Four-Membered Metallacyclic Complexes of Platinum, Palladium, and Nickel

A Thesis submitted by

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For my Parents
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William Henderson

ABSTRACT

Chapter 1 reviews the literature concerning the principal synthetic routes to metallaclobutane, metallaclobutan-3-one ($\eta^3$-oxodimethylene), and four-membered cyclic ylide complexes of platinum, palladium, and nickel, which contain the M-C-X-C ring system ($X = C$, $S$, or $P$).

The preparation and characterisation of the first examples of metallathietane-3,3-dioxide complexes of platinum, palladium, and nickel, $[\text{M}(\text{CHR}(S(O)_{2}\text{CHR}))L_{2}]$, are presented in Chapter 2. The molecular structures of three of these complexes establish the presence of puckered four-membered rings, together with the presence of a heteroallylic contribution to the bonding.

Preliminary investigations into the reactivity of these metallathietane-3,3-dioxide complexes are detailed in Chapter 3. Ligand substitution reactions of the complex $[\text{Pt}(\text{CHPhS(O)_{2}CHPh})(\text{SEt}_{2})_{2}]$ afford a range of platinathietane-3,3-dioxide complexes. A study of the reactions of platinathietane-3,3-dioxide complexes with alkyl isocyanides shows that phenyl substituted complexes undergo ligand substitution, whereas benzoyl or methoxycarbonyl substituted complexes undergo a ring insertion reaction to afford the zwitterionic complexes $[\text{Pt}(\text{CH(COR)(O)S(O)C(COR)C:-S(CHR')})_{2}]$. 

Chapter 4 describes the synthesis of platinathietane-3-oxide complexes, crystallographic and n.m.r. data indicating the presence of puckered and non-fluxional four-membered ring systems, with the sulphynyl oxygen in an equatorial environment. The sulfoxide and equatorial benzoyl groups of the complex $[\text{Pt}(\text{CH(COPh)(O)CH(COPh))}(\text{PPh}_{3})_{2}]$ co-ordinate to palladium(II) or rhodium(I) centres to afford five-membered chelate ring products.

The final Chapter describes the synthesis of diphenyl-substituted oxodimethylene complexes of platinum and palladium using the dianion $\text{K}_{2}[\text{PhCH(O)CHPh}]$. The molecular structure of the complex $[\text{Pt}(\eta^{3}-\text{CHPhC(O)CHPh})(\text{AsPh}_{3})_{2}]$ establishes the presence of an $\eta^{3}$-oxodimethylene ligand. The fluxional behaviour of these diphenyl oxodimethylene complexes is shown to be dependent on the mode of substitution of the phenyl rings on the oxodimethylene ligand, with cis-diequatorial complexes being rigid in solution, and the trans-disubstituted complex trans-$[\text{Pt}(\eta^{3}-\text{CHPhC(O)CHPh})(\text{PPh}_{3})_{2}]$ being fluxional.
STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1984 and September 1987, under the supervision of Dr. R. D. W. Kemmitt. The work has not been, and is not concurrently being presented for any other degree.

Date: .......................  Signed: ..........................
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ABBREVIATIONS & SYMBOLS

GENERAL AND PHYSICAL:

Å - Angström unit
br - Broad
°C - Centigrade
\text{cm}^{-1} - Wave number
\text{cm}^3 - Cubic centimetres
d - Doublet
g - Gramme
Δ - Heat
Hz - Hertz
h - Hour
i.r. - Infrared
MHz - Megahertz
m.p. - Melting point
m - Medium (i.r.); Multiplet (n.m.r.)
\text{mmHg} - Millimetres of mercury
mmol - Millimole
min - Minute
n.m.r. - Nuclear magnetic resonance
p.p.m. - Parts per million
{^{31}\text{P}} - Phosphorus decoupled
{^{1}\text{H}} - Proton decoupled
q - Quartet
s - Singlet (n.m.r.); Strong (i.r.)
t - Tertiary (chemical); Triplet (n.m.r.)
vs - Very strong
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<tr>
<td>acac</td>
<td>Anion of pentane-2,4-dione</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-Bipyridine</td>
</tr>
<tr>
<td>Buⁿ</td>
<td>n-Butyl</td>
</tr>
<tr>
<td>Buᵗ</td>
<td>t-Butyl</td>
</tr>
<tr>
<td>COD</td>
<td>cis,cis-Cyclo-octa-1,5-diene</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl anion</td>
</tr>
<tr>
<td>Cy</td>
<td>Cyclohexyl</td>
</tr>
<tr>
<td>dba</td>
<td>Dibenzylideneacetone</td>
</tr>
<tr>
<td>dcpe</td>
<td>1,2-Bis-(dicyclohexylphosphino)ethane</td>
</tr>
<tr>
<td>diglyme</td>
<td>Diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulphoxide</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-Bis-(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dpm</td>
<td>Anion of 2,2,6,6-tetramethyl-3,5-heptanedione- (dipivaloylmethane)</td>
</tr>
<tr>
<td>dpmm</td>
<td>Bis-(diphenylphosphino)methane</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>Me₂bipy</td>
<td>4,4'-Dimethyl-2,2'-bipyridine</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>phen</td>
<td>1,10-Phenanthroline</td>
</tr>
<tr>
<td>PMDTA</td>
<td>N,N,N',N&quot;-Pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>Pri</td>
<td>iso-Propyl</td>
</tr>
<tr>
<td>py</td>
<td>Pyridine</td>
</tr>
<tr>
<td>SacSac</td>
<td>Anion of pentane-2,4-dithione</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TEEDA</td>
<td>N₅,N₅,N',N'-Tetraethylenediamine</td>
</tr>
<tr>
<td>TMEDA</td>
<td>N₅,N₅,N',N'-Tetramethylethylenediamine</td>
</tr>
<tr>
<td>tol</td>
<td>Tolyl</td>
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CHAPTER 1

Four-Membered Metallacyclic Complexes of Platinum, Palladium, and Nickel
1.1 INTRODUCTION

Considerable interest in the chemistry of transition-metalliclyclobutane complexes has arisen, since such complexes have been invoked as intermediates in several transition-metal mediated reactions of organic molecules.\textsuperscript{1,2,3} Thus, for example, the olefin metathesis reaction is one such reaction, the mechanism of which is considered to proceed via an interconversion of metallacyclobutane and olefin-carbene complexes,\textsuperscript{2,3} as outlined in Scheme 1. Platinacyclobutane complexes have attracted special attention,\textsuperscript{1} since these complexes, and their reaction products, are often highly stable and thus provide readily accessible models for the bonding and reactivity of metallacyclobutane complexes in general.

This first Chapter summarises the literature on the principal synthetic routes available for the synthesis of metallacyclobutane complexes, and their derivatives which contain the M-C-X-C ring system (X = non-metal), for the metals platinum, palladium, and nickel. A review of platinacyclobutane chemistry has appeared.\textsuperscript{1} The syntheses of a number of highly puckered metallacyclobutan-3-one complexes, which contain a degree of \( \eta^3 \)-allylic character, are also described, together with the syntheses of various four-membered cyclic phosphorus and sulphur ylide complexes.
1.2 SYNTHESIS OF METALLACYCLOBUTANE COMPLEXES OF PLATINUM, PALLADIUM, AND NICKEL

Metallacyclobutane complexes of platinum, palladium, and nickel have been synthesised via several routes, which may be classified into two broad groups; (i) ring opening reactions of cyclopropanes and related ring systems, and (ii) miscellaneous synthetic methods, including syntheses from unstrained reagents.

1.2.1 Ring opening reactions of cyclopropanes and other three membered ring systems

The first example of a platinacyclobutane complex was prepared by Tipper in 1955, who found that cyclopropane reacted with hexachloroplatinic(IV) acid, \( \text{H}_2[\text{PtCl}_6] \), in acetic anhydride, to give a complex of empirical formula \( \text{PtCl}_2(\text{C}_3\text{H}_6) \) which was later identified as a tetrameric platinacyclobutane complex (1). The tetrameric complex (1) reacted with pyridine to form the monomeric platinacyclobutane (2), the structure of which was established by an X-ray study. The synthetic method of Tipper, utilising \( \text{H}_2[\text{PtCl}_6] \), cannot be extended to the synthesis of substituted platinacyclobutane complexes, pyrylium ion salts being formed instead, as illustrated for example in equation 1.

\[
\text{H}_2[\text{PtCl}_6] + 2 \text{Me}_2\text{CMe} + 4(\text{RCO})_2\text{O} \rightarrow \text{[Et} \bigg[\text{R}_2\text{R} \bigg]_2[\text{PtCl}_4]^{2+} + 4\text{RCO}_2\text{H} + 2\text{H}_2\text{O}
\]

A general synthetic method for the synthesis of substituted tetrameric
platinum(IV) cyclobutanes (3) involves the reaction of a cyclopropane
derivative (4) (R = alkyl or aryl) with Zeise's dimer (5), as shown in
equation 2, and many examples of platincyclobutanes have been prepared
via this method.\textsuperscript{1,10,11} Except in the case of polycyclic platincyclo-
butanes described later, the structures of the tetrameric platincyclo-
butanes of type (3) have not been fully investigated.

\[
\begin{array}{c}
\text{(5)} \\
\text{(4)} \\
\text{(3)}
\end{array}
\]

The tetrameric platincyclobutanes (3) readily react with nitrogen or
oxygen donor ligands (for example pyridine, 2,2'-bipyridine, and tetra-
hydrofuran) to give monomeric platincyclobutane complexes typified by
\[\text{[Pt(CH}_2\text{CH}_2\text{CH}_2\text{X}_2\text{L}_2]} \quad (X = \text{halide, } L = \text{N or O-donor ligand}).\] A large number
of typical examples of monomeric platincyclobutanes prepared by this
method are given in Refs. 1, 10 and 11. The oxygen donor complexes are
somewhat less stable than the nitrogen donor complexes. This is
typified by the reaction of (1) with tetrahydrofuran, which presumably
forms the bis(tetrahydrofuran) complex \[\text{[Pt(CH}_2\text{CH}_2\text{X}_2\text{Cl}_2(\text{THF})}_2]\], which
loses tetrahydrofuran on removal of the solvent to afford the original
tetramer (1).\textsuperscript{12} An isolable complex is formed between (1) and 1,4-dioxane,
and may contain bridging 1,4-dioxane ligands.\textsuperscript{6}

Experiments involving competitive ring opening of cyclopropanes have
established that the presence of electron-donating groups on the cyclo-
propane ring enhances the rate of ring opening.\textsuperscript{13,14} When electron-
withdrawing groups are present (for example CO\textsubscript{2}Me, COMe, or CN) no ring
opening of the substituted cyclopropane by platinum(II) is observed.\textsuperscript{14}
The proposed mechanism for the reaction of Zeise's dimer (5) with cyclo-
propanes involves initial electrophilic attack of platinum on the cyclopropane ring.\textsuperscript{12} There is often difficulty in determining the initial point of insertion of platinum into the cyclopropane ring, since rapid skeletal isomerisation reactions of the initially formed monomeric platinacyclobutanes may occur.\textsuperscript{1,15} An example of such a rearrangement is given by the reaction of phenylcyclopropane with Zeise's dimer (5) and then with pyridine, to initially afford the platinacyclobutane (6), which rearranges to an equilibrium mixture of (6) and (7), see Scheme 2.\textsuperscript{15} Steric effects also appear to bear an influence on cyclopropane ring opening, since electron-rich 1,1,2,2-tetramethylcyclopropane fails to react with Zeise's dimer (5).\textsuperscript{16}

The reactions of \textit{cis}-1,2-disubstituted cyclopropanes with Zeise's dimer (5) often lead to either no reaction,\textsuperscript{16} or formation of \( \eta^3 \)-allyl complexes,\textsuperscript{14} for example see Scheme 3. However, the ring opening reactions of cyclopropanes incorporated as part of polycyclic hydrocarbons have recently been shown to result in the formation of platinacyclobutanes. Thus, Zeise's dimer (5) reacts with the norbornyl systems (8) to afford the platinacyclobutane complexes (9), as depicted in equation 3.\textsuperscript{17,18} In a similar fashion, the bicyclo[X.1.0] (\( X = 4 \) or 6) hydrocarbons (10) afford the platinacyclobutane complexes (11), see equation 4.\textsuperscript{19} In contrast, the reaction of bicyclo[6.1.0]non-4-ene with Zeise's dimer (5) initially gives a dinuclear olefin complex (12), which
undergoes ring opening on heating, to afford the platinacyclobutane (13), as shown in Scheme 4.\textsuperscript{19,20} Treatment of (13) with pyridine afforded an unstable intermediate which reacted with 2,2'-bipyridine to give the rearranged platinacyclobutane (14), Scheme 4.\textsuperscript{19}

It is worth noting that magic angle spinning/cross polarisation $^{13}$C n.m.r. studies on the initially precipitated (tetrameric) platinacyclobutane complexes formed in the reaction of (5) with the various cyclopropane derivatives (8), see equation 3, before solubilisation with pyridine, reveal that the tetramers have the same exo-platinacyclobutane skeleton as the pyridine solubilised complexes (9).\textsuperscript{18}

Cyclopropane substitution in tetrameric platina(IV)cyclobutanes has
also been shown to be a synthetic route into platinacyclobutane complexes, for example phenylcyclopropane will displace cyclopropane from (1), as illustrated in equation 5.\(^{(12)}\)

\[
\begin{align*}
\left[\text{Cl}_2\text{Pt}\right]_4 + 4 \text{Ph} & \rightarrow \left[\text{Cl}_2\text{Pt}\right]_4 + 4 \text{Ph} \quad 5 \\
\end{align*}
\]

Scheme 4

In contrast to the reactions of the tetrameric platina(IV)cyclobutanes (3) with hard nitrogen or oxygen donor ligands, the reactions of (3) with soft ligands, for example tertiary phosphines or dialkyl sulphides, lead to the reductive elimination of cyclopropane and formation of [PtCl\(_2\)L\(_2\)] (L = soft donor ligand).\(^{(1,21)}\) Cyclopropane may also be eliminated from monomeric platina(IV)cyclobutanes, typified by (2), provided that the ligand is able to substitute for pyridine at the platinum centre.\(^{(1)}\) This may be prevented by use of chelating nitrogen donor ligands such as 2,2'-bipyridine or 1,10-phenanthroline.\(^{(1,21)}\)
Reduction of the platinum(IV) cyclobutane complex \([\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Cl}_2(\text{bipy})]\) (15) either electrochemically, or via treatment with sodium amalgam affords the platinum(II) cyclobutane complex (16) as depicted in equation 6.\textsuperscript{22} The 2,2'-bipyridine ligand of (16) may be displaced by tertiary phosphines or t-butyl isocyanide to give the complexes \([\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2)L_2]\) (L = PPh\(_3\), PMe\(_3\), PEt\(_3\) or Bu\(^+\)NC).\textsuperscript{22}

\[ \begin{array}{c}
\text{(bipy)Pt} \\
\text{Cl} \\
\text{Cl}
\end{array} \xrightarrow{\text{i or ii}} \begin{array}{c}
\text{(bipy)Pt} \\
\text{Cl}
\end{array} \]

i cathodic reduction  
ii Na(Hg)

6

A large number of metallacyclobutane complexes of platinum(II) and palladium(II) (17) have been synthesised via the insertion of a nucleophilic metal(0) centre into a carbon-carbon bond of an electron-deficient cyclopropane, as illustrated in equation 7.\textsuperscript{23-25} In these reactions the nucleophilic metal(0) centre inserts into the cyclopropane ring bond bearing the largest number of electron-withdrawing substituents. The complex \([\text{Pt}(\eta^2-\text{C}_2\text{H}_4)(\text{PPh}_3)_2]\) may alternatively be used in place of \(\text{ML}_n\).\textsuperscript{23,25} The triphenylarsine ligands of \([\text{Pt}(\text{C(CN)}_2\text{CH}_2\text{C(CN)}_2)(\text{AsPh}_3)_2]\) may be readily displaced by triethylphosphine or dimethylphenylphosphine.\textsuperscript{23}

In related chemistry a number of oxaplatinacyclobutane complexes (18)
are formed by the ring opening of tetracyano-oxirane by \([\text{PtL}_n]\)\textsuperscript{26} or the ring opening of tricyano-oxirane by \([\text{Pt}(\eta^2-C_2\text{H}_4)(\text{PPh}_3)_2]\),\textsuperscript{27} as depicted

\[
\begin{align*}
&\text{[PtL}_4]\text{ or }\text{[Pt}(\eta^2-C_2\text{H}_4)(\text{PPh}_3)_2] \\
&\quad + \quad \begin{tikzpicture}
    \node (A) at (0,0) {CN};
    \node (B) at (0.5,0) {CN};
    \node (C) at (1,0) {CN};
    \node (D) at (1.5,0) {CN};
    \node (E) at (0,1) {O};
    \node (F) at (1.5,1) {R};
    \node (G) at (0,0.5) {R};
    \node (H) at (1.5,0.5) {NC};
    \node (I) at (1.5,-0.5) {NC};
    \node (J) at (0,-0.5) {NC};
    \node (K) at (0.5,-0.5) {NC};
    \draw (A) -- (B) -- (C) -- (D);
    \draw (E) -- (A);
    \draw (E) -- (B);
    \draw (E) -- (C);
    \draw (E) -- (D);
    \draw (F) -- (E);
    \draw (G) -- (E);
    \draw (H) -- (E);
    \draw (I) -- (E);
    \draw (J) -- (E);
    \draw (K) -- (E);
\end{tikzpicture}
\rightarrow \begin{tikzpicture}
    \node (L) at (0,0) {L_2\text{Pt} \quad \text{(18)}};
    \node (M) at (0.5,0) {R \quad \text{NC}};
    \node (N) at (1,0) {NC \quad \text{CN}};
\end{tikzpicture}
\end{align*}
\]

\[R = \text{CN}, \quad L = \text{PPh}_3, \text{P}(\text{p-tol})_3 \text{ or AsPh}_3\]

\[R = \text{H}, \quad L = \text{PPh}_3\]

in equation 8. With zerovalet palladium complexes, (cyano)tricyano-ethenolate complexes (19) are formed, via unstable oxapalladacyclobutane complexes, as shown in Scheme 5.\textsuperscript{28} The oxaplatinacyclobutane complexes

\[
\begin{align*}
&\text{[PdL}_4] \\
&\quad + \quad \begin{tikzpicture}
    \node (A) at (0,0) {O};
    \node (B) at (0.5,0) {\text{CN}};
    \node (C) at (1,0) {\text{CN}};
    \node (D) at (1.5,0) {\text{CN}};
    \node (E) at (0,1) {\text{CN}};
    \node (F) at (1.5,1) {\text{CN}};
    \node (G) at (0,0.5) {\text{CN}};
    \node (H) at (1.5,0.5) {\text{CN}};
    \node (I) at (0,-0.5) {\text{CN}};
    \node (J) at (1.5,-0.5) {\text{CN}};
    \draw (A) -- (B) -- (C) -- (D);
    \draw (E) -- (A);
    \draw (E) -- (B);
    \draw (E) -- (C);
    \draw (E) -- (D);
    \draw (F) -- (E);
    \draw (G) -- (E);
    \draw (H) -- (E);
    \draw (I) -- (E);
    \draw (J) -- (E);
\end{tikzpicture}
\rightarrow \begin{tikzpicture}
    \node (L) at (0,0) {L_2\text{Pd} \quad \text{(19)}};
    \node (M) at (0.5,0) {\text{NC} \quad \text{Pd} \quad \text{O} \quad \text{CN}};
    \node (N) at (1,0) {\text{NC} \quad \text{CN}};
\end{tikzpicture}
\end{align*}
\]

Scheme 5

are more robust, and require heating or treatment with alkyl phosphines to effect conversion to the analogous tricyanoethenolate complexes (19).\textsuperscript{27-29} The reaction of phenyl substituted cyano-oxiranes with zero-valent platinum or palladium does not result in oxametallacyclobutane formation, instead deoxygenation occurs to give the phosphine oxide, and a metal-olefin complex.\textsuperscript{30}

Other strained three-membered rings may also be ring opened by zero-valent platinum. The reaction of 1,2-diphenyl-3-dicyanomethylenecyclopropene with \([\text{Pt}(\eta^2-C_2\text{H}_4)(\text{PPh}_3)_2]\) gives the four-membered ring complex
In refluxing tetrahydrofuran, (20) is converted to the cyano-bridged dimeric species (21), which may be converted back to (20) via addition of triphenylphosphine, Scheme 6. Ring opening of related cyclopropenones gives the related platinacyclobutenone complexes (22), as illustrated in equation 9. The complex PtLₙ is either

\[
Ptn + \begin{array}{c} \text{R} \\ \text{R}
\end{array} \rightarrow \begin{array}{c} \text{L}_n \text{Pt} \\ \text{R}'
\end{array}
\]

\[\text{(22)} \quad L = \text{PPh}_3\]

\[R = \text{H}, \quad R' = \text{Me}; \quad R = R' = \text{Me}, \text{Ph}\]

