (I86) (0.29g, 98%). N.m.r. spectra: ¹H (300 MHz), δ 7.98-7.29 (m, 20H, Ph), 1.43 (m, 6H, P–CH₂, PPr₃), 1.29 (m, 6H, CH₂, PPr₃), 0.86 [t, 9H, CH₃, PPr₃, 3J(HH) 7]; 13C-{¹H}, δ 23.58 [d, P–CH₂, PPr₃, 1J(PCS) 37], 17.74 [d, CH₂, PPr₃, 2J(PCS) 1], 15.43 [d, CH₃, PPr₃, 3J(PCS) 15]; 31P-{¹H}, δ 38.16 {s, P(1), 2J(PtP(1)) 115}, 3.95 [d, PPh₃, 1J(PtP) 3928, 2J(PP) 32], and -3.77 p.p.m. {d, PPr₃, 1J(PtP) 3591, 2J(PP) 32}.

(ix) [Pt(OP(O)(Ph)O)(PPr₃)(AsPh₃)] (I87)

The complex [{PtBr₂(PPr₃)₂}] (0.20g, 0.19 mmol) with triphenylarsine (0.12g, 0.39 mmol) and phenylphosphonic acid (I75) (0.06g, 0.38 mmol) gave white microcrystals of
(187) (0.30g, 97%). N.m.r. spectra: \(^1\)H (300 MHz), \(\delta\) 8.08-7.30 (m, 20H, Ph), 1.52-1.26 (m, 12H, CH₂, PPr₃), 0.87 [t, 9H, CH₃, PPr₃, \(^3\)J(HH) 7]; \(^{13}\)C-\(^1\)H, \(\delta\) 23.96 [d, P-CH₂, PPr₃, \(^1\)J(PC) 37], 17.61 [d, CH₂, PPr₃, \(^2\)J(PC) 2], 15.24 [d, CH₃, PPr₃, \(^3\)J(PC) 15]; \(^{31}\)P-\(^1\)H, \(\delta\) 38.72 (s, P(1), \(^2\)J[PnP(1)] 137), and -6.66 p.p.m. [s, PPr₃, \(^1\)J(PtP) 3550].

(x) \([\text{Pt}(\text{OP}(\text{O})(\text{Ph})\text{O})(\text{PET}_{3})(\text{AsPh}_{3})]\) (188)

The complex \([\text{PtBr}_{2}(\text{PET}_{3})]_2\) (0.20g, 0.21 mmol) with triphenylarsine (0.13g, 0.43 mmol) and phenylphosphonic acid (175) (0.07g, 0.44 mmol) gave white microcrystals of (188) (0.32g, 98%). N.m.r. spectra: \(^1\)H (300 MHz), \(\delta\) 8.10-7.32 (m, 20H, Ph), 1.38 (m, 6H, P-CH₂, PPr₃), 0.99 [dt, 9H, CH₃, PPr₃, \(^3\)J(PH) 17, \(^3\)J(HH) 7]; \(^{13}\)C-\(^1\)H, \(\delta\) 14.19 [d, P-CH₂, PPr₃, \(^1\)J(PC) 39], 7.93 [d, CH₃, PPr₃, \(^2\)J(PC) 3]; \(^{31}\)P-\(^1\)H, \(\delta\) 38.72 (s, P(1), \(^2\)J[PnP(1)] 137), P), and 2.82 p.p.m. [s, PPr₃, \(^1\)J(PtP) 3564].

(xi) \([\text{Pt}(\text{OP}(\text{O})(\text{Me})\text{O})(\text{PPh}_{3})_2]\) (189).\(\text{H}_2\text{O}\)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and methylphosphonic acid (176) (0.03g, 0.31 mmol) gave white microcrystals of (189).\(\text{H}_2\text{O}\) (0.20g, 89%). N.m.r. spectra: \(^1\)H (300 MHz), \(\delta\) 7.89-6.63 (m, 30H, Ph), 3.21 (s, br, 2H, H₂O), 1.40 [d, 3H, Me, \(^2\)J(P(1)H) 16], \(^{13}\)C-\(^1\)H, \(\delta\) 17.09 (d, Me, \(^1\)J[P(1)C] 124); \(^{31}\)P-\(^1\)H, \(\delta\) 46.80 (t, P(1), \(^2\)J[PnP(1)] 122, \(^3\)J[PP(1)] 10), and 7.25 p.p.m. (d, PPh₃, \(^1\)J(PtP) 3848, \(^3\)J[P(1)P] 10).

(xii) \([\text{Pt}(\text{OP}(\text{O})(\text{Me})\text{O})(\text{PMePh}_{2})_2]\) (190).\(\text{CH}_2\text{Cl}_2\)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and methylphosphonic acid (176) (0.03g, 0.31 mmol) gave white microcrystals of (190).\(\text{CH}_2\text{Cl}_2\) (0.19g, 91%). N.m.r. spectra: \(^1\)H (300 MHz), \(\delta\) 7.76-7.18 (m, 20H, Ph), 5.29 (s, 2H, CH₂Cl₂), 1.76 [d, 6H, Me, PMePh₂, \(^2\)J(PH) + \(^4\)J(PH)] 11, \(^3\)J(PtH) 50], 1.43 [d, 3H, Me, \(^2\)J(P(1)H) 16]; \(^{13}\)C-\(^1\)H, \(\delta\) 53.37 (s, CH₂Cl₂), 17.24 [d, Me, \(^1\)J[P(1)C] 124], 14.08 [d, Me, PMePh₂, \(^1\)J(PC) + \(^3\)J(PC)] 44]; \(^{31}\)P-\(^1\)H, \(\delta\) 47.32 (s, P(1), \(^2\)J[PnP(1)] 112), and -7.47 p.p.m. [s, PMePh₂, \(^1\)J(PtP) 3755].
The complex \([\text{PtCl}_2\text{(cod)}]\) (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and methylphosphonic acid (176) (0.03g, 0.31 mmol) gave white microcrystals of \((191)_2\text{H}_2\text{O}\) (0.18g, 95%). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 8.11-7.09 (m, 20H, Ph), 2.96-2.15 (m, br, 4H, CH\(_2\), dppe), 2.20 (s, br, 2H, H\(_2\text{O}\)), 1.47 (d, 3H, Me, \(^2\text{J(P-P)}\) 16); \(^3\text{C}-\{\text{H}\}\), too insoluble; \(^{31}\text{P}-\{\text{H}\}\), \(\delta\) 50.68 (s, P(1), \(^2\text{J(PP)}\) 107), and 31.26 p.p.m. (s, dppe, \(^1\text{J(P-P)}\) 3696).

The complex \([\text{PtCl}_2\text{(AsPh}_3\text{)}\text{]}}\) (0.30g, 0.34 mmol) with methylphosphonic acid (176) (0.035g, 0.37 mmol) gave pale yellow microcrystals of \((194)_2\text{H}_2\text{O}\) (0.30g, 96%). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.88-6.97 (m, 30H, Ph), 3.12 (s, br, 2H, H\(_2\text{O}\)), 1.47 (d, 3H, Me, \(^2\text{J(P-P)}\) 16); \(^3\text{C}-\{\text{H}\}\), \(\delta\) 17.55 (d, Me, \(^1\text{J[P-C]}\) 124); \(^{31}\text{P}-\{\text{H}\}\), \(\delta\) 49.47 (t, P(1), \(^2\text{J(PP)}\) 112, \(^3\text{J[PP]}\) 5), and -12.25 p.p.m. (d, dppe, \(^1\text{J(P-P)}\) 3547, \(^3\text{J[P-P]}\) 5).

The complex \([\text{cis-}[\text{PtCl}_2\text{(AsPh}_3\text{)}\text{]}}\) (0.30g, 0.34 mmol) with methylphosphonic acid (176) (0.035g, 0.37 mmol) gave pale yellow microcrystals of \((194)_2\text{H}_2\text{O}\) (0.30g, 96%). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.88-6.97 (m, 30H, Ph), 3.12 (s, br, 2H, H\(_2\text{O}\)), 1.47 (d, 3H, Me, \(^2\text{J(P-P)}\) 16); \(^3\text{C}-\{\text{H}\}\), \(\delta\) 17.55 (d, Me, \(^1\text{J[P-C]}\) 124); \(^{31}\text{P}-\{\text{H}\}\), \(\delta\) 52.03 p.p.m. (s, P(1), \(^2\text{J(P-P)}\) 156).
(xvii) \([\text{Pt(O} \text{P(O)(OPh)(OPh)})_2\text{(PPh}_3)_2](195)\text{H}_2\text{O}\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and phenyl dihydrogen phosphate (177) (0.05g, 0.29 mmol) gave white microcrystals of \((195)\text{H}_2\text{O}\) (0.24g, 98%). N.m.r. spectra: \(^1\text{H}\) (90 MHz), \(\delta\) 8.2-6.8 (m, 35H, Ph), 2.7 (s, br, 2H, H\(_2\text{O}\)); \(^{31}\text{P}-(\text{H})\), \(\delta\) 18.96 (s, P(1)), \(^2\text{J}[\text{PtP(1)}] 147\), and 6.66 p.p.m. [s, PPh\(_3\), \(^1\text{J}(\text{PtP}) 3936\)].

(xviii) \([\text{Pt(O} \text{P(O)(OPh)(OPh)})_2\text{(PMePh}_2)_2](196)\text{H}_2\text{O}\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and phenyl dihydrogen phosphate (177) (0.05g, 0.29 mmol) gave white microcrystals of \((196)\text{H}_2\text{O}\) (0.20g, 94%). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.42-6.66 (m, 25H, Ph), 3.23 (s, br, 2H, H\(_2\text{O}\)), 1.67 \([d, 6\text{H}, \text{Me}, \text{PMePh}_2, (^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})) 11\]); \(^{13}\text{C}-(\text{H})\), \(\delta\) 14.00 \([d, \text{Me}, \text{PMePh}_2, (^1\text{J}(\text{PC}) + ^3\text{J}(\text{PC})) 44\]); \(^{31}\text{P}-(\text{H})\), \(\delta\) 18.78 (s, P(1)), \(^2\text{J}[\text{PtP(1)}] 142\), and -8.01 p.p.m. [s, PMePh\(_2\), \(^1\text{J}(\text{PtP}) 3823\)].

(xix) \([\text{Pt(O} \text{P(O)(OPh)(OPh)})_2\text{(dppp)}](197)\text{CH}_2\text{Cl}_2\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and phenyl dihydrogen phosphate (177) (0.05g, 0.29 mmol) gave white microcrystals of \((197)\text{CH}_2\text{Cl}_2\) (0.22g, 94%). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.93-6.69 (m, 25H, Ph), 5.27 (s, 2H, CH\(_2\text{Cl}_2\)), 2.81-1.92 (m, 6H, CH\(_2\)), dppp); \(^{13}\text{C}-(\text{H})\), too insoluble; \(^{31}\text{P}-(\text{H})\), \(\delta\) 19.56 (s, P(1)), \(^2\text{J}[\text{PtP(1)}] 146\), and -11.50 p.p.m. [s, dppp, \(^1\text{J}(\text{PtP}) 3594\)].

(xx) \([\text{Pt(O} \text{P(O)(OPh)(OPh)})_2\text{(dppb)}](198)\text{H}_2\text{O}\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and phenyl dihydrogen phosphate (177) (0.05g, 0.29 mmol) gave white microcrystals of \((198)\text{H}_2\text{O}\) (0.21g, 96%). Complex \((198)\text{H}_2\text{O}\) was too insoluble for n.m.r. spectroscopy.

(xxii) \([\text{Pt(O} \text{P(O)(OPh)(OPh)})_2\text{(AsPh}_3)_2](199)\text{H}_2\text{O}\)

The complex \(\text{cis-[PtCl}_2(\text{AsPh}_3)_2]\) (0.30g, 0.34 mmol) with phenyl dihydrogen phosphate (177) (0.06g, 0.34 mmol) gave pale yellow microcrystals of \((199)\text{H}_2\text{O}\) (0.33g, 97%).
N.m.r. spectra: $^1$H (90 MHz), $\delta$ 7.7-7.0 (m, 35H, Ph), 2.1 (s, br, 2H, H$_2$O); $^{31}$P-{$^1$H}, $\delta$ 23.60 p.p.m. [s, P(1), $^2$J(PtP) 181].

(xxii) $[\text{Pt}2\{\text{OP(O)(Ph)O}\}\{\text{PPh}_3\}_2] (200)$

The complex $[\text{PtCl}_2\text{(cod)}] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and phenylarsonic acid (0.06g, 0.30 mmol) gave white microcrystals of (200) (0.24g, 97%). N.m.r. spectra: $^1$H (90 MHz), $\delta$ 8.2-6.9 (m, 35H, Ph); $^{31}$P-{$^1$H}, $\delta$ 8.27 p.p.m. [s, PPh$_3$, $^1$J(PtP) 3690].

(xxiii) $[\text{Pt}2\{\text{OP(O)(Ph)O}\}\{\text{PPh}_3\}_2] (201).\text{CH}_2\text{Cl}_2$

The complex $[\text{PtCl}_2\text{(cod)}] (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and phenylarsonic acid (0.06g, 0.30 mmol) gave white microcrystals of (201).CH$_2$Cl$_2$ (0.23g, 97%). N.m.r. spectra: $^1$H (300 MHz), $\delta$ 8.11-6.73 (m, 25H, Ph), 5.27 (s, 2H, CH$_2$Cl$_2$), 2.66-2.15 (m, 4H, CH$_2$, dppe); $^{13}$C-{$^1$H}, $\delta$ 53.17 (s, CH$_2$Cl$_2$), 26.28 [d, P–CH$_2$, dppe, $^1$J(PC) + $^3$J(PC) 51]; $^{31}$P-{$^1$H}, $\delta$ 30.05 p.p.m. [s, dppe, $^1$J(PtP) 3560].

(xxiv) $[\text{Pt}2\{\text{OP(O)(Ph)O}\}\{\text{dppe}\}_2] (202).\text{H}_2\text{O}$

The complex $[\text{PtCl}_2\text{(cod)}] (0.10g, 0.27 mmol) with dppe (0.12g, 0.28 mmol) and phenylarsonic acid (0.06g, 0.30 mmol) gave white microcrystals of (202).H$_2$O (0.22g, 97%). N.m.r. spectra: $^1$H (300 MHz), $\delta$ 7.87-7.17 (m, 25H, Ph), 3.36 (s, br, 2H, H$_2$O), 2.45 (m, 4H, P–CH$_2$, dppe), 2.03-1.90 (m, 4H, CH$_2$, dppe); $^{13}$C-{$^1$H}, $\delta$ 25.58 [d, P–CH$_2$, dppe, $^1$J(PC) 40], 22.85 (s, CH$_2$, dppe); $^{31}$P-{$^1$H}, $\delta$ 3.23 p.p.m. [s, dppe, $^1$J(PtP) 3525].

(xxv) $[\text{Pt}2\{\text{OP(O)(Ph)O}\}\{\text{AsPh}_3\}_2] (203)$

The complex cis-$[\text{PtCl}_2\{\text{AsPh}_3\}_2] (0.30g, 0.34 mmol) with phenylarsonic acid (0.07g, 0.35 mmol) gave pale yellow microcrystals of (203) (0.33g, 96%). N.m.r. spectra: $^1$H (90 MHz), $\delta$ 8.2-6.9 p.p.m. (m, 35H, Ph).

Reactions of Platinaphosphonato complexes

(i) Decomposition of complex (18I).H$_2$O

A solution of $[\text{Pt}\{\text{OP(O)(Ph)O}\}\{\text{PBzPh}_2\}_2] (18I).\text{H}_2\text{O} (0.10g, 0.11 mmol) in dichloro-
methane (30 cm³) was stirred in air for 48h at room temperature. Evaporation to dryness under reduced pressure afforded a pale brown oil, which was shown to contain several products by $^{31}$P-$^1$H n.m.r. spectroscopy. The oil was dissolved in dichloromethane (ca. 5 cm³) and light petroleum was added until the cloud-point was reached. On standing, colourless crystals were formed, which were filtered, washed with light petroleum and dried in vacuo. An X-ray crystal structure determination identified the product as $\text{cis-}[\text{Pt} \{\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\} _2]$ (204, R = Ph) (ca. 0.015g, 17%).

(ii) Reaction with carbon monoxide

(a) A slow stream of carbon monoxide was bubbled through either a dichloromethane or THF (ca. 40 cm³) solution of $[\text{Pt}\{\text{OP(0)(Ph)}_2\}(\text{PPh}_3)_2]$ (179) (0.10g, 0.11 mmol) for 5h at room temperature. Evaporation to dryness under reduced pressure afforded an orange oil, $^{31}$P-$^1$H n.m.r. spectrum, $\delta$ 23.15 p.p.m. [s, PPh₃, $^1$J(PtP) 2798, 2837!], and 15.07 p.p.m. [s, PhP(O)(OH)₂]; $\nu$C=O at 1820 and 2040 cm⁻¹. Dissolution of the oil in dichloromethane (ca. 5 cm³) followed by addition of light petroleum afforded, on standing, a pale brown powder, shown to contain both complex (179) and phenylphosphonic acid (175) along with the suspected cluster compound (205). The following reactions of the unknown complex (205) were all carried out directly on the orange oil obtained by the treatment of carbon monoxide on complex (179) as described above.

(b) Reaction in dichloromethane in air

The orange oil was dissolved in dichloromethane (ca. 30 cm³) and stirred in air for 48h. Removal of the solvent under reduced pressure afforded a pale brown oil, shown to contain only $[\text{Pt}\{\text{OP(O)(Ph)}_2\}(\text{PPh}_3)_2]$ (179) by $^{31}$P-$^1$H n.m.r. spectroscopy.

(c) Reaction with diphenylacetylene

A solution of the oil in dichloromethane (30 cm³) with diphenylacetylene (0.10g, 0.56 mmol) was stirred for 12h at room temperature. Evaporation to dryness under reduced pressure afforded a pale brown oil, which was shown to contain $[\text{Pt} \{\text{PhC≡CPh}\}(\text{PPh}_3)_2]$¹⁷⁹ as the major component by $^{31}$P-$^1$H n.m.r. spectroscopy.
(d) Reaction with dimethyl acetylenedicarboxylate

A solution of the oil in dichloromethane with dmad (0.08g, 0.56 mmol) was stirred for 5h at room temperature. Work-up as in (c) afforded a pale orange oil, which was shown to contain [Pt(MeO2CC≡CCO2Me)(PPh3)2]152 as the major component by 31P-{1H} n.m.r. spectroscopy.

(e) Reaction with HCl

A slow stream of gaseous hydrogen chloride was passed through a solution of the oil in dichloromethane for 5 min. Evaporation to dryness under reduced pressure afforded a white solid which was identified as a mixture of cis-[PtCl2(PPh3)2] and phenylphosphonic acid (175) by 31P-{1H} n.m.r. spectroscopy.


A slow stream of carbon monoxide was bubbled through a dichloromethane solution of (195).H2O (0.10g, 0.11 mmol) for 5h at room temperature. Evaporation to dryness under reduced pressure afforded an orange oil, the metal component of which was shown to be identical to that obtained in (a), as shown by 31P-{1H} n.m.r. spectroscopy.

(g) Reaction of [Pt(OP(O)(OPh)O)(PMePh2)2] (180) with carbon monoxide

A slow stream of carbon monoxide was bubbled through a dichloromethane solution of (180) (0.10g, 0.13 mmol) for 5h at room temperature. Evaporation to dryness under reduced pressure afforded an orange oil; 31P-{1H} n.m.r. spectrum, δ 5.18 p.p.m. [s, PmPMe2, 1J(PtP) 2644, 2684!], and 15.40 p.p.m. [s, PhP(O)(OH)2]. As in (a), attempts to isolate a solid product resulted in the formation of mixtures as shown by 31P-{1H} n.m.r. spectroscopy.

Reaction of [Pt(OP(O)(OPh)O)(PPh3)2] (179) with ammonia

Complex (179) (0.10g, 0.11 mmol) was added to liquid ammonia (ca. 20 cm³) at -44°C and the mixture was stirred at this temperature for 1h. Evaporation of the ammonia at room temperature afforded a white solid residue, 31P-{1H} n.m.r. spectrum, δ 10.43 p.p.m. [s,
Attempts to recrystallise this solid invariably resulted in the reformation of the starting complex (179), as shown by $^{31}$P-$^1$H n.m.r. spectroscopy.

(iii) Reaction with tin(II) chloride

(a) A solution of $\left[\text{Pt}\left\{\text{OP}(\text{O})(\text{Ph})\text{O}\right]\right]_2(\text{PPh}_3)_2$ (179) (0.10g, 0.11 mmol) in dichloromethane (20 cm$^3$) with tin(II) chloride (0.06g, 0.32 mmol) was stirred for 3h at room temperature. Evaporation to dryness under reduced pressure afforded a pale yellow powder which was shown to contain several products by $^{31}$P-$^1$H n.m.r. spectroscopy. $^{31}$P-$^1$H n.m.r. spectrum of main component, $\delta$ 23.22 [d, PPh$_3$, $^3$J(PtP) 2485, $^2$J(PP) 20], and 12.59 p.p.m. [t, PPh$_3$, $^1$J(PtP) 3645, $^2$J(PP) 20].

(b) Reaction with SnCl$_2$ and triphenylphosphine

A solution of $\left[\text{Pt}\left\{\text{OP}(\text{O})(\text{Ph})\text{O}\right]\right]_2(\text{PPh}_3)_2$ (179) (0.10g, 0.11 mmol) in dichloromethane (20 cm$^3$) with tin(II) chloride (0.06g, 0.32 mmol) and triphenylphosphine (0.03g, 0.11 mmol) was stirred for 3h at room temperature. Evaporation to dryness under reduced pressure afforded a pale yellow powder which was shown to contain the major component from (a) and phenylphosphonic acid (175) as the only phosphorus containing species by $^{31}$P-$^1$H n.m.r. spectroscopy.

(c) Reaction of cis-[PtCl$_2$(PPh$_3$)$_2$] with SnCl$_2$ and triphenylphosphine

A solution of cis-[PtCl$_2$(PPh$_3$)$_2$] (0.10g, 0.13 mmol) in dichloromethane (30 cm$^3$) with tin(II) chloride (0.07g, 0.37 mmol) and triphenylphosphine (0.035g, 0.13 mmol) was stirred for 3h at room temperature. Evaporation to dryness under reduced pressure afforded a pale yellow powder, shown to contain the major component from (a) as the only phosphorus containing product by $^{31}$P-$^1$H n.m.r. spectroscopy. The powder was dissolved in dichloromethane (15 cm$^3$), the solution was filtered, and the addition of light petroleum afforded pale yellow microcrystals (0.14g, 87%), assigned as [PtCl(SnCl$_3$)(PPh$_3$)$_3$] (206).

(d) Hydroformylation using $\left[\text{Pt}\left\{\text{OP}(\text{O})(\text{Ph})\text{O}\right\}\text{(dppb)}\right](184)/\text{SnCl}_2$

The hydroformylation was carried out in a 100 cm$^3$, glass-lined Roth autoclave, fitted
with a thermostated heating jacket and pressure head connected to a cylinder of synthesis
gas (CO:H$_2$, 1:1). The complex (184) (0.05g, 0.06 mmol) and tin(II) chloride (0.04g, 0.21
mmol) were dissolved in toluene (10 cm$^3$). The autoclave was purged with nitrogen and the
catalyst solution and styrene (15 cm$^3$, 131 mmol) were then added. The autoclave was then
flushed twice with synthesis gas (50 atm) and then charged with synthesis gas (100 atm)
and brought to a constant 50°C for 24h. After cooling, the pressure was released, and the
reaction mixture was distilled to separate the catalyst. The percentage conversion and the
ratio of branched to chain products were determined by integration using $^1$H (90 MHz)
n.m.r. spectroscopy. Percentage conversion of styrene to either the chain or the branched
product was ca. 70%. The ratio of branched to chain products was ca. 3:1.
TABLE 9
M.p.'s, analytical<sup>a</sup> and selected i.r.<sup>b</sup> data for the platinaphosphonato complexes (179)-(191).H<sub>2</sub>O.

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Analysis (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>v&lt;sub&gt;P=O&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(179)</td>
<td>143</td>
<td>57.7 (57.6)</td>
<td>4.4 (4.0)</td>
<td>1220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(180)</td>
<td>&gt;220</td>
<td>51.0 (51.1)</td>
<td>4.1 (4.1)</td>
<td>1225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(181).H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>132</td>
<td>51.0 (51.1)</td>
<td>4.1 (4.1)</td>
<td>1220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(182).H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>178</td>
<td>50.2 (50.1)</td>
<td>4.0 (4.0)</td>
<td>1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(183).CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>137</td>
<td>48.1 (48.1)</td>
<td>3.8 (3.9)</td>
<td>1210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(184)</td>
<td>183</td>
<td>52.2 (52.5)</td>
<td>4.1 (4.2)</td>
<td>1220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(185).H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>&gt;220</td>
<td>51.6 (51.4)</td>
<td>3.6 (3.8)</td>
<td>1235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(186)</td>
<td>175</td>
<td>51.2 (51.2)</td>
<td>5.4 (5.3)</td>
<td>1210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(187)</td>
<td>216</td>
<td>48.2 (48.5)</td>
<td>5.1 (5.0)</td>
<td>1215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(188)</td>
<td>208</td>
<td>46.5 (46.5)</td>
<td>4.7 (4.5)</td>
<td>1225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(189).H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>&gt;220</td>
<td>53.7 (53.4)</td>
<td>4.4 (4.2)</td>
<td>1220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(190).CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&gt;220</td>
<td>43.0 (43.4)</td>
<td>3.5 (3.7)</td>
<td>1220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(191).H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>&gt;220</td>
<td>46.2 (46.0)</td>
<td>3.9 (4.1)</td>
<td>1190</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated values given in parentheses;
<sup>b</sup> Recorded as KBr discs;
<sup>c</sup> All bands s.
### TABLE 10
M.p.'s, analytical* and selected i.r. data for the platinaphosphonato, phosphato and arsonato complexes (192).CH₂Cl₂ - (203).