[Pt(PPh₃)₄] for diphenylcyclopropenone, or [Pt(η²-C₂H₄)(PPh₃)₂] for the methylcyclopropenones. In the case of methylcyclopropenone, an intermediate η²-C₄C cyclopropenone complex (23) was detected at low tempera-
In contrast to these reactions, the reactions of [Pt(PPh$_3$)$_2$X] (X = C$_2$H$_4$, CS$_2$, or PPh$_3$) or [Pd(PPh$_3$)$_4$] with thiirane-1,1-dioxide rings afforded only the η$^2$-olefin complexes (24). 34 Similarly, no ring opening is observed when zerovalent platinum is treated with a number of methylenecyclopropanes, 35 1,2-dimethylcyclopropene, 36 or thiirane and its S-oxide. 37 The ring opening of a co-ordinated phosphirene ring has recently been reported. Thus, the three-membered ring of (25) is opened by zerovalent platinum or palladium to afford the phosphametallacyclobutene complexes (26), see equation 10. 38

$$[M(\eta^2-C_2H_4)L_2] + \text{Ph} \stackrel{Ph}{\text{Ph}} \text{Ph} \rightarrow \text{L}_2M_{\text{Ph}} \text{Ph} \text{W(CO)}_6$$

(25)  (26)

When cyclopropabenzene (27) is treated with the zerovalent nickel complexes [Ni(COD)PR$_3$)$_2$] (R = Et or Bu$^n$), [Ni(PPh$_3$)$_4$] or [Ni(C$_2$H$_4$)$_3$] in the presence of TMEDA, or when 7,7-bis(trimethylsilyl)cyclopropabenzene (28) is reacted with [Ni(C$_2$H$_4$)$_3$] in the presence of TMEDA, TEEDA, PMDTA, or 2,2'-bipyridine the nickelacyclobutabenzene complexes (29) are isolated, as illustrated in equation 11. 39,40 In contrast, the reaction of (27) with [Ni(COD)PMe$_3$)$_2$] results in cyclopropabenzene dimerisation
to give the bismethanonickelacyclotridecahexaene complex (30). The TMEDA ligand of (29, R = SiMe$_3$, L = TMEDA) is readily substituted by tertiary phosphine ligands. The reaction of 7,7-difluorocyclopropabenzene (31) with [Ni(COD)L$_2$] (L = PMe$_3$, PEt$_3$, or L$_2$ = dcpe), [Ni(PPh$_3$)$_4$], or with [Ni(C$_2$H$_4$)$_3$] in the presence of TMEDA or bipy affords the propellane complexes (32) (L = PMe$_3$, PEt$_3$, PPh$_3$; L$_2$ = dcpe, bipy, or TMEDA),

\[
\begin{align*}
R_2 + \text{NiLn} & \rightarrow L_2\text{Ni} \\
(27), R = H & \\
(28), R = \text{SiMe}_3 & \\
(29) & \\
R = \text{H}; L = \text{PEI}_3, \text{PBu}_3, \text{or} \\
& \text{PPh}_3; L_2 = \text{TMEDA} \\
R = \text{SiMe}_3; L_2 = \text{TMEDA, TEEDA, PMDTA, or bipy} & \\
(30) & \\
\end{align*}
\]

as shown in equation 11. The reaction of (31) with [Ni(C$_2$H$_4$)$_3$] in the presence of TEEDA has also been reported to afford a nine-membered difluoromethano-bridged nickelacycle.

The reactions of the cyclopropabenzenes (27), (28) and (31) with the palladium complex [Pd($\eta^5$-C$_5$H$_5$($\eta^3$-C$_3$H$_5$))] (33) in the presence of trimethylphosphine are summarised in Scheme 7. The cyclopropabenzenes (28) and
(31) give analogous products to those yielded by reaction with zerovalent nickel.\textsuperscript{40,42} The reaction of (27) with (33) and trimethylphosphine shows markedly different behaviour, giving the \( \sigma \)-benzyl complex (35), and a palladacyclobutabenzenne complex (34) has been postulated as an intermediate.\textsuperscript{44}

1.2.2 Synthesis of metallacyclobutanes and derivatives by miscellaneous methods

A number of methods have been described for the synthesis of metallacyclobutane complexes of platinum and nickel from unstrained reagents.

Thermolysis of the complexes cis-[Pt(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{2}L\textsubscript{2}] (L = PE\textsubscript{t}\textsubscript{3}, PPr\textsubscript{3}, or PCy\textsubscript{3}) affords highly thermally stable platinacyclobutane complexes (36), equation 13.\textsuperscript{45-47} The reaction proceeds via dissociation of a phosphine ligand followed by intramolecular oxidative addition of a distal C-H bond, and reductive elimination of CMe\textsubscript{3} to afford the platinacycle.\textsuperscript{45,47}
The platinacyclobutanes \([\text{Pt}(\text{CH}_2\text{CMeRCH}_2\text{PEt}_3)_2]\) \((R = \text{CH}_2\text{CD}_3, \text{Pr}^n, \text{or} \text{CH}_2\text{CD}_2\text{CH}_3)\) are formed in low yield in the thermolysis reactions of dialkylbis(triethylphosphine)platinum complexes, which also afford platinacyclopentanes and -hexanes.\(^{48}\) Similarly, the bis(neopentyl)nickel complex (37) reacts to form the nickelacyclobutane (38) at 0°C, see Scheme 8.\(^{49}\) This methodology has also been recently employed in the synthesis of metallacyclobutanes and metalla-3-silacyclobutanes of, for example, rhodium,\(^{50}\) iridium,\(^{50}\) and thorium.\(^{51}\)

A platina-3-silacyclobutane complex (39) has been formed by treatment of a bis(trimethylsilyl)methyl complex with t-butyl lithium, a sterically hindered base, equation 14.\(^{52}\)

A number of perfluorinated metallacyclobutane derivatives have been synthesised via reaction of octafluorocyclo-octatetraene (40) with low-valent metal complexes. The reaction of \([\text{Ni(COD)}_2]\) with (40) in the
presence of two mole equivalents of t-butyl isocyanide yields the nickelacyclobutane derivative (41, M=Ni, L=Bu^tNC), containing the perfluoro[3.3.1]octadienediy ligand, see Scheme 9. Complex (41, M=Ni, L=Bu^tNC) reacts with excess t-butyl isocyanide or tertiary phosphine to afford the five co-cordinate adducts (42) (L' = Bu^tNC, PMe3, or PPh3), Scheme 9. However, the reaction of [Ni(COD)]2 with (40) in the presence of trimethylphosphine or dimethylphenylphosphine affords the fluoro-olefin complexes [Ni(1,2,5,6-η^6-octafluorocyclo-octatetraene)L2] (L = PMe3 or PMe2Ph). In contrast to the reactions with nickel, the reactions of zerovalent platinum and palladium complexes with (40) result in the formation of perfluoro[3.3.1]octadienediy complexes (41, M=Pt or Pd) regardless of whether phosphines or t-butyl isocyanide are used as ancillary ligands.
An iminoplatinacyclobutene complex (44), analogous to (20) and (22), has been synthesised via the reaction of the platinum-cyclohexyne complex (43) with t-butyl isocyanide, equation 15.55

\[
\begin{align*}
(\text{Ph}_3\text{P})_2\text{Pt} & \quad \text{H} \quad \text{N} \quad \text{Bu}^+ \quad \text{NC} \\
\quad (43) & \quad \rightarrow \quad \text{Ph}_3\text{P} & \quad \text{Bu}^+ \quad \text{NC} \\
\quad (44) & \quad \text{H} \quad \text{N} \quad \text{Bu}^+ \quad \text{NC}
\end{align*}
\]

Finally, both cationic (46)56 and anionic (47)57 platinum(IV)cyclobutane complexes have been synthesised by treatment of the pyridinium ylide complexes (45) [available from the thermolysis of platinum(IV)cyclobutanes] with carbon monoxide or hydrogen iodide respectively, see Scheme 10. The reaction of (2, X=Cl) with hydrogen iodide also afforded (47).57

\[
\begin{align*}
\text{py-Pt-CH}_{\text{Et}} & \quad \text{py-Pt-CH}_{\text{Et}} \\
\quad (45) & \quad \rightarrow \quad \text{X} \\
\quad (46) & \quad \rightarrow \quad \text{X} \\
\quad (47) & \quad \text{pyH}^+
\end{align*}
\]
1.3 Bonding in Metallacyclobutane Complexes

The various bonding descriptions proposed for platinacyclobutanes have been previously summarised,\(^1\) however, certain points will be emphasised here for comparative purposes with metallacyclobutan-3-one-(\(\eta^3\)-oximethylenemethane) complexes, which are described in Section 1.4, and in Chapter 5.

There have been many structural studies of metallacyclobutane complexes of platinum and nickel (see for example Refs. 1, 11, 20, 22, 40, 47, and 53), for which the structural data indicate the metallacyclobutane formulation to be correct. The simplest model for bonding in metallacyclobutanes of platinum, palladium, and nickel, involves the bonding of an anionic \(\text{C}_3\text{H}_6\text{H}^{2-}\) type ligand (with sp\(^3\) hybridised carbon atoms) to a \(\text{d}^6\)-metal(IV) or \(\text{d}^8\)-metal(II) centre resulting in the formation of two, two-centre, two-electron metal-carbon \(\sigma\) bonds. However the ease with which platinum(IV)cyclobutanes undergo reductive elimination of cyclopropane on treatment with \(\pi\)-acceptor ligands led McQuillen to propose a synergic bonding interaction in these systems based upon overlap of Walsh orbitals of cyclopropane with suitable platinum orbitals, as shown in Figure 1.\(^{14}\) This model allows the description of all possible cases between metal-cyclopropane(A) and metallacyclobutane(B) formulations, analogous to the Dewar-Chatt model for the bonding of olefins to metal centres,\(^{58}\) see Figure 2. Thus, if the back-bonding is strong, due to the presence of electron-withdrawing substituents on the cyclopropane, then the platinacyclobutane description is most appropriate. The linear combination of cyclopropane Walsh orbitals with suitable platinum orbitals to form platinacyclobutane molecular orbitals has also been considered.\(^{59}\) These platinum-cyclopropane bonding models are of most use in describing the intermediates involved in the insertion of a metal.
i-iii Electron donation from Walsh orbital to empty metal orbital.
iv Back-donation from filled metal d-orbital to antibonding cyclopropane orbital.

Figure 1

atom into a cyclopropane ring.\textsuperscript{1,24}

1.4 METALLACYCLOBUTAN-3-ONE($\eta^3$-OXODIMETHYLENYLMETHANE) COMPLEXES

A number of metallacyclobutan-3-one complexes of platinum(II), palladium(II), osmium(II), and iridium(III) have recently been synthesised. Single-crystal X-ray diffraction studies on several of these complexes have demonstrated that their structures differ markedly from those of
metallacyclobutanes. The four-membered metallacyclobutan-3-one rings are characteristically highly puckered (48), with fold angles typically around 50°, when compared to platinacyclobutanes, for which fold angles lie in the range 0-30°.1,11,22,47 Furthermore, the metallacyclobutan-

![Diagram](48)

3-one complexes also display somewhat lengthened metal-carbon and carbon-oxygen bonds, and short carbon-carbon bonds, with the oxygen atom tipped out of the CCC plane towards the metal atom. These complexes are subsequently considered to contain a significant contribution from the δ^3-allylic type representation (49), and are therefore better described as δ^3-oxodimethylenemethane complexes. However, there is some confusion in the literature on the nomenclature used to describe these compounds, and they are alternatively described as oxoallyl, oxyallyl, and δ^3-β-diketonate(2-) complexes. A detailed description of the bonding in oxodimethylenemethane complexes is presented in Chapter 5.

The first examples of 1,3-disubstituted oxodimethylenemethane-metal complexes (2,4-disubstituted metallacyclobutan-3-one complexes) (50, M = Pt or Pd; L = PPh₃, PMePh₂, PMe₂Ph, or AsPh₃; R = CO₂Me or CO₂Et) were obtained by treatment of a benzene solution of the zerovalent metal complex [Pt(PPh₃)₄], [Pt(PMe₂Ph)₄], [Pt(PMe₂Ph)₄], [Pt(AsPh₃)₄], [Pd(PPh₃)₄], or [Pd(AsPh₃)₄] with either the methyl or ethyl ester of 3-oxopentane-2,4-dioic acid in the presence of air, as shown in equation 16.60-63

High yield syntheses of a variety of palladium derivatives (50, M = Pd; R = CO₂Me, L = PPh₃, PMePh₂, PMe₂Ph, PEr₃, AsPh₃ or L₂ = bipy; R = CO₂Et, L = PPh₃, AsPh₃ or L₂ = bipy; R = CO₂Pr, L₂ = bipy) were obtained via treat-
ment of the palladium(0) precursor $[\text{Pd}_2(\text{dba})_3].\text{CHCl}_3$ with the dialkyl ester of 3-oxopentane-2,4-dioic acid, and an excess of a donor ligand in the presence of air.$^{62,63}$ These reactions are believed to proceed via an intermediate zerovalent platinum or palladium dioxygen complex of the type $[\text{M(O}_2\text{)}\text{L}_2]$, since the reaction of $[\text{Pd(O}_2\text{)}\text{XPPh}_3)_2]$ with the dimethyl ester of 3-oxopentane-2,4-dioic acid afforded the oxodimethylene-methane complex (50, $\text{M} = \text{Pd}, \text{R} = \text{CO}_2\text{Me}, \text{L} = \text{PPh}_3$).$^{62}$ Similarly, the reaction of $[\text{Pt(O}_2\text{)}\text{XPPh}_3)_2]$ with the dimethyl ester of 3-oxopentane-2,4-dioic acid afforded the peroxo-ring complex (51), which could be converted into (50, $\text{M} = \text{Pt}, \text{R} = \text{CO}_2\text{Me}, \text{L} = \text{PPh}_3$) by further reaction with the ketone and triphenylphosphine.$^{61}$ Treatment of the carbonate complexes $[\text{Pt}((\text{CO}_3))\text{L}_2]$ with the esters of 3-oxopentane-2,4-dioic acid, $\text{RCH}_2\text{COCH}_2\text{R}$, ($\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}, \text{or CO}_2\text{Pr}^n$), and with heptane-2,4,6-trione afforded high yields of the respective platinum oxodimethylene-methane complexes (50, $\text{M} = \text{Pt}; \text{R} = \text{CO}_2\text{Me}, \text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{AsPh}_3$, or $\text{L}_2 = \text{dppe}; \text{R} = \text{CO}_2\text{Et}, \text{L} = \text{PPh}_3, \text{AsPh}_3; \text{R} = \text{CO}_2\text{Pr}^n, \text{L} = \text{PPh}_3$,}
AsPh₃; R = COMe, L = PPh₃ or AsPh₃).⁶¹,⁶⁴

Palladium(II) chloride reacts with mono-substituted acetones in water to afford 2-hydroxyallyl complexes (52, R = OEt) and (53, R = Me). These react with a number of nitrogen donor ligands to yield a series of chloro-σ-alkyl complexes (54), which can be transformed into the monosubstituted palladium oxodimethylenemethane complexes (55, R = Me, L₂ = bipy), (56, R = OEt, L₂ = bipy), (57, R = Me, L₂ = Me₂bipy), (58, R = OEt, L₂ = Me₂bipy), (59, R = Me, L₂ = phen), and (60, R = OEt, L₂ = phen), as illustrated in Scheme 11.⁶⁵ Displacement of the 2,2'-bipyridine ligand

\[
\begin{align*}
\text{Cl} & \quad \text{Pd} \quad \text{COR} \\
& \quad \text{OH} \\
(52), (53) \quad \rightarrow \quad \left[ \text{Pd} \quad \text{COR} \right]^{\text{ClO}_4^-} \\
& \quad \text{i} \quad \text{ii} \quad \text{iii} \quad \text{iv}
\end{align*}
\]

\[
\begin{align*}
\text{L} & \quad \text{Pd} \quad \text{Cl} \\
& \quad \text{CH₂COCH₂COR} \\
(54) \quad \rightarrow \quad (55) - (60)
\end{align*}
\]

i bipy, AgClO₄, ii L = bipy, Me₂bipy, or phen
iii Tl(acac), iv K(acac)

Scheme 11

of (55) and (56) with phosphine ligands leads to a new series of palladium oxodimethylenemethane complexes.⁶⁶,⁶⁷

The reaction of [Pt(acac)₂] with tri-σ-chlorophenylphosphine in chloroform afforded the monosubstituted platinum oxodimethylenemethane complex (61) in 49% yield, as depicted in Scheme 12.⁶⁸ In a related reaction, treatment of [Pt(acac)₂] with triphenylphosphine and
Al(OEt)Et₂ afforded the complex (62), which eliminated ethane on recrystallisation from tetrahydrofuran, and may have generated the oxodimethyleneenemethane complex (63), although formulated by the authors as [Pt(CH₂COCHCOMeXPPh₃)₂], see Scheme 12.⁶⁹ Treatment of [Pt(acac)₂] with triphenylphosphine in hot methanol afforded the complex [Pt(acacXPPh₃)₂(acac)], and when this mixture was kept at 60°C for more than four hours, a novel dinuclear oxodimethyleneenemethane complex (64) was produced, together with a small amount of (63).⁷⁰ Complex (64) may be considered as a bridging trianion of acetylacetonate, and can be isolated as its acac⁻ or PF₆⁻ salts.

\[
\begin{align*}
\text{(Ph₃P)₂Pt} & \quad \text{(acac or PF₆)} \rightarrow \\
\text{Pt(PPh₃)₂} & \quad \text{(acac or PF₆)}
\end{align*}
\]

(64)

The reaction of PdCl₂ or [PdCl₄]²⁻ with heptane-2,4,6-trione in water afforded the palladium acetylacetionate derivative (65), which yielded the palladaoxodimethyleneenemethane complex (50, M = Pd, R = COMe, L₂ = bipy) on treatment with 2,2'-bipyridine in dichloromethane, equation 17.⁶³ In
contrast, the reaction of $[\text{PdCl}_4]^{2-}$ with the dimethyl ester of 3-oxo-pentanedioic acid in water afforded the complex (66), which could also be converted into an oxodimethylenemethane complex (50, $M=\text{Pt, } R=\text{CO}_2\text{Me}$, $L=\text{PPh}_3$) on treatment with triphenylphosphine.

The monosubstituted oxodimethylenemethane complexes may act as ligands toward other metal centres, such as in the complexes (67).  

The first examples of unsubstituted oxodimethylenemethane complexes were provided by the reactions of the cationic iridium(I) complexes $[\text{IrL}_4]\text{Cl}$ ($L=\text{PM}_{3}$ or $\text{AsMe}_3$) with the enolate salt of acetone, affording the unsubstituted complexes (68), as shown in equation 18. A more
convenient route into unsubstituted oxodimethyleneemethane complexes of iridium, osmium, and platinum utilises the reactivity of the silyl enol ether (69) with low-valent metal complexes. Thus, treatment of [

\[
[\text{Os(CO)}_2(\text{PPh}_3)_3], [\text{IrH(CO)(PPh}_3)_3], [\text{IrH(CO)}_2(\text{PPh}_3)_2], \text{trans-[IrCl(CO)-(PPh}_3)_2], \text{and [Pt(trans-stilbene)(PPh}_3)_2}\]

with (69) afford the oxodimethyleneemethane complexes (70), (71), and (72) respectively, as illustrated in Scheme 13.72,73

\[
\text{Scheme 13}
\]

There has been considerable interest in the cyclo coupling of the diradical oxodimethyleneemethane (73) with alkenes and 1,3-dienes as a route into five- and seven-membered rings.74 For example, the reaction of the \(\alpha,\alpha'\)-dibromoketone (74) with \([\text{Fe}_2(\text{CO})_9]\) generates an oxodimethyleneemethane intermediate (75) which undergoes a \([3+4]\) cyclo coupling
reaction with furan to give the bicyclic ketone (76), see Scheme 14. \(^{75}\)

![Scheme 14](image)

This dehalogenation reaction bears a resemblance to the reaction of 3-chloro-2-chloromethylprop-1-ene with \([\text{Fe}_2(\text{CO})_9]\) in which a similar dehalogenation occurs, and a highly stable \(\eta^4\)-trimethylenemethane iron complex has been isolated, see equation 19. \(^{76}\) Following the isolation of stable, isoelectronic \(\eta^3\)-oxodimethylenemethane complexes of osmium(II) and iridium(III), (70) and (71) respectively, \(^{72,73}\) it has been suggested that the \([\text{Fe}_2(\text{CO})_9]\) mediated cyclocoupling reactions of \(\alpha,\alpha'\)-dibromo-ketones with olefins proceeds via an \(\eta^3\)-oxodimethylenemethane complex of
iron, and this may be of the type (77), in which the basic oxodimethylene-

enemethane oxygen co-ordinates to the liberated iron(II) bromide.\(^7\)

The palladium-trimethylenemethane complex (78) has been proposed as
an intermediate in the palladium-catalysed cycloaddition of trimethylene-
methane to oleins,\(^7\), and is isoelectronic with the oxodimethylenemethane
complexes of platinum and palladium, for example (72). A metallacyclic
form (79), related to the \(\eta^3\)-complex (78) has also been considered;\(^7\)\(^8\),\(^7\)
this is discussed in greater detail in Chapter 5.

1.5 FOUR-MEMBERED CYCLIC YLIDE COMPLEXES

A large number of ylide-stabilised four-membered metallacyclic com-
plexes have recently been synthesised by the reaction of phosphorus or
sulphur ylides with metal halide complexes, and two recent reviews on
the co-ordination chemistry of ylides have appeared.\(^8\)\(^0\),\(^8\)\(^1\)

Reactions of the trimethylphosphine complexes \([M\text{Cl}_2(P\text{Me}_3)_2]\) \((M=\text{Ni},
Pd, \text{or Pt})\) with phosphorus ylides \(R_1R_2R_3\text{P}^+\text{CH}_2\) afford products which
vary markedly according to the ylide substituents \(R\), and the metal \(M\).
Treatment of \([\text{NiCl}_2(P\text{Me}_3)_2]\) with two mole equivalents of \(\text{Me}_2\text{P}^-\text{CH}_2\)
initially yields the complex \([\text{NiCl(CH}_2\text{PMe}_3)_2\text{PMe}_3]\)Cl, which then reacts with more ylide in tetrahydrofuran to give a mixture of the dinuclear species (80) and (81).\textsuperscript{82,83} These reactions are considered to proceed via a transylidation process. The monomeric form (82) has been detected in the gas phase, and the existence of (82) is also suggested by the ease of interconversion of (80) and (81) in solution.\textsuperscript{82,83} A single-crystal X-ray diffraction study of (80) has confirmed the presence of chelating and bridging ylide moieties.\textsuperscript{84} The proximity of the phosphorus atom to the nickel in the four-membered ring, together with its puckering (fold angle = 43.9°) have been interpreted in terms of a transannular Ni–P interaction occurring via contributions from the heterocylic representations (83) and (84) to the metallacyclic
The reactions of palladium and platinum complexes with $\text{Me}_3\text{P}^-\text{CH}_2$ have also been investigated. Thus, when the complex $[\text{PdCl}_2(\text{PMes})_2]$ is treated with $\text{Me}_3\text{P}^-\text{CH}_2$ in benzene, a mixture of the ionic chelate complex (85) and the dimer (86), [analogous to the nickel complex (81)] is isolated, as depicted in Scheme 15. The low solubility of (85) in benzene prevents its subsequent transformation to (86). The platinum and bromo analogues of (85) have also been reported, and are considered to be in equilibrium with the dimeric species (87), see equation 20.

The reactions of $[\text{PdCl}_2(\text{PMes})_2]$ with the ylides 1-methyl-1-methylene-$\lambda^5$-phospholane and -phosphorinane, $\text{R}_2\text{MeP}^-\text{CH}_2$ [R$_2$ = -(CH$_2$)$_n$ - or -(CH$_2$)$_5$-]
proceed with complete transylidation to afford the spirocyclic dinuclear ylide complexes (88), as illustrated in equation 21.\(^5\) In contrast, however, the reaction of \([\text{NiCl}_2(\text{PMe}_3)_2]\) with \(R_2\text{MeP}--\text{CH}_2\) \(R_2 = -(\text{CH}_2)_n-\),

\[
2[\text{PdCl}_2(\text{PMe}_3)_2] + 8R_2\text{MeP}--\text{CH}_2
\]

\[
-4[R_2\text{MeP}]\text{Cl}
\]

\[
-4\text{PMe}_3
\]

Contrastingly, the reaction of \([\text{NiCl}_2(\text{PMe}_3)_2]\) with \(Bu^t\text{MeP}--\text{CH}_2\) afforded only monomeric complexes (89), as depicted in equation 22.\(^7\) The formation of monomeric structures for the bulky t-butyl ylides is probably a result of a minimisation of steric effects, with monomers of the type (89) better able to accommodate the steric bulk of a t-butyl group. Although the steric requirements of the phospholane and phosphorinane ylides are low, the unexpected formation of their monomeric complexes (89) has been attributed to the presence of a small CPC angle in the heterocycle, concomitant with an opening of the ylidic CPC angle, which in turn may favour a greater degree of hetero-\(\pi\)-allylic character in these complexes.\(^7\)

The reaction of \([\text{PtCl}_2(\text{PMe}_3)_2]\) with \(Bu^t\text{MeP}--\text{CH}_2\) did not afford a monomeric complex of type (89), and instead the cationic ylide complex (90) was obtained, as a result of the reduced lability of trimethylphos-
The reaction of the bis(diphenylphosphinomethanide) complexes 

\[ [M(Ph_2PCHPPh_2)_2] \quad (M = Ni, Pd or Pt) \]

with \( Me_3P—\overline{\text{CH}_2} \) or \( Et_2MeP—\overline{\text{CH}_2} \) leads to formation of complexes (91) which contain both a chelating diphenyl phosphinomethanide ligand together with a chelating ylide ligand, see equation 24. The structure of the platinum complex has been confirmed by a structural study.

A number of chelating sulphur ylide complexes of nickel and palladium have similarly been synthesised. The reaction of \( [NiCl(SacSac)\text{phosphine}]^+ \) with an excess of \( Me_2S(O)—\overline{\text{CH}_2} \) afforded the chelating sulphur ylide complex (92), characterised by an X-ray study. The palladium sulphur...
The phase transfer catalysis technique has also been employed with success in the synthesis of sulphur ylide complexes. Thus, reaction of $\text{trans-}[\text{PdCl}_2(\text{PPh}_3)_2]$ with two equivalents of $\text{Me}_2\text{S(O)}-\overline{\text{CH}}_2$ in tetrahydrofuran is reported to afford a mixture of the chelate ylide complexes (94), (95, $L=\text{PPh}_3$) and the bis-(monodentate ylide) complex $\text{cis-}[\text{Pd}(\text{CH}_2\text{S(O)}\text{Me})_2(\text{PPh}_3)_2]_2$.$^{91}$ However, under phase transfer catalysis conditions, the reactions of $\text{trans-}[\text{PdCl}_2(\text{PPh}_3)_2]$ with trimethylsulphoxonium iodide in chloroform/aqueous sodium hydroxide in the presence of tetra-$n$-butyl ammonium iodide or 18-crown-6 as a phase transfer catalyst afford either pure (94) or (95, $L=\text{PPh}_3$) alone, depending on the quantity of base employed.$^{91}$ Bridge-splitting reactions of (93) with triphenylphosphine, triphenylphosphite, trimethylphosphite, or pyridine also afford a series of compounds (95) [$L=\text{PPh}_3, \text{P(OPh)}_3, \text{P(OMe)}_3$, or py].$^{92}$
Sulphur ylide complexes have also been prepared in aqueous solution by the reaction of \((\text{NH}_4)_2\text{[PdCl}_4]\) with trimethylsulphoxonium iodide in sodium hydroxide solution, affording complexes (93) and (96), depending on the conditions.\(^\text{93}\) By means of further reaction of (93) with trimethylsulphoxonium iodide in basic solution, the complexes (97) and (98) were produced, also dependent on the conditions employed.\(^\text{93}\) The reaction of (96) with chelating ligands such as dithiolates or the acetylacetonate anion affords stable chelate ligand ylide complexes (99), \(\text{L} = \text{acac, S}_2\text{P(OEt)}_2, \text{S}_2\text{COEt, or S}_2\text{CNET}_2\), comparable with the SacSac complex (92).\(^\text{89}\) Treatment of (97) with iodine afforded an unstable complex formulated as \([\text{Pd(CH}_2\text{S}(\text{O})(\text{Me})\text{CH}_2]_2\text{I}_2\]) which decomposed rapidly to yield (93).\(^\text{92}\) The reactions of (96)-(98) with hydroiodic acid also afforded (93), and the reaction of (97) with hydrochloric acid gave the chloro-analogue of (93).\(^\text{92}\)

Single-crystal X-ray diffraction studies have been carried out on the phosphorus ylide complexes (80)\(^\text{84}\) and (91, \(\text{M} = \text{Pt}\)),\(^\text{88}\) and on the sulphur ylides (92),\(^\text{89}\) (96),\(^\text{93}\) and (97).\(^\text{92}\) These four-membered ring cyclic ylides characteristically contain puckered ylide rings and short carbon-phosphorus or carbon-sulphur bonds. For example, the four-membered ring of (96) is folded about the C-C axis by 31.7°, and the CH₂-S bond distances
[average 1.71(2) Å] are somewhat shorter than the S-CH₃ bond distances [average 1.756(20) Å]. This bond shortening has been interpreted in terms of a partial retention of ylidic character, and contributions to the metallacyclic bonding from heteroallylic representations such as (83) and (84) have been proposed. This is described in greater detail in the following Chapter.
CHAPTER 2

Synthesis of Metallathietane-3,3-dioxide Complexes of Platinum, Palladium and Nickel
2.1 INTRODUCTION

The synthesis of metallacyclobutane complexes of platinum, palladium, and nickel may be achieved via a range of synthetic methods, as described in Chapter 1. However, many of these methods have drawbacks and do not provide routes to metallacyclic complexes containing either a wide variety of donor ligands or the presence of a functionality in the metallacyclic ring.

One of the classical methods for the synthesis of metal-carbon bonds involves the reaction of a carbanion source with a metal-halide complex.\textsuperscript{94} The application of this methodology via the use of 1,3-difunctional reagents of the type (100) has provided routes to a range of four-membered metallacyclic complexes of main group as well as early transition metals. Thus, for example metallacyclobutane complexes of titanium, zirconium, and hafnium, and silametallacyclobutane complexes of titanium, zirconium, niobium, and molybdenum (101) are obtained by treatment of [MX\textsubscript{2}C\textsubscript{p}]- (X=Cl, I) with (100, R=Me, M=MgBr), or with the related magnesium-containing reagent [CH\textsubscript{2}MgCH\textsubscript{2}SiMe\textsubscript{2}]\textsubscript{n} respectively.\textsuperscript{95,96} The recent application of 1,3-difunctionalised reagents in the synthesis of both unsaturated\textsuperscript{97} and spirocyclic\textsuperscript{98} metallacycles has also been described, as illustrated in equations 25 and 26. Although there are no reports of the synthesis of platinum, palladium, or nickel metallacyclobutanes (or derivatives thereof) using 1,3-difunctional organometallic reagents, the use of longer chain \(\alpha,\omega\)-difunctional reagents in metallacyclic synthesis has received more widespread success, as in for example, the synthesis of metallacyclo-
pentane and -hexane complexes of platinum(II)\(^{99}\) and titanium(IV),\(^{100}\) as shown in equation 27.

\[
\text{CH}_2(\text{MgBr})_2 \xrightarrow{1. [\text{TiCl}_2\text{Cp}_2]} \xrightarrow{2. \text{SiCl}_4} \text{Cp}_2\text{Ti} \overset{\text{Si}}\text{TiCp}_2
\]

The 1,3-difunctional reagents \(M_2[\text{PhCHS(O)}_2\text{CHPh}]\) (102, \(M = \text{Li}\))\(^{101}\) or (103, \(M = \text{K}\))\(^{102}\) and \(K_2[\text{PhCHC(O)}\text{CHPh}]\) (104),\(^{102}\) readily available via the deprotonation of dibenzyl sulphone and dibenzyl ketone (1,3-diphenyl acetone) respectively, can be viewed as precursors to the 2,4-disubstituted metallathietane-3,3-dioxide (105) and 1,3-disubstituted-\(\eta^3\)-oxo-dimethylenemethane (2,4-disubstituted metallacyclobutan-3-one) (106) systems respectively. As part of this thesis, the reactions of (102)-(104)
with various platinum, palladium, and nickel dichloride complexes have been investigated, and the results are presented in this Chapter, and also in Chapter 5.

The complex cis-[PtCl₂(PET₃)₂] is known to react with molecules containing 'acidic' C-H protons, such as acetone, nitromethane and phenylacetylene, in the presence of silver(I) oxide, to afford complexes containing platinum-carbon σ-bonds, see equation 28. The platinaoxo-

\[
\text{cis-}[\text{PtCl}_2(\text{PET}_3)_2] + \text{RH} \xrightarrow{\text{Ag}_2\text{O}} \text{cis-}[\text{PtCl}(\text{R})(\text{PET}_3)_2] \\
(\text{R} = \text{CH}_2\text{COMe, CH}_2\text{NO}_2)
\]

or

\[
\text{trans-}[\text{PtR}_4(\text{PET}_3)_2] \\
(\text{R} = \text{C} : \text{CPh})
\]

dimethylenemethane complex (50, M = Pt, R = CO₂Me, L = PPh₃) has similarly been synthesised by the reaction of cis-[PtCl₂(PPh₃)₂] with the dimethyl ester of 3-oxopentane-2,4-dioic acid and silver(I) oxide in dichloro-

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{R} \\
\text{O} \\
\end{array}
(107), \ R = \text{COPh} \\
(108), \ R = \text{CO}_2\text{Me}
\]

The rôle of silver(I) oxide in these reactions is to act as both a halide abstracting reagent and a strong base. The 1,3-disubstituted dimethyl sulphones RCH₂S(O)₂CH₂R (107, R = COPh), and (108, R = CO₂Me) contain activated methylene groups, and the reactions of (107) and (108) with metal-dichloride complexes in the presence of silver(I) oxide, giving metallathietane-3,3-dioxide complexes (105), are also described in this Chapter.

-35-
2.2 PREPARATION OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES

Treatment of the complexes cis- or trans-[MCl₂L₂] (cis-complex; M = Pt, L = AsPh₃, PPh₃, or SET₂; M = Ni, L₂ = dppe; trans-complex; M = Pd, L = PPh₃, PMe₃, or PEt₃; M = Ni, L = PMe₃) with one equivalent of the 1,3-difunctional organolithium reagent (102) in THF at low temperature affords, in moderate to excellent yields the metallathietane-3,3-dioxide complexes (109)-(116), as depicted in equation 29. Treatment of cis-

\[
\text{cis-} \quad \text{or} \quad [MCl₂L₂] + (102) \quad \text{THF, } -78°C \quad 29
\]

\[
\begin{align*}
(109), & \ M = \text{Pt, } L = \text{AsPh}_3 \\
(110), & \ M = \text{Pt, } L = \text{PPh}_3 \\
(111), & \ M = \text{Pt, } L = \text{SEt}_2 \\
(112), & \ M = \text{Pd, } L = \text{PPh}_3 \\
(113), & \ M = \text{Pd, } L = \text{PMe}_3 \\
(114), & \ M = \text{Pd, } L = \text{PET}_3 \\
(115), & \ M = \text{Ni, } L = \text{PMe}_3 \\
(116), & \ M = \text{Ni, } L₂ = \text{dppe}
\end{align*}
\]

[PtCl₂(AsPh₃)₂] or trans-[PdCl₂(PPh₃)₂] with the corresponding organopotassium reagent (103) under analogous conditions similarly affords comparable yields of (109) and (112) respectively. The reaction of palladium(II) acetate with trimethylphosphine and (102) also affords complex (113) in moderate yield. The platinum and palladium complexes (109)-(114) are isolated as white to pale yellow air-stable solids, whereas the nickel complexes are isolated as orange to red-orange solids which are somewhat air-sensitive, particularly in solution.

High yield syntheses of a range of platina- and palladathietane-3,3-dioxide complexes containing benzoyl ring substituents may be achieved
by treatment of the complexes cis-[PtCl₂L₂] or trans-[PdCl₂L₂] (L = tertiary phosphine or triphenylphosphite) (obtained in situ by reaction of [MCl₂(CO)] with two mole equivalents of L), with diphenacyl sulphone (107) in refluxing dichloromethane in the presence of silver(I) oxide, to give the metallathietane-3,3-dioxide complexes (117, M = Pt, L = PPh₃), (118, M = Pt, L = PMePh₂), (119, M = Pt, L = PMe₂Ph), (120, M = Pt, L = PMe₃), (121, M = Pt, L = PET₃), (122, M = Pt, L = PBu₃), (123, M = Pt, L = POPh₃), (124, M = Pd, L = PPh₃), (125, M = Pd, L = PMePh₂), (126, M = Pd, L = PMe₂Ph), (127, M = Pd, L = PMe₃), (128, M = Pd, L = PET₃), and (129, M = Pd, L = PBu₃), as illustrated in equation 30. Similarly, cis-[PtCl₂(PPh₃)₂] and trans-[PdCl₂(PPh₃)₂] react with the dimethyl ester of 2,2'-sulphonyldiacetic acid (108) in refluxing dichloromethane in the presence of excess silver(I) oxide to afford the methoxycarbonyl substituted metallathietane-3,3-dioxide complexes (130, M = Pt, L = PPh₃) and (131, M = Pd, L = PPh₃), equation 30. Complexes (117)-(131) were isolated as white to pale yellow air-stable microcrystalline to crystalline solids.

\[
\begin{align*}
\text{cis-}[\text{PtCl}_2L_2] & \quad \text{or} \quad \text{trans-}[\text{PdCl}_2L_2] \\
\Delta, \text{CH}_2\text{Cl}_2 & \quad \text{excess Ag}_2\text{O} \\
\text{RCH}_2\text{S(O)}_2\text{CH}_2\text{R} & \quad 30 \\
\end{align*}
\]

(117) - (129) \( R = \text{COPh} \)

(130), (131) \( R = \text{CO}_2\text{Me} \)
2.3 STRUCTURAL PROPERTIES OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES

Single-crystal X-ray diffraction studies for three of these metallathietane-3,3-dioxide complexes have been carried out to establish the molecular geometry and nature of the bonding in these complexes. The two platinum complexes (109) and (117) containing phenyl and benzoyl ring substituents respectively, and the palladium complex (125) have had their molecular structures determined, and a summary of the important bond lengths and angles are given in Tables 1 and 2 respectively.

The general molecular structure of these metallathietane-3,3-dioxide complexes is summarised in Figure 3, which also gives the crystallographic numbering system. All three complexes crystallise with solvent molecules incorporated in cavities in the lattice, as indicated in Tables 1 and 2. There are no short intermolecular contacts between the metal complexes and the solvent molecules. The molecular structure of (109) is illustrated in Figures 4 and 5, and the molecular structures of (117) and (125) are illustrated in Figures 6 and 7 respectively.