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Analysis (%)</th>
<th>ν₁₅₄₃ or ν₁₅₄₃* (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(192).CH₂Cl₂</td>
<td>&gt;220</td>
<td>44.4 (44.2)</td>
<td>3.7 (3.9)</td>
</tr>
<tr>
<td>(193)</td>
<td>&gt;220</td>
<td>48.1 (48.7)</td>
<td>4.3 (4.3)</td>
</tr>
<tr>
<td>(194).H₂O</td>
<td>173</td>
<td>48.3 (48.3)</td>
<td>3.9 (3.8)</td>
</tr>
<tr>
<td>(195).H₂O</td>
<td>&gt;220</td>
<td>54.8 (55.4)</td>
<td>3.9 (4.1)</td>
</tr>
<tr>
<td>(196).H₂O</td>
<td>183</td>
<td>49.2 (48.9)</td>
<td>4.1 (4.2)</td>
</tr>
<tr>
<td>(197).CH₂Cl₂</td>
<td>&gt;220</td>
<td>47.1 (47.2)</td>
<td>3.8 (3.8)</td>
</tr>
<tr>
<td>(198).H₂O</td>
<td>&gt;220</td>
<td>50.6 (50.3)</td>
<td>4.2 (4.3)</td>
</tr>
<tr>
<td>(199).H₂O</td>
<td>&gt;220</td>
<td>50.7 (50.6)</td>
<td>3.7 (3.7)</td>
</tr>
<tr>
<td>(200)</td>
<td>177</td>
<td>54.9 (54.9)</td>
<td>4.2 (3.8)</td>
</tr>
<tr>
<td>(201).CH₂Cl₂</td>
<td>174</td>
<td>45.9 (45.1)</td>
<td>3.8 (3.5)</td>
</tr>
<tr>
<td>(202).H₂O</td>
<td>151</td>
<td>48.9 (48.6)</td>
<td>4.2 (4.2)</td>
</tr>
<tr>
<td>(203)</td>
<td>200</td>
<td>50.9 (50.1)</td>
<td>3.8 (3.5)</td>
</tr>
</tbody>
</table>

* Calculated values given in parentheses;

b Recorded as KBr discs;

c All bands s.
CHAPTER 5

The Synthesis and Reactivity of [Amino Acid (2-)-N,O]platinum(II) Complexes
5.1 INTRODUCTION

The formation of four-membered metallacycles containing metal bonds to carbon, nitrogen, oxygen or sulphur has been described in Chapters 2, 3 and 4. The use of silver(I) oxide in these preparations has shown the versatility of this reagent in the high yield production of metal-containing ring compounds. These results led to an investigation into the possibility of forming five-membered rings by treating suitable substrates with cis-platinum dichloride complexes in the presence of silver(I) oxide. This chapter describes the use of amino acid derivatives (207) to produce the corresponding complexes (208), which contain metal-nitrogen and metal-oxygen bonds.

\[ C\text{[H]}_2\text{[O]} \quad L = \text{donor ligand} \]

N-acetyl derivatives of the amino acids glycine (207, \( R^1 = H, R^2 = \text{COMe} \)), dl-alanine (207, \( R^1 = \text{Me}, R^2 = \text{COMe} \)), dl-methionine (207, \( R^1 = \text{CH}_2\text{CH}_2\text{SMe}, R^2 = \text{COMe} \)) and l-phenylalanine (207, \( R^1 = \text{CH}_2\text{Ph}, R^2 = \text{COMe} \)) were employed in these reactions, along with the N-formyl and N-trifluoroacetyl derivatives of glycine (207, \( R^1 = H, R^2 = \text{CHO} \) or \( \text{COF}_3 \)). The use of l-proline to produce a bicyclic system was also studied.

5.2 SYNTHESIS OF [AMINO ACID(2-)-N,O]BIS(LIGAND)PLATINUM(II) COMPLEXES

Treatment of the complexes cis-[PtCl_2L_2] (\( L = \text{PPh}_3, \text{PMePh}_2, \text{PBzPh}_2; L_2 = \text{dpmm, dppe, dppp, dppb or cod} \)) {prepared in situ by the reaction of [PtCl_2(cod)] with either two mole equivalents of \( L \) or one equivalent of \( L_2 \)} with one equivalent of N-acetylglycine and an excess of silver(I) oxide in refluxing dichloromethane afforded, in high yield, the complexes (209)-(216), Scheme 43.
Similarly, complexes (217)-(223) may be prepared using N-acetyl-d/-alanine, complexes (224)-(230) using N-acetyl-d/-methionine and complexes (231)-(238) using N-acetyl-l-phenylalanine instead of N-acetylglycine.

Also, complexes (239) or (240) may be synthesised using N-formylglycine or N-trifluoroacetylglucose as the source of the chelating fragment.
Complexes (241)-(243) may also be prepared in a similar manner using l-proline with silver(I) oxide in refluxing dichloromethane in the presence of cis-[PtCl$_2$L$_2$] (L = PPh$_3$; L$_2$ = dppp or dppb).

![Chemical structure](image)

All the complexes were isolated as air stable, white to pale yellow microcrystalline solids with the exception of (241) which was greeny-yellow in colour.

Attempts to obtain palladium analogues using [PdCl$_2$(dppp)] with silver(I) oxide, resulted in the formation of several unidentified species, as shown by $^{31}$P-$^1$H n.m.r. spectroscopy. Also, attempts to obtain a platinum analogue using unacetylated $dl$-methionine with silver(I) oxide in the presence of cis-[PtCl$_2$(PPh$_3$)$_2$], resulted in the formation of numerous products, as shown by $^{31}$P-$^1$H n.m.r. spectroscopy.

### 5.3 STRUCTURAL PROPERTIES OF [N-ACETYLGLYCINATO(2-)-N,O]BIS-(LIGAND)PLATINUM(II) COMPLEXES

A single crystal X-ray diffraction study was carried out on the N-acetylglycinato complex (213) in order to investigate its molecular geometry and to compare the structure with other platinum(II)-glycinate compounds in which the amino acid acts as a chelating ligand. Important bond lengths and angles are presented in Table 11, whilst the molecular structure is illustrated in Figure 14 along with the crystallographic numbering system. Important structural data for related compounds, together with that for (213) and free glycine are presented in Table 12.

The structure consists of a chelating N-acetylglycinato(2-) ligand coordinated to a Pt(dppe) fragment so as to give the platinum atom a distorted square planar environment. The platinum atom lies in the least squares plane defined by itself and its four coordinating neighbours, the twist angle between planes P(1)–Pt–P(2) and N(1)–Pt–O(1) being 5.0°.
TABLE 11*

Selected bond lengths and angles for [Pt{N(COMe)CH₂C(O)O}(dppe)] (213)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (A)</th>
<th>Angle</th>
<th>()</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – P(1)</td>
<td>2.245 (4)</td>
<td>P(1) – Pt – P(2)</td>
<td>86.3 (1)</td>
</tr>
<tr>
<td>Pt – P(2)</td>
<td>2.240 (4)</td>
<td>P(1) – Pt – O(1)</td>
<td>94.4 (3)</td>
</tr>
<tr>
<td>Pt – N(1)</td>
<td>2.060 (11)</td>
<td>P(2) – Pt – N(1)</td>
<td>100.6 (4)</td>
</tr>
<tr>
<td>Pt – O(1)</td>
<td>2.097 (10)</td>
<td>O(1) – Pt – N(1)</td>
<td>78.8 (5)</td>
</tr>
<tr>
<td>N(1) – C(1)</td>
<td>1.433 (18)</td>
<td>Pt – O(1) – C(2)</td>
<td>117.8 (11)</td>
</tr>
<tr>
<td>C(1) – C(2)</td>
<td>1.485 (22)</td>
<td>O(1) – C(2) – C(1)</td>
<td>116.2 (15)</td>
</tr>
<tr>
<td>C(2) – O(1)</td>
<td>1.232 (19)</td>
<td>C(2) – C(1) – N(1)</td>
<td>114.6 (13)</td>
</tr>
<tr>
<td>C(2) – O(2)</td>
<td>1.245 (19)</td>
<td>Pt – N(1) – C(1)</td>
<td>112.1 (9)</td>
</tr>
<tr>
<td>N(1) – C(3)</td>
<td>1.258 (19)</td>
<td>C(1) – C(2) – O(2)</td>
<td>118.7 (17)</td>
</tr>
<tr>
<td>C(3) – O(3)</td>
<td>1.278 (16)</td>
<td>O(1) – C(2) – O(2)</td>
<td>125.0 (19)</td>
</tr>
<tr>
<td>C(3) – C(4)</td>
<td>1.538 (22)</td>
<td>Pt – N(1) – C(3)</td>
<td>127.8 (12)</td>
</tr>
<tr>
<td>P(1) – C(5)</td>
<td>1.811 (13)</td>
<td>C(1) – N(1) – C(3)</td>
<td>120.0 (14)</td>
</tr>
<tr>
<td>P(2) – C(6)</td>
<td>1.847 (14)</td>
<td>N(1) – C(3) – O(3)</td>
<td>122.4 (18)</td>
</tr>
<tr>
<td>C(5) – C(6)</td>
<td>1.533 (19)</td>
<td>C(4) – C(3) – O(3)</td>
<td>114.5 (16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N(1) – C(3) – C(4)</td>
<td>123.1 (15)</td>
</tr>
</tbody>
</table>

Pt – N(1) – C(1) – H(1A) Torsion 127.59
Pt – N(1) – C(1) – H(1B) Torsion -114.05
Pt – N(1) – C(3) – O(3) Torsion 4.07

* See Figure 14 for crystallographic numbering system.
Figure 14
Molecular structure of [Pt{N(CO)Me}CH₂C(O)O(dppe)] (213).
<table>
<thead>
<tr>
<th>Bond or Angle$^a$</th>
<th>Glycine</th>
<th>trans-Pt(Gly)$_2$ (55)</th>
<th>trans-Pt(Gly)$_2$ (57)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bond Length (Å) or Angle (°)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.060 (11)</td>
<td>2.037 (4)</td>
</tr>
<tr>
<td>Pt – N(1)</td>
<td></td>
<td>2.067 (10)</td>
<td>2.002 (4)</td>
</tr>
<tr>
<td>Pt – O(1)</td>
<td></td>
<td>1.474 (5)</td>
<td>1.496 (7)</td>
</tr>
<tr>
<td>N(1) – C(1)</td>
<td></td>
<td>1.523 (5)</td>
<td>1.510 (8)</td>
</tr>
<tr>
<td>C(1) – C(2)</td>
<td></td>
<td>1.255 (5)</td>
<td>1.232 (19)</td>
</tr>
<tr>
<td>C(2) – O(1)</td>
<td></td>
<td>1.252 (5)</td>
<td>1.245 (19)</td>
</tr>
<tr>
<td>C(2) – O(2)</td>
<td></td>
<td>78.5 (5)</td>
<td>80.6</td>
</tr>
<tr>
<td>N(1) – Pt – O(1)</td>
<td></td>
<td>111.8 (5)</td>
<td>109.7</td>
</tr>
<tr>
<td>N(1) – C(1) – C(2)</td>
<td>116.2 (15)</td>
<td>116.7 (17)</td>
<td></td>
</tr>
<tr>
<td>N(1) – C(1) – C(2)</td>
<td>117.4 (3)</td>
<td>120.7 (5)</td>
<td></td>
</tr>
<tr>
<td>C(1) – C(2) – C(2)</td>
<td>125.3 (3)</td>
<td>122.5 (38)</td>
<td></td>
</tr>
<tr>
<td>C(1) – C(2) – O(2)</td>
<td>125.0 (19)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* See Figure 14 for numbering system.
The Pt-N(1)-C(1)-C(2)-O(1) ring is only slightly distorted from planarity, C(1) being the most deviated atom from the least squares plane at a distance of -0.041 Å away. This non-planarity makes the hydrogen atoms H(1A) and H(1B) inequivalent in the solid state [Torsion angles Pt-N(1)-C(1)-H(1A) = 127.6°; Pt-N(1)-C(1)-H(1B) = -114.1°], however their equivalence in solution is discussed in Section 5.4.1. The acetyl group is attached to N(1) such that the carbonyl oxygen O(3) sits closer to the phosphine ligand than does the methyl group, presumably for steric reasons. The atoms C(3), O(3) and C(4) lie close to the Pt-N(1)-C(1)-C(2)-O(1) plane [Torsion angle O(3)-C(3)-N(1)-Pt = 4.1°].

The Pt-N(1) and Pt-O(1) distances [2.060(11) and 2.097(10) Å respectively] compare well to those of other glycinato complexes of platinum(II), even though in the latter cases, the Pt-N bond is coordinate. Within the N-acetylglycinate ligand, the N(1)-C(1) and C(1)-C(2) distances are slightly shorter than the corresponding distances in the other glycinate complexes, and are also shorter than those of free glycine itself. However, a significant difference arises in the comparison of the carboxylate bond distances. The structure of (213) shows a C(2)-O(2) double bond distance of 1.245(19) Å and a C(2)-O(1) single bond distance of 1.232(19) Å; a reversal of the expected geometry. The carboxylate groups of other glycinate chelates of platinum do not show this behaviour, the C(2)-O(2) double bond distance being significantly less than the value for the C(2)-O(1) single bond. A similar anomaly also occurs in the N-acetyl section of the ligand, the C(3)-O(3) ‘carbonyl’ distance of 1.278(16) Å being 0.020 Å longer than the ‘singly’ bonded C(3)-N(1) of 1.258(19) Å. These bond lengths indicate that the C(2)-O(2) and C(3)-O(3) carbonyl groups are highly delocalised and that the contribution of the resonance hybrid (244) to the structure of (213) is of consequence.

\[\text{(244)}\]
Further electron delocalisation through the platinum atom as in (245), may then be envisaged, although there is no evidence to support this structure.

\[
\text{(dppe)Pt}
\]

The bond angles in the glycinate chelate ring agree well with those of previously reported structures, the largest difference occurring with the N(1)–C(1)–C(2) angle, which at 114.6(13)°, is over 3° greater than the previous largest value.\(^{181-183}\) The chelate angle at the platinum atom is 78.8(5)°, smaller than those of prior investigations,\(^{181-183}\) which is probably due to the presence of a relatively large chelating phosphine ligand, opposing the glycinate fragment. The angles around N(1) seem to support the structure (244), which predicts trigonal planar geometry rather than the pyramidal environment expected for the structure shown in Scheme 43. The internal Pt–N(1)–C(1) angle is 112.1(9)°, however this is restricted in order to accommodate the 5-membered ring. The external angles at N(1) are 120.0(14)° and 127.8(12)° respectively, much closer to the value of 120.0° expected for an sp\(^2\) hybridised N(1) than 109.5° for an sp\(^3\) pyramidal atom. The angles around N(1) add to 359.9°, again indicating a planar hybridisation.

5.4 NMR SPECTRA OF [AMINO ACID(2-)-N,O]BIS(LIGAND)PLATINUM(II) COMPLEXES

5.4.1 \(^1\)H N.m.r. Spectra

The room temperature \(^1\)H n.m.r. spectra for all the new complexes are consistent with the structures shown in Section 5.2. The spectra of complexes which contain an N-acetyl function all show a sharp singlet in the region \(\delta 1.09-2.12\) p.p.m. which is assigned to the methyl protons of this group.

The \(^1\)H n.m.r. spectra of complexes (209)-(216), which contain an N-acetylglucose
residue, all contain a signal in the region $\delta$ 4.15-4.53 p.p.m. which can be assigned to the methylene group of the ring. The two protons of this group are equivalent due to rapid inversion of the ring and in the spectrum of complex (216), in which there are no phosphines present, they appear as a singlet with platinum-195 satellites $[^2]J(PtH)$ 21 Hz]. When phosphines are present in the complexes, the signal appears as a doublet with platinum-195 satellites due to a four bond phosphorus-31 coupling of magnitude 2-3 Hz. The three bond platinum-195 coupling to these protons is between 18 and 25 Hz.

The apparent planarity of the ring in solution is again indicated in the spectrum of complex (216) which shows that there are only two types of olefinic proton in the cod ligand, one type on the double bond coordinated opposite oxygen and the other on the one coordinated opposite nitrogen. Also, in complex (212), the dppe methylene protons are equivalent and are observed as a doublet of doublets due to phosphorus-31 coupling.

The $^1$H n.m.r. spectra of complexes (217)-(223) which contain an N-acetyl-dl-alaninato fragment all show a complex signal in the region $\delta$ 4.24-4.71 p.p.m. which contains platinum-195, phosphorus-31 and proton coupling assignable to the methine proton of the five-membered ring. The spectrum of the dppe derivative (221) is sufficiently resolved to show a doublet of doublet of quartets with two sets of phosphorus-31 coupling and a three bond proton coupling to the adjacent methyl group. This methyl group itself appears as a doublet in the range $\delta$ 1.47-1.82 p.p.m. The dppe methylene protons in complex (220) are not equivalent, one being cis to the $\alpha$-methyl group and the other trans. Thus two separate resonances are observed as doublets of doublets of doublets with coupling to each other and to both phosphorus nuclei, Figure 15.

The $^1$H n.m.r. spectra of complexes (224)-(230) all contain a singlet between $\delta$ 2.03 and 2.20 p.p.m. due to the methyl group attached to sulphur. The ring proton is observed as a multiplet in the region $\delta$ 4.27-4.68 p.p.m. The two methylene groups of the $\alpha$-carbon side chain generally appear as multiplets or are masked by signals due to the phosphine ligand. However, for complexes (225) and (227), four separate resonances are observed and in the case of the latter complex, both the lower field signals may be resolved into doublets of
Figure 15
Room temperature $^1$H n.m.r. spectrum at 300MHz for the methine (a), and methylene (b) protons of the complex $[\text{Pt}((\text{COMe})\text{CH}(\text{CH}_3)\text{C}(\text{O})\overline{\text{O}})(\text{dppm})]$ (220).
doublets of doublets, these signals being due to the protons of the methylene group attached directly to the sulphur atom (coupling to each other and to the adjacent inequivalent methylene protons). The dppm methylene protons in complex (227) again show different chemical shifts, due to being either cis or trans to the CH₂CH₂SCH₃ side chain, and are observed as doublets of doublets of doublets.

In complexes (231)-(238) the methine ring proton is again observed as a multiplet, apart from in complex (238) where the absence of phosphorus-31 coupling simplifies the signal to a doublet of doublets, with a three-bond platinum-195 coupling constant of 38 Hz. The four olefinic protons of the cod ligand of this complex appear at four different chemical shifts since they are either opposite oxygen or nitrogen and either cis or trans to the benzyl side chain. The methylene protons of this side chain are diastereotopic and therefore occur at different chemical shifts. They couple to each other and to the ring proton and are each observed as a doublet of doublets.

The proton n.m.r. signals for complexes (241)-(243) are not well resolved and are therefore difficult to assign. The bridgehead proton appears as a broad signal between δ 4.50 and 4.91 p.p.m. but it is difficult to extract any other information from the spectra due to the broadness of the signals.

**5.4.2 ¹³C-(¹H) N.m.r. Spectra**

The ¹³C-(¹H) n.m.r. spectra of the new complexes which contain an N-acetyl group show the presence of two non-equivalent carbonyl groups. The signal for the C(2) carbonyl group appears in the range δ 182.35-193.15 p.p.m. and usually shows coupling to either one or both phosphine ligands in the respective complexes, although any platinum-195 coupling is not discernible. The C(3) carbonyl group appears between δ 168.15 and 175.55 p.p.m. and is observed as a singlet, even though its attached methyl group sometimes appears as a doublet, with ^4J(PC) in the range 1-5 Hz.

For complexes (209)-(216) the ring methylene group appears as a singlet between δ 49.90 and 56.26 p.p.m. The spectrum for the cod derivative (216) shows two distinct resonances with platinum-195 satellites for the alkene carbons of the coordinated ligand.
For complexes (217)-(223), the ring methine carbon appears as a singlet in the range δ 58.65-61.99 p.p.m. and its attached methyl group is observed as a singlet to higher field, between δ 21.66 and 23.55 p.p.m.

The $^{13}$C-$^1$H n.m.r. spectra for complexes (224)-(230), which contain an N-acetyl-d/-methionine residue, all show a singlet in the range δ 62.22-65.99 p.p.m. for the methine carbon of the five-membered ring. The S-methyl group is observed as a singlet between δ 15.17 and 15.64 p.p.m. and the methylene groups of the side chain are also observed as singlets, in the range δ 29.22-36.96 p.p.m.

For complexes (231)-(238), the ring methine carbon appears as a singlet as does its adjacent methylene carbon. The chiral nature of the methine carbon is shown in the spectrum of complex (233) where the four methyl groups of the two dimethylphenylphosphine ligands occur as doublets at 4 different chemical shifts. The spectrum of complex (238) shows four singlets for the four olefinic carbons of the cycloocta-1,5-diene ligand and also four singlets for the methylene carbons of the same ligand. In both cases, coupling to platinum-195 was not discernible.

For complexes (241)-(243) the bridgehead carbon atom appears as a singlet in the range δ 63.00-64.11 p.p.m. The other three carbon atoms in the L-proline ring all appear as singlets in the ranges δ 50.26-51.53 p.p.m., δ 29.43-30.16 p.p.m. and δ 24.25-24.88 p.p.m. The carbonyl carbon appears as a weak signal between δ 184.47 and 184.99 p.p.m.

### 5.4.3 $^{31}$P-$^1$H and $^{19}$F-$^1$H N.m.r. Spectra

The $^{31}$P-$^1$H n.m.r. spectra of the new complexes containing phosphine ligands indicate the presence of two non-equivalent phosphorus nuclei in each case. Hence the spectra show second order AB patterns with corresponding platinum-195 satellites, for example for complex (213), resonances at δ 40.14 [d, $^1$J(PtP) 3071, $^2$J(PP) 13 Hz] and δ 26.72 [d, $^1$J(PtP) 3931, $^2$J(PP) 13 Hz] are observed.

Assigning the signals is facilitated by the large difference in the one bond platinum-195, phosphorus-31 coupling constants $^1$J(PtP). Thus, P(2) (Figure 16) which lies trans to oxygen experiences a larger platinum-195 coupling than P(1) which is trans to nitrogen and
hence the signal at $\delta$ 26.72 p.p.m. is assigned to P(2). For the acetylated complexes, the difference between $^1J[PtP(1)]$ and $^1J[PtP(2)]$ is usually greater than 800 Hz, the range of $^1J[PtP(1)]$ being 2608-3184 Hz and that for $^1J[PtP(2)]$ being 3512-4063 Hz. In a similar manner, the assignment of P(1) and P(2) in complexes (241)-(243) can be made, although $^1J[PtP(1)]$ and $^2J[PtP(2)]$ are a lot closer in magnitude, the difference being less than 450 Hz.

The $^{19}F-^{1}H$ n.m.r. spectrum of complex (240) shows a doublet at $\delta$ -67.69 p.p.m. with a five bond phosphorus-31 coupling constant of 2 Hz. Platinum-195 satellites are also observed, the value of $^4J(PtF)$ being 21 Hz.

5.5 IR SPECTRA OF [AMINO ACID(2-)-N,O]BIS(LIGAND)PLATINUM(II) COMPLEXES

The i.r. spectra of all the new compounds are dominated by the carbonyl absorptions, which occur within the range 1570-1680 cm$^{-1}$. With the exception of (240) and (241)-(243), all the compounds show two intense bands in this region, due to the carboxylate and amide stretches. The lower frequency band can be assigned to the amide stretch and lies between 1570 and 1620 cm$^{-1}$, about 60 cm$^{-1}$ lower than the carboxylate band (range 1640-1680 cm$^{-1}$). For compound (240), the two bands overlap due to the increase in frequency of the amide stretch in going from an acetyl to a trifluoroacetyl group. Compounds (241)-(243) show just one band in this region, between 1660 and 1670 cm$^{-1}$ due to the presence of only one carbonyl group.

The carboxylate stretching frequencies agree well with those of compounds (56) and (57) (1639 and 1640 cm$^{-1}$ respectively) in which the mono-anion of glycine is acting as a chelate towards platinum.
5.6 REACTIONS OF [AMINO ACID(2-)-N,O]BIS(LIGAND)PLATINUM(II) COMPLEXES

5.6.1 Ligand Substitution Reactions

The cycloocta-1,5-diene complexes (216) and (238) readily undergo simple ligand displacement reactions with mono or bidentate tertiary phosphines to yield the corresponding phosphine complexes. Thus treatment of (216) with two equivalents of triphenylphosphine or methylidiphenylphosphine in dichloromethane afforded the complexes (209) or (210) respectively, whereas treatment of (216) with one equivalent of dppp yielded complex (214). Complexes (231) and (236) may be obtained from (238) by a similar methodology.

The displacement of a phosphine ligand by an alkyl isocyanide has been proven to be an effective way of obtaining a single geometrical isomer of a metallacyclic complex which contains two different donor ligands. Thus the reaction of the triphenylphosphine complex (231) with t-butyl isocyanide was studied, in an attempt to obtain mono-substituted complexes and to determine the stereochemistry of the product. Treatment of (231) with one mole equivalent of t-butyl isocyanide in dichloromethane afforded complex (246) in good yield.

![Complex (246)](image)

The complex could not be isolated as a solid, but as a pale brown oil, thus making purification difficult. The $^{31}$P-$^{1}$H n.m.r. spectrum of the product shows a single peak with corresponding platinum-195 satellites [$^{1}$J(PtP) 2913 Hz], which indicates that the remaining phosphine is bound trans to nitrogen rather than oxygen. The i.r. spectrum shows two carbonyl stretches and a band at 2220 cm$^{-1}$, indicative of a terminal isocyanide ligand. The $^{1}$H n.m.r. spectrum shows the presence of one t-butyl group per phosphine
ligand. Therefore, the substitution of a triphenylphosphine ligand in complex (231) by t-butyl isocyanide is stereospecific, the isocyanide ligand coordinating trans to the oxygen atom of the chelating fragment, as shown for complex (246).

5.6.2 Reactions with Ethanol

At room temperature, the phosphine complexes (209) and (224) do not react with ethanol, the complexes being quantitatively retrievable after being stirred for 24 hours in this solvent. However, if the solution is warmed to over 50°C, decomposition of the complexes occurs, with the formation of numerous products as indicated by $^{31}$P-$^1$H n.m.r. spectroscopy.