The co-ordination around the metal atoms in all three complexes is


TABLE 1

Bond lengths for the complexes [M(CHRS(0)CHR)\textsubscript{2}]\textsuperscript{a}

<table>
<thead>
<tr>
<th>Bond length ( (\text{A}) )</th>
<th>Complex</th>
<th>( (109) \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O} )</th>
<th>( (117) \cdot 2\text{CH}_2\text{Cl}_2 )</th>
<th>( (125) \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M-E(1) )\textsuperscript{b}</td>
<td>2.422(2)</td>
<td>2.327(3)</td>
<td>2.295(1)</td>
<td></td>
</tr>
<tr>
<td>( M-E(2) )\textsuperscript{b}</td>
<td>2.403(2)</td>
<td>2.285(3)</td>
<td>2.311(2)</td>
<td></td>
</tr>
<tr>
<td>( M-C(1) )</td>
<td>2.063(21)</td>
<td>2.106(10)</td>
<td>2.148(6)</td>
<td></td>
</tr>
<tr>
<td>( M-C(2) )</td>
<td>2.082(21)</td>
<td>2.125(11)</td>
<td>2.122(6)</td>
<td></td>
</tr>
<tr>
<td>( M-S )</td>
<td>2.792(5)</td>
<td>2.840(5)</td>
<td>2.770(2)</td>
<td></td>
</tr>
<tr>
<td>( C(1)-S )</td>
<td>1.725(23)</td>
<td>1.762(11)</td>
<td>1.749(5)</td>
<td></td>
</tr>
<tr>
<td>( C(2)-S )</td>
<td>1.758(20)</td>
<td>1.755(11)</td>
<td>1.738(5)</td>
<td></td>
</tr>
<tr>
<td>( S-O(1) )</td>
<td>1.439(19)</td>
<td>1.439(9)</td>
<td>1.433(5)</td>
<td></td>
</tr>
<tr>
<td>( S-O(2) )</td>
<td>1.436(17)</td>
<td>1.445(8)</td>
<td>1.435(4)</td>
<td></td>
</tr>
<tr>
<td>( C(1)-H(1) )</td>
<td>1.080</td>
<td>0.97(7)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( C(2)-H(2) )</td>
<td>1.080</td>
<td>0.96(8)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Figure 3 for crystallographic numbering system;
\textsuperscript{b} \( E = \text{As} \) or \( P \).
TABLE 2a

Bond, plane and torsion angles for the complexes [M(CHS(O)2CHR)L2]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>E(1)—M—E(2) b</td>
<td>98.1(1)</td>
<td>98.5(1)</td>
<td>97.7(1)</td>
<td></td>
</tr>
<tr>
<td>E(1)—M—C(2) b</td>
<td>92.0(6)</td>
<td>91.9(3)</td>
<td>94.0(2)</td>
<td></td>
</tr>
<tr>
<td>E(2)—M—C(1) b</td>
<td>95.8(6)</td>
<td>94.2(3)</td>
<td>93.6(1)</td>
<td></td>
</tr>
<tr>
<td>C(1)—M—C(2)</td>
<td>74.3(8)</td>
<td>75.4(4)</td>
<td>74.7(2)</td>
<td></td>
</tr>
<tr>
<td>M—C(1)—S</td>
<td>94.6(10)</td>
<td>94.0(4)</td>
<td>90.0(2)</td>
<td></td>
</tr>
<tr>
<td>M—C(2)—S</td>
<td>92.9(10)</td>
<td>93.6(5)</td>
<td>91.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)—S—C(2)</td>
<td>92.0(10)</td>
<td>94.8(5)</td>
<td>95.9(3)</td>
<td></td>
</tr>
<tr>
<td>C(1)—S—O(1)</td>
<td>112.2(12)</td>
<td>113.7(6)</td>
<td>110.9(3)</td>
<td></td>
</tr>
<tr>
<td>C(1)—S—O(2)</td>
<td>110.7(10)</td>
<td>108.7(6)</td>
<td>112.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(2)—S—O(1)</td>
<td>115.8(11)</td>
<td>114.1(5)</td>
<td>112.8(3)</td>
<td></td>
</tr>
<tr>
<td>C(2)—S—O(2)</td>
<td>107.4(11)</td>
<td>106.6(5)</td>
<td>107.9(2)</td>
<td></td>
</tr>
<tr>
<td>Twist c</td>
<td>6.78</td>
<td>6.48(36)</td>
<td>3.47(13)</td>
<td></td>
</tr>
<tr>
<td>Fold d</td>
<td>24.56</td>
<td>15.25(56)</td>
<td>30.19(22)</td>
<td></td>
</tr>
<tr>
<td>P(1)—M—C(2)—H(2) torsion</td>
<td>-</td>
<td>-47.42</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>P(2)—M—C(1)—H(1) torsion</td>
<td>-</td>
<td>-71.41</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

a See Figure 3 for crystallographic numbering system;
b E = As or P;
c ∠E(1)—M—E(2)/C(1)—M—C(2);
d ∠C(1)—M—C(2)/C(1)—S—C(2).
FIGURE 4
Molecular structure of the complex $[\text{Pt(CHPhS(O)}\text{CHPh})(\text{AsPh}_3)_2]$ \(109\) with phenyl hydrogen atoms omitted.
FIGURE 5
Molecular structure of (109) with only attached carbon atoms of phenyl rings illustrated (shaded circles).
FIGURE 6
Molecular structure of [Pt(CH(COPh)S(O)₂CH(COPh))(PPh₃)₂] (117) with triphenylphosphine carbon atoms other than those bonded to phosphorus, and hydrogen atoms of phenyl rings being omitted.
FIGURE 7
Molecular structure of the complex [Pd(CH(COPh)S(O)2CH(COPh))2(PMePh2)2] (125) with all hydrogen atoms omitted.
effectively square-planar, the twist angles between the E(1)-M-E(2) and C(1)-M-C(2) planes (E = As or P) being in the range 3.47-6.78°. Overall, the molecular structures of these metallathietane-3,3-dioxide complexes bear a strong resemblance to those of related platinacyclobutane complexes. The complexes (109), (117), and (125) contain non-planar four-membered ring systems, the fold angles between the planes C(1)-M-C(2) and C(1)-S-C(2) being 24.56°, 15.25°, and 30.19° for (109), (117), and (125) respectively. Studies on a number of platinacyclobutane complexes have established fold angles in the range 0-30°. The fold angles for the metallathietane-3,3-dioxide complexes also lie within the range of 9-35° found for thietane-1,1-dioxide, C-C-C-S(O)₂ ring systems. Some structural data for a number of these thietane-1,1-dioxide ring systems, together with selected data for the metallathietane-3,3-dioxide complexes for comparison, are presented in Table 3. Puckering in four-membered rings results in a decrease in eclipsing strain, concomitant with an increase in angle strain until a minimum energy balance between the two opposing effects is achieved. Interestingly, the 1,3-dithietane oxide ring systems CCl₂SCCl₂S(O)₂ and CX₂S(O)₂CX₂S(O)₂ (X = H, F, Cl, or Br) have been shown to contain planar rings, but the ring system CH₂SCH₂S(O) is puckered by 39.3°, with the oxygen in an equatorial environment.

An examination of the X-ray data contained in Table 3 reveals that the metallathietane-3,3-dioxide complexes have shorter C-S bond distances and larger C-S-C bond angles than for thietane-1,1-dioxides. Thus, for the thietane-1,1-dioxides these values lie in the ranges 1.792-1.865 Å and 77.6-82.2°, whereas the corresponding ranges for the metallathietane-3,3-dioxide complexes are 1.742-1.759 Å, and 92.0-95.9°. These data may be interpreted in terms of a reduction in ring strain of the four-
<table>
<thead>
<tr>
<th>Ring</th>
<th>Fold angle (^\circ)^b</th>
<th>(&lt;\text{C-C}&gt;^\circ)</th>
<th>Mean bond distance ((\AA))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-S</td>
<td>S=O</td>
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<tr>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 1" /></td>
<td>35(^b)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 2" /></td>
<td>9</td>
<td>82.2</td>
<td>1.793</td>
<td>1.411</td>
</tr>
<tr>
<td><img src="image" alt="Structure 3" /></td>
<td>22.5</td>
<td>80.2(3)</td>
<td>1.792(6)</td>
<td>1.456(4)</td>
</tr>
<tr>
<td><img src="image" alt="Structure 4" /></td>
<td>25.1</td>
<td>80.9(2)</td>
<td>1.834(5)</td>
<td>1.422(4)</td>
</tr>
<tr>
<td><img src="image" alt="Structure 5" /></td>
<td>31.3</td>
<td>77.6(8)</td>
<td>1.865(20)</td>
<td>1.445(20)</td>
</tr>
<tr>
<td>(109)</td>
<td>24.56</td>
<td>92.0(10)</td>
<td>1.742(22)</td>
<td>1.438(18)</td>
</tr>
<tr>
<td>(117)</td>
<td>15.25</td>
<td>94.8(5)</td>
<td>1.759(11)</td>
<td>1.442(9)</td>
</tr>
<tr>
<td>(125)</td>
<td>30.19</td>
<td>95.9(3)</td>
<td>1.744(5)</td>
<td>1.434(5)</td>
</tr>
</tbody>
</table>

\(^a\) \(<\text{C-C-C/C-S-C}\>; \(^b\) From n.m.r. data.
membered ring system on replacement of carbon by a substantially larger platinum or palladium atom. The presence of ring strain in a cyclic organic molecule often results in a lengthening of the ring bonds, as observed for example in cyclobutanes. Further examination of the X-ray data for the thietane-1,1-dioxides, Table 3, reveals that as a general rule, on increasing the number of substituents (particularly in equatorial environments) on the sulphur-bonded ring carbons, there is a decrease in the C-S-C bond angle with a concomitant increase in the C-S bond distance. The C-S-C bond angle for dimethyl sulphone, which possesses no ring strain, is 103.0°. The C-S-C bond angles for the metallathietane-3,3-dioxide complexes are intermediate between those of thietane-1,1-dioxides and dimethyl sulphone, suggesting that the metallacycles do contain a degree of ring strain. Therefore, C-S bond distances intermediate between those of thietane-1,1-dioxides and dimethyl sulphone might also be expected. However, the C-S bond distances of the metallacycles (average 1.749 Å) appear slightly shorter than those of dimethyl sulphone [average 1.778(17) Å]. This suggests that there is an additional C-S bond shortening in the metallacyclic complexes to that which would be expected via a reduction in ring strain on replacement of carbon with platinum or palladium.

A number of chelating phosphorus and sulphur ylide complexes (80), (91, M = Pt), (92), (96), and (97), see Chapter 1, and the cobalt complex (132), containing the MCH₂PMe₂CH₂ or MCH₂S(O)(Me)CH₂ ring systems, have been found to contain notably shortened metallacyclic C-P and C-S bonds. Thus, for example, in the palladium sulphur ylide complex (96) the CH₂-S bond distances are shorter [average 1.71(2) Å] than the CH₃-S bond distances [average 1.756(20) Å]. Similarly in the cobalt complex (132) the metallacyclic C-P bond distances average 1.726(9) Å, as
compared with average C-P distances in the PMe$_2$ group and trimethylphosphine ligands of 1.793(8) Å and 1.799(9) Å respectively. The shortening of the metallacyclic C-P bonds in the octahedral cobalt complex (132), which contains a planar ylide ring, has been interpreted in terms of a contribution from a heteroallylic representation (84), Chapter 1, to the metallacyclic bonding.\textsuperscript{84} Such a system may be constructed using a phosphorus d$_{x^2-y^2}$ orbital, Figure 8, and requires an approximately planar four-membered ring in order to maximise orbital overlap.\textsuperscript{84} In contrast to the planar cobalt complex (132), the four-membered ylide rings of the nickel, palladium, and platinum ylide complexes (80),\textsuperscript{84} (91, M = Pt),\textsuperscript{88} (96),\textsuperscript{93} and (97)\textsuperscript{92} are highly puckered, for example the fold angles of the four-membered rings of (80) and (96) are 43.9 and 31.7° respectively. A contribution to the bonding from a 'classical'-type n$^2$-heteroallylic representation (83) has been proposed to account for the large deviation from planarity of these systems, together with
the carbon-phosphorus bond shortening, and a similar description may be applied to the sulphur chelate ylide complexes.

The apparent shortening of the C-S bonds of the metalla-thietane-3,3-dioxide complexes (109), (117), and (125) (which also contain puckered rings) may be similarly interpreted in terms of a contribution from a heteroallylic-type representation (133) or (134) to the metallacyclic bonding. The representations (133) and (134) are analogous to the phosphorus representations (83) and (84), Chapter 1. An examination of the X-ray data for the metalla-thietane-3,3-dioxide complexes (117) and (125) indicates that the palladium complex (125) is substantially more puckered than the platinum complex (117), and appears to have slightly shorter C-S bonds [although the C-S bonds of (117) and (125) are equal within the 3σ range]. This suggests that the contribution from (133) is important, since an increased contribution from this η³-type representation would be expected to both increase the fold angle of the ring, and shorten the C-S bonds.

A number of η³-oxodimethylenemethane(metallacyclobutan-3-one) complexes of platinum, palladium, and iridium, Chapter 1, contain highly puckered four-membered rings (48) and a large contribution from an η³-allylic (oxodimethylenemethane) representation (49) is considered to account for the non-planarity of these complexes. X-ray studies of these systems have indicated that the palladium complexes are more puckered with shorter C-C bonds, and therefore have a greater degree of η³-allylic
character (49) than their platinum analogues.\textsuperscript{60-64}

A consequence of considering an allylic contribution to the bonding in metallathietane-3,3-dioxide complexes is that the bond order of the sulphur-oxygen bonds is predicted to be less than two. However, the S=O bond distances for (109), (117), and (125) are identical, within experimental error, at around 1.438 Å, the values lying within the range of 1.411-1.456 Å observed for a range of thietane-1,1-dioxide ring systems, see Table 3.

Interestingly, structural studies on the lithiated sulphones \([\text{PhS(O)₂CHRLi.L}]_2\) (135, \(R=\text{H}, L=\text{TMEDA}\)),\textsuperscript{115} (136, \(R=\text{Ph}, L=\text{TMEDA}\)),\textsuperscript{116} and (137, \(R=\text{CH:CH}_2, L=\text{diglyme}\)),\textsuperscript{117} reveal that these compounds contain very short S-CH bonds, due to 'sulphenolate'-like character (138), but the corresponding lengthening of the S=O bonds for (135) and (136) is of a much smaller magnitude, and is undetectable in the case of (137).

Thus, for example, the S-CH bond distance for (135) of 1.608(3) Å is comparable with the C=S bond of thioformaldehyde [C=S bond distance 1.6108(9) Å],\textsuperscript{118} and is much shorter than the S-CH bond distance of the parent methyl phenyl sulphone (S-CH 1.761 Å).\textsuperscript{115,119} However, the S=O bond distances of (135) [average 1.460(2) Å] are comparable with those of methyl phenyl sulphone [average S=O 1.459 Å].\textsuperscript{115,119} Hence, in the metallathietane-3,3-dioxide complexes (109), (117), and (125), which show a small degree of C-S bond shortening, a smaller undetectable amount
of S=0 bond lengthening may be expected, and thus the S=0 bond distances in these systems appear normal.

The platinum-carbon bond distances for the platinathietane-3,3-dioxide complexes (109) and (117) are similar to those in phosphine-containing platinacyclobutanes, for example, the average Pt-C bond distances in (17, \(M = \text{Pt}, L = \text{PPh}_3, R = \text{H}, R' = \text{Ph}, R'' = \text{CN}\)) and (36, \(L = \text{PPh}_3\)) are 2.148, and 2.083 Å respectively.\(^{25,47}\) Thus, as a result of the relatively large range of platinum-carbon bond distances in platinacyclobutanes, together with an absence of suitable examples for comparison, it is difficult to conclusively assign any lengthening of the platinum-carbon bonds in the metallathietane-3,3-dioxide compounds, as would be predicted as a result of an allylic contribution (133) or (134) to the bonding. The long palladium-carbon bonds of (125) [average Pd-C 2.135 Å], as compared to the platinum-carbon bonds of (117) [average Pt-C 2.116 Å] are consistent with a greater allylic contribution in the palladium complex (125), as described previously, however, the presence of a more basic phosphine (of higher trans influence) in (125) will also tend to lengthen the palladium-carbon bonds. Similarly, highly non-planar metal \(\eta^1\)-oxodimethylenemethane complexes of platinum(II) and palladium(II)\(^{50}\), Chapter 1, also show longer metal-carbon bonds in the palladium complexes compared to the platinum complexes, and this can be taken as evidence for a greater allylic contribution (49) in the palladium complexes.\(^{60-64}\) The \(\eta^1\)-benzylic complexes (139) also show longer metal-carbon bond lengths for palladium when compared to platinum.\(^{120}\) In contrast, however, a recent study of the isostructural \(\sigma\)-alkyl complexes \(\text{cis-}[\text{M(CH}_3)_2(\text{PMePh}_2)_2]\) (\(M = \text{Pt, Pd}\)) conversely demonstrates a shortening of the metal-carbon bond (with a concomitant lengthening of the metal-phosphorus bond) when the metal is changed from platinum to palladium.\(^{121}\) These observations appear
to be consistent with a hetero-\(\pi\)-allylic contribution (133) to the bonding in metallathietane-3,3-dioxide complexes.

The platinum-carbon bonds of (109) are somewhat shorter than those of (117) and (125), presumably as a result of the low \textit{trans} influence of the triphenylarsine ligands.

It is interesting to note that the metalla-3-silacyclobutane complexes \([\text{Os(CH}_2\text{SiMe}_2\text{CH}_2\text{(PMe}_3)_4}]\) (140)\(^{122}\) and \([\text{Ir(CH}_2\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_5\text{Me}_5\text{XPPh}_3)]}\) (141)\(^{50}\) contain, respectively, planar and slightly puckered (fold angle 18.9°) metallacyclic rings in which the C-Si bonds are significantly shorter than the exocyclic C-Si bonds. Thus, in (141) the average Si-CH\(_2\) bond distance is 1.836(8) Å, as compared with an average Si-CH\(_3\) bond distance of 1.888(9) Å. This is identical to the behaviour displayed by a number of cyclic ylide and metallathietane-3,3-dioxide complexes described previously. That the carbon-silicon bond shortening is effected by the presence of a metallacyclic silicon atom may be demonstrated by an examination of the X-ray data for the related rhodacyclobutane complex \([\text{Rh(CH}_2\text{CMe}_2\text{CH}_2(\eta^5\text{-C}_5\text{Me}_5\text{XPPh}_3)]}\),\(^{50}\) in which all the C-C distances around the metallacyclic quaternary carbon are essentially identical. This silicon-carbon bond shortening in the complexes (140) and (141) may possibly arise as a result of a heteroallylic contribution (142) to the metallacyclic bonding \textit{via} utilisation of a silicon d-orbital, as described previously for a phosphorus heteroallylic representation, Figure 8. In contrast, silametallacyclobutanes of early transition metals (101) \((M=\text{Ti}, \text{V})\).
Zr, Nb, Mo) do not display metallacyclic carbon silicon bond shortening.\(^{96,123}\)

All three metallathietane-3,3-dioxide complexes (109), (117), and (125) exist as the 'trans'-isomer, with one of the phenyl or benzoyl substituents in a pseudo-axial environment, and the other in a pseudo-equatorial environment, as a result of the puckering of the four-membered ring. Thus, for example in (109), the As(1)-Pt-C(2)-C(9) and As(2)-Pt-C(1)-C(3) torsion angles are 81.1 and 46.3° respectively, where C(3) and C(9) are the attached carbon atoms of equatorial and axial phenyl substituents respectively. Similarly, the sulphonyl oxygen atoms also adopt pseudo-axial and -equatorial positions. Pseudo-axial-equatorial substitution has also been shown to be the favoured configuration in puckered 2,4-disubstituted metallacyclobutan-3-one (1,3-disubstituted \(\eta^3\)-oxodimethylenemethane) complexes (50) of platinum\(^{61,63,64}\) and palladium,\(^{62}\) see Chapter 1. However, recent calculations on the metallacyclobutane complexes \([M(CHR^1CH_2CHR^2)Cl_4]\) (M = Cr, W; \(R^1 = Me, R^2 = Me, Et\)) indicate that the stability of the 2,4-disubstituted isomers decrease in the order \(e > a, e > a, a = a\) (\(a =\) axial, \(e =\) equatorial substituent), Figure 9, as a result of 2,4-cross-ring non-bonded interactions, which are greatest between axial substituents.\(^{124}\) Isomerisation studies on 2,4-diphenylthietane-1,1-dioxides have also established that the phenyl substituents in the more stable isomer occupy pseudo-equatorial environments.\(^{106}\)

However, in the four co-ordinate square planar metallathietane-3,3-dioxide
complexes (109), (117), and (125), it would seem likely that torsional effects between equatorial substituents and the bulky cis-phosphine or -arsine ligands will destabilise the diequatorial isomer, resulting in the observed axial equatorial isomer, Figure 9.

Attempts to isomerise a trans-metallathietane-3,3-dioxide system, by treatment of (109) with excess sodium hydride in THF, or (110) with excess n-butyl lithium in THF, followed by quenching with $^{2}H_{2}$-water did not lead to replacement of any metallathietane-3,3-dioxide hydrogen atoms by deuterium. Thus, it is not possible to say whether the formation of a trans-2,4-disubstituted isomer is a consequence of kinetic or thermodynamic control. The observation that 2,4-diphenylthietane-1,1-dioxides appear more acidic than the platinathietane-3,3-dioxide rings in (109) and (110) (trans-2,4-diphenylthietane-1,1-dioxide is readily isomerised to its cis-diequatorial isomer on treatment with sodium methoxide in methanol) is an indication of a reduction in acidity by replacement of a CH$_2$ moiety by a sterically bulky, electron-donating PtL$_2$ ($L$=AsPh$_3$ or PPh$_3$) moiety. The reduction in ring strain on going from a thietane-1,1-dioxide ring to a platinathietane-3,3-dioxide ring does not appear to form an important contribution to the reduction in acidity of the latter, since non-strained dibenzyl sulphone is itself readily deprotonated by n-butyl lithium.
It is finally worth noting that as a result of the trans-substitution of the metallathietane-3,3-dioxide systems, these molecules are chiral, and an examination of the unit cell contents for (117) reveals that one molecule of both enantiomers co-crystallise from solution in a centrosymmetric unit cell.

2.4 N.M.R. SPECTRA OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES

The n.m.r. spectroscopic properties of all the metallathietane-3,3-dioxide complexes may be interpreted in terms of a rapidly inverting metallacycle, Figure 10, resulting in magnetic equivalence of the axial (Ha and Ha') and equatorial (He and He') metallathietane-3,3-dioxide ring protons. However, a planar metallathietane-3,3-dioxide ring system would also account for the observed spectroscopic data.