The formation of the acetylene complex (247) from the carbonato complex (157) by refluxing in ethanol in the presence of diphenylacetylene, Scheme 44, led to an investigation of the reactions of the N-acetyl amino acid complexes in ethanol with donor ligands.

\[
\text{(Ph}_3\text{P)}_2\text{Pt} + \text{PhC}≡\text{CPh} \xrightarrow{\text{EtOH (reflux)}} \text{(Ph}_3\text{P)}_2\text{Pt} \text{ C} \text{ C} \text{ C}
\]

Scheme 44

Thus, the reaction of diphenylacetylene with either (209) or (231) in ethanol at 60°C led to the formation of complex (247) in good yield. A similar reaction using excess triphenylphosphine instead of an acetylene, led to the precipitation of a bright yellow solid, which was tentatively assigned as tetrakis(triphenylphosphine)platinum(0) based on the formation of $\text{trans-}[\text{PtHCl(PPh}_3)_2]$ on its reaction with HCl and complex (248) on its reaction with dimethyl acetylenedicarboxylate.

\[
\text{(Ph}_3\text{P)}_2\text{Pt} \xrightarrow{\text{CO}_2\text{Me}} \text{ C} \text{ C} \text{ C} \text{ C} \text{ CO}_2\text{Me}
\]

(248)
5.6.3 Reactions with Sulphur Dioxide

The reaction of complexes (209) or (218) with sulphur dioxide in ethanol, led to the formation of complexes (249, $L = \text{PPh}_3$ or $\text{PMePh}_2$) in good yield. Comparison of $^{31}\text{P}-^{1}\text{H}$ n.m.r. and i.r. spectra with those of authentic samples, made by the method of Barlex et al.,\textsuperscript{187} led to the identification of the products.

$$[\text{Pt(SO}_3\text{Et})_2L_2]$$

(249)

The $^{31}\text{P}-^{1}\text{H}$ n.m.r. spectrum of complex (249, $L = \text{PPh}_3$) shows a singlet with $^{1}J(\text{PtP})$ 2988 Hz. This coupling constant strongly suggests that the complex adopts a cis stereochemistry, as its value is far greater than that expected for a trans complex. However, an X-ray crystal structure determination on the bis(methylsulphonate)bis(triphenylphosphine)-platinum(II) complex assigned its stereochemistry at trans,\textsuperscript{188} though it should be noted that its mode of preparation differed significantly from that used by Barlex et al. and in the present work. Nevertheless, it should be noted that a crystal structure determination may not be representative of the bulk sample, and that in some cases, trans isomers crystallise preferentially to their cis counterparts, owing to closer packing in the crystal.\textsuperscript{189}

Mechanisms suggested for the formation of bis(alkylsulphonate) ligands include the insertion of sulphur dioxide into the metal-oxygen bond of an intermediate metal-alkoxy species, or the cleavage of a metal-ligand bond by alkylsulphurous acid, produced by the dissolving of sulphur dioxide in an alcohol, Scheme 45.\textsuperscript{188}

\begin{align*}
\text{cis-[MX}_2\text{L}_2] & \xrightarrow{2\text{ROH} \text{-2HX}} \text{cis-[M(OR)]_2L}_2 \\
\text{cis-[MX}_2\text{L}_2] & \xrightarrow{2\text{SO}_2} \text{cis-[M(SO}_3\text{R)]_2L}_2 \\
2\text{SO}_2 + 2\text{ROH} & \rightarrow 2\text{HSO}_3\text{R}
\end{align*}

Scheme 45
Once formed, complexes of the type (250) may then isomerise, as for the bis(methyl-sulphonate) complex on crystallisation, although a solution of (249, L = PPh₃) on standing for 24h showed no change, as shown by ³¹P-¹H n.m.r. spectroscopy.

Reaction of the triphenylphosphine complex (231) with sulphur dioxide in dichloromethane, led to the formation of a product whose ³¹P-¹H n.m.r. spectrum showed a singlet at δ 6.33 p.p.m. with ¹J(PtP) = 3870 Hz. Attempts to identify this product were unsuccessful. The methyldiphenylphosphine complex (218) reacted with sulphur dioxide in dichloromethane to give a number of products. The main component in the ³¹P-¹H n.m.r. spectrum of the reaction mixture was an AB pattern with platinum-195 satellites, [¹J(PtP) = 2317 and 4182 Hz], however attempts to isolate this product were not successful.

5.6.4 Reactions with Carbon Monoxide

When carbon monoxide was bubbled through a dichloromethane solution of the phosphine complexes (209) or (224), no reaction occurred as observed by ³¹P-¹H n.m.r. spectroscopy. However, when the triphenylphosphine complex (209) was dissolved in ethanol and carbon monoxide bubbled through the solution for five hours, complete conversion to a new product was seen to have occurred. The ³¹P-¹H n.m.r. spectrum showed a singlet at δ 20.93 p.p.m. with corresponding platinum-195 satellites [¹J(PtP) = 3254 Hz]. When the reaction was repeated with the N-trifluoroacetylglycinato complex (240), ¹⁹F-¹H n.m.r. spectroscopy indicated that the chelate ring had been removed from the platinum, by the appearance of a singlet whose shift corresponded to free N-trifluoroacetylglucose. Due to these observations, and by analogy with the sulphur dioxide reactions (Section 5.6.3), the product of these reactions was tentatively assigned as (257, R = Et).

\[
\text{[Pt(CO₂R)_₂(PPh₃)₂]}
\]

(251)

The methoxycarbonyl derivative (251, R = Me), was previously synthesised by Werner and Beck,¹⁹⁰ who assigned the stereochemistry of their product as trans on the basis of dipole moment measurements, later confirmed by a crystal structure determination.¹⁹¹
\[ ^{31}\text{P}-\{^1\text{H}\} \text{ n.m.r. shift quoted for this product was } \delta 16.4 \text{ p.p.m., but no value for } ^{1}J(\text{PtP}) \text{ was} \]

\[ \text{given.}^{190} \text{ As a change of } R \text{ group in compound (251) from methyl to ethyl would be expected to have only a minimal effect on the } ^{31}\text{P}-\{^1\text{H}\} \text{ n.m.r. spectrum of a particular isomer, the compound obtained from complexes (209) or (240) with carbon monoxide in ethanol is unlikely to be the trans product, and was therefore assigned cis geometry.} \]

A re-investigation into the reaction of cis-[Pt(OAc)\(_2\)(PPh\(_3\))\(_2\)] with carbon monoxide in methanol\(^{187}\) was carried out to see if the complex cis or trans-(251, R = Me) could be isolated from the reaction. Barlex et al. described the reaction and obtained the product trans-[Pt(CO\(_2\)Me)(OAc)(PPh\(_3\))\(_2\)] (252) as a precipitate in approximately 50% yield.\(^{187}\) The reaction was repeated, and complex (252) was obtained as a white precipitate, comparison of i.r. spectral data confirming the product.\(^{187}\) Examination of the filtrate by \(^{31}\text{P}-\{^1\text{H}\} \text{n.m.r. spectroscopy showed that only a single phosphorus-containing compound was remaining, the chemical shift and platinum-195 coupling constant of which were very close to those obtained for cis-(251, R = Et), however the shift was significantly different to that obtained for trans-(251, R = Me) as described by Werner and Beck.}^{190} \text{Thus, the compound was assigned as cis-(251, R = Me). The } ^{31}\text{P}-\{^1\text{H}\} \text{n.m.r. spectrum of the unfiltered reaction mixture showed that the two products were formed in approximately a 1:1 ratio, thus explaining the yield which Barlex et al. obtained. The } ^1\text{H n.m.r. spectrum of cis-[Pt(CO}_2\text{Et})\(_2\)(PPh\(_3\))\(_2\)] \text{shows the presence of two equivalent ethyl groups and the i.r. spectrum shows carbonyl absorptions at 1805 and 1840 cm}^{-1}. \]

5.6.5 Attempted Insertion Reactions

The ability of dmad to insert into the metal-nitrogen bonds of 4-membered metallacycles has been described in the literature\(^{126}\) and in Chapter 3. This led to an investigation of whether the same acetylene would insert into the metal-nitrogen bond of a five-membered metallacycle. Treatment of complex (209) with excess dmad in dichloromethane, both at room temperature or at reflux, resulted in no reaction. The mechanism for insertion suggested in Chapter 3 involved the attack of a nucleophilic nitrogen lone pair on the electron deficient carbon atoms of the acetylene. But as the X-ray crystal structure of
complex (213) indicated, the lone pair on the nitrogen atom is delocalised and has therefore lost some of its nucleophilic character. Hence, no reaction may have been predicted. However, the l-proline complex (241) has no acetyl group attached to its nitrogen atom and so the nucleophilicity of its lone pair has not been diminished, and therefore a reaction would be more probable. Hence, a dichloromethane solution of complex (241) was stirred with excess dmad for 4h. The $^{31}$P-$^1$H n.m.r. spectrum of the reaction mixture showed a reaction had occurred, although a large number of signals indicated numerous products. The reaction was repeated using one mole equivalent of dmad, and on this occasion a major product was seen in the $^{31}$P-$^1$H n.m.r. spectrum, which showed an AB pattern with platinum-195 satellites. Attempts to isolate and identify the product failed with decomposition of the complex.

Complex (241) was also reacted with hexafluorobut-2-yne in the same manner as the four-membered metallacyclic complex (137), to see if any polymer-type substance or insertion product was formed. Hexafluorobut-2-yne was condensed onto a THF solution of complex (241) which was then stirred whilst being allowed to warm to room temperature. The solution was solidified by the formation of a gel-like substance, which when desiccated, yielded a pale brown powder, identical by i.r. to the powder obtained from the reaction of complex (137) with this acetylene. There was no evident reaction when an N-acetyl containing metal complex was treated with hexafluorobut-2-yne in the same manner.

5.7 CONCLUSION

The preparation of new five-membered metallacycles containing platinum-oxygen and platinum-nitrogen bonds may be achieved in high yield via the treatment of cis-[PtCl$_2$L$_2$] ($L$ = donor ligand) with silver(I) oxide and the N-acetyl derivatives of the amino acids glycine, $dl$-alanine, $dl$-methionine and $l$-phenylalanine or the free amino acid $l$-proline in refluxing dichloromethane. A single crystal X-ray diffraction study of the N-acetylglycinato complex (213) shows the presence of a slightly puckered five-membered chelate ring with extensive electron delocalisation in the carboxyl and amide groups. N.m.r. studies on the N-acetyl-
glycinato complexes, indicate that in solution, the ring flips, making the $\alpha$-CH$_2$ protons equivalent.

Simple ligand displacement reactions of these complexes have been investigated, as have the reactions with carbon monoxide and sulphur dioxide in ethanol, which give the cis-bis(ethoxycarbonyl) and cis-bis(ethylsulphonate) complexes respectively. Complex (241), which contains an $l$-proline residue, reacts with hexafluorobut-2-yne to yield a polymeric material.

5.8 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. Tables 13 and 14 show microanalytical results, m.p.'s and i.r. spectroscopic data and Tables 15 and 16 show $^{31}$P-$\{^1$H$\}$ n.m.r. spectroscopic data for compounds (209)-(243). All $^1$H n.m.r. spectra were recorded on a Bruker AM 300 spectrometer operating at 300.13 MHz. The $^{13}$C-$\{^1$H$\}$ n.m.r. data for the aromatic region between 140 and 120 p.p.m. are omitted for clarity. The compounds N-acetylglycine, N-acetyl-$dl$-methionine, N-acetyl-$l$-phenylalanine, $l$-proline, t-butyl isocyanide, diphenylacetylene, dmad (Aldrich), N-acetyl-$dl$-alanine, $dl$-methionine (Sigma), carbon monoxide (BOC), sulphur dioxide (BDH) and hexafluorobut-2-yne (Fluorochem) were used as supplied from commercial sources. Absolute ethanol (BDH) and methanol (BDH) were dried over activated molecular sieves prior to use. The compounds [PtCl$_2$(cod)]$_{123}$ [PdCl$_2$(cod)]$_{125}$ cis-[Pt(OAc)$_2$(PPh$_3$)$_2$]$_{158}$ benzylidiphenylphosphine, $^{177}$ N-formylglycine$^{192}$ and N-trifluoroacetylglycine$^{193}$ were prepared as described in the literature.

Preparation of [Amino Acid(2-)-N,O]bis(ligand)platinum(II) complexes

Two equivalents of tertiary phosphine or one equivalent of chelating tertiary phosphine, followed by one equivalent of respective amino acid derivative, and an excess of silver(I) oxide were added in succession to a stirred solution of [PtCl$_2$(cod)] in dichloromethane (ca. 45 cm$^3$), and the mixture was refluxed for 4h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish
brown oil. Dissolution of the oil in dichloromethane (ca. 5 cm\(^3\)) followed by addition of light petroleum afforded, on standing, a white to pale yellow microcrystalline solid, which was recrystallised from dichloromethane - light petroleum, and dried in vacuo.

(i) \([\text{Pt}\{\text{N(COMe)CH,C(O)O}\}\{(\text{PPh})_2\}] (209)\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (209) (0.21g, 93%). N.m.r. spectra: \(^1\text{H}, \delta 7.73-7.12\) (m, 30H, Ph), 4.25 [dd, 2H, CH\(_2\), \(^4\text{J}(\text{PH}) 1,3, \(^3\text{J}(\text{PtH}) 25\)], 1.39 (s, 3H, CH\(_3\)); \(^1^3\text{C}-\{^1\text{H}\}, \delta 183.88\) [d, CO, \(^3\text{J}(\text{PC}) 2\], 170.84 (s, CO), 55.54 (s, CH\(_2\)) and 20.00 p.p.m. \([d, \text{CH}_3, \text{J}(\text{PC}) 3\].

(ii) \([\text{Pt}\{\text{N(COMe)CH,C(O)O}\}\{(\text{PMePh})_2\}] (210)\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (210) (0.17g, 89%). N.m.r. spectra: \(^1\text{H}, \delta 7.58-7.17\) (m, 20H, Ph), 4.30 \([d, 2\text{H}, \text{CH}_2, \text{J}(\text{PH}) 3, \text{J}(\text{PtH}) 23\]), 2.04 \([d, 3\text{H}, \text{Me}, \text{PMMePh}_2, \text{J}(\text{PH}) + \text{J}(\text{PH}) 11, \text{J}(\text{PtH}) 35\)], 1.76 \([d, 3\text{H}, \text{Me}, \text{PMMePh}_2, \text{J}(\text{PH}) + \text{J}(\text{PH}) 10, \text{J}(\text{PtH}) 24\], 1.60 (s, 3H, CH\(_3\)); \(^1^3\text{C}-\{^1\text{H}\}, \delta 184.10\) [d, CO, \(^3\text{J}(\text{PC}) 3\], 171.35 (s, CO), 55.41 (s, CH\(_2\)), 20.14 \([d, \text{CH}_3, \text{J}(\text{PC}) 4\], 13.69 \([d, \text{Me}, \text{PMMePh}_2, \text{J}(\text{PC}) + \text{J}(\text{PC}) 45\]), and 13.40 p.p.m. \([d, \text{Me}, \text{PMMePh}_2, \text{J}(\text{PC}) + \text{J}(\text{PC}) 39\].

(iii) \([\text{Pt}\{\text{N(COMe)CH,C(O)O}\}\{(\text{PBzPh})_2\}] (211)\)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with benzylidiphenylphosphine (0.16g, 0.58 mmol) and N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (211) (0.22g, 94%). N.m.r. spectra: \(^1\text{H}, \delta 7.72-6.11\) (m, 30H, Ph), 4.53 \([d, 2\text{H}, \text{CH}_2, \text{J}(\text{PH}) 3, \text{J}(\text{PtH}) 25\]), 3.85-3.62 \([m, 4\text{H}, \text{CH}_2, \text{PBzPh}_2\], 1.93 (s, 3H, CH\(_3\)); \(^1^3\text{C}-\{^1\text{H}\}, \delta 183.67\) [d, CO, \(^3\text{J}(\text{PC}) 2\], 171.78 (s, CO), 56.26 (s, CH\(_2\)), 38.09 \([d, \text{CH}_2, \text{PBzPh}_2, \text{J}(\text{PC}) + \text{J}(\text{PC}) 36\], 34.57 \([d, \text{CH}_2, \text{PBzPh}_2, \text{J}(\text{PC}) + \text{J}(\text{PC}) 31\], and 21.18 p.p.m. (s, CH\(_3\)).

(iv) \([\text{Pt}\{\text{N(COMe)CH,C(O)O}\}\{(\text{dppm})\}] (212)\). \text{CH}_2\text{Cl}_2

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and
N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (212).CH₂Cl₂ (0.19g, 90%). N.m.r. spectra: ¹H, δ 7.80-7.28 (m, 20H, Ph), 5.27 (s, 2H, CH₂Cl₂), 4.33 [dd, 2H, CH₂, dppm, ²J(Ph) 9,11], 4.13 [d, 2H, CH₂, ⁴J(Ph) 2, ³J(PtH) 21], 1.86 (s, 3H, CH₃); ¹³C-{¹H}, δ 188.22 [d, CO, ²J(PC) 3], 172.07 (s, CO), 53.39 (s, CH₂), 53.27 (s, CH₂Cl₂), 49.11 [dd, CH₂, dppm, ¹J(PC) 31,32], and 19.56 p.p.m. [d, CH₃, ⁴J(PC) 3].

(v) \([\text{Pt}\{\text{N(COMe)CH₃C(O)O}\}(\text{dppe})\}] (213)

The complex \([\text{PtCl₂(cod)}]\) (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (213) (0.18g, 94%). N.m.r. spectra: ¹H, δ 7.91-7.27 (m, 20H, Ph), 4.22 [d, 2H, CH₂, ⁴J(Ph) 2, ³J(PtH) 18], 2.28-1.92 (m, 4H, CH₂, dppe), 1.70 (s, 3H, CH₃); ¹³C-{¹H}, δ 187.24 (s, CO), 170.13 (s, CO), 54.10 (s, CH₂), 35.15 [dd, CH₂, dppe, ¹J(PC) 40, ³J(PC) 13], 24.40 [dd, CH₂, dppe, ¹J(PC) 36, ³J(PC) 6], and 19.57 p.p.m. [d, CH₃, ⁴J(PC) 5]. X-ray quality crystals of (213) were grown slowly from dichloromethane - light petroleum, in air.

(vi) \([\text{Pt}\{\text{N(COMe)CH₃C(O)O]\}(\text{dppp})\}] (214)

The complex \([\text{PtCl₂(cod)}]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (214) (0.18g, 92%). N.m.r. spectra: ¹H, δ 7.83-7.28 (m, 20H, Ph), 4.15 [d, 2H, CH₂, ⁴J(Ph) 3, ³J(PtH) 23], 2.32 (m, 4H, P-CH₂, dppp), 1.88 (m, 2H, CH₂, dppp), 1.39 (s, 3H, CH₃); ¹³C-{¹H}, δ 184.86 [d, CO, ³J(PC) 3], 170.11 (s, CO), 55.12 (s, CH₂), 27.78 [dd, P-CH₂, dppp, ¹J(PC) 41, ³J(PC) 9], 21.17 [dd, P-CH₂, dppp, ¹J(PC) 38, ³J(PC) 7], 19.57 [d, CH₃, ⁴J(PC) 5], and 18.49 p.p.m. (s, CH₂, dppp).

(vii) \([\text{Pt}\{\text{N(COMe)CH₃C(O)O}\}(\text{dppb})\}] (215)

The complex \([\text{PtCl₂(cod)}]\) (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (215) (0.19g, 95%). N.m.r. spectra: ¹H, δ 7.74-7.20 (m, 20H, Ph), 4.20 [d, 2H, CH₂, ⁴J(Ph) 3, ³J(PtH) 24], 2.87-1.43 (m, 8H, CH₂, dppb), 1.37 (s, 3H, CH₃); ¹³C-{¹H}, δ 184.56 [d, CO, ³J(PC) 3], 170.43 (s, CO), 54.76 (s, CH₂), 25.67 (m, P-CH₂, dppb), 23.72 [d, P-CH₂, dppb, ¹J(PC) 38], 19.57 [d, CH₃, ⁴J(PC) 5].
21.57 (s, 2 x CH₂, dppb), and 19.54 p.p.m. [d, CH₃, ^4J(PC) 5].

(viii) [Pt[N(COMe)CH(CH₃)C(0)O](cod)] (216)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with N-acetylglycine (0.035g, 0.30 mmol) gave white microcrystals of (216) (0.10g, 89%). N.m.r. spectra: ¹H, δ 6.39 [m, 2H, CH, cod, ^2J(PtH) 74], 5.38 [m, 2H, CH, cod, ^2J(PtH) 56], 4.19 [s, 2H, CH₂, ^3J(PtH) 21], 2.74-2.21 (m, 8H, CH₂, cod), 2.00 (s, 3H, CH₃); ^13C-{¹H}, δ 184.55 (s, CO), 175.55 (s, CO), 97.63 [s, CH, cod, ^1J(PtC) 139], 95.67 [s, CH, cod, ^1J(PtC) 161], 55.58 (s, CH₂), 32.20 (s, CH₂, cod), 27.81 (s, CH₂, cod), and 23.02 p.p.m. (s, CH₃).

(ix) [Pt[N(COMe)CH(CH₃)C(0)O](PPh₃)₂] (217)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N-acetyl-d/-alanine (0.04g, 0.29 mmol) gave white microcrystals of (217) (0.22g, 96%). N.m.r. spectra: ^1H, δ 7.87-7.12 (m, 30H, Ph), 4.41 (m, 1H, CH), 1.71 [d, 3H, CHCH₃, ^3J(HH) 7], 1.44 [s, 3H, C(0)CH₃]; ^13C-{¹H}, δ 189.57 (s, CO), 170.50 (s, CO), 61.23 (s, CH), 21.81 (s, CHCH₃), and 19.66 p.p.m. [d, C(O)CH₃, ^4J(PC) 3].

(x) [Pt[N(COMe)CH(CH₃)C(0)O](PMePh₂)₂] (218)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and N-acetyl-d/-alanine (0.04g, 0.30 mmol) gave white microcrystals of (218) (0.18g, 92%). N.m.r. spectra: ^1H, δ 7.76-7.11 (m, 20H, Ph), 4.50 (m, 1H, CH), 1.98 [d, 3H, Me, PMePh₂, ^3J(PH) + ^4J(PH)] 11, ^3J(PtH) 33], 1.77 [d, 3H, Me, PMePh₂, ^3J(PH) + ^4J(PH)] 11, ^3J(PtH) 37], 1.71 [d, 3H, CHCH₃, ^3J(HH) 7], 1.64 [s, 3H, C(O)CH₃]; ^13C-{¹H}, δ 187.25 [d, CO, ^3J(PC) 3], 170.73 (s, CO), 61.36 (s, CH), 22.49 (s, CHCH₃), 19.47 [d, C(O)CH₃, ^4J(PC) 4], and 13.59 p.p.m. [d, 2 x P-CH₃, PMePh₂, ^1J(PC) + ^3J(PC)] 39.

(xi) [Pt[N(COMe)CH(CH₃)C(0)O](PBzPh₂)₂] (219)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with benzyldiphenylphosphine (0.16g, 0.58 mmol) and N-acetyl-d/-alanine (0.04g, 0.30 mmol) gave white microcrystals of (219) (0.22g, 93%). N.m.r. spectra: ^1H, δ 7.72-6.30 (m, 30H, Ph), 4.71 (m, 1H, CH), 4.06 (m,
2H, CH₂, PbzPh₂), 3.59 (m, 2H, CH₂, PbzPh₂), 1.94 [s, 3H, C(O)CH₃], 1.82 [d, 3H, CHCH₃, 3J(HH) 7]; 13C-{¹H}, δ 186.76 (s, CO), 171.09 (s, CO), 61.99 (s, CH), 37.78 [d, CH₂, PbzPh₂], 1J(PC) + 3J(PC) 35], 34.50 [d, CH₂, PbzPh₂, 1J(PC) + 3J(PC) 31], 22.52 (s, CHCH₃), and 20.45 p.p.m. [d, C(O)CH₃, 4J(PC) 2].

(xii) [Pt(N(COME)CH(CH₃)C(O)O)(dppm)] (220)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and N-acetyl-d/-alanine (0.04g, 0.30 mmol) gave white microcrystals of (220) (0.18g, 94%).

N.m.r. spectra: ¹H, δ 7.83-7.17 (m, 20H, Ph), 4.62 [ddd, 1H, CH₂, dppm, 2J(PH) 9,11, 2J(HH) 16], 4.24 (m, 1H, CH), 4.01 [ddd, 1H, CH₂, dppm, 2J(PH) 10,12, 2J(HH) 16], 1.88 [s, 3H, C(O)CH₃], 1.58 [d, 3H, CHCH₃, 3J(HH) 7]; 13C-¹H, δ 190.76 (s, CO), 171.33 (s, CO), 58.65 (s, CH), 48.76 [dd, CH₂, dppm, 1J(PC) 31,32], 23.55 (s, CHCH₃), and 18.53 p.p.m. [d, C(O)CH₃, 4J(PC) 2].

(xiii) [Pt(N(COME)CH(CH₃)C(O)O)(dppe)] (221)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and N-acetyl-d/-alanine (0.04g, 0.30 mmol) gave white microcrystals of (221) (0.18g, 92%).

N.m.r. spectra: ¹H, δ 8.07-7.22 (m, 20H, Ph), 4.38 [ddq, 1H, CH, 4J(PH) 1,5, 3J(HH) 7], 2.69-2.35 (m, 4H, CH₂, dppe), 1.64 [s, 3H, C(O)CH₃], 1.47 [d, 3H, CHCH₃, 3J(HH) 7]; 13C-¹H, δ 189.30 [d, CO, 3J(PC) 2], 169.15 (s, CO), 59.76 (s, CH), 35.00 [dd, CH₂, dppe, 1J(PC) 40, 3J(PC) 13], 24.02 [dd, CH₂, dppe, 1J(PC) 42, 3J(PC) 6], 23.25 (s, CHCH₃), and 18.34 p.p.m. [d, C(O)CH₃, 4J(PC) 4].

(xiv) [Pt(N(COME)CH(CH₃)C(O)O)(dppp)] (222)

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and N-acetyl-d/-alanine (0.04g, 0.30 mmol) gave white microcrystals of (222) (0.18g, 95%).

N.m.r. spectra: ¹H, δ 7.91-6.94 (m, 20H, Ph), 4.33 (m, 1H, CH), 2.68-2.05 (m, 6H, CH₂, dppp), 1.55 [d, 3H, CHCH₃, 3J(HH) 7], 1.38 [s, 3H, C(O)CH₃]; 13C-¹H, δ 187.93 [d, CO, 3J(PC) 3], 169.44 (s, CO), 61.06 (s, CH), 28.10 [dd, P-CH₂, dppp, 1J(PC) 38, 3J(PC) 10], 23.17 [dd, P-CH₂, dppp, 1J(PC) 36, 3J(PC) 7], 22.34 (s, CHCH₃), 18.94 (s, CH₂, dppp), and
18.77 p.p.m. [d, C(O)CH₃, 4J(PCM) 4].

(xv) \([Pt\{N(\text{COMe})CH(CH₂)C(O)\hat{O}\}(dppb)] (223)\)

The complex \([PtCl₂(cod)] (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and N-acetyl-d/-alanine (0.04g, 0.30 mmol) gave white microcrystals of (223) (0.19g, 94%). N.m.r. spectra: ¹H, δ 7.82-7.11 (m, 20H, Ph), 4.36 (m, 1H, CH), 2.70-2.15 (m, 8H, CH₂, dppb), 1.62 [d, 3H, CHCH₃, ³J(HH) 7], 1.38 [s, 3H, C(O)CH₃]; ¹³C-{¹H}, δ 187.78 [d, CO, ³J(PCM) 3], 169.86 (s, CO), 60.61 (s, CH), 25.62 (m, P-CH₂, dppb), 23.72 (m, P-CH₂, dppb), 21.87 (s, 2 x CH₂, dppb), 21.66 (s, CHCH₃), and 18.95 p.p.m. [d, C(O)CH₃, 4J(PCM) 4].

(xvi) \([Pt\{N(\text{COMe})CH(CH₂CH₂SCH₂)C(O)\hat{O}\}(PPh₃₂)] (224)\)

The complex \([PtCl₂(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N-acetyl-d/-methionine (0.055g, 0.29 mmol) gave white microcrystals of (224) (0.24g, 98%). N.m.r. spectra: ¹H, δ 7.84-7.12 (m, 30H, Ph), 4.34 (m, 1H, CH), 2.42 (m, 2H, S-CH₂), 2.22 (m, 2H, CHCH₂), 2.13 (s, 3H, S-CH₃), 1.56 [s, 3H, C(O)CH₃]; ¹³C-{¹H}, δ 184.91 (m, CO), 171.87 (s, CO), 65.12 (s, CH), 36.29 (s, S-CH₂), 31.03 (s, S-CH₃), 20.55 [d, C(O)CH₃, 4J(PCM) 3], and 15.36 p.p.m. (s, S-CH₃).

(xvii) \([Pt\{N(\text{COMe})CH(CH₂CH₃SCH₂)C(O)\hat{O}\}(PMePh₂₂)] (225)\)

The complex \([PtCl₂(cod)] (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and N-acetyl-d/-methionine (0.055g, 0.29 mmol) gave white microcrystals of (225) (0.20g, 94%). N.m.r. spectra: ¹H, δ 7.68-7.15 (m, 20H, Ph), 4.45 (m, 1H, CH), 2.70 (m, 1H, S-CH₂), 2.57 (m, 1H, S-CH₂), 2.42 (m, 1H, CHCH₂), 2.27 (m, 1H, CHCH₂), 2.17 (s, 3H, S-CH₃), 1.99 [d, 3H, Me, PMePh₂, ²J(PH) + ⁴J(PH)] 11], 1.74 [s, 3H, C(O)CH₃], 1.72 [d, 3H, Me, PMePh₂, ²J(PH) + ⁴J(PH)] 11]; ¹³C-{¹H}, δ 185.62 (m, CO), 171.65 (s, CO), 65.12 (s, CH), 36.77 (s, S-CH₂), 30.87 (s, CHCH₂), 20.36 [d, C(O)CH₃, ⁴J(PCM) 2], 15.40 (s, S-CH₃), and 13.28 p.p.m. (m, 2 x Me, PMePh₂).

(xviii) \([Pt\{N(\text{COMe})CH(CH₂CH₂SCH₂)C(O)\hat{O}\}(PBzPh₂₂)] (226)\)

The complex \([PtCl₂(cod)] (0.10g, 0.27 mmol) with benzylidiphenylphosphine (0.16g,
0.58 mmol) and N-acetyl-d/-l-methionine (0.055g, 0.29 mmol) gave white microcrystals of (226) (0.24g, 95%). N.m.r. spectra: $^1$H, δ 7.41-6.25 (m, 30H, Ph), 4.68 (m, 1H, CH), 4.05 (m, 2H, P-CH$_2$, PBzPh$_2$), 3.55 (m, 2H, P-CH$_2$, PBzPh$_2$), 2.83 (m, 2H, S-CH$_2$), 2.66-2.42 (m, 2H, CHCH$_2$), 2.20 (s, 3H, S-CH$_3$), 2.05 [s, 3H, C(O)CH$_3$]; $^{13}$C-{ $^1$H}, δ 185.22 (m, CO), 172.41 (s, CO), 65.99 (s, CH), 37.67 [d, CH$_2$, PBzPh$_2$, $^1$J(PC) + $^3$J(PC) 35], 36.86 (s, S-CH$_2$), 34.30 [d, CH$_2$, PBzPh$_2$, $^1$J(PC) + $^3$J(PC) 31], 31.02 (s, CHCH$_2$), 21.45 [d, C(O)CH$_3$, $^4$J(PC) 2], and 15.64 p.p.m. (s, S-CH$_3$).

(xix) $[\text{Pt(N(COMe)CH(CH$_2$CH$_2$SCH$_3$)C(O)O)}](\text{dpdm})] \cdot \text{H$_2$O}$

The complex $[\text{PtCl$_2$(cod)}]$ (0.10g, 0.27 mmol) with dpdm (0.11g, 0.29 mmol) and N-acetyl-d/-l-methionine (0.055g, 0.29 mmol) gave white microcrystals of (227).H$_2$O (0.20g, 94%). N.m.r. spectra: $^1$H, δ 7.84-7.30 (m, 20H, Ph), 4.64 [ddd, 1H, CH$_2$, dpdm, $^2$J(PH) 9,11, $^2$J(HH) 16], 4.30 (m, 1H, CH), 4.03 [ddd, 1H, CH$_2$, dpdm, $^2$J(PH) 10,12, $^2$J(HH) 16], 2.95 [ddd, 1H, S-CH$_2$, $^2$J(HH) 12, $^3$J(HH) 5,11], 2.69 [ddd, 1H, S-CH$_2$, $^2$J(HH) 12, $^3$J(HH) 6,11], 2.34 (s, br, 2H, H$_2$O), 2.31-2.19 (m, 1H, CHCH$_2$), 2.15-2.02 (m, 1H, CHCH$_2$), 2.08 (s, 3H, S-CH$_3$), 1.89 [s, 3H, C(O)CH$_3$]; $^{13}$C-{ $^1$H}, δ 188.58 (s, CO), 171.19 (s, CO), 62.22 (s, CH), 48.64 [dd, CH$_2$, dpdm, $^1$J(PC) 31,32], 36.01 (s, S-CH$_2$), 29.22 (s, CHCH$_2$), 18.74 [d, C(O)CH$_3$, $^4$J(PC) 3], and 15.41 p.p.m. (s, S-CH$_3$).

(xx) $[\text{Pt(N(COMe)CH(CH$_2$CH$_2$SCH$_3$)C(O)O)}](\text{dppe})] \cdot \text{H$_2$O}$

The complex $[\text{PtCl$_2$(cod)}]$ (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and N-acetyl-d/-l-methionine (0.055g, 0.29 mmol) gave white microcrystals of (228) (0.20g, 95%). N.m.r. spectra: $^1$H, δ 8.05-7.30 (m, 20H, Ph), 4.39 (m, 1H, CH), 2.66-1.91 (m, 6H, CH$_2$, dppe + S-CH$_2$ + CHCH$_2$), 2.03 (s, 3H, S-CH$_3$), 1.68 [s, 3H, C(O)CH$_3$], 1.49 (m, 2H, CH$_2$, dppe); $^{13}$C-{ $^1$H}, δ 187.24 [d, CO, $^3$J(PC) 3], 169.33 (s, CO), 63.31 (s, CH), 36.36 (s, S-CH$_2$), 34.66 [dd, P-CH$_2$, dppe, $^1$J(PC) 41, $^3$J(PC) 12], 29.56 (s, CHCH$_2$), 18.92 [d, C(O)CH$_3$, $^4$J(PC) 3], 17.78 [dd, P-CH$_2$, dppe, $^1$J(PC) 41, $^3$J(PC) 7], and 15.24 p.p.m. (s, S-CH$_3$).
The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and N-acetyl-\textit{dl}-methionine (0.055g, 0.29 mmol) gave white microcrystals of \((229).\text{H}_2\text{O}\) (0.20g, 91%). N.m.r. spectra: \(\text{^1H}\), \(\delta\) 7.84-7.22 (m, 20H, Ph), 4.27 (m, 1H, CH), 2.65-1.92 (m, 12H, 3 x CH₂, dppp + S-CH₂ + CHCH₂ + H₂O), 2.13 (s, 3H, S-CH₃), 1.48 [s, 3H, C(O)CH₃]; \(\text{^{13C}-[\text{^1H}]}\), \(\delta\) 186.09 [d, CO, \(\text{^3J(PC)}\) 3], 169.93 (s, CO), 64.90 (s, CH), 36.96 (s, S-CH₂), 30.58 (s, CHCH₂), 28.07 [dd, P-CH₂, dppp, \(\text{^1J(PC)}\) 40, \(\text{^3J(PC)}\) 9], 23.37 [dd, P-CH₂, dppp, \(\text{^1J(PC)}\) 38, \(\text{^3J(PC)}\) 5], 19.61 [d, C(O)CH₃, \(\text{^4J(PC)}\) 4], 18.75 (s, CH₂, dppp), and 15.17 p.p.m. (s, S-CH₃).

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and N-acetyl-\textit{dl}-methionine (0.055g, 0.29 mmol) gave white microcrystals of \((230).\text{H}_2\text{O}\) (0.20g, 91%). N.m.r. spectra: \(\text{^1H}\), \(\delta\) 7.75-7.17 (m, 20H, Ph), 4.27 (m, 1H, CH), 2.68-1.89 (m, 10H, 3 x CH₂, dppb + S-CH₂ + CHCH₂), 2.13 (s, 3H, S-CH₃), 1.58-1.26 (m, 2H, CH₂, dppb), 1.47 [s, 3H, C(O)CH₃]; \(\text{^{13C}-[\text{^1H}]}\), \(\delta\) 186.18 (m, CO), 170.73 (s, CO), 64.57 (s, CH), 36.57 (s, S-CH₂), 30.91 (s, CHCH₂), 25.40 (m, P-CH₂, dppb), 23.78 [dd, P-CH₂, dppb, \(\text{^1J(PC)}\) 41, \(\text{^3J(PC)}\) 3], 21.53 (s, 2 x CH₂, dppb), 19.86 [d, C(O)CH₃, \(\text{^4J(PC)}\) 3], and 15.17 p.p.m. (s, S-CH₃).

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N-acetyl-\textit{l}-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of \((231).\text{H}_2\text{O}\) (0.23g, 90%). N.m.r. spectra: \(\text{^1H}\), \(\delta\) 7.83-7.02 (m, 35H, Ph), 4.62 (m, 1H, CH), 3.50 [dd, 1H, CH₂, \(\text{^2J(HH)}\) 14, \(\text{^3J(HH)}\) 5], 3.39 [dd, 1H, CH₂, \(\text{^2J(HH)}\) 14, \(\text{^3J(HH)}\) 7], 2.13 (s, br, 2H, H₂O), 1.43 (s, 3H, CH₃); \(\text{^{13C}-[\text{^1H}]}\), \(\delta\) 185.61 [d, CO, \(\text{^3J(PC)}\) 3], 172.22 (s, CO), 67.44 (s, CH), 42.69 (s, CH₂), and 20.52 p.p.m. [d, CH₃, \(\text{^4J(PC)}\) 5].

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with methyl diphenylphosphine (0.11g,
0.55 mmol) and N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (232).H₂O (0.20g, 91%). N.m.r. spectra: 1H, δ 7.93-6.93 (m, 25H, Ph), 4.85 (m, 1H, CH₂), 3.53 [dd, 1H, CH₂, 1H, (HH) 14, 3(J(HH) 5)], 3.20 [dd, 1H, CH₂, 1H, (HH) 14, 3(J(HH) 5)], 2.24 (s, br, 2H, H₂O), 1.94 [d, 3H, Me, PMePh₂, 1J(PH) + 4J(PH) 12, 3(J(PtH) not discernible], 1.88 [s, 3H, C(O)CH₃], 1.30 [d, 3H, Me, PMePh₂, 2J(PH) + 4J(PH) 10, 3(J(PtH) not discernible]; 13C-{1H}, δ 186.15 [d, CO, 3(J(PC) 5)], 172.81 (s, CO), 66.74 (s, CH), 41.50 (s, CH₂), 20.40 [d, C(O)CH₃, 4(J(PC) 4), 17.97 [d, Me, PMePh₂, 1J(PC) + 3(J(PC) 48], and 12.83 p.p.m. [d, Me, PMePh₂, 1J(PC) + 3(J(PC) 40].

(xxv) [Pt{(N(COMe)CH(CH₂Ph)C(O)O)2(PMe₂Ph)₂} (233)]

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with dimethylphenylphosphine (0.08g, 0.58 mmol) and N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (233) (0.17g, 93%). N.m.r. spectra: 1H, δ 7.47-6.89 (m, 15H, Ph), 4.90 (m, 1H, CH), 3.50 [dd, 1H, CH₂, 1H, (HH) 13, 3(J(HH) 6)], 3.17 [dd, 1H, CH₂, 1H, (HH) 13, 3(J(HH) 5)], 1.95 [s, 3H, C(O)CH₃], 1.90 [d, 3H, Me, PMePh₂, 1J(PH) + 4J(PH) 12, 3(J(PtH) 37], 1.55 [d, 3H, Me, PMePh₂, 1J(PH) + 4J(PH) 11, 3(J(PtH) 22], 1.38 [d, 3H, Me, PMePh₂, 1J(PH) + 4J(PH) 11, 3(J(PtH) 21]; 13C-{1H}, δ 186.11 [d, CO, 3(J(PC) 3)], 173.23 (s, CO), 67.24 (s, CH), 41.48 (s, CH₂), 20.58 [d, C(O)CH₃, 4(J(PC) 4), 18.68 [d, Me, PMePh₂, 1J(PC) + 3(J(PC) 47], 12.12 [d, Me, PMePh₂, 1J(PC) + 3(J(PC) 40], 11.95 [d, Me, PMePh₂, 1J(PC) + 3(J(PC) 42], and 11.40 p.p.m. [d, Me, PMePh₂, 1J(PC) + 3(J(PC) 43].

(xxvi) [Pt{(N(COMe)CH(CH₂Ph)C(O)O)(PMe₂Ph)₂} (234).H₂O]

The complex [PtCl₂(cod)] (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (234).H₂O (0.20g, 92%). N.m.r. spectra: 1H, δ 7.90-7.16 (m, 25H, Ph), 4.52 (m, 1H, CH), 4.46 [ddd, 1H, CH₂, dppm, 1J(PH) 9, 11, 2(J(HH) 16)], 3.86 [ddd, 1H, CH₂, dppm, 1J(PH) 9, 12, 2(J(HH) 16)], 3.31 [dd, 1H, CHCH₂, 1H, (HH) 13, 3(J(HH) 5)], 3.09 [dd, 1H, CHCH₂, 1H, (HH) 13, 3(J(HH) 5)], 2.10 (s, br, 2H, H₂O), 1.77 (s, 3H, CH₃); 13C-{1H}, δ 189.10 (s, CO), 171.47 (s, CO), 64.60 (s,
The complex [Pt\textsubscript{2}(cod)] (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (235).CH\textsubscript{2}Cl\textsubscript{2} (0.21g, 88%). N.m.r. spectra: \textsuperscript{1}H, \(\delta\) 7.98-6.81 (m, 25H, Ph), 5.24 (s, 2H, CH\textsubscript{2}Cl\textsubscript{2}), 4.51 (m, 1H, CH), 3.15 [dd, 1H, CHCH\textsubscript{2}, \(J\textsubscript{HH}\) 13, \(J\textsubscript{HH}\) 4]; 3.03 [dd, 1H, CHCH\textsubscript{2}, \(J\textsubscript{HH}\) 13, \(J\textsubscript{HH}\) 7], 2.83-2.23 (m, 2H, P-CH\textsubscript{2}, dppe), 1.94 (m, 1H, P-CH\textsubscript{2}, dppe), 1.42 (m, 1H, P-CH\textsubscript{2}, dppe), 1.29 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C-{\textsuperscript{1}H}, \(\delta\) 187.88 [d, CO, \(J\textsubscript{PC}\) 2], 170.08 (s, CO), 66.02 (s, CH), 53.15 (s, CH\textsubscript{2}Cl\textsubscript{2}), 43.22 (s, CHCH\textsubscript{2}), 34.99 [dd, P-CH\textsubscript{2}, dppe, \(J\textsubscript{PC}\) 40, \(J\textsubscript{PC}\) 13], 17.80 [dd, P-CH\textsubscript{2}, dppe, \(J\textsubscript{PC}\) 38, \(J\textsubscript{PC}\) 7], and 18.55 p.p.m. [d, CH\textsubscript{3}, \(J\textsubscript{PC}\) 4].

The complex [Pt\textsubscript{2}(cod)] (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (236).H\textsubscript{2}O (0.20g, 89%). N.m.r. spectra: \textsuperscript{1}H, \(\delta\) 7.84-6.89 (m, 25H, Ph), 4.38 (m, 1H, CH), 3.27 [dd, 1H, CHCH\textsubscript{2}, \(J\textsubscript{HH}\) 13, \(J\textsubscript{HH}\) 4]; 3.00 [dd, 1H, CHCH\textsubscript{2}, \(J\textsubscript{HH}\) 13, \(J\textsubscript{HH}\) 8], 2.57-2.01 (m, 8H, 3 x CH\textsubscript{2}, dppe + H\textsubscript{2}O), 1.09 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C-{\textsuperscript{1}H}, \(\delta\) 193.15 (m, CO), 170.49 (s, CO), 67.55 (s, CH), 43.48 (s, CHCH\textsubscript{2}), 28.62 [dd, P-CH\textsubscript{2}, dppp, \(J\textsubscript{PC}\) 40, \(J\textsubscript{PC}\) 10], 22.97 [dd, P-CH\textsubscript{2}, dppp, \(J\textsubscript{PC}\) 33, \(J\textsubscript{PC}\) 5], 19.23 [d, CH\textsubscript{3}, \(J\textsubscript{PC}\) 4], and 18.62 p.p.m. (s, CH\textsubscript{2}, dppp).

The complex [Pt\textsubscript{2}(cod)] (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (237).H\textsubscript{2}O (0.21g, 92%). N.m.r. spectra: \textsuperscript{1}H, \(\delta\) 7.79-7.04 (m, 25H, Ph), 4.57 (m, 1H, CH), 3.33 [dd, 1H, CHCH\textsubscript{2}, \(J\textsubscript{HH}\) 14, \(J\textsubscript{HH}\) 6], 3.22 [dd, 1H, CHCH\textsubscript{2}, \(J\textsubscript{HH}\) 14, \(J\textsubscript{HH}\) 5], 3.11-1.75 (m, br, 8H, 3 x CH\textsubscript{2}, dppe + H\textsubscript{2}O), 1.56 (m, 2H, CH\textsubscript{2}, dppb), 1.38 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C-{\textsuperscript{1}H}, \(\delta\)
186.57 [d, CO, 3J(PC) 3], 171.29 (s, CO), 66.26 (s, CH), 41.97 (s, CHCH2), 25.57 (m, P-CH2, dppb), 22.72 [d, P-CH2, dppb, 1J(PC) 35], 21.45 (s, 2 x CH2, dppb), and 19.62 p.p.m. [d, CH3, 4J(PC) 4].

(***)[Pt(N(COMe)CH(CH2Ph)C(O)O)(cod)] (238)

The complex [PtCl2(cod)] (0.10g, 0.27 mmol) with N-acetyl-l-phenylalanine (0.06g, 0.29 mmol) gave white microcrystals of (238) (0.11g, 80%). N.m.r. spectra: 1H, δ 7.41-7.18 (m, 5H, Ph), 5.80 [m, 1H, CH, cod, 2J(PtH) 76], 5.16 [m, 1H, CH, cod, 2J(PtH) 52], 4.70 [dd, 1H, CHCH2Ph, 3J(HH) 3.6, 3J(PtH) 38], 4.57 [m, 1H, CH, cod, 2J(PtH) 56], 3.31 [dd, 1H, CHCH2Ph, 2J(HH) 13, 3J(HH) 3], 2.96 [dd, 1H, CHCH2Ph, 2J(HH) 13, 3J(HH) 6], 2.73-1.63 (m, 8H, CH2, cod), 2.12 (s, 3H, CH3); 13C-{1H}, δ 185.67 (s, CO), 174.77 (s, CO), 98.38 (s, CH, cod), 97.29 (s, CH, cod), 96.99 (s, CH, cod), 91.72 (s, CH, cod), 67.24 (s, CHCH2Ph), 41.19 (s, CHCH2Ph), 32.94 (s, CH2, cod), 30.55 (s, CH2, cod), 29.44 (s, CH2, cod), 25.93 (s, CH2, cod), and 22.15 p.p.m. (s, CH3).

(***i)[Pt(N(CHG)CH,C(G)6l(PPh,Xl(239).CH,CN

The complex [PtCl2(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N-formylglycine (0.03g, 0.29 mmol) gave pale yellow microcrystals of (239).CH2Cl2 (0.24g, 98%). N.m.r. spectra: 1H, δ 7.62-7.08 (m, 31H, Ph + CHO), 5.22 (s, 2H, CH2Cl2), 4.33 [s, 2H, CH2, 3J(PtH) 23]; 13C-{1H}, δ 184.25 (s, CO), 168.15 (s, CO), 53.36 (s, CH2Cl2), and 49.90 p.p.m. (s, CH2).

(***ii)[Pt(N(COCF3)CH2C(O)O)(PPh3)2] (240)

The complex [PtCl2(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N-trifluoroacetylglycine (0.05g, 0.29 mmol) gave white microcrystals of (240) (0.23g, 96%). N.m.r. spectra: 1H, δ 7.77-6.66 (m, 30H, Ph), 4.38 [d, 2H, CH2, 4J(PH) 3, 3J(PtH) 22]; 13C-{1H}, δ 182.35 (s, CO), 52.94 (s, CH2), C(O)CF3 were not discernible; 19F-{1H}, δ -67.69 p.p.m. [d, CF3, 5J(PF) 2, 4J(PtF) 21].
The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and \(l\)-proline (0.035g, 0.30 mmol) gave greeny-yellow microcrystals of \((241).\text{H}_2\text{O}\) (0.21g, 92%). N.m.r. spectra: \(^1\text{H}, \delta 7.74-7.21\) (m, 30H, Ph), 4.88 (m, 1H, CH), 2.70 (m, 2H, CH\(_2\)), 2.46 (s, br, 2H, H\(_2\)O), 2.02 (m, 2H, CH\(_2\)), 1.67 (m, 2H, CH\(_2\)); \(^{13}\text{C}-\{^1\text{H}\}, \delta 184.47\) (m, CO), 64.11 (s, CH), 51.53 (s, CH\(_2\)), 30.16 (s, CH\(_2\)), and 24.88 p.p.m. (s, CH\(_2\)).

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and \(l\)-proline (0.035g, 0.30 mmol) gave pale yellow microcrystals of \((242)\) (0.18g, 92%). N.m.r. spectra: \(^1\text{H}, \delta 8.42-7.25\) (m, 20H, Ph), 4.50 (m, 1H, CH), 2.94 (m, 2H, CH\(_2\)), 2.52-1.26 (m, 10H, 3 x CH\(_2\), dppp + 2 x CH\(_2\)); \(^{13}\text{C}-\{^1\text{H}\}, \delta 184.86\) (m, CO), 63.03 (s, CH), 50.60 (s, CH\(_2\)), 29.85 (s, CH\(_2\)), 24.25 (s, CH\(_2\)), 23.59 (m, 2 x P-CH\(_2\), dppp), and 18.57 p.p.m. (s, CH\(_2\), dppp).

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and \(l\)-proline (0.035g, 0.30 mmol) gave pale yellow microcrystals of \((243).\text{CH}_2\text{Cl}_2\) (0.20g, 90%). N.m.r. spectra: \(^1\text{H}, \delta 7.88-7.34\) (m, 20H, Ph), 5.29 (s, 2H, CH\(_2\)Cl\(_2\)), 4.91 (m, 1H, CH), 2.91-1.20 (m, 14H, 4 x CH\(_2\), dppb + 3 x CH\(_2\)); \(^{13}\text{C}-\{^1\text{H}\}, \delta 184.99\) [d, CO, \(^3\text{J}(\text{PC}) 2\)], 63.00 (s, CH), 53.15 (s, CH\(_2\)Cl\(_2\)), 50.26 (s, CH\(_2\)), 29.43 (s, CH\(_2\)), 27.68 [d, P-CH\(_2\), dppb, \(^1\text{J}(\text{PC}) 38\)], 25.45 [d, CH\(_2\), dppb, \(^2\text{J}(\text{PC}) 4\)], 24.79 (s, CH\(_2\)), 23.80 [d, P-CH\(_2\), dppb, \(^1\text{J}(\text{PC}) 40\)], and 20.74 p.p.m. (s, CH\(_2\), dppb).

Attempted preparation of \([\text{Pd}[\text{N(COMe)}\text{CH}(_2)\text{CH}_2\text{SCH}_2\text{C(O)}\text{O}]](\text{dppp})]\)

The complex \([\text{PdCl}_2(\text{cod})]\) (0.10g, 0.35 mmol) with dppp (0.15g, 0.36 mmol) and \(N\)-acetyl-\(d\)-l-methionine (0.07g, 0.37 mmol) gave, after filtration of the reaction mixture, a deep red solution. Evaporation to dryness under reduced pressure afforded a deep red oil which quickly turned dark brown in the presence of air. Dissolution of the oil in
dichloromethane, followed by the addition of light petroleum yielded a brown solid. The $^{31}$P-$^1$H n.m.r. spectrum of both the oil and the solid indicated the presence of a number of unidentified products.

(xxxvii) Attempted preparation of $[Pt\{NHCH(CH_2CH_2SCH_3)C(O)\O\}(PPh_3)_2]$  

The complex $[PtCl_2(cod)]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and $dl$-methionine (0.04g, 0.27 mmol) gave a pale brown solid. The $^{31}$P-$^1$H n.m.r. spectrum of the solid indicated the presence of numerous unidentified species, and further purification was not attempted.

Reactions of $[\text{Amino Acid(2-)-N,O}1\text{bis(ligand)platinum(II)}$ complexes

(i) Ligand substitution reactions

(a) $[Pt\{N(COMe)CH_2C(O)\O\}(cod)]$ (216) with triphenylphosphine

A solution of $[Pt\{N(COMe)CH_2C(O)\O\}(cod)]$ (216) (0.10g, 0.24 mmol) in dichloromethane (ca. 30 cm$^3$) with triphenylphosphine (0.13g, 0.50 mmol) was stirred for 15 min at room temperature. The mixture was then evaporated to dryness under reduced pressure to afford a colourless oil which was crystallised from dichloromethane - light petroleum to afford white microcrystals of $[Pt\{N(COMe)CH_2C(O)\O\}(PPh_3)_2]$ (209) (0.19g, 95%), identified by $^{31}$P-$^1$H n.m.r. spectroscopy.

(b) $[Pt\{N(COMe)CH_2C(O)\O\}(cod)]$ (216) with methyldiphenylphosphine

A solution of (216) (0.10g, 0.24 mmol) in dichloromethane (30 cm$^3$) with methyldiphenylphosphine (0.1g, 0.50 mmol) was stirred for 30 min at room temperature. Work-up as in (a) afforded white microcrystals of $[Pt\{N(COMe)CH_2C(O)\O\}(PMePh_2)_2]$ (210) (0.16g, 94%), identified by $^{31}$P-$^1$H n.m.r. spectroscopy.