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

The $^1$H n.m.r. spectra of all the platinum-phosphine or -phosphite complexes appear as the A part of an AA'MXX' spin system (M = $^{195}$Pt, X = $^{31}$P), to give a complex resonance consisting of an intense inner doublet, a weaker outer doublet, together with two very weak outer doublets some distance from the centre of the resonance. This second-order spectrum arises due to the presence of chemically equivalent but magnetically non-equivalent phosphorus-31 nuclei, and is illustrated for
complex (117) in Figure 11. Corresponding satellite features due to coupling to platinum-195 are observed, with values of $^2J(PtH)$ for the benzoyl substituted phosphine complexes typically around 60 Hz. For the phenyl substituted platinum complexes (109)-(111) the increase in $^2J(PtH)$ from 70.0 Hz for (80) to 84.9 Hz for (109) to 98.9 Hz for (111) is consistent with the decrease in trans influence of the ligands in the order PPh$_3$ > AsPh$_3$ > SEt$_2$. Values of $|^3J(PH)_{trans} + ^3J(PH)_{cis}|$ for the platinum-phosphine complexes are typically around 9-10 Hz for the benzoyl substituted complexes, and 11.6 Hz for the phenyl substituted complex (110). These values of $^2J(PtH)$ and $|^3J(PH)_{trans} + ^3J(PH)_{cis}|$ are similar to the values observed for the platinacyclobutane complex (36, $L = PPr_3^+$), which shows $^2J(PtH)$ 75.2 Hz and $J(PH)$ 10.3 Hz. The palladium metallathietane-3,3-dioxide complexes containing phosphine ligands yield similar Pd-CH $^1$H n.m.r. spectral features, although these signals are commonly poorly resolved, giving a broad single resonance from which it was not possible to measure a value of $J(PH)$. The dppe nickel complex (116) shows Ni-CH proton signals which appear first-order, as a doublet of doublets with $^3J(PH_{cis})$ ca. 5 Hz, and $^3J(PH_{trans})$ ca. 8 Hz.

The $^1$H n.m.r. spectra of the metallathietane-3,3-dioxide complexes (119) and (126) containing the dimethylphenylphosphine ligand illustrate the chiral nature of the carbon atoms of the metallacycle, causing the two methyl groups bonded to the phosphorus to become chemically non-equivalent (diastereotopic). This results in signals for the two methyl resonances Me(A) and Me(B) being observed, Figure 12, even though free rotation about the metal-phosphorus bond would be expected. This feature has similarly been observed in 1,3-disubstituted oxodimethylenemethane complexes of platinum and palladium.61-64

Identical $^1$H n.m.r. spectra for the phenyl substituted palladium com-
FIGURE 11
Room temperature $^1$H n.m.r. spectrum at 300 MHz for the Pt-CH protons of $[\text{Pt}(\text{CH(COPh)}\text{S(O)COPh})\text{CH(COPh)}\text{]}(\text{PPh}_3)_2] (117)$.
plex (114) and the benzoyl substituted platinum complex (118) were obtained at room and low (-90°C) temperatures, consistent with either a planar metallacycle, or a metallacycle undergoing rapid ring inversion at low temperature. Since these complexes contain puckered four-membered rings in the solid state, a fluxional metallacycle is more probable.

2.4.2 $^{13}$C-{$^1$H} and $^{31}$P-{$^1$H} N.m.r. Spectra

The $^{13}$C-{$^1$H} n.m.r. spectra for the metallathietane-3,3-dioxide complexes exhibit the expected features for a planar or rapidly inverting metallacycle, with the ring carbon atoms showing large couplings to either platinum-195 or phosphorus-31, or both. Since the complexes containing phosphine ligands have chemically equivalent but magnetically non-equivalent phosphorus nuclei, the observed spectra are second-order, appearing as the A part of an AMXX' spin-system ($M = ^{195}$Pt, $X = ^{31}$P), giving a doublet of doublets with a small central feature, as illustrated for complex (119) in Figure 13.

The values of $^1J$(PtC) for the phenyl substituted complexes (109)-(111) lie in the range 505.7-609.3 Hz, according to the trans influence of the accompanying ligand, with the diethyl sulphide complex (111) showing, as expected, the largest coupling. The values of $^1J$(PtC) and $|^2J$(PC)$_{trans}$ + $^2J$(PC)$_{cis}$| for the phenyl and benzoyl or methoxycarbonyl substituted
FIGURE 13

Room temperature $^{13}$C-$^1$H n.m.r. spectrum at 75.5 MHz for the Pt-CH carbon atoms of the complex \([\text{Pt(CH(COPh)S(O)}_2\text{CH(COPh)}](\text{PMe_2Ph})_2\) (119).CH$_2$Cl$_2$.

★ = CH$_2$Cl$_2$ of crystallisation
complexes are comparable with those of platinacycllobutanes,\(^1\) for example the complex \([\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_3)_2]\) shows \(^{1}J(\text{PtC}) 400\) Hz, and \(^{2}J(\text{PC}) 80\) Hz.\(^{22}\)

The assignment of the ring carbons was confirmed by a proton-coupled \(^{13}\text{C}\) n.m.r. spectrum of the triphenylarsine complex (119), which yielded a doublet for the Pt-CH protons, with \(^{1}J(\text{CH}) 143.5\) Hz. Values of \(^{1}J(\text{CH})\) have been used to examine the degree of hybridisation of carbon atoms, with an increase in s-character effecting an increase in \(^{1}J(\text{CH})\).\(^{128}\) A contribution to the bonding in metallathietane-3,3-dioxide complexes from a heteroallylic representation such as (133) would be expected to effect an increase in the s-character of the carbon orbitals employed in bonding to the hydrogen atom and phenyl substituent (the hybridisation of carbon in allylic systems is sp\(^2\)). The value of \(^{1}J(\text{CH})\) for (109) is slightly larger than that observed for the parent dibenzyl sulphone \(^{1}J(\text{CH}) 138.4\) Hz, and this may tentatively be taken as evidence of a contribution from the heteroallylic representation (133).

The carbonyl carbon atoms of the benzoyl substituents of complexes (117) and (119) show coupling to platinum-195, with \(^{2}J(\text{PtC})\) being 35 and 32 Hz respectively, although no three-bond phosphorus coupling was discernible.

The \(^{13}\text{C}-\{^1\text{H}\}\) n.m.r. spectra of the complexes (119) and (126) containing the dimethylphenylphosphine ligand again demonstrate the chiral nature of the ring carbons, as described in Section 2.4.1 (see Figure 12), with two sets of methyl resonances again being observed.

The room temperature \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectra for all the metallathietane-3,3-dioxide complexes containing phosphine or triphenylphosphite ligands consist of a single resonance, with the platinum complexes showing the expected coupling to platinum-195, values of \(^{1}J(\text{PtP})\) being 2532 Hz for the phenyl substituted complex (110), and in the range 2705-2817 Hz.
for the benzoyl and methoxycarbonyl substituted phosphine complexes (117), (122) and (130).

2.5 I.R. SPECTRA OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES

Infrared spectra of molecules containing a sulphone function typically show two intense bands assigned to the symmetric ($v_{sym}$) and antisymmetric ($v_{asym}$) stretches of the sulphone group, which commonly lie in the respective ranges 1120-1160 cm$^{-1}$, and 1310-1350 cm$^{-1}$. The phenyl substituted metallathietane-3,3-dioxide complexes (109)-(116) show values in the ranges 1097-1118 cm$^{-1}$ and 1264-1278 cm$^{-1}$, whereas the benzoyl and methoxycarbonyl substituted complexes show values in the ranges 1110-1126 cm$^{-1}$ and 1290-1310 cm$^{-1}$. The values of $v_{SO_2}$ for the phenyl substituted metallathietane-3,3-dioxides are lower than those reported for both dibenzyl sulphone $^{102}$ [$v_{SO_2}$ 1130 and 1308 cm$^{-1}$] and trans-2,4-diphenylthietane-1,1-dioxide $^{106}$ [$v_{SO_2}$ 1117 and 1312 cm$^{-1}$]. Variations in sulphonyl stretching frequencies in alkyl and aryl sulphones have been related to changes in the electron density of, and the steric bulk around, the sulphur atom. $^{130}$ An increase in the electron deficiency of the sulphur atom, and a decrease in the steric bulk of the substituents (which may occur via a reduction of the C-S-C bond angle) both result in an increase in the sulphone stretching frequencies.

Hence, the replacement of the $\beta$-CR$_2$ group of a thietane-1,1-dioxide ring by a larger, more strongly electron-donating PtL$_2$ moiety (to give a metallathietane-3,3-dioxide ring) results in an increase in the C-S-C bond angle, and a lowering of the SO$_2$ stretching frequencies. The values of $v_{SO_2}$ for the benzoyl substituted complexes are also lower than for diphenacyl sulphone ($v_{SO_2}$ 1145 and 1330 cm$^{-1}$). $^{131}$

Furthermore, a contribution to the metallacyclic bonding in metalla-
thietane-3,3-dioxides from a heteroallylic representation such as (133), see Section 3.2, would also be predicted to lower the SO₂ stretching frequencies. Examination of the i.r. spectroscopic data for the phenyl substituted metallathietane-3,3-dioxide complexes (Table 4), reveals an increase in νSO₂ on changing the metal atom from nickel to platinum. For the benzoyl substituted sulphones, the platinum and palladium complexes appear to have similar values of νSO₂ for any given ligand, within experimental error, see Table 5. Based upon the observed trends for dialkyl sulphones, the presence of a larger, more electron-rich platinum atom would be expected to decrease values of νSO₂. However, given that for the phenyl substituted complexes, those of platinum display the higher values of νSO₂, it would seem likely that the platinum complexes have a smaller contribution from the η²-heteroallylic representation (133) than do the nickel complexes. This is consistent with the structural studies on the benzoyl substituted platinum and palladium complexes, (117) and (125) respectively, see Section 2.3, which reveal that the palladium complex is more highly puckered and has slightly shorter C-S bonds, suggesting a larger contribution from the η²-heteroallylic representation (133). Studies on oxodimethylenemethane complexes of platinum and palladium, Chapter 1, have also shown that the palladium complexes contain a greater degree of η³-allylic character.

2.6 CONCLUSION

The preparation of the new metallathietane-3,3-dioxide complexes of platinum(II), palladium(II), and nickel(II) may be achieved via treatment of the dichloride complexes cis- or trans-[MCl₂L₂] (M = Ni, Pd, Pt; L = donor ligand) with the 1,3-dianionic reagent [PhCHS(O)₂CHPh]²⁻ in tetrahydrofuran, or by reaction of cis-[PtCl₂L₂] or trans-[PdCl₂L₂] with
the activated dialkyl sulphones \( R\text{CH}_2\text{S(O)}_2\text{CH}_2\text{R} \) \((R = \text{COPh or CO}_2\text{Me})\) in the presence of silver(I) oxide in dichloromethane.\(^{133}\) Single-crystal X-ray diffraction studies have been carried out on three of these complexes, establishing the presence of puckered four-membered rings which display trans-axial-equatorial substitution. The X-ray data also suggest a heteroallylic contribution in the bonding of the organic ligand to the metal. The n.m.r. spectroscopic properties of these metallathietane-3,3-dioxide complexes are similar overall to those found in platinacyclobutanes.

2.7 EXPERIMENTAL

Microanalytical results, m.p.'s, and i.r. spectroscopic data (Tables 4 and 5), together with n.m.r. spectroscopic data are presented for all newly isolated compounds. 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 \(^1\text{H}\) n.m.r. spectra were recorded at room temperature in \([^2\text{H}_2]\)-chloroform, unless otherwise stated, on a Bruker Spectrospin WH 400 spectrometer operating at 400.13 MHz, a Bruker AM 300 spectrometer operating at 300.13 MHz, or on a JEOL 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 \(^{13}\text{C}-[^1\text{H}]\) n.m.r. spectra were recorded in \([^2\text{H}_2]\)-chloroform at room temperature on a Bruker Spectrospin WH 400 spectrometer operating at 100.62 MHz, and 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
$\delta$ 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-FX60 spectrometer operating at 24.15 MHz with
$[P(OH)_{4}]^{+}$ in $[^2H]_{2}$-water (0.0 p.p.m.) as external reference, or on
a Bruker Spectrospin WH 400 spectrometer operating at 162 MHz with
$H_3PO_4$ as external reference, with positive values to high frequency
(low-field). 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
palladathietane-3,3-dioxide complexes were recrystallised in air. The
compounds dimethylphenylphosphine, n-butyl lithium (2.5 mol dm$^{-3}$), tri-
ethylphosphine, tri-n-butylphosphine, triphenylphosphite (Aldrich),
silver(I) oxide (BDH), 1,2-bis-(diphenylphosphino)ethane (Lancaster),
and methyldiphenylphosphine (Strem) were used as supplied from commercial
sources. Sodium hydride (Aldrich) was washed with light petroleum prior
to use, to remove mineral oil. The compounds cis-$[PtCl_2(AsPh_3)_{2}]$,\textsuperscript{135}
cis-$[PtCl_2(PPh_3)_{2}]$,\textsuperscript{136} cis-$[PtCl_2(SEt)_{2}]$,\textsuperscript{137} trans-$[PdCl_2(PPh_3)_{2}]$,\textsuperscript{138}
trimethylphosphine,\textsuperscript{139} trans-$[PdCl_2(PMe_3)_{2}]$,\textsuperscript{140} $[Pd([O_2CMe]_2)]$,\textsuperscript{141} trans-
$[PdCl_2(NCPh)_{2}]$,\textsuperscript{142} trans-$[NiCl_2(PMe_3)_{2}]$,\textsuperscript{143} $[NiCl_2(dppe)]$,\textsuperscript{144} $[PtCl_2(COD)]$,\textsuperscript{99}
$[PdCl_2(COD)]$,\textsuperscript{145} diphencayl sulphone,\textsuperscript{104} and 2,2'-sulphonyldiacetic acid
dimethyl ester (78)\textsuperscript{105} were prepared as described in the literature. The
platinum metal salts were obtained on loan from Johnson Matthey p.l.c.

The lithium reagent $Li_2[PhCHS(O)_2CHPh]$(102) was prepared as an approxi-
mately 0.2 mol dm$^{-3}$ solution in THF, as described in the literature,\textsuperscript{101}
except that a stoichiometric quantity of n-butyl lithium was employed. The solution was estimated for total base content by hydrolysis of a 5.0 cm³ aliquot in water (ca. 20 cm³), followed by titration of the liberated hydroxide with hydrochloric acid, using phenolphthalein indicator. The reagent K₂[PhCHS(O)₂CHPh] (103) was prepared in liquid ammonia solution as described in the literature. The ammonia was allowed to boil away, and the resulting solid was dissolved in THF to give a solution of approximately 0.2 mol dm⁻³, which was standardised as for (102).

Preparation of trans-2,4-diphenyl-1,1-bis(ligand)metallahietane-3,3-dioxide complexes using [PhCHS(O)₂CHPh]⁻; general method

One mole equivalent of M₂[PhCHS(O)₂CHPh] (M' = Li or K), prepared as above, was added dropwise to a stirred suspension or solution of cis- or trans-[MCl₂L₂] or [Pd(O₂CMe)₂(PMe₃)₂] (generated from palladium(II) acetate and trimethylphosphine) in THF (ca. 50 cm³) at -78°C. The mixture was stirred for 10 min. at -78°C, and for a further 4h at room temperature to give a clear pale-yellow to brown solution. Evaporation to dryness under reduced pressure gave an oil which was washed with light petroleum (30 cm³). The residual solid was extracted into dichloromethane (30 cm³), and the solution filtered. The volume of the filtrate was reduced to ca. 15 cm³ under reduced pressure, and light petroleum added to the cloud point. Cooling to -20°C for 24h gave a microcrystalline solid which was recrystallised and dried in vacuo (ca. 0.4 mmHg).

(i) [Pt(CHPhS(O)₂CHPh)(AsPh₃)₂] (109).PhMe. The compound cis-[PtCl₂(AsPh₃)₂] (1.60 g, 1.82 mmol) and K₂[PhCHS(O)₂CHPh] (103) gave white microcrystals of (109).PhMe (1.929 g, 94%) on recrystallisation from dichloromethane-toluene. N.m.r. spectra: ¹H (400 MHz), δ 7.3-6.9 (m, 45H, Ph), 4.24 [s,
Reaction of cis-[PtCl₂(AsPh₃)₂] (0.40 g, 0.46 mmol) with Li₂[PhCHS(O)₂CHPh](102) gave white microcrystals of (109).CH₂Cl₂.2H₂O (0.429 g, 80%) on recrystallisation from dichloromethane-light petroleum. X-ray quality crystals were grown slowly from dichloromethane-light petroleum, in air.

(ii) [Pt(CHPhS(O)₂CHPh)(PPh₃)₂](110).0.5PhMe. The compound cis-[PtCl₂(PPh₃)₂] (0.80 g, 1.01 mmol) and Li₂[PhCHS(O)₂CHPh](102) gave white microcrystals of (110).0.5PhMe (0.82 g, 81%) on recrystallisation from dichloromethane-toluene. N.m.r. spectra: ¹H (400 MHz), δ 7.5-6.8 (m, 42.5H, Ph), 3.99 [d, second-order, 2H, Pt-CH, ¹³J(PtH) 11.6, ²J(PtH) 70.0], and 2.35 p.p.m. (s, 1.5H, Me, PhMe); ¹³C-{¹H} (100 MHz), δ 56.27 [dd, second-order, Pt-CH, ¹²J(PC) 90.4, ¹¹J(PtC) 505.7], and 18.9 p.p.m. (s, Me, PhMe); ³¹P-{¹H} (162 MHz, [¹H]-chloroform), δ 16.26 p.p.m. [s, ¹¹J(PtP) 2532].

(iii) [Pt(CHPhS(O)₂CHPh)(SEt₂)₂](111). The compound cis-[PtCl₂(SEt₂)₂] (1.00 g, 2.24 mmol) and Li₂[PhCHS(O)₂CHPh](102) gave white microcrystals of (111) (0.83 g, 60%) on recrystallisation from dichloromethane-light petroleum. N.m.r. spectra: ¹H (400 MHz), δ 7.5-7.1 (m, 10H, Ph), 4.40 [s, 2H, Pt-CH, ²J(PtH) 98.9], 2.43-2.15 (m, 8H, CH₂, SEt₂), and 1.16 p.p.m. [t, 12H, CH₃, SEt₂, ³J(HH) 7.4]; ¹³C-{¹H} (100 MHz), δ 47.85 [s, Pt-CH, ¹¹J(PtC) 609.3], 29.55 (s, CH₂, SEt₂), and 13.05 p.p.m. (s, CH₃, Et₂S).

(iv) [Pd(CHPhS(O)₂CHPh)(PPh₃)₂](112). The compound trans-[PdCl₂(PPh₃)₂] (0.50 g, 0.71 mmol) and Li₂[PhCHS(O)₂CHPh](102) gave pale yellow micro-

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2H, Pt-CH, ²J(PtH) 84.9], and 2.36 p.p.m. (s, 3H, Me, PhMe); ¹³C-{¹H} (100 MHz), δ 51.95 [s, Pt-CH, ¹J(PtC) 566.1, ¹¹J(CH) 143.5 (d from ¹³C spectrum)], and 19.5 p.p.m. (s, Me, PhMe).
crystals of (112) (0.32 g, 52%) on recrystallisation from dichloromethane-light petroleum. N.m.r. spectra: $^1$H (400 MHz), $\delta$ 7.5-6.8 (m, 40H, Ph), and 3.57 p.p.m. [d, second-order, 2H, Pd-CH, $|3J(\text{PH})_{\text{trans}} + 3J(\text{PH})_{\text{cis}}| 9.0]$; $^{13}$C-{$^1$H} (100 MHz), $\delta$ 53.10 p.p.m. [dd, second-order, Pd-CH, $|2J(\text{PC})_{\text{trans}} + 2J(\text{PC})_{\text{cis}}| 141.1]$; $^{31}$P-{$^1$H} (24 MHz), $\delta$ 21.58 p.p.m. (s).

Reaction of trans-[PdCl$_2$(PPh$_3$)$_2$] (0.30 g, 0.43 mmol) with K$_2$[PhCHS(0)$_2$CHPh] (103) gave complex (112) (0.21 g, 56%) on recrystallisation from dichloromethane-light petroleum.

(v) [Pd(CHPhS(0)$_2$CHPh)(PMe$_3$)$_2$] (113). The compound [Pd(O$_2$CMe)$_2$(PMe$_3$)$_2$], prepared in situ from [[Pd(O$_2$CMe)$_2$]$_3$ (0.275 g, 0.409 mmol) and trimethylphosphine (0.3 cm$^3$, 3 mmol), and Li$_2$[PhCHS(O)$_2$CHPh] (102) gave white microcrystals of (113) (0.35 g, 57%) on recrystallisation from dichloromethane-light petroleum. N.m.r. spectra: $^1$H (400 MHz), $\delta$ 7.36-7.04 (m, 10H, Ph), 3.62 [d, second-order, 2H, Pd-CH, $|3J(\text{PH})_{\text{trans}} + 3J(\text{PH})_{\text{cis}}|$ ca. 7], and 1.06 p.p.m. [d, second-order, 18H, Me, PMe$_3$, $|2J(\text{PH}) + 4J(\text{PH})|$ 8.07]; $^{13}$C-{$^1$H} (100 MHz), $\delta$ 49.55 [dd, second-order, Pd-CH, $|2J(\text{PC})_{\text{trans}} + 2J(\text{PC})_{\text{cis}}| 112.1$], and 15.93 p.p.m. [t, second-order, CH$_3$, PMe$_3$, $|1J(\text{PC}) + 3J(\text{PC})| 12.9$]; $^{31}$P-{$^1$H} (24 MHz), $\delta$ 21.38 p.p.m. (s).