(c) $[Pt\{N(COMe)CH_2C(O)\O\}(cod)]$ (216) with dppp

A solution of (216) (0.10g, 0.24 mmol) in dichloromethane (30 cm$^3$) with dppp (0.11g, 0.27 mmol) was stirred for 20 min at room temperature. Work-up as in (a) afforded white microcrystals of $[Pt\{N(COMe)CH_2C(O)\O\}(dppp)]$ (214) (0.17g, 98%), identified by $^{31}$P-$^1$H n.m.r. spectroscopy.
(d) $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{cod})]$ (238) with triphenylphosphine

A solution of $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{cod})]$ (238) (0.10g, 0.20 mmol) in dichloromethane (30 cm$^3$) with triphenylphosphine (0.11g, 0.42 mmol) was stirred for 30 min at room temperature. Work-up as in (a) afforded white microcrystals of $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{PPh}_3)_2]$ (231) (0.18g, 97%), identified by $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectroscopy.

(e) $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{cod})]$ (238) with dppp

A solution of (238) (0.10g, 0.20 mmol) in dichloromethane (30 cm$^3$) with dppp (0.09g, 0.22 mmol) was stirred for 15 min at room temperature. Work-up as in (a) afforded white microcrystals of $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{dppp})]$ (236) (0.16g, 98%), identified by $^{31}\text{P}-\{^1\text{H}\}$ and $^1\text{H}$ n.m.r. spectroscopy.

(f) $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{PPh}_3)_2]$ (231).H$_2$O with t-butyl isocyanide

t-Butyl isocyanide (0.02g, 0.24 mmol) in dichloromethane (10 cm$^3$) was added dropwise to a stirred solution of $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{PPh}_3)_2]$ (231).H$_2$O (0.20g, 0.21 mmol) in dichloromethane (30 cm$^3$), and the mixture was stirred for 4h at room temperature. Evaporation to dryness under reduced pressure afforded a pale brown oil (0.15g, 84%) which resisted attempts using numerous solvent mixtures to yield a solid sample of $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{O}](\text{CNBu'})(\text{PPh}_3)]$ (246).H$_2$O. (Found: C, 53.3; H, 4.6; N, 3.1. C$_{34}$H$_{35}$N$_2$O$_3$P$_{2}$Pt.H$_2$O requires C, 53.5; H, 4.8; N, 3.7%); i.r. (CHCl$_3$), $\nu_{\text{C=O}}$ at 2220s cm$^{-1}$; $\nu_{\text{C=O}}$ at 1660s and 1610s cm$^{-1}$. N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 7.74-7.00 (m, 20H, Ph), 4.61 (m, 1H, CH), 3.21 [dd, 1H, CH$_2$, $^2$J(HH) 13, $^3$J(HH) 5], 3.10 [dd, 1H, CH$_2$, $^2$J(HH) 13, $^3$J(HH) 5], 2.20 (s, br, 2H, H$_2$O), 1.80 [s, 3H, C(O)CH$_3$], 1.08 [s, 9H, Me, Bu']; $^{31}\text{P}-\{^1\text{H}\}$ (36.2 MHz), $\delta$ 8.08 p.p.m. [s, PPh$_3$, $^1$J(PtP) 2913].

(ii) Reactions with Ethanol

(a) Reaction at room temperature

A solution of either $[\text{Pt}[\text{N}(\text{COMe})\text{CH}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2]$ (209) (0.10g) or $[\text{Pt}[\text{N}(\text{COMe})\text{CH}(\text{CH}_2\text{CH}_2\text{SCH}_3)\text{C}(\text{O})\text{O}](\text{PPh}_3)_2]$ (224) (0.10g) in absolute ethanol (30
cm$^3$) was stirred for 24h at room temperature. Evaporation to dryness under reduced pressure afforded a colourless oil which contained the respective starting materials, as shown by $^{31}$P-{$^1$H} n.m.r. spectroscopy.

(b) **Reaction at 60°C**

A solution of the complex $[\text{Pt}\{\text{N(COMe)}\text{CH}_2\text{C(O)}\text{O}\}\{\text{PPh}_3\}_2]$ (209) (0.10g) in absolute ethanol (30 cm$^3$) was stirred and heated to 60°C for 1h. Evaporation to dryness under reduced pressure afforded a brown oil, shown to contain numerous products by $^{31}$P-{$^1$H} n.m.r. spectroscopy.

(c) **Reaction of $[\text{Pt}\{\text{N(COMe)}\text{CH}_2\text{C(O)}\text{O}\}\{\text{PPh}_3\}_2]$ (209) with diphenylacetylene in ethanol**

The complex (209) (0.15g, 0.18 mmol) with diphenylacetylene (0.12g, 0.67 mmol) in absolute ethanol (25 cm$^3$) was stirred and heated to 60°C for 1.5h. The mixture was cooled to 0°C and the pale yellow precipitate was filtered off. By comparison with data for an authentic sample, $^{31}$P-{$^1$H} n.m.r. spectroscopy showed the product to be $[\text{Pt}(\text{PhOCPh})(\text{PPh}_3)_2]$ (247) (0.13g, 81%).

(d) **Reaction of $[\text{Pt}\{\text{N(COMe)}\text{CH(CH}_2\text{Ph})\text{C(O)}\text{O}\}\{\text{PPh}_3\}_2]$ (231),H$_2$O with diphenylacetylene in ethanol**

The complex (231),H$_2$O (0.20g, 0.21 mmol) with diphenylacetylene (0.12g, 0.67 mmol) in absolute ethanol (25 cm$^3$) was stirred and heated to 60°C for 1.5h. Work-up as in (c) afforded pale yellow microcrystals of $[\text{Pt}(\text{PhC=CPh})(\text{PPh}_3)_2]$ (247) (0.16g, 85%), identified by $^{31}$P-{$^1$H} n.m.r. spectroscopy.$^{179}$

(e) **Reaction of $[\text{Pt}\{\text{N(COMe)}\text{CH}_2\text{C(O)}\text{O}\}\{\text{PPh}_3\}_2]$ (209) with triphenylphosphine in ethanol**

The complex (209) (0.15g, 0.18 mmol) with triphenylphosphine (0.18g, 0.69 mmol) in absolute ethanol (25 cm$^3$) was stirred and heated to 60°C for 2h. The mixture was cooled to 0°C and a bright yellow precipitate (0.20g) was filtered off.

A slow stream of gaseous hydrogen chloride was passed through a dichloromethane solution of the yellow product (0.10g) for 3 min. Evaporation to dryness under reduced
pressure afforded a white solid, which was shown to contain *trans*-[PtHCl(PPh₃)₂] by 
^{31}P-{¹H} n.m.r. spectroscopy.

To a solution of the yellow product (0.10g) in dichloromethane (20 cm³), was added
dmad (0.07g, 0.50 mmol), and the mixture was stirred for 30 min at room temperature.
Evaporation of the solvent under reduced pressure yielded an orange oil, shown to contain
[Pt(Me₂CC=CCO₂Me)(PPh₃)₂] (248) by ^{31}P-{¹H} n.m.r. spectroscopy.¹⁷⁹

(iii) Reactions with Sulphur Dioxide

(a) Reaction of [Pt(N(COMe)CH>>C(0)O)(PPh₃)₂] (209) with sulphur dioxide in
ethanol

A slow stream of sulphur dioxide was passed through an ethanol solution of (209)
(0.15g, 0.18 mmol) for 20 min at room temperature. Evaporation to dryness under reduced
pressure afforded a colourless oil which was crystallised from dichloromethane - light
petroleum to afford the white solid cis-[Pt(SO₃Et)₂(PPh₃)₂] (249, L = PPh₃) (0.14g, 83%).
I.r. spectra: νSO₂ at 1260s and 1100s cm⁻¹. ^{31}P-{¹H} n.m.r. spectrum (36.2 MHz), δ 25.51
p.p.m. [s, PPh₃, ^{1}J(PtP) 2988].

(b) Reaction of [Pt(N(COMe)CH(CH₃)C(0)₆XPMePh₂)₂] (218) with sulphur
dioxide in ethanol

A slow stream of sulphur dioxide was passed through an ethanol solution of (218)
(0.10g, 0.14 mmol) for 20 min at room temperature. Work-up as in (a) afforded the white
solid cis-[Pt(SO₃Et)₂(PMePh₂)₂] (249, L = PMePh₂) (0.09g, 79%). I.r. spectra: νSO₂ at
1250s and 1100s cm⁻¹. ^{31}P-{¹H} n.m.r. spectrum (36.2 MHz), δ 15.08 p.p.m. [s, PMePh₂,
^{1}J(PtP) 2811].

(c) Reaction of [Pt(N(COMe)CH(CH₂Ph)C(0)O)(PPh₃)₂] (237).H₂O with sulphur
 dioxide in dichloromethane

A slow stream of sulphur dioxide was passed through a dichloromethane solution of
(237).H₂O (0.20g, 0.21 mmol) for 20 min at room temperature. Work-up as in (a) afforded
a white solid (0.14g). N.m.r. spectra: ^{1}H (90 MHz), δ 7.8-7.0 (m, Ph); ^{31}P-{¹H} (36.2
MHz), δ 6.33 p.p.m. [s, PPh₃, ^{1}J(PtP) 3870].
(d) Reaction of \( \text{[Pt}(\text{NMe}_{3})\text{CH}(\text{CH}_{2} \text{C}(\text{O})\text{O})\text{PPh}_{3})_{2} \) (218) with sulphur dioxide in dichloromethane

A slow stream of sulphur dioxide was passed through a dichloromethane solution of (218) (0.15g, 0.21 mmol) for 20 min at room temperature. Work-up as in (a) afforded a white solid which was shown to contain one main component and several lesser species by \( ^{31}\text{P-}^{1}\text{H} \) n.m.r. spectroscopy. \( ^{31}\text{P-}^{1}\text{H} \) n.m.r. spectrum (36.2 MHz) of the main component, \( \delta 3.87 \) [d, PMePh\(_{2}\), \( ^{1}J(\text{PtP}) 2317, ^{2}J(\text{PP}) 22 \)], and -5.68 p.p.m. [d, PMePh\(_{2}\), \( ^{1}J(\text{PtP}) 4182, ^{2}J(\text{PP}) 22 \)].

(iv) Reactions with Carbon Monoxide

(a) Reaction in dichloromethane

A slow stream of carbon monoxide was passed through a stirred dichloromethane solution of either \( \text{[Pt}(\text{NMe}_{3})\text{CH}(\text{CH}_{2} \text{C}(\text{O})\text{O})\text{PPh}_{3})_{2} \) (209) (0.10g, 0.12 mmol) or \( \text{[Pt}(\text{NMe}_{3})\text{CH}(\text{CH}_{2} \text{CH}_{2} \text{SCH}_{3})\text{C}(\text{O})\text{O})\text{PPh}_{3})_{2} \) (224) (0.10g, 0.11 mmol) for 5h at room temperature. Evaporation to dryness under reduced pressure yielded, in each case, a colourless oil which, by \( ^{31}\text{P-}^{1}\text{H} \) n.m.r. spectroscopy, was shown to contain unreacted starting material.

(b) Reaction of \( \text{[Pt}(\text{NMe}_{3})\text{CH}(\text{CH}_{2} \text{C}(\text{O})\text{O})\text{PPh}_{3})_{2} \) (209) with carbon monoxide in ethanol

A slow stream of carbon monoxide was passed through an ethanol solution of (209) (0.20g, 0.24 mmol) for 5h at room temperature. Removal of the solvent under reduced pressure afforded a pale orange oil which was crystallised from dichloromethane - light petroleum to give a pale brown powdery solid, formulated as cis-[Pt(CO\(_{2}\)Et)\(_{2}\)(PPh\(_{3}\))\(_{2}\)] (251, \( R = \text{Et} \)) (0.15g, 72%). I.r. spectrum, \( v_{\text{C=O}} \) at 1805s and 1840s cm\(^{-1}\). N.m.r. spectra: \( ^{1}\text{H} \) (300 MHz), \( \delta 7.74-6.71 \) (m, 180H, Ph), 2.84 [q, CH\(_{2}\), Et, \( ^{3}J(\text{HH}) 7 \)], 0.26 [t, CH\(_{3}\), Et, \( ^{3}J(\text{HH}) 7 \); \( ^{31}\text{P-}^{1}\text{H} \) (36.2 MHz), \( \delta 20.93 \) p.p.m. [s, PPh\(_{3}\), \( ^{1}J(\text{PtP}) 3254 \)].

(c) Reaction of \( \text{[Pt}(\text{NOCF}_{3})\text{CH}(\text{CH}_{2} \text{C}(\text{O})\text{O})\text{PPh}_{3})_{2} \) (240) with carbon monoxide in ethanol

A slow stream of carbon monoxide was passed through an ethanol solution of (240) (0.15g, 0.17 mmol) for 5h at room temperature. Evaporation to dryness under reduced
pressure yielded a pale brown oil whose $^{31}$P-$^1$H n.m.r. spectrum was identical to that obtained for (251, $R = $ Et). $^{19}$F-$^1$H n.m.r. spectrum of the oil, $\delta$ -75.95 p.p.m. (s, CF$_3$, N-trifluoroacetylglycine).

(d) **Reaction of cis-[Pt(OAc)$_2$(PPh$_3$)$_2$] with carbon monoxide in methanol**

A slow stream of carbon monoxide was passed through a stirred methanolic solution of cis-[Pt(OAc)$_2$(PPh$_3$)$_2$] (0.20g, 0.24 mmol) for 5h at room temperature. The solution was then filtered to separate white microcrystals of trans-[Pt(CO$_2$Me)(OAc)(PPh$_3$)$_2$] (252) (0.09g, 45%). The filtrate was evaporated to dryness to yield a pale brown oil which was crystallised from dichloromethane - light petroleum, to give the pale brown solid cis-[Pt(CO$_2$Me)$_2$(PPh$_3$)$_2$] (251, $R = $ Me) (0.09g, 45%). N.m.r. spectrum: $^{31}$P-$^1$H (36.2 MHz), $\delta$ 20.86 p.p.m. [s, PPh$_3$, $^3J$(PtP) 3259].

(v) **Attempted insertion reactions**

(a) **Reaction of [Pt{N(COMe)CH$_2$CH$_2$CHC(O)O}](PPh$_3$)$_2$ (209) with dmad** Dmad (0.20g, 1.41 mmol) was added dropwise to a stirred dichloromethane solution of (209) (0.10g, 0.12 mmol) and the mixture was stirred for 15h at room temperature. Evaporation of the solvent under reduced pressure afforded a colourless oil, which was shown, by $^{31}$P-$^1$H n.m.r. spectroscopy, to contain unreacted (209).

The reaction was repeated with the mixture being refluxed for an additional 6h, however $^{31}$P-$^1$H n.m.r. spectroscopy again indicated the presence of unreacted (209).

(b) **Reaction of [Pt{NCH$_2$CH$_2$CH$_2$CHC(O)O}](PPh$_3$)$_2$ (241).H$_2$O with excess dmad**

Dmad (0.20g, 1.41 mmol) was added dropwise to a dichloromethane solution of (241).H$_2$O (0.10g, 0.12 mmol) and the mixture was stirred for 4h at room temperature. Evaporation of the solvent under reduced pressure afforded a pale brown oil, which was shown to contain numerous products by $^{31}$P-$^1$H n.m.r. spectroscopy.
(c) Reaction of [Pt(NCH2CH2CH2C(O)O)(PPh3)2] (241).H2O with one equivalent of dmad

Dmad (0.04g, 0.26 mmol) was added to a dichloromethane solution of (241).H2O (0.20g, 0.24 mmol) and the mixture was stirred for 3h at room temperature. Evaporation of the solvent under reduced pressure afforded a pale brown oil, which was shown to contain a major component by 31P-{1H} n.m.r. spectroscopy. N.m.r. spectrum: 31P-{1H} (36.2 MHz), δ 16.83 [d, PPh3, J(PtP) 3914, J(PP) 20], and 2.96 p.p.m. [d, PPh3, J(PtP) 3645, J(PP) 20].

(d) Reaction of [Pt(NCH2CH2CH2C(O)O)(PPh3)2] (241).H2O with hexafluorobut-2-yne

Hexafluorobut-2-yne (ca. 1.00g, 6.17 mmol) was condensed onto a THF solution of (241).H2O (0.10g, 0.12 mmol) at -78°C. The stirred solution was allowed to warm to room temperature, during which time, the mixture solidified into a pale brown gel. Desiccation of the gel under vacuum yielded a pale brown powder (0.80g) which was washed with dichloromethane and dried in air. The product was identified as being identical to that obtained from complex (137).H2O with hexafluorobut-2-yne, (Chapter 3), by i.r. spectroscopy.

(e) Reaction of [Pt(N(COMe)CH(CH3)C(O)O)(PPh3)2] (217) with hexafluorobut-2-yne

Hexafluorobut-2-yne (ca. 1.00g, 6.17 mmol) was condensed onto a THF solution of (217) (0.10g, 0.12 mmol) at -78°C. The stirred solution was allowed to warm to room temperature with no evident reaction. Evaporation of the solvent under reduced pressure afforded a colourless oil, which was shown to contain unreacted (217) by 31P-{1H} n.m.r. spectroscopy.
TABLE 13
M.p.'s, analytical\(^a\) and selected i.r.\(^b\) data for the complexes \([\text{Amino Acid}(2-)-\text{N,O}]\text{bis(ligand)platinum(II)}\), derived from N-acetyl, N-formyl and N-trifluoroacetylglutamic and N-acetyl-dl-alanine.

<table>
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<th>Complex</th>
<th>m.p. (°C)</th>
<th>Analysis (%)</th>
<th>(v \text{C=O (cm}^{-1} \text{)} )(^c)</th>
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<td>50.7 (50.7)</td>
<td>4.7 (4.4)</td>
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<tr>
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<td>142</td>
<td>57.9 (58.5)</td>
<td>4.5 (4.5)</td>
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<tr>
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<td>50.5 (50.9)</td>
<td>3.9 (4.1)</td>
</tr>
<tr>
<td>(214)</td>
<td>&gt;220</td>
<td>50.9 (51.4)</td>
<td>4.4 (4.3)</td>
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<tr>
<td>(215)</td>
<td>217</td>
<td>52.2 (52.2)</td>
<td>4.5 (4.3)</td>
</tr>
<tr>
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<td>171</td>
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<td>3.9 (4.1)</td>
</tr>
<tr>
<td>(217)</td>
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<td>58.1 (58.0)</td>
<td>4.6 (4.4)</td>
</tr>
<tr>
<td>(218)</td>
<td>128</td>
<td>50.9 (51.4)</td>
<td>4.6 (4.6)</td>
</tr>
<tr>
<td>(219)</td>
<td>&gt;220</td>
<td>58.8 (58.9)</td>
<td>4.9 (4.7)</td>
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<td>218</td>
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<td>4.7 (4.5)</td>
</tr>
<tr>
<td>(223)</td>
<td>&gt;220</td>
<td>52.7 (52.8)</td>
<td>4.6 (4.7)</td>
</tr>
<tr>
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<tr>
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<td>53.9 (54.1)</td>
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\(^a\) Calculated values given in parentheses; \(^b\) Recorded as KBr discs; \(^c\) All bands s.
<table>
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<tr>
<th>Complex</th>
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<th>Amide</th>
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<td>1580</td>
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<td>1580</td>
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<td>1580</td>
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<tr>
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<td>1580</td>
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<td>1570</td>
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<td>1580</td>
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<td>1570</td>
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<tr>
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<td>1590</td>
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<td>4.7 (4.5) 1.7 (1.7)</td>
<td>1660</td>
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</tr>
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* Calculated values given in parentheses;  
  b Recorded as KBr discs;  
  c All bands s.
### TABLE 15

$^{31}$P-$^1$H n.m.r. data$^a$ for complexes (209)-(223), (239).CH$_2$Cl$_2$ and (240).

<table>
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<th>Complex</th>
<th>$\delta$ P(1)$^b$ (p.p.m.)</th>
<th>$^1$J[PtP(1)] (Hz)</th>
<th>$\delta$ P(2)$^b$ (p.p.m.)</th>
<th>$^1$J[PtP(2)] (Hz)</th>
<th>$^2$J[P(1)P(2)] (Hz)</th>
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</tr>
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<td>(239).CH$_2$Cl$_2$</td>
<td>12.86</td>
<td>3137</td>
<td>6.43</td>
<td>3730</td>
<td>24</td>
</tr>
<tr>
<td>(240)</td>
<td>8.21</td>
<td>3184</td>
<td>4.92</td>
<td>3926</td>
<td>24</td>
</tr>
</tbody>
</table>

$^a$ At 36.2 MHz in dichloromethane, at room temperature;

$^b$ See Figure 16.
### TABLE 16

31P-{1H} n.m.r. data for complexes (224)-(238) and (241)-(243).

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ P(1) (^b) (p.p.m.)</th>
<th>1J[PtP(1)] (Hz)</th>
<th>δ P(2) (^b) (p.p.m.)</th>
<th>1J[PtP(2)] (Hz)</th>
<th>2J[P(1)P(2)] (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(224)</td>
<td>10.36</td>
<td>3044</td>
<td>6.09</td>
<td>4060</td>
<td>25</td>
</tr>
<tr>
<td>(225)</td>
<td>-2.66</td>
<td>3022</td>
<td>-9.99</td>
<td>3889</td>
<td>26</td>
</tr>
<tr>
<td>(226)</td>
<td>8.92</td>
<td>3105</td>
<td>1.80</td>
<td>3936</td>
<td>25</td>
</tr>
<tr>
<td>(227).H(_2)O</td>
<td>-53.85</td>
<td>2612</td>
<td>-67.38</td>
<td>3525</td>
<td>68</td>
</tr>
<tr>
<td>(228)</td>
<td>38.42</td>
<td>3057</td>
<td>27.73</td>
<td>3906</td>
<td>15</td>
</tr>
<tr>
<td>(229).H(_2)O</td>
<td>-8.16</td>
<td>2849</td>
<td>-10.70</td>
<td>3694</td>
<td>35</td>
</tr>
<tr>
<td>(230)</td>
<td>-2.01</td>
<td>2905</td>
<td>9.69</td>
<td>3916</td>
<td>30</td>
</tr>
<tr>
<td>(231).H(_2)O</td>
<td>10.58</td>
<td>3047</td>
<td>5.75</td>
<td>4058</td>
<td>24</td>
</tr>
<tr>
<td>(232).H(_2)O</td>
<td>-4.48</td>
<td>3052</td>
<td>-8.18</td>
<td>3938</td>
<td>27</td>
</tr>
<tr>
<td>(233)</td>
<td>-16.24</td>
<td>3003</td>
<td>-23.30</td>
<td>3770</td>
<td>25</td>
</tr>
<tr>
<td>(234).H(_2)O</td>
<td>-53.85</td>
<td>2639</td>
<td>-68.15</td>
<td>3574</td>
<td>78</td>
</tr>
<tr>
<td>(235).CH(_2)Cl(_2)</td>
<td>38.40</td>
<td>3069</td>
<td>26.58</td>
<td>3931</td>
<td>15</td>
</tr>
<tr>
<td>(236).H(_2)O</td>
<td>-8.17</td>
<td>2869</td>
<td>-12.15</td>
<td>3718</td>
<td>37</td>
</tr>
<tr>
<td>(237).H(_2)O</td>
<td>-3.83</td>
<td>2920</td>
<td>9.48</td>
<td>3960</td>
<td>30</td>
</tr>
<tr>
<td>(238)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(241).H(_2)O</td>
<td>8.48</td>
<td>3316</td>
<td>6.06</td>
<td>3696</td>
<td>29</td>
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<tr>
<td>(242)</td>
<td>-10.34</td>
<td>3025</td>
<td>-12.55</td>
<td>3362</td>
<td>37</td>
</tr>
<tr>
<td>(243).CH(_2)Cl(_2)</td>
<td>-4.43</td>
<td>3140</td>
<td>9.28</td>
<td>3569</td>
<td>30</td>
</tr>
</tbody>
</table>

\(^a\) At 36.2 MHz in dichloromethane, at room temperature;

\(^b\) See Figure 16.
CHAPTER 6

The Synthesis of Further Metallacyclic Complexes of Platinum and Palladium using Silver(I) Oxide
6.1 INTRODUCTION

The successful preparation of four- and five-membered metallacycles using silver(I) oxide led to an investigation into the use of further substrates which may react with this reagent in the presence of a cis-metal dichloride species to produce new ring systems. For a five-membered metallacyclic complex, the pre-requisite for the organic substrate is that it contains 'acidic' hydrogen atoms in a 1,4 relationship, so that on their removal, a metal atom can bridge these two positions, thus forming a ring. Such organic compounds which satisfy this requirement include dl-mandelic acid, 2-acetamidophenol, pyrrole-2-carboxylic acid, oxamide, oxamic acid and mercaptoacetic acid. The amino acid precursors 2-acetamidoacrylic acid and a-acetamidocinnamic acid were also used in these reactions, as was salicylamide, which contains 'acidic' hydrogen atoms in a 1,5 relationship so that a six-membered ring would result on its reaction under the above conditions.

6.2 SYNTHESIS OF METALLACYCLIC COMPLEXES OF PLATINUM AND PALLADIUM

Treatment of cis-[PtCl₂(PPh₃)₂] with one equivalent of dl-mandelic acid and an excess of silver(I) oxide in refluxing dichloromethane afforded complex (253) in high yield.

\[
\begin{align*}
\text{(Ph₃P)₂Pt} & \quad \text{Ph} \\
& \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{C} \quad \text{H} \\
& \quad \text{C} = \text{O}
\end{align*}
\]

(253)

Similarly, complex (254) may be prepared using 2-acetamidophenol, complex (255) using pyrrole-2-carboxylic acid, complex (256) using oxamide and complex (257) using salicylamide.

Treatment of the complexes cis-[PtCl₂L₂] (L = PPh₃, PMePh₂, PMe₂Ph, PBzPh₂; L₂ = dppm, dppe, dppp or dppb) (prepared in situ by the reaction of [PtCl₂(cod)] with either two mole equivalents of L or one equivalent of L₂) with one equivalent of a-acetamidocinnamic acid and an excess of silver(I) oxide in refluxing dichloromethane afforded, in high yield,
the complexes (258)-(265), Scheme 46.

Similarly, complexes (266)-(269) may be prepared using oxamic acid, complexes (270)-(274) using mercaptoacetic acid and complex (275) using 2-acetamidoacrylic acid.

Treatment of complexes cis-[PtCl₂L₂] (L = PPh₃ or L₂ = dppb) with excess silver(I)
oxide and 2-acetamidoacrylic acid in refluxing dichloromethane did not give products analogous to the dppm derivative (275). N.m.r. evidence and a subsequent crystal structure determination on a related analogue showed the products to have the metallaoxacyclopentenone framework, (276) and (280), as shown in Figure 17.

Analogous treatment of complexes [PtCl₂L₂] (L₂ = dppe or dppp) led to the formation of a mixture containing both the isomeric ring systems. When L₂ = dppe, no pure isomer could be isolated, however, when L₂ = dppp, crystallisation from the filtered reaction mixture led to the isolation of pure complex (279). Treatment of the complexes cis-[PtCl₂L₂] (L = PMePh₂ or PMe₂Ph) with 2-acetamidoacrylic acid and excess silver(I) oxide in refluxing dichloromethane, initially led to the formation of complexes (281) and (282), as seen by an appreciation of the platinum-195 coupling constants in their ³¹P-{¹H} n.m.r. spectra. Attempts to isolate these complexes by precipitation or crystallisation, led only to the isolation of complexes (277) and (278) in good yield.

The reason for the formation of the platinaoxacyclopentenone ring system in preference
to the expected product as formed for the dppm derivative (275) is unclear. Evidence from the above preparations indicates that initially, the platinum is bonded to the fragment via oxygen and nitrogen to give a structure of the type (A), Scheme 47.

When \( L_2 = \text{dppm} \), this arrangement is stable, however when other phosphines are present, isomerisation occurs to yield the observed product of structure type (B). Although no mechanistic evidence is available, the transformation can be seen to consist of a 1,3-shift of platinum from nitrogen to carbon followed by a 1,3-shift of hydrogen from that carbon onto nitrogen. When \( L = \text{PPh}_3 \) or \( L_2 = \text{dppb} \), complete isomerisation occurs during the main reaction, but when \( L_2 = \text{dppe} \) or \( \text{dppp} \), there is still a significant proportion of the initially formed product, of structure type (A), in the reaction mixture, even after prolonged
refluxing. When \( L = \text{PMePh}_2 \) or \( \text{PMe}_2\text{Ph} \), isomerisation occurs after filtration of the reaction mixture.

For the chelating phosphine complexes, the size of the ring made by the donor ligand and the metal seems to affect the likelihood of the formation of the metallaoxacyclopentenone ring, i.e. the larger the chelate ring, the more probable isomerisation is to occur. Hence the series:

\[
dppb > dppp > dppe > dpmm
\]

describes the ease of isomerisation of the respective phosphine complexes of structure type (A).

There is no observable isomerisation in any of the complexes (258)-(265), whose structures differ from type (A) (Scheme 47) only in the presence of a phenyl ring on the carbon-carbon double bond. A possible reason may be that steric interactions involving this phenyl ring with the phosphine ligand in the metallaoxacyclopentenone product, Figure 18(i), prevent any transformation.

Figure 18

Similarly, no isomerisation occurs to complex (255), even though the change in structure does not apparently lead to any increase in steric interactions, Figure 18(ii).

The palladium complexes (283) and (284) were obtained in high yield via the treatment of \([\text{PdCl}_2(\text{dppp})]\) with excess silver(I) oxide and either \(\alpha\)-acetamidocinnamic acid or 2-acetamidoacrylic acid respectively, in refluxing dichloromethane.

All the complexes were isolated as microcrystalline, air-stable solids. The complexes (253)-(269) and (275) were white to pale yellow in colour, complexes (270)-(274),

- 191 -
(276)-(280) and (284) were yellow and complex (283) was greeny-yellow.

6.3 STRUCTURAL PROPERTIES OF PLATINAOXACYCLOPENTENONE COMPLEXES

A single crystal X-ray diffraction study was carried out on the platinoaoxacyclopentenone derivative (278) in order to confirm its molecular geometry. Important bond lengths and angles are presented in Table 17 whilst the molecular structure is illustrated in Figure 19, along with the crystallographic numbering system, excepting the methyl and phenyl hydrogen atoms.

The structure consists of a five-membered ring containing a Pt(PMe$_2$Ph)$_2$ moiety. The co-ordination about the platinum atom is essentially square planar, the deviation of the metal atom from the least squares plane defined by itself and its four nearest neighbours being -0.008 Å. The Pt–C(3)–C(2)–C(1)–O(1) ring is effectively planar, O(1) being the most deviated atom from the least squares plane at a distance of 0.031 Å away. The non-hydrogen atoms of the nitrogen bonded side chain deviate only slightly from the plane of the ring, and are orientated such that atoms C(1)–C(2)–N(1)–C(4)–C(5) lie in a ‘W’ conformation.

The Pt–C(3) distance of 2.027(11) Å compares well to that of complex (285) [2.031(14) Å] although the Pt–O(1) distance of 2.086(6) Å is slightly longer [2.061(10) Å for (285)].\textsuperscript{194} The C(2)–C(3) double bond and C(1)–C(2) single bond lengths also agree well with those for (285) and are also comparable to those of metallaoxacyclopentenone complexes of iridium(III) and molybdenum(IV).\textsuperscript{194-196}

However, the C(1)–O(2) and C(1)–O(1) bond distances are significantly longer and
**TABLE 17**

Selected bond lengths and angles for \([\text{Pt}(\text{CH}=\text{C(NCOMe)}\text{C(O)}\text{O})(\text{PMe}_2\text{Ph})_2] (278)\)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – P(1)</td>
<td>2.316 (3)</td>
<td>(\text{P}(1) – \text{Pt} – \text{P}(2))</td>
<td>100.2 (1)</td>
</tr>
<tr>
<td>Pt – P(2)</td>
<td>2.207 (2)</td>
<td>P(1) – Pt – O(1)</td>
<td>87.0 (2)</td>
</tr>
<tr>
<td>Pt – O(1)</td>
<td>2.086 (6)</td>
<td>P(2) – Pt – C(3)</td>
<td>94.6 (3)</td>
</tr>
<tr>
<td>Pt – C(3)</td>
<td>2.027 (11)</td>
<td>C(3) – Pt – O(1)</td>
<td>82.2 (3)</td>
</tr>
<tr>
<td>C(3) – C(2)</td>
<td>1.331 (13)</td>
<td>Pt – C(3) – C(2)</td>
<td>110.5 (8)</td>
</tr>
<tr>
<td>C(2) – C(1)</td>
<td>1.498 (14)</td>
<td>Pt – O(1) – C(1)</td>
<td>111.8 (6)</td>
</tr>
<tr>
<td>C(1) – O(1)</td>
<td>1.267 (11)</td>
<td>O(1) – C(1) – C(2)</td>
<td>117.0 (8)</td>
</tr>
<tr>
<td>C(1) – O(2)</td>
<td>1.244 (10)</td>
<td>C(1) – C(2) – C(3)</td>
<td>118.3 (9)</td>
</tr>
<tr>
<td>C(3) – H(3)</td>
<td>0.82 (8)</td>
<td>C(2) – C(1) – O(2)</td>
<td>120.7 (10)</td>
</tr>
<tr>
<td>C(2) – N(1)</td>
<td>1.420 (12)</td>
<td>O(1) – C(1) – O(2)</td>
<td>122.3 (10)</td>
</tr>
<tr>
<td>N(1) – C(4)</td>
<td>1.346 (15)</td>
<td>C(1) – C(2) – N(1)</td>
<td>111.9 (8)</td>
</tr>
<tr>
<td>C(4) – C(5)</td>
<td>1.498 (15)</td>
<td>C(3) – C(2) – N(1)</td>
<td>129.7 (10)</td>
</tr>
<tr>
<td>C(4) – O(3)</td>
<td>1.233 (13)</td>
<td>C(2) – N(1) – C(4)</td>
<td>129.3 (9)</td>
</tr>
<tr>
<td>P(1) – C(21)</td>
<td>1.794 (5)</td>
<td>N(1) – C(4) – C(5)</td>
<td>113.8 (11)</td>
</tr>
<tr>
<td>P(1) – C(27)</td>
<td>1.800 (10)</td>
<td>N(1) – C(4) – O(3)</td>
<td>124.5 (10)</td>
</tr>
<tr>
<td>P(1) – C(28)</td>
<td>1.837 (11)</td>
<td>C(5) – C(4) – O(3)</td>
<td>121.7 (11)</td>
</tr>
<tr>
<td>P(2) – C(11)</td>
<td>1.803 (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(2) – C(17)</td>
<td>1.817 (11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(2) – C(18)</td>
<td>1.823 (11)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* See Figure 19 for crystallographic numbering system.
Figure 19
Molecular structure of $[\text{Pt} (\text{CH}=\text{C(NHCOMe)}\text{C}(\text{O})\text{O}) (\text{PMe}_2\text{Ph})_2]$ (278).
and shorter respectively than those of previously reported complexes, and are within 0.03 Å of each other.\textsuperscript{194-196} A similar effect was seen for the N-acetylglucinato complex (213), Chapter 5, where this anomaly was explained in terms of a contribution to the structure of a resonance hybrid form. Hence, using the same methodology to account for the irregularity in the carboxylate bond distances of complex (278), there must be a contribution of the hybrid structure (286) to the final description of the complex.

As this effect is not seen in the other metallaoxacyclofenone complexes and that the C(2)–C(3) double bond and C(2)–C(1) single bond lengths compare well to those of the other complexes, then further electron delocalisation throughout the ring can be disregarded. The bond distances within the C(2) acetamido side chain show no great deviation from the expected values for such a group.

The bond angles in complex (278) compare well with the corresponding angles in (285).\textsuperscript{194} The only major difference occurs around C(1), where the angles C(2)–C(1)–O(2) and C(2)–C(1)–O(1) are several degrees removed from the values for complex (285) [124.1(16) and 113.7(15)° respectively].\textsuperscript{194} This may be explained in terms of the irregular bond distances within the carboxylate group slightly altering its molecular geometry with respect to the other complex.
6.4 NMR SPECTRA OF METALLACYCLIC COMPLEXES OF PLATINUM AND PALLADIUM

6.4.1 1H N.m.r. Spectra

The room temperature 1H n.m.r. spectra for all the new ring systems are consistent with the structures shown in Section 6.2.

In complexes (270), (271) and (274), the α-methylene group of the mercaptoacetate ligand appears as either a doublet or a doublet of doublets [4J(PH) in the range 1-3 Hz] with platinum-195 satellites [3J(PtH) = 18-20 Hz]. In the spectrum of complex (273), the signal is too broad to elucidate any coupling and complex (272) is too insoluble for n.m.r. studies.

The spectra of complexes (266)-(269) show the N-H proton as a broad multiplet between δ 4.42 and 5.63 p.p.m., although the two-bond platinum-195 coupling constants can be resolved and lie in the range 100-106 Hz.

The room temperature 1H n.m.r. spectra of complexes (258)-(265) all show a singlet between δ 1.44 and 1.98 p.p.m. due to the N-acetyl methyl group. The signal for the olefinic proton is masked by the signals for the aromatic protons and is not seen in any of the spectra. The 1H n.m.r. spectrum of the dimethylphenylphosphine complex (260) indicates that the four methyl groups of the two phosphine ligands are inequivalent. This is probably caused by the steric interference between the phenyl ring of the chelating fragment and the acetyl function. This may either force the acetyl group to be orientated such that its carbonyl oxygen and methyl carbon are not coincidental with the plane of the five-membered ring, as was seen for the [N-acetylglycinato(2-)N,0] complex (213), or it may force the ring itself to pucker. The effect of this is also indicated by the non-equivalence of the four methylene protons of the benzylidiphenylphosphine ligands in complex (261), and is again shown in the 1H n.m.r. spectrum of the dppm analogue (262), whose temperature dependence is illustrated in Figure 20.

At -30°C, two distinct signals are observed for the dppm methylene protons, each exhibiting both phosphorus-31 and proton coupling. The framework of the dppm chelate ring, Pt–P–C–P, would be expected to be planar,197 hence the non-equivalence of its CH2 protons is unlikely to be due to any puckering of this ring. Thus, the two signals arise from
Figure 20
Variable temperature $^1$H n.m.r. spectra, at 300 MHz, of 
$[\text{Pt}(\text{N(COMe)C(=CHPh)C(O)}\text{O})(\text{dppm})] \ (262)$ in the range 
$\delta \ 3.85-5.05$ p.p.m.
the non-planarity of the $\gamma$-acetamidocinnamato residue with respect to the plane of the Pt(dppm) moiety.

On raising the temperature, the two signals broaden and begin to coalesce until at the high temperature limit (+90°C) just one signal is observed as an overlapping doublet of doublets with platinum-195 satellites. At this limit, the dppm methylene protons are equivalent, probably because the molecule has enough energy to either allow the acetyl group to rotate or to permit the ring to flip. The molecule may then approximate to a planar system, and hence a single resonance is seen.

The room temperature $^1$H n.m.r. spectrum of the related dppm complex (275) shows a sharp doublet of doublets for the dppm methylene protons, indicating that they are equivalent. In this case, there are no steric restrictions confining the chelating dianionic fragment, which may then adopt a planar geometry, making the two methylene protons equivalent.

The room temperature $^1$H n.m.r. spectra of the platinoaxacyclopentenone complexes (276)-(280) all show a sharp singlet for the N-acetyl methyl group. The olefinic proton generally appears as a doublet of doublets, just to high field of the aromatic region of the spectrum, with a $^2J$(PtH) of 112-124 Hz. The signal for the N-H proton of complexes (276)-(280) could not be seen and is presumably hidden underneath the signals for the aromatic protons.

The palladium complexes (283) and (284), have $^1$H n.m.r. spectra consistent with the structures indicated in Section 6.2 and comparable to those of their platinum analogues.

6.4.2 $^{13}$C-$^1$H N.m.r. Spectra

As with the $^1$H n.m.r. spectra, the $^{13}$C-$^1$H n.m.r. spectra are consistent with the structures shown in Section 6.2.

In the spectra of the sufficiently soluble mercaptoacetate complexes (270), (271) and (273), the carbonyl group appears either as a doublet or a doublet of doublets and its $\alpha$-methylene group appears as a singlet. In both cases, coupling to platinum-195 is not discernible.
In complexes (258)-(265), the carbonyl groups appear either as a doublet or a singlet between $\delta$ 170.43 and 178.21 p.p.m. The N-acetyl methyl group appears as a doublet [$^4J(\text{PC}) = 3-4 \text{ Hz}$] in the range of $\delta$ 20.44-21.97 p.p.m. The olefinic carbons could not be confidently assigned due to their positioning within the aromatic region of the spectrum. The methylene carbon of the dppm ligand of complex (262) appears as a doublet of doublets at $\delta$ 46.49 p.p.m.

The ring carbonyl group of the platinoxacyclopentenone complexes (276)-(280) appears as a doublet of doublets, owing to coupling to two inequivalent phosphorus-31 nuclei. The N-acetyl carbonyl group appears as a singlet in the range $\delta$ 167.39-167.95 p.p.m. The olefinic carbon atom bonded to platinum is observed as a doublet of doublets with $^2J(\text{P}_{\text{trans}}\text{C}) = 98-104 \text{ Hz}$ and $^2J(\text{P}_{\text{cis}}\text{C}) = 6-9 \text{ Hz}$. In complex (276) coupling of this signal to platinum-195 is observable with $^1J(\text{PtC}) = 755 \text{ Hz}$. The signal for the other olefinic carbon atom appears within the aromatic region and could not be assigned, whilst the methyl group of the N-acetyl moiety appears as a singlet between $\delta$ 24.19 and 24.46 p.p.m.

The $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectra for the palladium complexes (283) and (284) resemble those of their platinum analogues, taking into consideration the absence of any metal coupling in the spectra.

### 6.4.3 $^{31}\text{P}-\{^1\text{H}\}$ N.m.r. Spectra

The $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectra of all the new complexes, apart from (256) and (272), show an AB spin pattern, with those containing platinum also showing platinum-195 satellites. For complex (256), a singlet was observed with $^1J(\text{PtP})$ 3188 Hz, whilst complex (272) was too insoluble for $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectroscopy.

The signals for the remaining platinum complexes were assigned on the basis of the magnitude of the one-bond platinum-195 coupling constants. As all the complexes contain either a carboxylate or phenolic oxygen atom bound to the platinum, then the phosphorus atom lying trans to this group was labelled P(2). In the $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectra, the highest value of $^1J(\text{PtP})$ for a particular complex was always associated with the signal for P(2).

In the platinoxacyclopentenone complexes (276)-(280), P(1) lies trans to carbon and
\( ^1J[\text{PtP}(1)] \) occurs in the range 1897-2012 Hz whereas \( ^1J[\text{PtP}(2)] \) has values between 3813 and 4153 Hz. For the mercaptoacetate complexes, P(1) is trans to sulphur and \( ^1J[\text{PtP}(1)] \) has values ranging between 2344 and 2848 Hz, whilst \( ^1J[\text{PtP}(2)] \) has a range of 3086-3743 Hz. In complex (253), both P(1) and P(2) lie trans to oxygen, however by comparison of the spectrum with those for other complexes containing a triphenylphosphine ligand opposing a carboxylate group, P(2) was assigned the signal with \( ^1J(\text{PtP}) = 3904 \) Hz, whereas the signal with \( ^1J(\text{PtP}) = 3286 \) Hz was assigned to P(1). The rest of the complexes contain phosphine ligands trans to oxygen and nitrogen. However, there is still a sufficient difference in the size of the platinum-195 coupling constants to assign the signals to P(1) and P(2) without doubt, for example, for complex (266), a resonance at \( \delta \) 9.90 p.p.m., \( ^1J(\text{PtP}) = 3784 \) Hz may be assigned to P(2) and \( \delta \) 11.40 p.p.m., \( ^1J(\text{PtP}) = 3184 \) Hz assigned to P(1).

The \( ^{31}\text{P}-\{^1\text{H}\} \) n.m.r. signals for the two palladium complexes were tentatively assigned on the basis of their relative chemical shifts. In their platinum analogues, the signal for P(1) was generally to low field of that for P(2). Hence, for complex (283), the signal at \( \delta \) 5.34 p.p.m. was assigned to P(2), whilst in complex (284), the signal at \( \delta \) -5.38 p.p.m. was assigned to P(2).

### 6.5 I.R. SPECTRA OF METALLACYCLIC COMPLEXES OF PLATINUM AND PALLADIUM

The i.r. spectra of the new compounds are consistent with the structures shown in Section 6.2. Hence carbonyl absorptions are seen for complex (253) at 1660 cm\(^{-1}\), for (254) at 1600 cm\(^{-1}\) and for complex (255) at 1650 cm\(^{-1}\). The i.r. spectrum for complex (257) shows a carbonyl band at 1600 cm\(^{-1}\) and a peak assigned to the N-H stretch at 3355 cm\(^{-1}\).

The i.r. spectra of compounds (258)-(265) show two carbonyl absorption peaks in the ranges 1580-1600 cm\(^{-1}\) and 1650-1660 cm\(^{-1}\) assigned to the amide and carboxylate stretches respectively. The spectrum of complex (275) is, as expected, similar to those of complexes (258)-(265), carbonyl stretches appearing at 1590 and 1660 cm\(^{-1}\). The spectra of the mercaptoacetate complexes (270)-(274) show a single carbonyl band between 1610 and
For complexes (276)-(280), the i.r. spectra show two carbonyl absorptions, in the ranges 1620-1640 cm\(^{-1}\) and 1670-1680 cm\(^{-1}\) and a peak in the region 3280-3370 assigned to the N-H stretch.

The two palladium complexes, (283) and (284), have i.r. spectra similar to those of their platinum analogues, the N-H and carbonyl frequencies of which occur within the same ranges.

The i.r. spectrum of compound (256) shows two carbonyl absorptions, at 1660 and 1640 cm\(^{-1}\), and an N-H stretch at 3360 cm\(^{-1}\). The spectra for compounds (266)-(269) also show two carbonyl bands, in the range 1700-1640 cm\(^{-1}\), and an N-H stretch between 3370 and 3360 cm\(^{-1}\). However, the i.r. spectra of complexes (256) and (266)-(269) also show a band between 2240 and 2140 cm\(^{-1}\) which is absent in the spectra of the other complexes. This latter absorption may be due to a coupling of two fundamental vibrations which appear in other parts of the spectrum, or it may be related to the zwitterionic structures shown in Figure 21. A similar band has been noted in the i.r. spectra of simple amino acids, and this has been associated with their dipolar structure.\(^{197}\) Precedents for the structures shown in Figure 21 were given by the X-ray crystal structures of compounds (213) and (278), both of which indicated that zwitterionic resonance forms made a contribution to the overall description of the complexes.

![Figure 21](image-url)
6.6 CONCLUSION

The preparation of new metallacyclic complexes of platinum(II) and palladium(II) may be achieved in high yield via the treatment of cis-[MCl₂L₂] (M = Pt or Pd; L = donor ligand) with either d,l-mandelic acid, 2-acetamidophenol, pyrrole-2-carboxylic acid, oxamide, salicylamide, a-acetamidocinnamic acid, oxamic acid or 2-acetamidoacrylic acid in refluxing dichloromethane in the presence of silver(I) oxide. Isomerisation of the initially formed product from the reaction of cis-[MCl₂L₂] (M = Pt, L = PPh₃, PMePh₂, PMe₂Ph₂, L₂ = dppp or dpbb; M = Pd, L₂ = dppp) with 2-acetamidoacrylic acid in the presence of silver(I) oxide, led to the formation of a metallaoxacyclopentenone ring, the structure of which was confirmed by a single crystal X-ray diffraction study. The metallacyclic ring is effectively planar and there is significant electron delocalisation within the carboxylate group. N.m.r. and i.r. studies were used to confirm the structures of the other new complexes.

6.7 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. Variable temperature ¹H n.m.r. spectra were recorded in [₂H₃]-chloroform (-30°C to +30°C) and [₂H₆]-DMSO (+50°C to +90°C), on a Bruker AM-300 spectrometer operating at 300.13 MHz. The ¹³C-¹H n.m.r. data for the aromatic region between δ 140 and 120 p.p.m. are omitted for clarity. The compounds d,l-mandelic acid, 2-acetamidophenol, pyrrole-2-carboxylic acid, oxamide, salicylamide, a-acetamidocinnamic acid, oxamic acid, mercaptoacetic acid, 2-acetamidoacrylic acid, and dpnm (Aldrich) were used as supplied from commercial sources. The compounds [PtCl₂(cod)],¹²³ [PdCl₂(cod)]¹²⁵ and benzylidiphenylphosphine¹⁷⁷ were prepared as described in the literature.

**Preparation of metallacyclic complexes: general method**

Two equivalents of tertiary phosphine or one equivalent of chelating tertiary phosphine, followed by one equivalent of respective organic substrate, and an excess of silver(I) oxide were added in succession to a stirred solution of [MCl₂(cod)] (M = Pt or Pd) in
dichloromethane (ca. 45 cm$^3$), and the mixture was refluxed for 6h. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish-brown oil. Dissolution of the oil in dichloromethane (ca. 5 cm$^3$) followed by addition of light petroleum afforded, on standing, a white to yellow microcrystalline solid, which was recrystallised from dichloromethane - light petroleum, and dried in vacuo.

(i) $\text{[Pt(O}(\text{OC}(\text{H})\text{PhC(O))})\text{(PPh}_3)_2\text{]}(253)\text{.H}_2\text{O}$

The complex $\text{[PtCl}_2\text{(cod)] (0.10 g, 0.27 mmol)}$ with triphenylphosphine (0.15 g, 0.57 mmol) and $dl$-mandelic acid (0.045 g, 0.29 mmol) gave white microcrystals of $\text{(253).H}_2\text{O}$ (0.22 g, 92%). (Found: C, 59.7; H, 4.3. $\text{C}_{44}\text{H}_{36}\text{O}_3\text{P}_2\text{Pt.H}_2\text{O}$ requires C, 59.5; H, 4.3%), m.p. 123°C; v$\text{C=O}$ at 1660s cm$^{-1}$. N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 7.87-6.96 (m, 35 H, Ph), 5.53 [d, 1H, C-H, $^1\text{J}$(PH) 8, $^3\text{J}$(PtH) 43], 2.20 (s, br, 2H, H$_2$O); $^{13}\text{C}$-[1H], $\delta$ 190.65 [dd, CO, $^3\text{J}$(PC) 4, 7], 81.65 [d, CH, $^3\text{J}$(PC) 2]; $^{31}\text{P}$-[1H] (36.2 MHz); $\delta$ 10.87 [d, P(2), $^1\text{J}$(PtP(2)] 3904, $^2\text{J}$(P(1)P(2)] 27), and 9.69 p.p.m. [d, P(1), $^1\text{J}$(PtP(1)] 3286, $^2\text{J}$(P(2)P(1)] 27).

(ii) $\text{[Pt(o-N(COMe)C=H=CC(G)G)(PPh}_3)_2\text{]}(254)$

The complex $\text{[PtCl}_2\text{(cod)] (0.10 g, 0.27 mmol)}$ with triphenylphosphine (0.15 g, 0.57 mmol) and 2-acetamidophenol (0.045 g, 0.30 mmol) gave white microcrystals of (254) (0.20 g, 85%). (Found: C, 60.9; H, 4.4; N, 1.8. $\text{C}_{44}\text{H}_{37}\text{NO}_2\text{P}_2\text{Pt}$ requires C, 60.8; H, 4.3; N, 1.6%), m.p. Above 220°C; v$\text{C=O}$ at 1600s cm$^{-1}$. N.m.r. spectra: $^1\text{H}$ (90 MHz), $\delta$ 7.8-6.1 (m, 34 H, Ph), 1.7 (s, 3H, CH$_3$); $^{13}\text{C}$-[1H], $\delta$ 171.22 (s, CO), 21.35 [d, CH$_3$, $^4\text{J}$(PC) 4]; $^{31}\text{P}$-[1H] (36.2 MHz); $\delta$ 10.80 [d, P(1), $^1\text{J}$(PtP(1)] 3184, $^2\text{J}$(P(2)P(1)] 22], and 3.40 p.p.m. [d, P(2), $^1\text{J}$(PtP(2)] 3798, $^2\text{J}$(P(1)P(2)] 22).

(iii) $\text{[Pt(NCH=CH=CC(O))}(\text{PPh}_3)_2\text{]}(255)\text{.H}_2\text{O}$

The complex $\text{[PtCl}_2\text{(cod)] (0.10 g, 0.27 mmol)}$ with triphenylphosphine (0.15 g, 0.57 mmol) and pyrrole-2-carboxylic acid (0.03 g, 0.27 mmol) gave white microcrystals of (255).H$_2$O (0.22 g, 96%). (Found: C, 57.9; H, 3.9; N, 1.7. $\text{C}_{44}\text{H}_{33}\text{NO}_2\text{P}_2\text{Pt.H}_2\text{O}$ requires C, 58.2; H, 4.1; N, 1.7%), m.p. Above 220°C; v$\text{C=O}$ at 1650s cm$^{-1}$. N.m.r. spectra: $^1\text{H}$ (300 MHz), $\delta$ 7.49-7.11 (m, 30H, Ph), 6.64 (m, 1H, CH), 5.75 (m, 1H, CH), 5.28 (m, 1H, CH),
1.91 (s, br, 2H, H₂O); ¹³C-{¹H}, too insoluble; ³¹P-¹H) (36.2 MHz); δ 14.87 {d, P(1),
¹¹P(1)] 3313, ²J[P(2)P(1)] 24}, and 5.95 p.p.m. {d, P(2), ¹¹P(2)] 3599, ²J[P(1)P(2)]
24}.