Reaction of trans-[PdCl$_2$(PMe$_3$)$_2$] (0.10 g, 0.30 mmol) with Li$_2$[PhCHS(O)$_2$CHPh] (102) gave compound (113) (0.106 g, 69%) on recrystallisation from dichloromethane-light petroleum.

(vi) [Pd(CHPhS(0)$_2$CHPh)(PEt$_3$)$_2$] (114).CH$_2$Cl$_2$. Triethylphosphine (0.5 cm$^3$, 3.4 mmol) was added to a stirred suspension of trans-[PdCl$_2$(NCPh)$_2$] (0.412 g, 1.07 mmol) in toluene (20 cm$^3$), the resulting pale yellow solution stirred for 1h, and evaporated to dryness under reduced pressure to afford a solid which was washed with light petroleum (20 cm$^3$). The resulting solid, and Li$_2$[PhCHS(O)$_2$CHPh] (102) gave white microcrystals of
(114). CH₂Cl₂ (0.37 g, 51%) on recrystallisation from dichloromethane-light petroleum. N.m.r. spectra: \(^1\)H (400 MHz), δ 7.46-7.11 (m, 10H, Ph), 5.35 (s, 2H, CH₂Cl₂), 3.55 [d, second-order, 2H, Pd-CH, \(\text{^3J(PH)trans} + \text{^3J(PH)cis}\) not discernible], 1.40 (m, 12H, CH₂, PEt₃), and 0.97 p.p.m. (m, 18H, CH₂, PEt₃); \(^1\)H (400 MHz, \([^2\text{H}_2]\)-dichloromethane, -90°C) identical to room temperature spectrum; \(^1^3\)C-{\(^1\)H} (100 MHz), δ 50.19 [dd, second-order, Pd-CH, \(\text{^2J(PC)trans} + \text{^2J(PC)cis}\) 106.4], 15.94 (m, second-order, CH₂, PEt₃), and 8.19 p.p.m. (s, CH₂, PEt₃); \(^31\)P-{\(^1\)H} (162 MHz, \([^2\text{H}_1]\)-chloroform), δ 11.38 p.p.m. (s).

(vi) \([\text{Ni(CHPhS(O)₂CHPh)}(\text{PMe₃})₂]\) (115). The compound trans-[NiCl₂(PMe₃)₂] (0.30 g, 1.06 mmol) and Li₂[PhCHS(O)₂CHPh] (102) gave red-orange crystals of (115) (0.11 g, 23%) on recrystallisation from dichloromethane-toluene at -20°C. N.m.r. spectra: \(^1\)H (90 MHz), δ 7.6-7.0 (m, 10H, Ph), 3.36 [d, filled-in, second-order, 2H, Ni-CH, \(\text{^3J(PH)trans} + \text{^3J(PH)cis}\) ca. 10], and 1.02 p.p.m. [d, second-order, 18H, Me, PMe₃, \(\text{^2J(PH)trans} + \text{^2J(PH)cis}\) ca. 8]; \(^1^3\)C-{\(^1\)H} (75.5 MHz), δ 49.28 [dd, second-order, Ni-CH, \(\text{^2J(PC)trans} + \text{^2J(PC)cis}\) 72.9], and 15.87 p.p.m. [t, second-order, Me, PMe₃, \(\text{^1J(PC)trans} + \text{^3J(PC)cis}\) 13.6]; \(^31\)P-{\(^1\)H} (24 MHz), δ -12.91 p.p.m. (s).

(viii) \([\text{Ni(CHPhS(O)₂CHPh)}(\text{dppe})]\) (116). The compound [NiCl₂(dppe)] (0.35 g, 0.66 mmol) and Li₂[PhCHS(O)₂CHPh] (102) gave orange microcrystals of (116) (0.21 g, 28%) on recrystallisation from dichloromethane-light petroleum. N.m.r. spectrum: \(^1\)H (90 MHz), δ 7.8-6.7 (m, 30H, Ph), 4.0 [dd, 2H, Ni-CH, \(^3\)J(PH cis) ca. 5, \(^3\)J(PH trans) ca. 8], and 2.2-1.7 p.p.m. (m, 4H, CH₂, dppe).

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Preparation of metallathietane-3,3-dioxide complexes using silver(I) oxide; general method

Two equivalents of tertiary phosphine or triphenyl phosphite, followed by one equivalent of diphenacyl sulphone (107) or sulphonyldiacetic acid dimethyl ester (108), 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. 30 cm³), and the mixture was refluxed for 4h. 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 cm³) 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) \([\text{Pt}\left(\text{CH(COPh)}\right)_2\text{CH(COPh)}\left(\text{PPh}_3\right)_2]\) (117).CH₂Cl₂.0.5H₂O. The complex [PtCl₂(COD)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and diphenacyl sulphone (107) (0.082 g, 0.27 mmol) gave white microcrystals of (117).CH₂Cl₂.0.5H₂O (0.23 g, 77%). N.m.r. spectra:

\(^1\text{H}\) (300 MHz), \(\delta\) 7.5-6.9 (m, 40H, Ph), 5.31 (s, 2H, CH₂Cl₂), 4.86 [d, second-order, 2H, Pt-CH, \(|^3\text{J(Ph)}\text{trans} + ^3\text{J(Ph)}\text{cis}| 9.20, ^2\text{J(Ph)} 61.79], \) and 1.81 p.p.m. (s, br, 1H, H₂O); \(^{13}\text{C}-\{^1\text{H}\} (75.5 MHz), \(\delta\) 196.30 [s, CO, \(^2\text{J(PtC)} 35.0], 54.58 [dd, second-order, Pt-CH, \(|^2\text{J(PC)}\text{trans} + ^2\text{J(PC)}\text{cis}| 87.08, ^1\text{J(PtC)} 446.2], \) and 53.4 p.p.m. (s, CH₂Cl₂); \(^{31}\text{P}-\{^1\text{H}\} (24 MHz), \(\delta\) 13.31 p.p.m. [s, \(^1\text{J(PtP)} 2817]. \) X-ray quality crystals of (117).2CH₂Cl₂ were grown slowly from dichloromethane-light petroleum, in air.

(ii) \([\text{Pt}\left(\text{CH(COPh)}\right)_2\text{CH(COPh)}\left(\text{PMePh}_2\right)_2]\) (118).CH₂Cl₂.0.5H₂O. The complex [PtCl₂(COD)] (0.12 g, 0.32 mmol) with methyldiphenylphosphine (0.13 g, 0.65 mmol) and diphenacyl sulphone (107) (0.098 g, 0.33 mmol) gave white microcrystals of (118).CH₂Cl₂.0.5H₂O (0.241 g, 76%). N.m.r.
spectra: $^1$H (300 MHz), $\delta$ 7.80-7.00 (m, 30H, Ph), 5.30 (s, 2H, CH$_2$Cl$_2$), 4.80 [d, second-order, 2H, Pt-CH, $|^3$J(PH)$_{trans}$ + $^3$J(PH)$_{cis}$| 9.0, $^2$J(PtH) 59.9], 2.08 p.p.m. (s, br, 1H, H$_2$O), and 1.62 p.p.m. [d, second-order, 6H, Me, PMe$_2$Ph, $|^2$J(PH) + $^4$J(PH)| 8.55, $^3$J(PtH) 29.3]; $^1$H (300 MHz, [${^2}$H]$_2$-dichloromethane, -90°C) identical to room temperature spectrum; $^{13}$C-$^1$H (75.5 MHz), $\delta$ 196.20 [s, CO, $^2$J(PtC) not discernible], 55.45 [dd, second-order, Pt-CH, $|^2$J(PC)$_{trans}$ + $^2$J(PC)$_{cis}$| 84.96, $^1$J(PtC) 412.5], 53.4 (s, CH$_2$Cl$_2$), and 13.54 p.p.m. [dd, second-order, Me, PMe$_2$Ph, $|^1$J(PC) + $^3$J(PC)| 46.3, $^2$J(PtC) not discernible]; $^{31}$P-$^1$H (24 MHz), $\delta$ -4.24 p.p.m. [s, $^1$J(PtP) 2759].

(iii) [Pt{CH(COPh)S(O)$_2$CH(COPh)}(PMe$_2$Ph)](119).CH$_2$Cl$_2$. The complex [PtCl$_2$(COD)] (0.25 g, 0.67 mmol) with dimethylphenylphosphine (0.19 g, 1.37 mmol) and diphenacyl sulphone (107) (0.20 g, 0.67 mmol) gave white microcrystals of (119).CH$_2$Cl$_2$ (0.41 g, 71%). N.m.r. spectra: $^1$H (300 MHz), $\delta$ 8.06 7.27 (m, 20H, Ph), 5.34 (s, 2H, CH$_2$Cl$_2$), 4.89 [d, second-order, 2H, Pt-CH, $|^3$J(PH)$_{trans}$ + $^3$J(PH)$_{cis}$| ca. 9, $^2$J(PtH) 60.06], 1.48 [d, second-order, 6H, Me, PMe$_2$Ph, $|^2$J(PH) + $^4$J(PH)| 9.34, $^3$J(PtH) 30.2], and 1.26 p.p.m. [d, second-order, 6H, Me, PMe$_2$Ph, $|^2$J(PH) + $^4$J(PH)| 9.41, $^3$J(PtH) 28.7]; $^{13}$C-$^1$H (75.5 MHz), $\delta$ 197.23 [s, CO, $^2$J(PtC) 32.0], 55.31 [dd, second-order, Pt-CH, $|^2$J(PC)$_{trans}$ + $^2$J(PC)$_{cis}$| 84.39, $^1$J(PtC) 384.5], 15.92 [dd, second-order, Me, PMe$_2$Ph, $|^1$J(PC) + $^3$J(PC)| 48.0, $^2$J(PtC) not discernible], and 14.34 p.p.m. [dd, second-order, Me, PMe$_2$Ph, $|^1$J(PC) + $^3$J(PC)| 46.75, $^2$J(PtC) not discernible]; $^{31}$P-$^1$H (24 MHz), $\delta$ -17.95 p.p.m. [s, $^1$J(PtP) 2734].

(iv) [Pt{CH(COPh)S(O)$_2$CH(COPh)}(PMe$_3$)$_2$](120). The complex [PtCl$_2$(COD)] (0.15 g, 0.401 mmol) with trimethylphosphine (0.1 cm$^3$, 1.0 mmol) and diphenacyl sulphone (107) (0.121 g, 0.401 mmol) gave white microcrystals
of (120) (0.184 g, 71%). N.m.r. spectra: $^1$H (400 MHz), $\delta$ 8.12-7.37 (m, 10H, Ph), 4.80 [d, second-order, 2H, Pt-CH, $|{^3J(\text{PH})_{\text{trans}} + ^3J(\text{PH})_{\text{cis}}}|$ 9.57, $^2J(\text{PtH})$ 58.06], and 1.41 p.p.m. [d, second-order, $|{^2J(\text{PH}) + ^4J(\text{PH})}|$ 9.44, $^3J(\text{PtH})$ 29.55]; $^{13}$C-$^1$H (75.5 MHz), $\delta$ 197.52 [s, CO, $^2J(\text{PtC})$ not discernible], 55.10 [dd, second-order, Pt-CH, $|{^3J(\text{PC})_{\text{trans}} + ^3J(\text{PC})_{\text{cis}}}|$ 84.59, $^1J(\text{PtC})$ ca. 354], and 16.97 p.p.m. [dd, second-order, Me, PMe$_3$, $|{^1J(\text{PC}) + ^3J(\text{PC})}|$ 47.6, $^2J(\text{PtC})$ not discernible]; $^{31}$P-$^1$H (24 MHz), $\delta$ -28.84 p.p.m. [s, $^1J(\text{PtP})$ 2705].

(v) $[\text{Pt}(\text{CH(COPh)}S(\text{O})_2\text{CH(COPh)})\{\text{PET}_3\}](121)\cdot 0.5\text{CH}_2\text{Cl}_2$. The complex $[\text{PtCl}_2(\text{COD})]$ (0.21 g, 0.56 mmol) with triethylphosphine (0.14 g, 1.18 mmol) and diphenacyle sulphone (107) (0.17 g, 0.57 mmol) gave white microcrystals of (121) $0.5\text{CH}_2\text{Cl}_2$ (0.35 g, 81%). N.m.r. spectra: $^1$H (300 MHz), $\delta$ 8.20-7.35 (m, 10H, Ph), 5.25 (s, 1H, CH$_2$Cl$_2$), 4.62 [d, second-order, 2H, Pt-CH, $|{^3J(\text{PH})_{\text{trans}} + ^3J(\text{PH})_{\text{cis}}}|$ 9.0, $^2J(\text{PtH})$ 69.2], 1.71 (m, 12H, CH$_2$, PET$_3$), and 0.99 p.p.m. (m, 18H, CH$_3$, PET$_3$); $^{31}$P-$^1$H (24 MHz), $\delta$ 2.42 p.p.m. [s, $^1J(\text{PtP})$ 2739].

(vi) $[\text{Pt}(\text{CH(COPh)}S(\text{O})_2\text{CH(COPh)})\{\text{PBu}_3\}^\text{n}](122)$. The complex $[\text{PtCl}_2(\text{COD})]$ (0.20 g, 0.535 mmol) with tri-n-butylphosphine (0.22 g, 1.09 mmol) and diphenacyle sulphone (107) (0.162 g, 0.536 mmol) gave white microcrystals of (122) (0.37 g, 77%). N.m.r. spectra: $^1$H (400 MHz), $\delta$ 8.33-7.31 (m, 10H, Ph), 4.58 [d, second-order, 2H, Pt-CH, $|{^3J(\text{PH})_{\text{trans}} + ^3J(\text{PH})_{\text{cis}}}|$ ca. 9, $^2J(\text{PtH})$ 59.0], 1.80-1.09 (m, 36H, CH$_2$, PBu$_3$), and 0.81 p.p.m. [t, 18H, CH$_3$, PBu$_3$, $^3J(\text{HH})$ 7.14]; $^{31}$P-$^1$H (24 MHz), $\delta$ -6.25 p.p.m. [s, $^1J(\text{PtP})$ 2725].

(vii) $[\text{Pt}(\text{CH(COPh)}S(\text{O})_2\text{CH(COPh)})\{\text{P(OPh)}_3\}_2](123)$. The complex $[\text{PtCl}_2(\text{COD})]$ (0.225 g, 0.60 mmol) with triphenylphosphinite (0.38 g, 1.22 mmol) and diphenacyle sulphone (107) (0.181 g, 0.60 mmol) gave white micro-
crystals of (123) (0.24 g, 36%). N.m.r. spectra: \(^1\)H (300 MHz), \(\delta\) 8.02-6.83 (m, 40H, Ph), and 4.60 p.p.m. [d, second-order, 2H, Pt-CH, \(|^{3}J(\text{PH})_{\text{trans}} + ^{3}J(\text{PH})_{\text{cis}}|\) ca. 10, \(^{2}J(\text{PtH}) 70.1\)]; \(^{31}\)P-{\(\text{^1}H\)} (24 MHz), \(\delta\) 95.20 p.p.m. [s, \(\text{^1}J(\text{PtP}) 4976\)].

(viii) \([\text{Pd}(\text{CH}(\text{COPh})_2\text{S}(\text{O})_2\text{CH}(\text{COPh}))\text{(PPh}_3)_2]\) (124). \(\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}\). The complex [PdCl\(_2\)(COD)] (0.20 g, 0.70 mmol) with triphenylphosphine (0.367 g, 1.40 mmol) and diphenacyl sulphone (107) (0.211 g, 0.70 mmol) gave pale yellow microcrystals of (124). \(\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}\) (0.68 g, 94%). N.m.r. spectra: \(^1\)H (400 MHz), \(\delta\) 7.68-6.97 (m, 40H, Ph), 5.25 (s, 2H, \(\text{CH}_2\text{Cl}_2\)), 4.86 [d, second-order, 2H, Pd-CH, \(|^{3}J(\text{PH})_{\text{trans}} + ^{3}J(\text{PH})_{\text{cis}}|\) 9.83], and 1.90 (s, br, 2H, \(\text{H}_2\text{O}\)); \(^{13}\)C-{\(\text{^1}H\)} (75.5 MHz), \(\delta\) 196.13 (s, CO), and 52.15 p.p.m. [dd, second-order, Pd-CH, \(|^{2}J(\text{PC})_{\text{trans}} + ^{2}J(\text{PC})_{\text{cis}}|\) 100.61]; \(^{31}\)P-{\(\text{^1}H\)} (24 MHz), \(\delta\) 22.79 p.p.m. (s).

(ix) \([\text{Pd}(\text{CH}(\text{COPh})_2\text{S}(\text{O})_2\text{CH}(\text{COPh}))\text{(PMePh}_2)_2]\) (125). The complex [PdCl\(_2\)(COD)] (0.10 g, 0.35 mmol) with methyldiphenyolphosphine (0.15 g, 0.75 mmol) and diphenacyl sulphone (107) (0.105 g, 0.35 mmol) gave pale yellow microcrystals of (125) (0.247 g, 88%). N.m.r. spectra: \(^1\)H (400 MHz), \(\delta\) 7.58-6.98 (m, 30H, Ph), 4.39 [d, second-order, unresolved, 2H, Pd-CH, \(|^{3}J(\text{PH})_{\text{trans}} + ^{3}J(\text{PH})_{\text{cis}}|\) not discernible], and 1.43 p.p.m. [d, second-order, 6H, Me, PMePh\(_2\), \(|^{2}J(\text{PH}) + ^{4}J(\text{PH})|\) 7.7]; \(^{13}\)C-{\(\text{^1}H\)} (100 MHz), \(\delta\) 195.43 (s, CO), 52.45 [dd, second-order, Pd-CH, \(|^{2}J(\text{PC})_{\text{trans}} + ^{2}J(\text{PC})_{\text{cis}}|\) 104.08], and 12.00 p.p.m. [t, Me, PMePh\(_2\), \(|^{3}J(\text{PC}) + ^{3}J(\text{PC})|\) 27.2]; \(^{31}\)P-{\(\text{^1}H\)} (24 MHz, \(\text{[}^{2}\text{H}_1\text{-chloroform}]\), \(\delta\) 4.64 p.p.m. (s). X-ray quality crystals of (125). \(\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}\) were grown slowly from dichloromethane-light petroleum, in air.

(x) \([\text{Pd}(\text{CH}(\text{COPh})_2\text{S}(\text{O})_2\text{CH}(\text{COPh}))\text{(PMe}_2\text{Ph}_2)_2]\) (126). \(\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}\). The complex [PdCl\(_2\)(COD)] (0.15 g, 0.525 mmol) with dimethylphenylphosphine (0.19 g,
1.37 mmol) and diphenacyl sulphone (107) (0.158 g, 0.527 mmol) gave white microcrystals of (126). CH₂Cl₂ (0.38 g, 94%). N.m.r. spectra:

\(^1\text{H} (300 \text{ MHz}), \delta 8.20-7.18 \text{ (m, 20H, Ph)}, 5.29 \text{ (s, 2H, CH₂Cl₂)}, 4.47 \text{ [d, second-order, unresolved, 2H, Pd-CH, \(\text{^3}J(\text{PH})_{\text{trans}} + \text{^3}J(\text{PH})_{\text{cis}}\) not discernible]}, 1.34 \text{ [d, second-order, 6H, Me, PMe₂Ph, \(\text{^2}J(\text{PH}) + \text{^4}J(\text{PH})\) \(9.05\)}, \text{ and 1.05 p.p.m. [d, second-order, 6H, Me, PMe₂Ph, \(\text{^2}J(\text{PH}) + \text{^4}J(\text{PH})\) \(8.88\)}]; \(^{31}\text{P}-\{\text{^1}\text{H}\} (24 \text{ MHz}), \delta -7.87 \text{ p.p.m. (s)}.\)

(xi) \([\text{Pd}[\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}]\text{(PMe}_3\text{)}]_2(127)\). The complex \([\text{PdCl}_2(\text{COD})]\) (0.10 g, 0.35 mmol) with trimethylphosphine (0.1 cm³, 1.0 mmol) and diphenacyl sulphone (107) (0.106 g, 0.351 mmol) gave white microcrystals of (127) (0.18 g, 92%). N.m.r. spectra: \(^1\text{H} (300 \text{ MHz}), \delta 8.06-7.37 \text{ (m, 10H, Ph)}, 4.33 \text{ [d, second-order, unresolved, 2H, Pd-CH, \(\text{^3}J(\text{PH})_{\text{trans}} + \text{^3}J(\text{PH})_{\text{cis}}\) not discernible]}, \text{ and 1.23 p.p.m. [d, second-order, 18H, Me, PMe}_3\text{, \(\text{^2}J(\text{PH}) + \text{^4}J(\text{PH})\) \(8.9\)}, \text{ and 1.05 p.p.m. (m, 18H, CH}_3\text{, PEt}_3\text{); \(^{31}\text{P}-\{\text{^1}\text{H}\} (24 \text{ MHz}), \delta -18.35 \text{ p.p.m. (s)}.\)

(xii) \([\text{Pd}[\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}]\text{(PEt}_3\text{)}]_2(128)\). The complex \([\text{PdCl}_2(\text{COD})]\) (0.20 g, 0.70 mmol) with triethylphosphine (0.20 g, 1.69 mmol) and diphenacyl sulphone (107) (0.21 g, 0.7 mmol) gave white microcrystals of (128) (0.34 g, 77%). N.m.r. spectra: \(^1\text{H} (400 \text{ MHz}), \delta 8.15-7.43 \text{ (m, 10H, Ph)}, 4.19 \text{ [d, second-order, 2H, Pd-CH, \(\text{^3}J(\text{PH})_{\text{trans}} + \text{^3}J(\text{PH})_{\text{cis}}\) ca. 8.6]}, 1.77-1.54 \text{ (m, 12H, CH}_2\text{, PEt}_3\text{), and 1.05 p.p.m. (m, 18H, CH}_3\text{, PEt}_3\text{); \(^{31}\text{P}-\{\text{^1}\text{H}\} (24 \text{ MHz, [^2}\text{H}_1\text{-chloroform), \delta 13.92 p.p.m. (s).\)

(xiii) \([\text{Pd}[\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}]\text{(PBu}_3\text{)}]_2(129)\). The complex \([\text{PdCl}_2(\text{COD})]\) (0.10 g, 0.35 mmol) with tri-n-butylphosphine (0.22 g, 1.09 mmol) and diphenacyl sulphone (107) (0.16 g, 0.351 mmol) gave white microcrystals of (129) (0.26 g, 76%). N.m.r. spectrum: \(^{31}\text{P}-\{\text{^1}\text{H}\} (24 \text{ MHz}), \delta 5.45 \text{ p.p.m. (s).\)
(xiv) [Pt(CH\textsubscript{(CO\textsubscript{2}Me)}S(O)\textsubscript{2}CH(CH\textsubscript{2}Me)})\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}](130).\textsubscript{CH\textsubscript{2}}Cl\textsubscript{2}. The complex [PtCl\textsubscript{2}(COD)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and sulphonyldiacetic acid dimethyl ester (108) (0.056 g, 0.27 mmol) gave white microcrystals of (130).\textsubscript{CH\textsubscript{2}}Cl\textsubscript{2} (0.19 g, 70%). N.m.r. spectra: $^1\text{H}$ (90 MHz), $\delta$ 7.8-7.5 (m, 30H, Ph), 5.3 (s, 2H, CH\textsubscript{2}Cl\textsubscript{2}), 3.8 [d, second-order, 2H, Pt-CH, $|^3\text{J(\text{PH})}\text{trans} + ^3\text{J(\text{PH})cis}|$ ca. 9.5, $^2\text{J(\text{PH})}$ 65], and 3.1 p.p.m. (s, 6H, Me); $^{31}\text{P}$-$^1\text{H}$ (24 MHz), $\delta$ 14.52 p.p.m. [s, $^1\text{J(PtP)}$ 2798].

(xv) [Pd(CH\textsubscript{(CO\textsubscript{2}Me)}S(O)\textsubscript{2}CH(CH\textsubscript{2}Me)})\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}](131).\textsubscript{CH\textsubscript{2}}Cl\textsubscript{2}. The complex [PdCl\textsubscript{2}(COD)] (0.10 g, 0.35 mmol) with triphenylphosphine (0.184 g, 0.70 mmol) and sulphonyldiacetic acid dimethyl ester (108) (0.065 g, 0.35 mmol) gave white microcrystals of (131).\textsubscript{CH\textsubscript{2}}Cl\textsubscript{2} (0.22 g, 68%). N.m.r. spectrum: $^{31}\text{P}$-[$^1\text{H}$] (24 MHz), $\delta$ 25.01 p.p.m. (s).

*Attempted deuteration of (109).PhMe*

An excess of sodium hydride was added to a solution of (109).PhMe (0.10 g) in THF (5 cm\textsuperscript{3}), and the mixture was stirred for 48h. The solution was decanted from the unreacted hydride and an excess of [\textsuperscript{2}H\textsubscript{2}]-water (ca. 1 cm\textsuperscript{3}) added. The THF was removed under reduced pressure and the mixture extracted with dichloromethane (20 cm\textsuperscript{3}). The dichloromethane layer was separated, dried (MgSO\textsubscript{4}) and evaporated to dryness under reduced pressure to afford a white solid which was shown to be unreacted (109) by $^1\text{H}$ n.m.r. spectroscopy.

*Attempted deuteration of (110).0.5PhMe*

Excess (0.5 cm\textsuperscript{3}, 2.5 mol dm\textsuperscript{-3}) n-butyl lithium was added dropwise to a stirred solution of (110).0.5PhMe (0.10 g) in THF at -78°C to give a salmon-pink solution, which was allowed to warm to room temperature and stirred for a further 3h. The mixture was quenched with [\textsuperscript{2}H\textsubscript{2}]-water
(1 cm$^3$), and the THF was removed under reduced pressure. The residue was extracted with dichloromethane, dried ($\text{MgSO}_4$), and evaporated to dryness to give a white solid which was identified as unreacted (110) from its $^1$H n.m.r. spectrum.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Analysis (%)</th>
<th>ν(SO$_2$)(cm$^{-1}$)</th>
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<tbody>
<tr>
<td>(109).PhMe</td>
<td>94c</td>
<td>245-248d</td>
<td>59.4(59.8)</td>
<td>4.5(4.4)</td>
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<tr>
<td>(109).CH$_2$Cl$_2$.2H$_2$O</td>
<td>80e</td>
<td>245-248d</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(110).0.5PhMe</td>
<td>81</td>
<td>259-262d</td>
<td>63.8(63.6)</td>
<td>4.6(4.6)</td>
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<td>(111)</td>
<td>60</td>
<td>190-208e</td>
<td>41.9(42.5)</td>
<td>4.9(5.2)</td>
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<td>(112)</td>
<td>56, 52g</td>
<td>178-182d</td>
<td>68.5(68.6)</td>
<td>5.0(4.8)</td>
</tr>
<tr>
<td>(113)</td>
<td>57, 69h</td>
<td>195-197d</td>
<td>47.8(47.8)</td>
<td>6.0(6.0)</td>
</tr>
<tr>
<td>(114).CH$_2$Cl$_2$</td>
<td>51</td>
<td>176-178d</td>
<td>48.7(48.3)</td>
<td>6.7(6.6)</td>
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<tr>
<td>(115)</td>
<td>33</td>
<td>87g, 1</td>
<td>52.8(52.5)</td>
<td>7.3(7.1)</td>
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<tr>
<td>(116)</td>
<td>28</td>
<td>213-217d, 1</td>
<td>69.1(68.5)</td>
<td>5.4(5.2)</td>
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</tbody>
</table>

Subscripts:
- a Calculated values given in parentheses;
- b Recorded as KBr discs unless otherwise stated;
- c Using $K_2[PhCHSO_2CHPh]$(103);
- d With decomposition;
- e Using $Li_2[PhCHSO_2CHPh]$(102);
- f Decomposition to black solid, with no observed melting;
- g From palladium(II) acetate;
- h From trans-$[PdCl_2(PMe_3)_2]$;
- i Under nitrogen atmosphere;
- j Powder film between NaCl plates.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Analysis (%)</th>
<th>$\nu$(SO$_2$)(cm$^{-1}$)</th>
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</thead>
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<tr>
<td>(117).CH$_2$Cl$_2$.0.5H$_2$O</td>
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<td>185-190$^b$</td>
<td>56.9(57.2)</td>
<td>4.1(4.1)</td>
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<tr>
<td>(118).CH$_2$Cl$_2$.0.5H$_2$O</td>
<td>76</td>
<td>153-161$^c$</td>
<td>51.7(52.2)</td>
<td>4.1(4.2)</td>
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<td>71</td>
<td>111-116$^c$</td>
<td>45.8(46.3)</td>
<td>4.2(4.2)</td>
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<td>(120)</td>
<td>71</td>
<td>&gt;230$^d$</td>
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<td>4.7(4.7)</td>
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<td>81</td>
<td>218-222$^e$</td>
<td>44.4(44.2)</td>
<td>5.7(5.6)</td>
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<td>77</td>
<td>171-172</td>
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<td>7.4(7.6)</td>
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<td>36</td>
<td>74-82</td>
<td>55.4(56.0)</td>
<td>3.85(3.8)</td>
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<td>61.2(61.5)</td>
<td>4.6(4.5)</td>
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<tr>
<td>(125)</td>
<td>88</td>
<td>222-224$^f$</td>
<td>62.1(62.5)</td>
<td>4.6(4.8)</td>
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<tr>
<td>(126).CH$_2$Cl$_2$</td>
<td>94</td>
<td>103-106$^c$</td>
<td>51.7(51.6)</td>
<td>4.8(4.8)</td>
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<td>(127)</td>
<td>92</td>
<td>222-225$^g$</td>
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<td>5.4(5.4)</td>
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<tr>
<td>(128)</td>
<td>77</td>
<td>211-213$^e$</td>
<td>51.5(52.3)</td>
<td>6.5(6.6)</td>
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<tr>
<td>(129)</td>
<td>76</td>
<td>158-160</td>
<td>59.3(59.2)</td>
<td>8.3(8.2)</td>
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<tr>
<td>(130).CH$_2$Cl$_2$</td>
<td>70</td>
<td>&gt;230$^d$</td>
<td>51.7(51.0)</td>
<td>4.1(4.0)</td>
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<tr>
<td>(131).CH$_2$Cl$_2$</td>
<td>68</td>
<td>217-219$^e$</td>
<td>56.4(55.9)</td>
<td>4.5(4.4)</td>
</tr>
</tbody>
</table>

---

a. Calculated values given in parentheses;
b. Partial melting 155-165°C with gas evolution;
c. With gas evolution;
d. Decomposition above 230°C;
e. With decomposition;
f. Partial melting from 151-160°C;
g. All bands vs.
CHAPTER 3

Reactions of Metallathietane-3,3-dioxide Complexes: An Initial Study
3.1 INTRODUCTION

The reactions undergone by metallathietane-3,3-dioxide complexes may be compared with those of both metallacyclobutane and metallacyclobutan-3-one (n^3-oxodimethylenemethane) complexes (Chapter 1) and can be broadly classified according to the nature of the products formed. In many cases, these reactions result in cleavage of the somewhat strained MC_3 ring. For platinacyclobutanes, a range of reaction types have been reported, including hydrogenolysis to give alkanes, reductive elimination giving cyclopropanes, reactions giving ylide complexes,^146 reactions giving alkenes or alkene complexes,^146 and reactions giving n^3-allyl complexes. Platinacyclobutane chemistry has been extensively studied, and the various reaction types displayed by these complexes have been covered in a fairly recent review.^1 A brief examination of certain reactions of platinacyclobutanes and n^3-oxodimethylenemethane complexes will be outlined below, in order that a comparison may be made with the reactions of metallathietane-3,3-dioxide complexes.

Studies on platina(II)cyclobutanes^1,45 and platinaoxodimethylenemethane complexes^63,73 have shown that they are susceptible to electrophilic attack. Thus, for example, the oxidative addition of iodine, bromine, or cyanogen to the platinacyclobutane complex [Pt(CH_2CH_2CH_2XPEt_3)_2](36) affords 1,1-dimethylocyclopropane, equation 31, presumably via a short-lived six co-ordinate platina(IV)cyclobutane.^45 Although platina(IV)-cyclobutanes of the type [Pt(CH_2CH_2X_2)L_2], e.g. (2), are very stable when the donor ligand L is a hard nitrogen or oxygen donor, and X is a halide, treatment of these complexes with soft ligands such as tertiary phosphines or arsines, results in the reductive elimination of cyclopropane, as illustrated in equation 32.^1,21 However, the oxidative addition of trifluoriodomethane to the platina(II)cyclopentane [Pt(CH_2CH_2CH_2CH_2L_2]
results in no reaction when \( L = \text{PPh}_3 \), or formation of a stable six co-ordinated platina(IV) cyclopentane when \( L = \text{PBu}_3^n \), as depicted in equation 33.\(^{147}\)

\[
(\text{Et}_3\text{P})_2\text{Pt} + X_2 \rightarrow \begin{array}{c}
\text{Pt}
\\
\text{Pt}
\end{array} + (\text{Et}_3\text{P})_2\text{Pt}X_2
\]

\[X = 1, \text{Br, CN}\]  

\[
\begin{array}{c}
\text{Cl} \\
\text{py}
\end{array} + 2\text{L} \rightarrow \begin{array}{c}
\text{Cl} \\
\text{py}
\end{array} + 2\text{py} + \text{PtCl}_2\text{L}_2
\]

\[
(\text{Bu}_3\text{P})_2\text{PtCl}_3 + \text{CF}_3\text{I} \rightarrow \begin{array}{c}
\text{CF}_3 \\
\text{I}
\end{array}
\]

In contrast to platina(IV) cyclobutan es, ligand substitution readily occurs with the platina(II) cyclobutane \([\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{bipy}]\) \((16)\), using phosphines or t-butyl isocyanide to give very stable platinacyclobutane complexes \([\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{L}_2]\) \((L = \text{PPh}_3, \text{PMe}_3, \text{PET}_3, \text{or Bu}^t\text{NC})\).\(^{22}\) Treatment of these platinacyclobutanes with either carbon monoxide or sulphur dioxide results in ring insertion to afford five-membered ring products, equation 34.\(^{22}\)

\[
\text{L}_2\text{Pt} + X(\text{O})_n \rightarrow \text{L}_2\text{Pt}
\]

\[X = \text{C, n = 1, L}_2 = \text{bipy}\]

\[X = \text{S, n = 2, L} = \text{PMe}_3\]

Ring expansion reactions of platina(II) cyclobutanes have been accomplished via the solvolysis of the complexes \([\text{Pt}(\text{CH}_2\text{CR}_1(\text{CHR}_2\text{OR}_3)\text{CH}_2)\text{Cl}_2\text{L}_2]\) \((R_1 = \text{H, Me, or Ph}; R_2 = \text{H or Me}; R_3 = \text{methanesulphonyl or 4-nitrobenzoyl}; L = \text{py or L}_2 = \text{bipy})\) to give the platinacyclopentanol complexes \([\text{Pt}(\text{CHR}_2\text{CR}_1(\text{OH})\text{CH}_2\text{CH}_2)\text{Cl}_2\text{L}_2]\).\(^{10}\) The platinaoxodimethylenemethane
(platinacyclobutan-3-one) complexes \([\text{Pt}(\eta^3-\text{CHRC(O)}\text{CHR})\text{L}_2]\) (50, \(M = \text{Pt}, \ R = \text{CO}_2\text{Me or COMe}, \ L = \text{PPh}_3 \text{ or AsPh}_3\)) undergo insertion of t-butyl isocyanide to afford the five-membered ring zwitterionic products (143).\(^{63}\)

\[
\begin{array}{c}
\text{Bu}^+\text{NC} \quad \text{R} = \text{Me or OMe} \\
\text{L} = \text{Bu}'\text{NC or PPh}_3
\end{array}
\]

(143)

3.2 REACTIONS OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES WITH IODOALKANES AND CHLORINE

The attempted oxidative addition of iodomethane to the benzoyl substituted platinathietane-3,3-dioxide complex (119) in refluxing dichloromethane afforded only unreacted starting material, and similarly treatment of (119) with an excess of trifluoriodomethane in a Carius tube also afforded only unreacted (119). This lack of reactivity, even though basic phosphines are present (which enhance oxidative addition), is in contrast to the behaviour displayed by bis-(tri-n-butylphosphine)-platinacyclopentane, which readily undergoes oxidative addition of trifluoriodomethane at room temperature, equation 33.\(^{147}\) The oxidative addition of chlorine to (117) afforded the complex \(\text{cis-[PtCl}_2(\text{PPh}_3)_2]\), similar to the treatment of the platinacyclobutane (36) with halogens,\(^{45}\) and may imply the formation of the thiirane dioxide \(\text{CH(COPh)S(O)}_2\text{CH(COPh)}\), although no attempt was made to identify organic products.

3.3 LIGAND SUBSTITUTION REACTIONS OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES

Reactions of the bis(diethyl sulphide) complex (111) with a range of ligands indicate that the diethyl sulphide ligands are weakly co-ordinated
to the platinum, as a result of the strong trans influence of the
-CHPhS(O)₂CHPh- diyl moiety. Thus, treatment of (111) with two mole
equivalents of methyldiphenylphosphine, trimethylphosphite, or triphenyl-
phosphite, or with one equivalent of dpmm affords, in high yields, the
phosphine or phosphite substituted platinathietane-3,3-dioxide complexes,

\[ [\text{Pt}([\text{CHPhS(O)}_2\text{CHPh}]L_2)](144, L = \text{PMePh}_2), (145, L = \text{P(OMe)}_3), (146, L = \text{P(OPh)}_3), \text{and (147, } L_2 = \text{dpmm}) \].

The presence of chelating dpmm in (147) was confirmed by the low-field chemical shift of the dpmm methylene
protons, by comparison with dpmm platinacyclopentane complexes.¹⁴⁸

Interestingly, treatment of (111) with greater than one mole equivalent
of 2,2'-bipyridine per platinum, or with a large excess of cyclo-oct-1,5-
diene in refluxing dichloromethane results in the displacement of only
one diethyl sulphide ligand per platinum, to afford the bipy- or COD-
bridged complexes (148) and (149), as depicted in equation 35. Integration
of the \(^1\)H n.m.r. spectra, together with the observation that the
chemical shifts of the methylene and methyl resonances are almost
identical with those of the parent diethyl sulphide complex (111) rules
out the possibility of a diethyl sulphide-bridged dimer.¹⁴⁹,¹⁵⁰ In con-
trast to (111), reactions of the related diphenyl complex cis-
\([\text{PtPh}_2(\text{SMe})_2]\) with ligands such as bipy and phen result in displacement
of both dimethyl sulphide ligands with no other dimethyl sulphide
complexes being identified.¹⁴⁹ Two platinathietane-3,3-dioxide ring
proton signals were observed for both (148) and (149), due to ring CH
groups cis and trans to the co-ordinated diethyl sulphide ligand, with
both resonances showing large coupling to platinum-195. Thus, for example,
the \(^1\)H n.m.r. spectrum of (148) shows platinathietane-3,3-dioxide ring
signals at \(\delta 4.94\) and \(4.36\) p.p.m., showing coupling to platinum-195 of
104.0 and 98.0 Hz respectively. The \(^{13}\)C-{\(^1\)H} and \(^1\)H n.m.r. spectra of
the COD complex (149) indicate that both olefinic groups of the COD ligand are co-ordinated to platinum, and, as a result of the 2,4-disubstitution of the four-membered metalla-cyle, these olefinic CH groups appear as two distinct resonances. Thus, in the $^{13}\text{C}$-$^1\text{H}$ n.m.r. spectrum of (149) the olefinic carbons appear as resonances at $\delta$ 103.39 and 101.38 p.p.m., showing coupling to platinum-195 of 84.8 and 70.5 Hz respectively. In the $^1\text{H}$ n.m.r. spectrum, the olefinic protons appear as a somewhat complex second-order resonance, due to proton-proton coupling. This inequivalence is also extended to the COD CH$_2$ groups, which give two resonances in the $^{13}\text{C}$-$^1\text{H}$ n.m.r. spectrum of (149), although again the $^1\text{H}$ n.m.r. signal for these protons was complex, and no inequivalence could be detected. Complexes containing bridging cyclo-octa-1,5-diene ligands have been noted previously, as in for example $[[\text{PtX}(\text{S}_2\text{CNEt}_2)]_2(\mu\text{-COD})]$ ($X=\text{Cl}^{151}$ or $\text{Me}^{152}$).

Treatment of (111) with one atmosphere pressure of carbon monoxide similarly resulted in the displacement of one diethyl sulphide ligand,
to afford the monocarbonyl derivative (150), equation 36. No evidence was observed, under these conditions, for the insertion of carbon monoxide into a platinum-carbon bond, to give a five-membered ring product. This is in contrast to the platinacyclobutane complex [Pt(CH$_2$CH$_2$CH$_2$)bipy], which undergoes insertion of carbon monoxide at room temperature, see equation 34.$^{22}$ The ring strain in a platinathietane-3,3-dioxide ring is expected to be less than that in a platinumcyclobutane ring, and this difference may influence the ability of a four-membered ring to undergo ring expansion with carbon monoxide. Treatment of cis-[PtMe$_2$(SMe)$_2$] with carbon monoxide has recently been shown to afford an analogous monocarbonyl complex cis-[PtMe$_2$(CO)(SMe)$_2$] (151).$^{153}$ The i.r. spectrum of (150) shows an intense platinum-carbonyl stretching band at 2070 cm$^{-1}$, together with strong sulphone stretching bands at 1116 and 1274 cm$^{-1}$. The value of $\nu$(CO) for (150) is slightly higher than that of (151)[$\nu$(CO) 2030 cm$^{-1}$], presumably as a result of the presence of electron-withdrawing phenyl and sulphonyl groups in (150). The $^1$H n.m.r. spectrum of (150) displays two platinathietane-3,3-dioxide ring proton signals at $\delta$ 4.20 and 4.15 p.p.m., showing coupling to platinum-195 of 102 and 88 Hz, for protons trans to diethyl sulphide and carbonyl ligands respectively.$^{153}$ These values of $^3J$(PtH) are slightly larger than the corresponding values of 89 and 78 Hz observed for (151).$^{153}$

A similar lack of reactivity towards ring expansion was observed when the platinathietane-3,3-dioxide complex (119) was treated with an excess
of sulphur dioxide in dichloromethane at 60°C, with only unreacted
starting material being isolated. Again, this is in marked contrast to
the platinacyclobutane [Pt(CH_2CH_2CH_2PMe_3)_2], which readily undergoes
sulphur dioxide insertion, equation 34. However some platinathietane-
3,3-dioxide complexes do undergo ring expansion when treated with alkyl
isocyanides, and this is discussed in Section 3.5.