(iv) \([\textit{Pt}\{\textit{N(H)(O)(O)NH}\}(\text{PPh}_3)_2\}\)(256).CHCl₃

The complex \([\textit{PtCl}_2\text{(cod)}]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57
mmol) and oxamide (0.025g, 0.28 mmol) gave white microcrystals which were
recrystallised from a saturated chloroform solution to give white crystals of (256).CHCl₃
(0.21g, 84%). (Found: C, 51.3; H, 3.5; N, 3.2. C₃₈H₃₂N₂O₂P₂Pt.CHCl₃ requires C, 50.6;
H, 3.6; N, 3.0%), m.p. 129°C; νₚₙ at 3360 cm⁻¹; ν₋ₓ at 2180 cm⁻¹; νₓ at 1660s and
1640s cm⁻¹. N.m.r. spectra: ¹H (90 MHz), δ 7.9-6.6 (m, 31H, Ph + CHCl₃), 4.9 [m, 2H,
NH, ²J(PtH) 77]; ¹³C-{¹H}, δ 168.51 (s, CO), 77.27 (s, CHCl₃); ³¹P-¹H) (36.2 MHz); δ
13.19 p.p.m. {s, PPh₃, ¹¹P(1)}1887.

(v) \([\textit{Pt}\{\textit{o-N(H)(C(O)(C=CHPh)C(0)O)}\}](\text{PPh}_3)_2\}\)(257).CH₂Cl₂

The complex \([\textit{PtCl}_2\text{(cod)}]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57
mmol) and salicylamide (0.04g, 0.29 mmol) gave white microcrystals of (257).CH₂Cl₂
(0.24g, 95%). (Found: C, 56.4; H, 4.1; N, 1.4. C₄₃H₃₅NO₂P₂Pt.CH₂Cl₂ requires C, 56.2;
H, 3.9; N, 1.5%), m.p. Above 220°C; νₚₙ at 3355 cm⁻¹; νₓ at 1600s cm⁻¹. N.m.r.
spectra: ¹H (300 MHz), δ 7.99-5.75 (m, 34H, Ph), 5.33 (s, 2H, CH₂Cl₂), 4.94 [d, 1H, N-H,
³J(PH) 6, ²J(PtH) 30]; ¹³C-{¹H}, δ 166.08 [d, CO, ³J(PC) 3], 54.19 (s, CH₂Cl₂); ³¹P-¹H)
(36.2 MHz); δ 16.37 {d, P(1), ¹¹P(1)] 3138, ²J[P(2)P(1)] 24}, and 11.98 p.p.m. {d, P(2),
¹¹P(2)] 24}.

(vi) \([\textit{Pt}\{\textit{N(COMe)(C=CHPh)(C(O)O)}\}](\text{PPh}_3)_2\}\)(258).H₂O

The complex \([\textit{PtCl}_2\text{(cod)}]\) (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57
mmol) and α-acetamidocinnamic acid (0.06g, 0.29 mmol) gave white microcrystals of
(258).H₂O (0.22g, 87%). (Found: C, 60.5; H, 4.4; N, 1.3. C₄₇H₃₉NO₃P₂Pt.H₂O requires C,
60.5; H, 4.4; N, 1.5%), m.p. Above 220°C; νₓ at 1650s and 1600s cm⁻¹. N.m.r. spectra:
¹H (300 MHz), δ 8.29-6.87 (m, 36H, Ph + =CH), 2.00 (s, br, 2H, H₂O), 1.53 (s, 3H, CH₃);
\[ ^{13}\text{C}-\{\text{H}\}, \delta \ 176.72 \text{ [d, CO, } ^{3}\text{J(PC)  3]}, 172.55 \text{ (s, CO)}, 21.97 \text{ (s, CH}_{3}\text{); } ^{31}\text{P}-\{\text{H}\} \ (36.2 \text{ MHz}); \delta \ 10.18 \text{ (d, P(1), } ^{1}\text{J[PtP(1)] } 3198, \ ^{2}\text{J[P(2)P(1)] } 24), \text{ and } 5.95 \text{ p.p.m. (d, P(2), } ^{1}\text{J[PtP(2)] } 4063, ^{2}\text{J[P(1)P(2)] } 24). \]

(vii) \[ [\text{Pt}\{\text{N(COMe)}C(=CHPh)C(O)O\}](\text{PMePh}_{2})_{2}] (259).\text{H}_{2}\text{O} \]

The complex \([\text{PtCl}_{2}(\text{cod})] \ (0.10 \text{g, 0.27 mmol}) \) with methyldiphenylphospine \((0.11 \text{g, 0.55 mmol}) \) and \(\alpha\)-acetamidocinnamic acid \((0.06 \text{g, 0.29 mmol}) \) gave white microcrystals of \((259).\text{H}_{2}\text{O} (0.18 \text{g, 82%}). \) (Found: C, 54.4; H, 4.4; N, 1.7. \( \text{C}_{37}\text{H}_{35}\text{NO}_{3}\text{P}_{2}\text{Pt.H}_{2}\text{O} \) requires C, 54.4; H, 4.5; N, 1.7%). m.p. 199°C; \( \nu_{\text{C=O}} \) at 1650s and 1580s cm\(^{-1}\). N.m.r. spectra: \( ^{1}\text{H} \) \((300 \text{ MHz}), \delta \ 7.78-7.11 \) \( \text{m, 26H, Ph } + \text{ =CH}) \), 2.17 \( \text{d, 3H, Me, PMePh}_{2}, \ ^{2}\text{J(PH) } + ^{4}\text{J(PH)} \) 12, \( ^{3}\text{J(PtH)} \) 32, 1.00 \( \text{br, 2H, H}_{2}\text{O}) \), 1.72 \( \text{s, 3H, CH}_{3}\), 1.72 \( \text{d, 3H, Me, PMePh}_{2}, \ ^{2}\text{J(PH) } + ^{4}\text{J(PH)} \) 11, \( ^{3}\text{J(PtH)} \) 27; \( ^{13}\text{C}-\{\text{H}\}, \delta \ 176.57 \) \[ \text{d, CO, } ^{3}\text{J(PC) 4}], 173.02 \text{ (s, CO)}, 21.50 \text{ [d, CH}_{3}\), \( ^{4}\text{J(PC) 4}], 15.80 \text{ [d, Me, PMePh}_{2}, \ ^{1}\text{J(PC) } + ^{3}\text{J(PC)] 46}], 13.36 \text{ [d, Me, PMePh}_{2}, \ ^{1}\text{J(PC) } + ^{3}\text{J(PC)] 40], } ^{31}\text{P}-\{\text{H}\} \ (36.2 \text{ MHz}); \delta \ -3.63 \text{ (d, P(1), } ^{1}\text{J[PtP(1)] } 3154, \ ^{2}\text{J[P(2)P(1)] } 25), \text{ and } -8.97 \text{ p.p.m. (d, P(2), } ^{1}\text{J[PtP(2)] } 3889, ^{2}\text{J[P(1)P(2)] } 25). \]

(viii) \[ [\text{Pt}\{\text{N(COMe)}C(=CHPh)C(O)O\}](\text{PMe}_{2}\text{Ph})_{2}] (260).\text{H}_{2}\text{O} \]

The complex \([\text{PtCl}_{2}(\text{cod})] \ (0.10 \text{g, 0.27 mmol}) \) with dimethylphenylphosphine \((0.08 \text{g, 0.58 mmol}) \) and \(\alpha\)-acetamidocinnamic acid \((0.06 \text{g, 0.29 mmol}) \) gave white microcrystals of \((260).\text{H}_{2}\text{O} (0.16 \text{g, 86%}). \) (Found: C, 46.9; H, 4.4; N, 2.2. \( \text{C}_{27}\text{H}_{31}\text{NO}_{3}\text{P}_{2}\text{Pt.H}_{2}\text{O} \) requires C, 46.8; H, 4.8; N, 2.0%). m.p. 111°C; \( \nu_{\text{C=O}} \) at 1660s and 1580s cm\(^{-1}\). N.m.r. spectra: \( ^{1}\text{H} \) \((300 \text{ MHz}), \delta \ 7.60-7.15 \) \( \text{m, 16H, Ph } + \text{ =CH}) \), 2.48 \( \text{s, br, 2H, H}_{2}\text{O}) \), 1.95 \( \text{d, 3H, Me, PMe}_{2}\text{Ph}, \ ^{2}\text{J(PH) } + ^{4}\text{J(PH)} \) 12, \( ^{3}\text{J(PtH)} \) 30, 1.87 \( \text{s, 3H, CH}_{3}\), 1.63 \( \text{d, 3H, Me, PMe}_{2}\text{Ph}, \ ^{2}\text{J(PH) } + ^{4}\text{J(PH)} \) 11, \( ^{3}\text{J(PtH)} \) 26), 1.46 \( \text{d, 3H, Me, PMe}_{2}\text{Ph}, \ ^{2}\text{J(PH) } + ^{4}\text{J(PH)} \) 11, \( ^{3}\text{J(PtH)} \) 25; \( ^{13}\text{C}-\{\text{H}\}, \delta \ 176.33 \text{ (s, CO)}, 173.93 \text{ (s, CO)}, 21.73 \text{ [d, CH}_{3}\), \( ^{4}\text{J(PC) 4}], 19.20 \text{ [d, Me, PMe}_{2}\text{Ph, } ^{1}\text{J(PC) } + ^{3}\text{J(PC)] 46}], 11.91 \text{ [d, Me, PMe}_{2}\text{Ph, } ^{1}\text{J(PC) } + ^{3}\text{J(PC)] 41], 11.48 \text{ [d, Me, PMe}_{2}\text{Ph, } ^{1}\text{J(PC) } + ^{3}\text{J(PC)] 40}], 11.35 \text{ [d, Me, PMe}_{2}\text{Ph, } ^{1}\text{J(PC) } + ^{3}\text{J(PC) 43], } ^{31}\text{P}-\{\text{H}\} \ (36.2 \text{ MHz}); \delta \ -16.19 \text{ (d, P(1), } ^{1}\text{J[PtP(1)] } 3105, ^{2}\text{J[P(2)P(1)] } 24), \text{ and } 21.40 \text{ p.p.m. (d, P(2), } ^{1}\text{J[PtP(2)] } 3745, ^{2}\text{J[P(1)P(2)] } 24). \)
The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with benzyldiphenylphosphine (0.16g, 0.58 mmol) and \(\alpha\)-acetamidocinnamic acid (0.06g, 0.29 mmol) gave white microcrystals of \((261)\).CH\(_2\)Cl\(_2\) (0.25g, 89\%). (Found: C, 57.7; H, 4.4; N, 1.4. \(C_{49}H_{43}NO_3P_2Pt.CH_2Cl_2\) requires C, 58.0; H, 4.4; N, 1.4\%), m.p. Above 220°C; \(\nu\text{C=O}\) at 1660s and 1600s cm\(^{-1}\). N.m.r. spectra: \(\delta\) 7.88-6.31 (m, 36H, Ph + =CH), 5.25 (s, 2H, CH\(_2\)), 4.56 [dd, 1H, CH\(_2\), PBzPh\(_2\), \(^2\)J(PH) 13, \(^2\)J(HH) 13], 4.16 [dd, 1H, CH\(_2\), PBzPh\(_2\), \(^2\)J(PH) 13, \(^2\)J(HH) 12], 3.90 [dd, 1H, CH\(_2\), PBzPh\(_2\), \(^2\)J(PH) 13, \(^2\)J(HH) 12], 3.54 [dd, 1H, CH\(_2\), PBzPh\(_2\), \(^2\)J(PH) 13, \(^2\)J(HH) 13], 1.98 (s, 3H, CH\(_3\)); \(\delta\) 176.22 [d, CO, \(^3\)J(PC) 2], 173.57 (s, CO), 53.33 (s, CH\(_2\)Cl\(_2\)), 39.63 [d, CH\(_2\), PBzPh\(_2\), \(^1\)J(PC) 35], 34.20 [d, CH\(_2\), PBzPh\(_2\), \(^1\)J(PC) 32], 21.89 [d, CH\(_3\), \(^4\)J(PC) 4]; \(\delta\) 8.51 (d, P(1), \(^1\)J[PtP(1)] 3245, \(^2\)J[P(2)P(1)] 22), and 3.60 p.p.m. (d, P(2), \(^1\)J[PtP(2)] 3945, \(^2\)J[P(2)P(2)] 22).

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and \(\alpha\)-acetamidocinnamic acid (0.06g, 0.29 mmol) gave white microcrystals of \((262)\).H\(_2\)O (0.20g, 93\%). (Found: C, 54.1; H, 4.0; N, 1.8. \(C_{36}H_{31}NO_3P_2Pt.H_2O\) requires C, 54.0; H, 4.1; N, 1.8\%), m.p. 216°C; \(\nu\text{C=O}\) at 1650s and 1590s cm\(^{-1}\). N.m.r. spectra: \(\delta\) 7.71-6.95 (m, 26H, Ph + =CH), 4.38 (m, br, 2H, CH\(_2\), dppm), 2.38 (s, br, 2H, H\(_2\)O), 1.53 (s, 3H, CH\(_3\)); \(\delta\) 4.82 [ddd, 1H, CH\(_2\), dppm, \(^2\)J(PH) 10,10, \(^2\)J(HH) 16], 4.07 [ddd, 1H, CH\(_2\), dppm, \(^2\)J(PH) 12,12, \(^2\)J(HH) 16]; \(\delta\) 4.42 [dd, 2H, CH\(_2\), dppm, \(^2\)J(PH) 11,11, \(^3\)J(PtH) 62]; \(\delta\) 178.21 [d, CO, \(^3\)J(PC) 2], 172.37 (s, CO), 46.49 [dd, CH\(_2\), dppm, \(^1\)J(PC) 33,33], 20.77 [d, CH\(_3\), \(^4\)J(PC) 3]; \(\delta\) -53.94 (d, P(1), \(^1\)J[PtP(1)] 2700, \(^2\)J[P(2)P(1)] 73), and -61.21 p.p.m. (d, P(2), \(^1\)J[PtP(2)] 3438, \(^2\)J[P(1)P(2)] 73).

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and \(\alpha\)-acetamidocinnamic acid (0.06g, 0.29 mmol) gave white microcrystals of \((263)\).CH\(_2\)Cl\(_2\)
(0.22g, 92%). (Found: C, 51.7; H, 4.1; N, 1.7. \(\text{C}_{37}\text{H}_{33}\text{NO}_{3}\text{P}_{2}\text{Pt.CH}_{2}\text{Cl}_{2}\) requires C, 51.8; H, 4.0; N, 1.6%). m.p. Above 220°C; \(\nu_{C=O}\) at 1650s and 1600s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 8.02-6.80 (m, 26H, Ph + =CH), 5.26 (s, 2H, \text{CH}_{2}\text{Cl}_2), 2.66-2.15 (m, 4H, \text{CH}_2, dppe), 1.46 (s, 3H, \text{CH}_3); \(^{13}\text{C}\{-^1\text{H}\}, \delta 177.26 [d, \text{CO}, ^3(J\text{PC}) 2], 170.43 (s, \text{CO}), 53.42 (s, \text{CH}_2\text{Cl}_2), 34.24 [dd, \text{CH}_2, \text{dppe}, ^1\text{J(\text{PC}) 42, ^3\text{J(\text{PC}) 11}], 23.65 [dd, \text{CH}_2, \text{dppe}, ^1\text{J(\text{PC}) 41, ^3\text{J(\text{PC}) 7]}, 20.44 [d, \text{CH}_3, ^4\text{J(\text{PC}) 4}; ^3\text{P}\{-^1\text{H}\} (36.2 MHz); \(\delta\) 39.91 [d, \text{P(1), ^1\text{J(PtP(1)) 3155, ^2\text{J(P(2)P(1)) 12}], and 30.15 p.p.m. [d, \text{P(2), ^1\text{J(PtP(2)) 3865, ^2\text{J(P(1)P(2)) 12].}

(xii) \(\text{[Pt(N(COMe)C(=CHPh)C(=O)O)(dppp)] (264).H}_2\text{O}\)

The complex \([\text{PtCl}_2(\text{cod})] (0.10g, 0.27 mmol) with \text{dppp} (0.12g, 0.29 mmol) and \(\alpha\)-acetamidocinnamic acid (0.06g, 0.29 mmol) gave white microcrystals of (264).\(\text{H}_2\text{O}\) (0.20g, 89%). (Found: C, 55.3; H, 4.3; N, 1.7. \(\text{C}_{38}\text{H}_{35}\text{NO}_{3}\text{P}_{2}\text{Pt.H}_2\text{O}\) requires C, 54.9; H, 4.4; N, 1.7%), m.p. Above 220°C; \(\nu_{C=O}\) at 1660s and 1590s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.83-6.79 (m, 26H, Ph + =CH), 2.66-1.97 (m, 8H, \text{CH}_2, \text{dppp} + \text{H}_2\text{O}), 1.44 (s, 3H, \text{CH}_3); \(^{13}\text{C}\{-^1\text{H}\}, \delta 176.83 [d, \text{CO}, ^3(J\text{PC}) 2], 170.78 (s, \text{CO}), 28.46 [dd, \text{P-CH}_2, \text{dppp}, ^1\text{J(\text{PC}) 32, ^3\text{J(\text{PC}) 8]}, 23.38 [dd, \text{P-CH}_2, \text{dppp}, ^1\text{J(\text{PC}) 38, ^3\text{J(\text{PC}) 4}], 20.87 [d, \text{CH}_3, ^4\text{J(\text{PC}) 3}], 18.83 (s, \text{CH}_2, \text{dppp}); ^3\text{P}\{-^1\text{H}\} (36.2 MHz); \(\delta\) -9.33 [d, \text{P(1), ^1\text{J(PtP(1)) 2966, ^2\text{J(P(2)P(1)) 35], and -11.42 p.p.m. [d, \text{P(2), ^1\text{J(PtP(2)) 3696, ^2\text{J(P(1)P(2)) 35].}

(xiii) \(\text{[Pt(N(COMe)C(=CHPh)C(=O)O)(dppb)] (265)}\)

The complex \([\text{PtCl}_2(\text{cod})] (0.10g, 0.27 mmol) with \text{dppb} (0.12g, 0.28 mmol) and \(\alpha\)-acetamidocinnamic acid (0.06g, 0.29 mmol) gave white microcrystals of (265) (0.21g, 94%). (Found: C, 56.6; H, 4.4; N, 1.8. \(\text{C}_{39}\text{H}_{37}\text{NO}_{3}\text{P}_{2}\text{Pt}\) requires C, 56.8; H, 4.5; N, 1.7%), m.p. Above 220°C; \(\nu_{C=O}\) at 1650s and 1580s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.87-6.79 (m, 26H, Ph + =CH), 3.16 (m, 2H, P-CH\(_2\), dppb), 2.66 (m, 2H, P-CH\(_2\), dppb), 2.14 (m, 4H, CH\(_2\), dppb), 1.52 (s, 3H, CH\(_3\)); \(^{13}\text{C}\{-^1\text{H}\}, \delta 177.02 [d, \text{CO}, ^3(J\text{PC}) 3], 171.84 (s, \text{CO}), 27.77 [d, \text{P-CH}_2, \text{dppb}, ^1\text{J(\text{PC}) 38], 25.48 [d, \text{CH}_2, \text{dppb}, ^2\text{J(\text{PC}) 4], 24.14 [d, \text{P-CH}_2, \text{dppb}, ^1\text{J(\text{PC}) 37], 21.57 (s, \text{CH}_2, \text{dppb}), 21.12 [d, \text{CH}_3, ^4\text{J(\text{PC}) 4]; ^3\text{P}\{-^1\text{H}\} (36.2 MHz); \(\delta\) 8.67 [d, \text{P(2), ^1\text{J(PtP(2)) 3892, ^2\text{J(P(1)P(2)) 30}, and -2.43 p.p.m. (d, \text{P(1),}}

- 207 -
$^{1}J[PtP(1)] \, 3047, \, ^{2}J[P(2)P(1)] \, 30$. 

(xiv) $[Pt\{N(H)C(O)C(O)O\}(PPh_{3})_{2}] \, (266) \cdot H_{2}O$

The complex $[PtCl_{2}(cod)]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and oxamic acid (0.025g, 0.28 mmol) gave white microcrystals of (266)$ \cdot H_{2}O$ (0.21g, 94%). (Found: C, 55.5; H, 3.8; N, 1.7. C$_{38}$H$_{31}$NO$_{3}$P$_{2}$Pt.H$_{2}$O requires C, 55.3; H, 4.0; N, 1.7%), m.p. Above 220°C; $v_{N-H}$ at 3360 cm$^{-1}$; $v_{\text{max}}$ at 2140 cm$^{-1}$; $v_{C=O}$ at 1700s and 1640s cm$^{-1}$. N.m.r. spectra: $^{1}H$ (90 MHz), $\delta$ 7.9-6.6 (m, 30H, Ph), 4.7 [m, 1H, N-H, $^2J$(PtH) 105], 2.0 (s, br, 2H, H$_{2}$O); $^{13}$C-{$^1H$}, $\delta$ 168.01 (s, CO), 166.17 (s, CO); $^{31}$P-{$^1H$} (36.2 MHz); $\delta$ 11.40 [d, P(1), $^1J[PtP(1)]$ 3184, $^2J[P(2)P(1)]$ 25], and 9.90 p.p.m. [d, P(2), $^1J[PtP(2)]$ 3784, $^2J[P(1)P(2)]$ 25].

(xv) $[Pt\{N(H)C(O)C(O)O\}(dppe)] \, (267)$

The complex $[PtCl_{2}(cod)]$ (0.10g, 0.27 mmol) with dppe (0.11g, 0.28 mmol) and oxamic acid (0.025g, 0.28 mmol) gave white microcrystals of (267) (0.18g, 98%). (Found: C, 49.0; H, 3.8; N, 2.2. C$_{28}$H$_{25}$NO$_{3}$P$_{2}$Pt requires C, 49.4; H, 3.7; N, 2.1%), m.p. Above 220°C; $v_{N-H}$ at 3360 cm$^{-1}$; $v_{\text{max}}$ at 2220 cm$^{-1}$; $v_{C=O}$ at 1690s and 1640s cm$^{-1}$. N.m.r. spectra: $^1H$ (300 MHz), $\delta$ 7.88-7.26 (m, 20H, Ph), 5.63 [m, 1H, N-H, $^2J$(PtH) 106], 2.61-2.33 (m, 4H, CH$_2$, dppe); $^{13}$C-{$^1H$}, too insoluble; $^{31}$P-{$^1H$} (300 MHz); $\delta$ 32.56 [d, P(2), $^1J[PtP(2)]$ 3605, $^2J[P(1)P(2)]$ 11], and 31.70 p.p.m. [d, P(1), $^1J[PtP(1)]$ 3150, $^2J[P(2)P(1)]$ 11].

(xvi) $[Pt\{N(H)C(O)C(O)O\}(dppp)] \, (268) \cdot CH_{2}Cl_{2}$

The complex $[PtCl_{2}(cod)]$ (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and oxamic acid (0.025g, 0.28 mmol) gave white microcrystals of (268)$ \cdot CH_{2}Cl_{2}$ (0.19g, 90%). (Found: C, 44.7; H, 3.6; N, 1.8. C$_{29}$H$_{27}$NO$_{3}$P$_{2}$Pt.CH$_{2}$Cl$_{2}$ requires C, 44.7; H, 3.7; N, 1.8%), m.p. Above 220°C; $v_{N-H}$ at 3360 cm$^{-1}$; $v_{\text{max}}$ at 2240 cm$^{-1}$; $v_{C=O}$ at 1690s and 1640s cm$^{-1}$. N.m.r. spectra: $^1H$ (90 MHz), $\delta$ 7.7-6.8 (m, 20H, Ph), 5.25 [m, 2H, CH$_2$Cl$_2$], 4.9 [m, 1H, N-H, $^2J$(PtH) 105], 2.9-1.7 (m, 6H, CH$_2$, dppp); $^{13}$C-{$^1H$}, $\delta$ 168.50 (s, CO), 166.39 (s, CO), 53.31 (s, CH$_2$Cl$_2$), 24.20 (m, P-CH$_2$, dppp), 18.87 (s, CH$_2$, dppp); $^{31}$P-{$^1H$} (36.2 MHz); $\delta$ -7.26 [d, P(2), $^1J[PtP(2)]$ 3447, $^2J[P(1)P(2)]$ 35], and -9.38 p.p.m. [d, P(1), $^1J[PtP(1)]$ 2949,
The complex [PtCl\(_2\)(cod)] (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and oxamic acid (0.025g, 0.28 mmol) gave white microcrystals of (269) (0.17g, 89%). (Found: C, 50.5; H, 4.1; N, 2.0. C\(_{30}\)H\(_{29}\)NO\(_3\)P\(_2\)Pt requires C, 50.8; H, 4.1; N, 2.0%), m.p. Above 220°C; \(v_{\text{N-H}}\) at 3370 cm\(^{-1}\); \(v_{\text{max}}\) at 2200 cm\(^{-1}\); \(v_{\text{C-O}}\) at 1690s and 1650s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.78-7.10 (m, 20H, Ph), 4.42 [m, 1H, N-H, \(^2\text{J}(\text{Pt-H})\) 100], 2.76 (m, 4H, P-CH\(_2\), dppb), 2.31 (m, 4H, CH\(_2\), dppb); \(^1\text{H}\) of (269) too insoluble; \(^3\text{P}\{-^1\text{H}\}\) (36.2 MHz); \(\delta\) 12.10 (d, P(2), \(^1\text{J}(\text{Pt-P(2)})\) 3660, \(^2\text{J}(\text{P(1)-P(2)})\) 29), and -2.30 p.p.m. (d, P(1), \(^1\text{J}(\text{Pt-P(1)})\) 2988, \(^2\text{J}(\text{P(2)-P(1)})\) 29).

(xviii) \([\text{Pt}(\text{SCH}_2\text{C(O)O})\text{(PPh}_3\text{)}_2]\) (270), CH\(_2\)Cl\(_2\)

The complex [PtCl\(_2\)(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and mercaptoacetic acid (0.025g, 0.27 mmol) gave yellow microcrystals of (270).CH\(_2\)Cl\(_2\) (0.21g, 87%). (Found: C, 53.3; H, 3.5. C\(_{38}\)H\(_{32}\)O\(_2\)P\(_2\)PtS.CH\(_2\)Cl\(_2\) requires C, 52.4; H, 3.8%), m.p. 147°C; \(v_{\text{C-O}}\) at 1650s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.58-7.12 (m, 30H, Ph), 5.33 (s, 2H, CH\(_2\)Cl\(_2\)), 3.60 [dd, 2H, CH\(_2\)], \(^4\text{J}(\text{PH})\) 1, \(^3\text{J}(\text{Pt-H})\) 18; \(^1\text{C}\{-^1\text{H}\}, \(\delta\) 190.68 [d, CO, \(^3\text{J}(\text{PC})\) 10], 53.25 (s, CH\(_2\)Cl\(_2\)), 30.41 (s, CH\(_2\)); \(^3\text{P}\{-^1\text{H}\}\) (36.2 MHz); \(\delta\) 21.68 (d, P(1), \(^1\text{J}(\text{Pt-P(1)})\) 2898, \(^2\text{J}(\text{P(1)-P(2)})\) 23), and 11.20 p.p.m. (d, P(2), \(^1\text{J}(\text{Pt-P(2)})\) 3743, \(^2\text{J}(\text{P(1)-P(2)})\) 23).

(xix) \([\text{Pt}(\text{SCH}_2\text{C(O)O})(\text{dppm})]\) (271), CH\(_2\)Cl\(_2\)

The complex [PtCl\(_2\)(cod)] (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and mercaptoacetic acid (0.025g, 0.27 mmol) gave yellow microcrystals of (271).CH\(_2\)Cl\(_2\) (0.18g, 88%). (Found: C, 44.5; H, 3.4. C\(_{27}\)H\(_{24}\)O\(_2\)P\(_2\)PtS.CH\(_2\)Cl\(_2\) requires C, 44.6; H, 3.4%), m.p. Above 220°C; \(v_{\text{C-O}}\) at 1610s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta\) 7.90-7.00 (m, 20H, Ph), 5.30 (s, 2H, CH\(_2\)Cl\(_2\)), 4.49 [dd, 2H, CH\(_2\), dppm, \(^2\text{J}(\text{PH})\) 11, \(^3\text{J}(\text{Pt-H})\) 53], 3.70 [d, 2H, CH\(_2\)], \(^4\text{J}(\text{PH})\) 3, \(^3\text{J}(\text{Pt-H})\) 20]; \(^1\text{C}\{-^1\text{H}\}, \(\delta\) 192.44 [dd, CO, \(^3\text{J}(\text{PC})\) 3, \(^1\text{J}(\text{PC})\) 31, \(^6\text{J}(\text{PC})\) 31], 53.29 (s, CH\(_2\)Cl\(_2\)), 43.06 [dd, CH\(_2\), dppm, \(^1\text{J}(\text{PC})\) 31, \(^6\text{J}(\text{PC})\) 31], 28.34 (s, CH\(_2\)); \(^3\text{P}\{-^1\text{H}\}\) (36.2 MHz); \(\delta\)
-44.87 \{d, P(1), ^1J(PtP(1)) 2344, ^2J(P(2)P(1)) 73\}, and -55.37 p.p.m. \{d, P(2), ^1J(PtP(2)) 3086, ^2J(P(1)P(2)) 73\}.

\((xx)\) \([\text{Pt}\{\text{SCH}_2\text{C(O)O}\}\{\text{dppe}\}\](272)\cdot\text{CH}_2\text{Cl}_2\)

The complex \([\text{PtCl}_2(\text{cod})] (0.10g, 0.27 mmol)\) with \(\text{dppe} (0.11g, 0.28 mmol)\) and mercaptoacetic acid \((0.025g, 0.27 mmol)\) gave yellow microcrystals of \((272)\cdot\text{CH}_2\text{Cl}_2\) (0.20g, 96\%). (Found: C, 45.0; H, 3.7. \(\text{C}_{28}\text{H}_{26}\text{O}_2\text{P}_2\text{PtS}.\text{CH}_2\text{Cl}_2\) requires C, 45.3; H, 3.7\%), m.p. 167°C; \(\nu_{\text{C=O}}\) at 1610s cm\(^{-1}\). Complex \((272)\cdot\text{CH}_2\text{Cl}_2\) was too insoluble for n.m.r. studies.

\((xxi)\) \([\text{Pt}\{\text{SCH}_2\text{C(O)O}\}\{\text{dppp}\}\](273)\cdot\text{CHCl}_3\)

The complex \([\text{PtCl}_2(\text{cod})] (0.10g, 0.27 mmol)\) with \(\text{dppp} (0.12g, 0.29 mmol)\) and mercaptoacetic acid \((0.025g, 0.27 mmol)\) gave yellow microcrystals which were recrystallised from a saturated chloroform solution to give yellow crystals of \((273)\cdot\text{CHCl}_3\) (0.19g, 86\%). (Found: C, 43.6; H, 3.6. \(\text{C}_{29}\text{H}_{28}\text{O}_2\text{P}_2\text{PtS}.\text{CHCl}_3\) requires C, 44.0; H, 3.6\%), m.p. Above 220°C; \(\nu_{\text{C=O}}\) at 1640s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 7.93-7.11 \text{ (m, 21H, Ph + CHCl}_3\text{)}, 3.37 \text{ (m, 2H, CH}_2\text{)}, 2.99 \text{ (m, 4H, P-CH}_2\text{, dppp)}, 2.44 \text{ (m, 2H, CH}_2\text{, dppp)}; \(\text{C}-\{^1\text{H}\}, \delta 190.89 \text{ [d, CO, }^3\text{J(\text{PC}) 11]}, 29.97 \text{ (s, CH}_2\text{)}, 23.43 \text{ [dd, P-CH}_2\text{, dppp, }^1\text{J(\text{PC}) 40, }^3\text{J(\text{PC}) 3]}, 21.93 \text{ [dd, P-CH}_2\text{, dppp, }^1\text{J(\text{PC}) 42, }^3\text{J(\text{PC}) 2]}, 19.08 \text{ (s, CH}_2\text{, dppp); }^3\text{P}-\{^1\text{H}\} (36.2 \text{ MHz}); \delta -1.10 \text{ [d, P(1), }^1\text{J(PtP(1)) 2832, }^2\text{J(P(2)P(1)) 34], and -7.76 \text{ p.p.m. }}\{\text{d, P(2), }^1\text{J(PtP(2)) 3374, }^2\text{J(P(1)P(2)) 34}\}.

\((xxii)\) \([\text{Pt}\{\text{SCH}_2\text{C(O)O}\}\{\text{dppb}\}\](274)\cdot\text{CH}_2\text{Cl}_2\)

The complex \([\text{PtCl}_2(\text{cod})] (0.10g, 0.27 mmol)\) with \(\text{dppb} (0.12g, 0.28 mmol)\) and mercaptoacetic acid \((0.025g, 0.27 mmol)\) gave yellow microcrystals of \((274)\cdot\text{CH}_2\text{Cl}_2\) (0.19g, 88\%). (Found: C, 46.9; H, 4.1. \(\text{C}_{30}\text{H}_{30}\text{O}_2\text{P}_2\text{PtS}.\text{CH}_2\text{Cl}_2\) requires C, 46.7; H, 4.0\%), m.p. Above 220°C; \(\nu_{\text{C=O}}\) at 1620s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 7.78-7.29 \text{ (m, 20H, Ph)}, 5.27 \text{ (s, 2H, CH}_2\text{Cl}_2\text{)}, 3.37 \text{ [d, 2H, CH}_2\text{, }^4\text{J(\text{PH}) 2, }^3\text{J(\text{PtH}) 18]}, 3.01 \text{ (m, 2H, P-CH}_2\text{, dppb)}, 2.35 \text{ (m, 4H, CH}_2\text{ + P-CH}_2\text{, dppb)}, 1.66 \text{ (m, 2H, CH}_2\text{, dppb); }^{13}\text{C}-\{^1\text{H}\}, \text{too insoluble; }^3\text{P}-\{^1\text{H}\} (36.2 \text{ MHz}); \delta 11.70 \text{ [d, P(2), }^1\text{J(PtP(2)) 3565, }^2\text{J(P(1)P(2)) 29], and}
9.48 p.p.m. \{d, P(1), J[PtP(1)] 2817, J[PtP(2)] 29\}.

(xxiii) \[
\text{Pt(N(COMe)C(=CH2)C(O)O)(dppm) (275)}
\]

The complex [PtCl\(_2\)(cod)] (0.10g, 0.27 mmol) with dppm (0.11g, 0.29 mmol) and 2-acetamidoacrylic acid (0.035g, 0.27 mmol) gave pale yellow microcrystals of (275) (0.17g, 89%). (Found: C, 50.7; H, 3.9; N, 2.0. \(\text{C}_{39}\text{H}_{27}\text{NO}_3\text{P}_2\text{Pt}\) requires C, 51.0; H, 3.8; N, 2.0%), m.p. Above 220°C; \(\nu_{\text{C=O}}\) at 1660s and 1590s cm\(^{-1}\). N.m.r. spectra: \(\nu_{\text{H}}\) (300 MHz), \(\delta 7.83-7.29\) (m, 20H, Ph), 5.76 [d, 1H, =CH\(_2\), 2J(PH) 2], 4.71 (s, 1H, =CH\(_2\)), 4.34 [dd, 2H, CH\(_2\), dppm, 2J(PH) 9,11], 2.10 (s, 3H, CH\(_3\)); \(\nu_{\text{C-}}\)\(*_{\text{H}}\), 5 179.03 [d, CO, 3J(PC) 3], 172.93 (s, CO), 144.60 (s, >C=), 105.35 (s, =CH\(_2\)), 47.91 [dd, CH\(_2\), dppm, 1J(PC) 32,32], 21.90 [d, CH\(_3\), 4J(PC) 2]; 31P-\(\{^1\text{H}\}\) (36.2 MHz), \(\delta -56.11\) \(\{d, P(1), J[PtP(1)] 3000, J[PtP(2)] 2714, J[P(2)P(1)] 71\},\) and -66.47 p.p.m. \{d, P(2), 1J[PtP(2)] 3472, 2J[P(1)P(2)] 71\}.

(xxiv) \[
\text{Pt(CH=C(NHCOMe)C(0)O)(PMePh\(_3\)) (276).CH\(_2\)Cl\(_2\)}
\]

The complex [PtCl\(_2\)(cod)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and 2-acetamidoacrylic acid (0.035g, 0.27 mmol) gave pale yellow microcrystals of (276) (0.25g, 99%). \(\text{C}_{41}\text{H}_{35}\text{NO}_3\text{P}_2\text{Pt.CH}_2\text{Cl}_2\) requires C, 54.1; H, 4.0; N, 1.5%), m.p. Above 220°C; \(\nu_{\text{N-H}}\) at 3280 cm\(^{-1}\); \(\nu_{\text{C=O}}\) at 1670s and 1630s cm\(^{-1}\). N.m.r. spectra: \(\nu_{\text{H}}\) (300 MHz), \(\delta 7.72-7.10\) (m, 31H, Ph + NH), 6.60 [dd, 1H, CH, 3J(PH) 8,12, 2J(PtPH) 112], 5.28 (s, 2H, CH\(_2\)Cl\(_2\)), 1.91 (s, 3H, CH\(_3\)); 13C-\(\{^1\text{H}\}\), \(\delta 180.99\) [dd, CO, 3J(PC) 2,13, 2J(PtC) 50], 167.39 (s, CO), 140.68 [dd, Pt-C, 2J(PC) 7,100, 1J(PtC) 755], 53.17 (s, CH\(_2\)Cl\(_2\)), 24.19 (s, CH\(_3\)); 31P-\(\{^1\text{H}\}\) (36.2 MHz), \(\delta 24.67\) \{d, P(1), 1J[PtP(1)] 2000, 2J[P(2)P(1)] 17\}, and 15.38 p.p.m. \{d, P(2), 1J[PtP(2)] 4153, 2J[P(1)P(2)] 17\}.

(xxv) \[
\text{Pt(CH=C(NHCOMe)C(O)O)(PMePh\(_3\)) (277)}
\]

The complex [PtCl\(_2\)(cod)] (0.10g, 0.27 mmol) with methyldiphenylphosphine (0.11g, 0.55 mmol) and 2-acetamidoacrylic acid (0.035g, 0.27 mmol) gave yellow microcrystals of (277) (0.16g, 82%). \(\text{C}_{31}\text{H}_{31}\text{NO}_3\text{P}_2\text{Pt}\) requires C, 51.5; H, 4.3; N, 1.9%), m.p. Above 220°C; \(\nu_{\text{N-H}}\) at 3360 cm\(^{-1}\); \(\nu_{\text{C=O}}\) at 1670s and 1640s cm\(^{-1}\). N.m.r. spectra: \(\nu_{\text{H}}\) (300 MHz), \(\delta 7.66-7.24\) (m, 21H, Ph + NH), 7.01 [dd, 1H, CH, 3J(PH) 8,12,
\[2J(\text{PtH}) \, 118],\ 1.94 \, (s, \ 3H, \ CH\_3),\ 1.88 \, [d, \ 3H, \ Me, \ PMePh\_2, \ 1^2J(\text{PtH}) + 4^J(\text{PtH})] \, 9, \ 3^J(\text{PtH}) \, 30],
\[1.73 \, [d, \ 3H, \ Me, \ PMePh\_2, \ 1^2J(\text{PtH}) + 4^J(\text{PtH})] \, 11, \ 3^J(\text{PtH}) \, 37]; \ 13^C-{1^H}, \ \delta \ 180.93 \, [dd, \ CO, \ 3^J(\text{PC}) \, 3, 12, \ 2^J(\text{PtC}) \, not \ discernible], \ 167.58 \, (s, \ CO), \ 139.59 \, [dd, \ Pt-C, \ 2^J(\text{PC}) \, 9, 102, \ 1^J(\text{PtC}) \, not \ discernible], \ 24.30 \, (s, \ CH\_3), \ 14.59 \, [d, \ Me, \ PMePh\_2, \ 1^J(\text{PC}) + 3^J(\text{PC})] \, 47], \ 13.24
\[d, \ Me, \ PMePh\_2, \ 1^J(\text{PC}) + 3^J(\text{PC})] \, 31]; \ ^3P-{1^H} \, (36.2 \, MHz), \ \delta \ 11.60 \, [d, \ P(1), \ 1^J[\text{PtP}(1)] \, 2012, \ 2^J[\text{PtP}(1)] \, 15], \ and \ -4.00 \, p.p.m. \ [d, \ P(2), \ 1^J[\text{PtP}(2)] \, 3989, \ 2^J[\text{PtP}(2)] \, 15].

\[\text{Pt(PtCl}\_2(\text{cod})\text{)(COMe)}\,\text{C(=CH\_2)}\,\text{C}(\text{=O})\text{)(PMePh)}\,\text{,}] \, (278), \ ^3P-{1^H} \, (36.2 \, MHz) \, n.m.r. \, spectrum, \ \delta \ -3.03 \, [d, \ P(1), \ 1^J[\text{PtP}(1)] \, 3125, \ 2^J[\text{PtP}(1)] \, 25], \ and \ -11.20 \, p.p.m. \ [d, \ P(2), \ 1^J[\text{PtP}(2)] \, 3896, \ 2^J[\text{PtP}(2)] \, 25].

(xxvi) \[\text{Pt(PtCl}\_2(\text{COD})\text{)(PtMePh)}\,\text{,}] \, (278)

The complex \[\text{PtCl}\_2(\text{cod})\] \, (0.10g, 0.27 mmol) with dimethylphenylphosphine \, (0.08g, 0.58 mmol) and 2-acetamidoacrylic acid \, (0.035g, 0.27 mmol) gave yellow microcrystals of \, (278) \, (0.13g, 81%). \ (Found: \ C, 41.9; \ H, 4.4; \ N, 2.3. \ C\text{\,}_{21}\text{H}\text{\,}_{27}\text{NO}_3\text{P}_{2}\text{Pt \, requires \ C, 42.1; \ H, \ 4.5; \ N, 2.3%, \ m.p. 200°c; \ \nu_N-H \ at \ 3370 \, cm\^{-1}; \ \nu_C=O \ at \ 1680s \ and \ 1620s \ cm\^{-1}. \ N.m.r. \ spectra: \ 1^H \, (300 \, MHz), \ \delta \ 7.81-7.21 \, (m, \ 12H, \ Ph + CH + NH), \ 2.05 \, (s, \ 3H, \ CH\_3), \ 1.69 \, [d, \ 6H, \ Me, \ PMePh\_2, \ 1^2J(\text{PtH}) + 4^J(\text{PtH})] \, 11, \ 3^J(\text{PtH}) \, 45], \ 1.54 \, [d, \ 6H, \ Me, \ PMePh\_2, \ 1^2J(\text{PtH}) + 4^J(\text{PtH})] \, 9, \ 3^J(\text{PtH}) \, 24]; \ 13^C-{1^H}, \ \delta \ 181.03 \, [dd, \ CO, \ 3^J(\text{PC}) \, 2, 14, \ 2^J(\text{PtC}) \, not \ discernible], \ 167.95 \, (s, \ CO), \ 137.52 \, [dd, \ Pt-C, \ 2^J(\text{PC}) \, 9, 104, \ 1^J(\text{PtC}) \, not \ discernible], \ 24.46 \, (s, \ CH\_3), \ 15.18 \, [dd, \ Me, \ PMePh\_2, \ 1^J(\text{PC}) \, 44, \ 3^J(\text{PC}) \, 3, \ 2^J(\text{PtC}) \, 56], \ 12.50 \, [d, \ Me, \ PMePh\_2, \ 1^J(\text{PC}) + 3^J(\text{PC})] \, 31, \ 2^J(\text{PtC}) \, 14]; \ ^3P-{1^H} \, (36.2 \, MHz), \ \delta \ -2.96 \, [d, \ P(1), \ 1^J[\text{PtP}(1)] \, 1995, \ 2^J[\text{PtP}(1)] \, 20], \ and \ -19.72 \, p.p.m. \ [d, \ P(2), \ 1^J[\text{PtP}(2)] \, 3887, \ 2^J[\text{PtP}(2)] \, 20]. \ \text{x-ray quality crystals} \, of \, (278) \, were \, grown \, slowly \, from \, dichloromethane \, - \, light \, petroleum, \, in \, air.

(xxvii) \[\text{Pt(N(COME)}\,\text{C(=CH\_2)}\,\text{C(=O)}\text{)(PMePh)}\,\text{,}] \, (282), \ ^3P-{1^H} \, (36.2 \, MHz) \, n.m.r. \, spectrum, \ \delta \ -15.81 \, [d, \ P(1), \ 1^J[\text{PtP}(1)] \, 3091, \ 2^J[\text{PtP}(1)] \, 24], \ and \ -22.61 \, p.p.m. \ [d, \ P(2), \ 1^J[\text{PtP}(2)] \, 3753, \ 2^J[\text{PtP}(2)] \, 24].

(xxviii) The complex \[\text{PtCl}\_2(\text{cod})\] \, (0.10g, 0.27 mmol) with dppe \, (0.11g, 0.28 mmol) and 2-acetamidoacrylic acid \, (0.035g, 0.27 mmol) gave a yellow powder, shown by \ ^3P-{1^H}
n.m.r. spectroscopy to contain two products: -

\[ \text{[Pt(\text{CH} = \text{C(NHCOMe)}\text{C(O)})]}(\text{dppe}) \], \quad \text{^31P} - \{^1\text{H}\} (36.2 \text{ MHz}) \text{ n.m.r. spectrum, } \delta 45.83 \text{ (s, P(1), } ^1\text{J(PtP(1))} 2012), \text{ and } 35.40 \text{ p.p.m. (s, P(2), } ^1\text{J(PtP(2))} 3923). \\

\[ \text{[Pt(N(COMe)C(=CH_{2})\text{C(O)})]}(\text{dppe}) \], \quad \text{^31P} - \{^1\text{H}\} (36.2 \text{ MHz}) \text{ n.m.r. spectrum, } \delta 38.13 \text{ (d, P(1), } ^1\text{J(PtP(1))} 3164, \text{ } ^2\text{J(P(2)P(1))} 15), \text{ and } 28.49 \text{ p.p.m. (d, P(2), } ^1\text{J(PtP(2))} 3911, \text{ } ^2\text{J(P(1)P(2))} 15). \\

(xxvii) \[ \text{[Pt(\text{CH} = \text{C(NHCOMe)}\text{C(O)})]}(\text{dppe}) \] (279)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppp (0.12g, 0.29 mmol) and 2-acetamidoacrylic acid (0.035g, 0.27 mmol) gave, after slow recrystallisation, yellow microcrystals of (279) (0.15g, 76%). (Found: C, 52.2; H, 4.1; N, 2.0. \(\text{C}_{32}\text{H}_{31}\text{NO}_{3}\text{P}_{2}\text{Pt}\) requires C, 52.3; H, 4.2; N, 1.9%), m.p. Above 220°C; \(\nu_{\text{N-H}}\) at 3290 cm\(^{-1}\); \(\nu_{\text{C=O}}\) at 1670 s and 1630 s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta 7.71-7.28\) (m, 21H, Ph + NH), 6.86 [dd, 1H, CH, \(^3\text{J(PT)} 8,12, \text{ } ^2\text{J(PT)} 10), 2.60 (m, 2H, P-CH\(_{2}\), dppp), 2.43 (m, 2H, P-CH\(_{2}\), dppp), 1.99 (m, 2H, CH\(_{2}\), dppp), 1.88 (s, 3H, CH\(_{3}\)); \(^{13}\text{C}\{-\text{H}\}, \delta 182.13\) [dd, CO, \(^3\text{J(PC)} 2,11, \text{ } ^2\text{J(PC)}\) not discernible], 167.62 (s, CO), 141.45 [dd, Pt-C, \(^2\text{J(PC)} 6,100, \text{ } ^1\text{J(PtC)}\) not discernible], 26.31 [dd, P-CH\(_{2}\), dppp, \(^1\text{J(PC)} 41, \text{ } ^3\text{J(PC)} 6)], 25.79 [d, P-CH\(_{2}\), dppp, \(^1\text{J(PC)} 32), 24.41 (s, CH\(_{3}\)), 19.64 (s, CH\(_{2}\), dppp), \(^{31}\text{P} - \{^1\text{H}\} (36.2 \text{ MHz}), \delta 1.85 \text{ (d, P(1), } ^1\text{J(PtP(1))} 1897, \text{ } ^2\text{J(P(2)P(1))} 27), \text{ and } -0.44 \text{ p.p.m. (d, P(2), } ^1\text{J(PtP(2))} 3818, \text{ } ^2\text{J(P(1)P(2))} 27). \\

(xxix) \[ \text{[Pt(N(COMe)C(=CH\(_{2}\))\text{C(O)})]}(\text{dppb}) \] (280)

The complex \([\text{PtCl}_2(\text{cod})]\) (0.10g, 0.27 mmol) with dppb (0.12g, 0.28 mmol) and 2-acetamidoacrylic acid (0.035g, 0.27 mmol) gave yellow microcrystals of (280) (0.18g, 89%). (Found: C, 53.0; H, 4.4; N, 1.8. \(\text{C}_{33}\text{H}_{33}\text{NO}_{3}\text{P}_{2}\text{Pt}\) requires C, 52.9; H, 4.4; N, 1.9%), m.p. Above 220°C; \(\nu_{\text{N-H}}\) at 3300 cm\(^{-1}\); \(\nu_{\text{C=O}}\) at 1680 s and 1630 s cm\(^{-1}\). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \(\delta 7.71-7.14\) (m, 21H, Ph + NH), 6.62 [dd, 1H, CH, \(^3\text{J(PT)} 7,11, \text{ } ^2\text{J(PT)} 124), \\

- 213 -
2.71 (m, 2H, P-CH₂, dppb), 2.31 (m, 2H, P-CH₂, dppb), 2.08 (m, 2H, CH₂, dppb), 1.88 (s, 3H, CH₃), 1.65 (m, 2H, CH₂, dppb); ¹³C-{¹H}, δ 181.71 [dd, CO, ³J(PC) 2,10, ²J(PtC) not discernible], 167.55 (s, CO), 142.14 [dd, Pt-C, ²J(PC) 8,98, ¹J(PtC) not discernible], 28.07 [d, P-CH₂, dppb, ¹J(PC) 39], 24.41 [d, P-CH₂, dppb, ¹J(PC) 34], 24.37 (s, CH₃), 24.25 (s, CH₂, dppb), 22.34 (s, CH₂, dppb); ³¹P-{¹H} (36.2 MHz), δ 14.00 (d, P(2), ¹J[Pt(P2)] 4004, ²J[P(1)P(2)] 20), and 13.13 p.p.m. (d, P(1), ¹J[Pt(P1)] 1941, ²J[P(1)P(2)] 20).

The complex [PtCl₂(cod)] (0.10g, 0.35 mmol) with dppp (0.15g, 0.36 mmol) and α-acetamidocinnamic acid (0.075g, 0.37 mmol) gave greeny-yellow microcrystals of (283).H₂O (0.24g, 93%). (Found: C, 61.8; H, 5.0; N, 1.9. C₃₈H₅₃NO₉P₂Pd.H₂O requires C, 61.6; H, 5.0; N, 1.9%), m.p. 220°C; νₐ₅ at 1640s and 1580s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.79-6.64 (m, 26H, Ph + =CH), 2.61-1.92 (m, 6H, P-CH₂, dppp + H₂O), 1.35 (m, 2H, CH₂, dppp), 1.33 (s, 3H, CH₃); ¹³C-{¹H}, δ 176.67 [d, CO, ³J(PC) 3], 170.15 (s, CO), 29.43 [dd, P-CH₂, dppp, ¹J(PC) 32, ³J(PC) 11], 24.15 [dd, P-CH₂, dppp, ¹J(PC) 32, ³J(PC) 7], 21.18 [d, CH₃, ⁴J(PC) 4], 19.22 (s, CH₂, dppp); ³¹P-{¹H} (36.2 MHz), δ 13.21 (d, P(1), ²J[P(2)P(1)] 54), and 5.34 p.p.m. (d, P(2), ²J[P(1)P(2)] 54).

The complex [PtCl₂(cod)] (0.10g, 0.35 mmol) with dppp (0.15g, 0.36 mmol) and 2-acetamidoacrylic acid (0.045g, 0.35 mmol) gave yellow microcrystals of (284).H₂O (0.19g, 82%). (Found: C, 57.8; H, 5.0; N, 2.0. C₃₂H₃₃NO₉P₂Pd.H₂O requires C, 57.8; H, 5.0; N, 2.1%), m.p. 143°C; νₐ₅ at 3370 cm⁻¹; νₐ₅ at 1670s and 1610s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.73-7.34 (m, 21H, Ph + NH), 6.69 [dd, 1H, CH, ³J(PH) 12,23], 2.54-2.39 (m, 4H, P-CH₂, dppp), 2.04-1.90 (m, 4H, CH, dppp + H₂O), 1.85 (s, 3H, CH₃); ¹³C-{¹H}, δ 179.54 [d, CO, ³J(PC) 12], 168.06 (s, CO), 144.14 [d, Pd-C, ²J(PC) 111], 28.33 [dd, P-CH₂, dppp, ¹J(PC) 32, ³J(PC) 8], 26.44 [dd, P-CH₂, dppp, ¹J(PC) 24, ³J(PC) 2], 24.76 (s, CH₃), 19.67 [d, CH₂, dppp, ²J(PC) 4]; ³¹P-{¹H} (36.2 MHz), δ 26.18 (d, P(1), ²J[P(2)P(1)] 54), and -5.38 p.p.m. (d, P(2), ²J[P(1)P(2)] 54).
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