3.4 REACTIONS OF PHENYL SUBSTITUTED METALLATHIETANE-3,3-DIOXIDE
COMPLEXES WITH ALKYL ISOCYANIDES

The reaction of the phenyl substituted platinathietane-3,3-dioxide
complex (109) with an excess of either t-butyl isocyanide or n-butyl
isocyanide in refluxing dichloromethane affords, in high yield, the
bis(isocyanide) complexes [Pt(CHPhS(0)CHPh)(CNR)_2] (152, R = Bu^t), and
(153, R = Bu^n), as shown in equation 37. The i.r. spectra of (152) and

\[ (109) \xrightarrow{excess\ RNC} (152), \ R = Bu^t \]
\[ (153), \ R = Bu^n \]

(152) and (153) show two intense bands at 2214 and 2188 cm\(^{-1}\) for (152), and at
2248 and 2232 cm\(^{-1}\) for (153), characteristic of two cis-terminal iso-
cyanide ligands. The room temperature \(^1\)H n.m.r. spectra of (152) and
(153) show a single platinathietane-3,3-dioxide ring proton resonance,
showing coupling to platinum-195 of 79.9 and 79.6 Hz for (152) and (153)
respectively. The metal-bonded isocyanide carbon signals were not
observed in the \(^{13}\)C-(\(^1\)H) n.m.r. spectra of (152) and (153) due to either
overlapping with the phenyl resonances or to the long relaxation time and
low nuclear Overhauser effect associated with these carbons as observed,
for example, in the complex $[\text{Pt}_3(\text{CNBu}^t)_6]$\textsuperscript{154}. Identical reactivity is displayed by the platinacyclobutane complex $[\text{Pt(CH}_2\text{CH}_2\text{CH}_2]\text{bipy}]$, which affords the complex $[\text{Pt(CH}_2\text{CH}_2\text{CH}_2(\text{CNBu}^t)_2]$ on treatment with t-butyl isocyanide.$^{22}$

Similarly, simple ligand substitution also occurs when the trimethylphosphine-palladium and trimethylphosphite-platinum complexes, (113) and (145) respectively, are treated with an excess of t-butyl isocyanide, to afford the monosubstituted complexes (154) and (155) respectively, as shown in equation 38. Complexes (154) and (155) display the expected i.r.

![Diagram](image)

and n.m.r. spectroscopic features for a monosubstituted metallathietane-3,3-dioxide ring system, with a single, intense terminal isocyanide band being observed at 2185 cm$^{-1}$ for (154) and at 2198 cm$^{-1}$ for (155).

3.5 REACTIONS OF BENZOYL AND METHOXYCARBONYL SUBSTITUTED METALLATHIETANE-3,3-DIOXIDE COMPLEXES WITH ALKYL ISOCYANIDES

3.5.1 Ligand Substitution Reactions with One Equivalent of Alkyl Isocyanide

Treatment of the platinum complex (117) with one equivalent of either t-butyl isocyanide or n-butyl isocyanide, or the palladium complex (128) with one equivalent of t-butyl isocyanide, affords the monosubstituted metallathietane-3,3-dioxide complexes $[\text{M}[\text{CH(OCPh)}\text{S(OCPh)}][\text{CNPh}]L]$ (156, $M=\text{Pt}$, $R=\text{Bu}^t$, $L=\text{PPh}_3$), (157, $M=\text{Pt}$, $R=\text{Bu}^n$, $L=\text{PPh}_3$), and (158, $M=\text{Pd}$, $R=\text{Bu}^t$, $L=\text{PET}_3$) in high yield. The i.r. and n.m.r. ($^1\text{H}$, $^{13}\text{C}$-$^1\text{H}$, and $^{31}\text{P}$-$^1\text{H}$) spectroscopic properties are characteristic for mono iso-
cyanide metallathietane-3,3-dioxide complexes. Thus, the $^1\text{H}$ and $^{13}\text{C-}[^1\text{H}]$ n.m.r. spectra show the presence of two inequivalent Pt-CH groups, with the one trans to the phosphine ligand displaying the larger $^2\text{J(\text{PC})}$ and $^3\text{J(\text{PH})}$ couplings. One of the carbonyl groups in the $^{13}\text{C-}[^1\text{H}]$ n.m.r. spectrum of (156) shows coupling to both the phosphorus ligand [$^3\text{J(\text{PC})}$ 3.9 Hz], and the platinum-195 nucleus [$^2\text{J(\text{PlC})}$ 44.5 Hz], whereas the other carbonyl group, presumably cis to the phosphine ligand, shows coupling to platinum-195 only, with $^2\text{J(\text{PlC})}$ ca. 37 Hz.

### 3.5.2 Ligand Substitution and Insertion Reactions with Excess Alkyl Isocyanide

Treatment of the platinathietane-3,3-dioxide complexes (117), (119), and (130) with an excess of either t-butyl isocyanide or n-butyl isocyanide in refluxing dichloromethane resulted in ring insertion to afford white to pale yellow crystalline complexes formulated as the zwitterionic five-membered ring products $[\text{Pt\{CH(COR)\text{S(O2)}\text{C(COR)}C:NHR'}\}(\text{CNR'})\text{L}]$ (159, $L = \text{PPh}_3$, $R = \text{Ph}$, $R' = \text{Bu}^t$), (160, $L = \text{PMe}_2\text{Ph}$, $R = \text{Ph}$, $R' = \text{Bu}^t$), (161, $L = \text{PPh}_3$, $R = \text{Ph}$, $R' = \text{Bu}^t$), and (162, $L = \text{PPh}_3$, $R = \text{OMe}$, $R' = \text{Bu}^t$) on the basis of their i.r. and n.m.r. spectroscopic properties, and a single-crystal X-ray diffraction study on a mixed isocyanide analogue, which is described in Section 3.6. The overall reaction is depicted in equation 39.

The spectroscopic properties of complexes (159)-(162) are almost identical with those of the related ketone complexes (143) containing a phosphine ligand. Thus, the $^1\text{H}$ n.m.r. spectra of (159)-(162) display a characteristic broad low-field signal at $>\delta$ 10 p.p.m. due to the acidic iminium proton, which is readily exchanged on shaking with alkaline $[^2\text{H}_2]$-water. This NH proton signal shows a large coupling to the trans phosphorus-31 nucleus to give a doublet, with values of $^4\text{J(\text{PH})}$ being around 14.4 Hz. Satellite features due to coupling to platinum-195 are also
observed, with $^3J(\text{PtH})$ in the range 78-95 Hz. Although this acidic proton is far removed from the phosphorus and platinum nuclei, this long-range coupling is similar to the large couplings observed between trans substituents in olefins. For the n-butyl isocyanide complex (161), the NH proton shows an additional coupling to the α-CH$_2$ protons of the inserted n-butyl group, to give a broad, complex multiplet, but no phosphorus or proton coupling could be resolved. The Pt-CH protons for (159)-(162) appear in the range $\delta$ 3.8-5.0 p.p.m., showing coupling to both the cis phosphine ligand, with $^3J(\text{PH})$ values in the range 10.7-11.2 Hz, and to the platinum-195 nucleus, with $^2J(\text{PtH})$ in the range 75.0-84.0 Hz. These values are similar to those of the parent platinathietane-3,3-dioxide complexes, Chapter 2. Two sets of t-butyl or n-butyl resonances are observed in the $^1H$ and $^{13}C-(^1H)$ n.m.r. spectra of (159)-(162) due to the two non-equivalent (co-ordinated and inserted) isocyanide moieties. By comparison of the chemical shifts of the two t-butyl resonances in (159) with that of the co-ordinated t-butyl isocyanide in the monosubstituted
complex (156), the higher field t-butyl resonance of (159) is assigned to the co-ordinated ligand.

The $^{31}\text{P}-^{1}\text{H}$ n.m.r. spectra of (159)-(162) show a single resonance with a relatively small coupling to platinum-195, as compared to the parent platinathietane-3,3-dioxide complexes (Chapter 2). Thus, values of $^1J(\text{PtP})$ for (159)-(162) lie in the range 1919-1997 Hz, whereas the values for the parent platinathietane-3,3-dioxide complexes lie in the range 2734-2817 Hz. This suggests that the phosphine ligand in (159)-(162) is trans to a high trans influence $\text{C}=\text{NHR}$ fragment.

The $^{13}\text{C}-^{1}\text{H}$ n.m.r. spectra of (159)-(162) are also consistent with their formulation as five-membered ring insertion products. The Pt-CH ring carbons of complexes (159) and (160) exhibit a large $^1J(\text{PtC})$ coupling of 614.0 and 569.8 Hz respectively, and the presence of a small phosphorus coupling of around 3.8 Hz is consistent with the assignment of these carbons cis to the co-ordinated phosphine ligand. Furthermore, the $\text{C}=\text{N}$ carbon appears as a weak resonance at $\delta$ 186.7 and 189.45 p.p.m. for (159) and (160) respectively, showing very large couplings to both the phosphorus-31 and platinum-195 nuclei. Thus, for example, the values of $^2J(\text{PC})$ and $^1J(\text{PtC})$ for the $\text{C}=\text{N}$ carbon of (160) are 114.5 and 798.1 Hz respectively, consistent with the assignment of an inserted isocyanide moiety trans to the co-ordinated phosphine ligand. The carbonyl resonances of (159) and (160) are assigned by their smaller values of $J(\text{PC})$ and $J(\text{PtC}).$ Thus the Pt-CH(COPh) carbonyl group of (160) appears at $\delta$ 194.92 p.p.m., showing coupling to platinum-195 of 34.7 Hz, these values being similar to those of the parent platinathietane-3,3-dioxide complex (119) [$\delta$ 197.23 p.p.m., $^2J(\text{PtC})$ 32.0 Hz]. The $\text{C}=\text{COPh}$ carbonyl appears as a peak at around $\delta$ 189 p.p.m. showing coupling to both platinum-195 and phosphorus-31 nuclei. Thus, for example, for complex (160) the values of $^3J(\text{PtC})$
and $^3J(\text{PC})$ for the $\hat{\text{C}}$-COPh carbonyl are 62.3 and 1.9 Hz respectively, these relatively large long-range couplings being consistent with the assignment of this group trans to the co-ordinated phosphine ligand. The 'carbanionic' ring carbon appears as a weak resonance at $\delta$ 120.8 p.p.m. in (159) and 120.3 p.p.m. in (160). A coupling of this carbon to platinum-195 of around 30 Hz was discernible only for (160), and the absence of an attached proton on this carbon is demonstrated by the presence of a single peak in the proton-coupled $^{13}$C n.m.r. spectrum of complex (160).

The i.r. spectra of (159)-(162) exhibit a number of weak, broad bands above 3000 cm$^{-1}$; assigned to, or at least in part to, the NH group, together with an intense band due to the co-ordinated isocyanide ligand in the range 2084-2260 cm$^{-1}$. The somewhat broad band in the range 1660-1686 cm$^{-1}$ is assigned to the benzoyl or methoxycarbonyl groups, and the C=N stretch is tentatively assigned as the strong band in the range 1560-1583 cm$^{-1}$. Finally, the sulphone group displays its characteristically intense stretching frequencies in the ranges 1124-1140 cm$^{-1}$, and 1297-1308 cm$^{-1}$.

In contrast to the above reactions with platinum, the reactions of benzoyl substituted palladathietane-3,3-dioxide complexes with an excess of t-butyl isocyanide afforded bright yellow oils, from which no pure complexes could be isolated.

3.5.3 A Possible Mechanism of Isocyanide Insertion into Metallathietane-
            3,3-Dioxide Ring Systems

As described in Sections 3.4 and 3.5.2, the two series of platinumthietane-3,3-dioxide complexes, containing either phenyl, or benzoyl or methoxycarbonyl ring substituents, react differently towards an excess of an alkyl isocyanide. Thus, the phenyl substituted complexes undergo simple ligand substitution, whereas the benzoyl and methoxycarbonyl
substituted complexes undergo a ring insertion reaction.

A possible mechanism for the insertion of an alkyl isocyanide into the platinathietane-3,3-dioxide ring system is outlined in Scheme 16. The generation of a monosubstituted metallathietane-3,3-dioxide complex (via the reaction of the initial platinathietane-3,3-dioxide complex with one equivalent of alkyl isocyanide, see Section 3.5.1) is followed by 'insertion' of a second molecule of isocyanide into a platinum-carbon bond. The differing reactivities of phenyl and benzoyl substituted complexes indicate that the presence of electron-withdrawing substituents on the platinathietane-3,3-dioxide ring is a prerequisite for the 'insertion' step. Although the mechanism of this insertion step is not strictly known, the pathway illustrated in Scheme 16 provides a very attractive route to the generation of the ring systems (159)-(162). Thus, platinum-carbon bond cleavage, affording an intermediate zwitterionic complex (163), followed by attack of the displaced carbanionic centre of (163) upon a co-ordinated isocyanide molecule would generate the isocyanide-inserted ring system (164). Finally, an inter- or intra-molecular proton shift from carbon to nitrogen would account for the formation of the observed zwitterionic complexes (159)-(162). The generation of the zwitterionic intermediate (163) is most readily accomplished when the platinathietane-3,3-dioxide ring substituent is an electron-withdrawing group, viz. COPh or CO₂Me, since the carbanionic centre which is generated in (163) will be stabilised via enolisation onto the benzoyl or methoxycarbonyl substituent. This would account for the lack of reactivity of phenyl substituted metallathietane-3,3-dioxide complexes (Section 3.4), since the zwitterionic intermediate of the type (163), but containing phenyl substituents, would be too unstable, due to the absence of enolic stabilisation of the carbanionic centre. Alterna-
tively, however, a concerted migration of a CH(COR) group onto a coordinated isocyanide molecule, again promoted by the presence of strongly electron-withdrawing substituents, would also result in the generation of the five-membered ring system (164). The actual insertion process may, in practice, be somewhere inbetween these two limiting descriptions.

It is noteworthy that the reactions of a number of triphenylphosphine-platinum cis-dialkyl or -diaryl complexes with isocyanides typically
result in substitution only. Thus, treatment of the dialkyl or diaryl complexes cis-[PtR₂(PPh₃)₂] (R=Me or Ph) with methyl or p-chlorophenyl isocyanides affords the substitution products cis-[PtR₂(CNR'X(PPh₃))] (R' = Me or p-C₆H₄Cl),¹⁵⁵ and the reactions of cis-[PtR₂(PMePh₂)₂] (R=Me or Ph) with p-chlorophenyl isocyanide, and cis-[PtMe₂(PMe₂Ph₂)] with p-methoxyphenyl isocyanide also afford analogous monosubstitution products.¹⁵⁵,¹⁵⁶ However, the presence of a more basic phosphine, such as triethylphosphine, does result in isocyanide insertion, such as in the reactions of cis-[PtR₂(PEt₃)₂] (R=Me or Ph) with methyl or p-chlorophenyl isocyanides, which afford cis- or trans-[PtR(CR=NR')(PEt₃)₂] (R' = Me or p-C₆H₄Cl).¹⁵⁵ Treatment of the platinacyclobutane complex [Pt(CH₂CH₂CH₂)bipy] (16) with t-butyl isocyanide also results in ligand substitution only, to afford [Pt(CH₂CH₂CH₂)(CNBu⁺)].²²

In contrast to the reactions of dialkyl or diaryl platinum complexes with isocyanides, the reactions of a range of complexes of the type trans-[PtR(X)L₂] (X = halide, R = alkyl or aryl, L = tertiary phosphine) with a number of isocyanides R'NC initially affords adducts of the form [PtR(CNR')L₂]⁺X⁻, which undergo a migratory insertion of isocyanide on heating, to give the iminoacyl complexes trans-[PtX(CR=NR')L₂].¹⁵⁵,¹⁵⁷-¹⁶⁰ The proposed mechanism for this insertion reaction is illustrated in Scheme 17,¹⁵⁷,¹⁵⁸ and bears a resemblance to the mechanism proposed for isocyanide insertion into metallathietane-3,3-dioxide rings (Scheme 16), in that the initial step involves displacement of a ligand from platinum by an isocyanide, forming a cationic platinum centre. Attack of the halide ion at the platinum subsequently effects the concerted migration of the alkyl or aryl residue R to the co-ordinated isocyanide of the intermediate (165), to generate the observed iminoacyl complex,¹⁵⁸ and a similar concerted alkyl migration process has been proposed for the
From the observations above, the presence of electron-withdrawing substituents on the α-carbon atoms of platinum-dialkyl species would appear to be a prerequisite for isocyanide insertion, with these electron-withdrawing groups stabilising the intermediate species in the insertion step. Consistent with this, a number of platinoxodimethylene-methane (platinacyclobutan-3-one) complexes (50), containing electron-withdrawing alkoxycarbonyl or acetyl substituents, Chapter 1, also readily undergo insertion reactions with t-butyl isocyanide to afford complexes (143), which are analogous to the sulphone complexes described in this Section. In order to further test the necessity of electron-withdrawing substituents for isocyanide insertion, the monosubstituted palladaoxodimethylene-methane complex (166), which was prepared by the literature method employed to prepare the ethyl ester analogue (56) (Chapter 1), was treated with an excess of t-butyl isocyanide in refluxing dichloromethane. This resulted in highly selective insertion.
into the Pd-CH(CO₂Me) bond only, to afford a high yield of the five-membered ring product (167), as illustrated in equation 40. No evidence of any complexes formed by insertion of isocyanide into the Pd-CH₂ bond was observed.

Complex (167) was characterised by its n.m.r. spectroscopic properties, which showed the characteristic features for the five-membered zwitterionic ring system. Thus, the NH proton appears as a characteristically broad peak at δ 10.68 p.p.m., of relative intensity one, and the Pd-CH₂ protons appear as a singlet of relative intensity two, at δ 2.75 p.p.m., indicating that insertion into the Pd-CH₂(CO₂Me) bond had occurred. The proton-coupled ¹³C n.m.r. spectrum of (167) is particularly diagnostic, and displays the expected triplet for the Pd-CH₂ group, showing ¹J(CH) 137.1 Hz. The C=O carbon appeared as a doublet in the ¹³C n.m.r. spectrum due to coupling to the NH proton, with ²J(CH) 5.3 Hz. Complex (167) was air-sensitive in solution, and decomposed over 12 hours to give a dark brown oil from which no pure complexes could be identified.

Treatment of the monosubstituted platinathetane-3,3-dioxide complex (156) with one equivalent of n-butyl isocyanide, or (157) with one equivalent of t-butyl isocyanide in refluxing dichloromethane afforded, in both cases, the zwitterionic ring-inserted product (168), as depicted in Scheme 18. The ¹H n.m.r. spectrum of (168) is consistent with the
presence of a co-ordinated t-butyl isocyanide ligand, together with an inserted C=NH$_n$Bu$^n$ moiety. Thus, the NH proton appears as a complex multiplet, as observed for the other inserted n-butyl isocyanide complex (161), as a result of coupling to platinum-195, phosphorus-31, and the $\alpha$-CH$_2$ protons of the n-butyl group. A comparison of the chemical shift for the t-butyl resonance of (168) with the t-butyl resonances in the monosubstituted and ring-inserted complexes, (156) and (159) respectively, confirms the presence of a co-ordinated, as opposed to an inserted, t-butyl isocyanide ligand. As to why only insertion of n-butyl isocyanide occurs is uncertain. Following the mechanism proposed in Scheme 16 for isocyanide insertion in platinathietane-3,3-dioxide complexes, preferential attack of the carbanionic centre on the co-ordinated n-butyl isocyanide ligand, in an intermediate of the type (163), would account for the selective formation of (168). The isocyanide carbon of an n-butyl isocyanide ligand would be expected to be more susceptible to nucleophilic attack than that of a t-butyl isocyanide ligand, as a result of steric
and electronic effects. It is also not possible to rule out the selective formation of a zwitterionic intermediate of the type (163) (Scheme 16) having the carbonanionic alkyl ligand trans to the t-butyl isocyanide, a geometry which would prohibit 'insertion' of t-butyl isocyanide. The possibility of substitution of one isocyanide for another in the monosubstituted complexes prior to insertion of n-butyl isocyanide also cannot be discounted.

3.6 MOLECULAR STRUCTURE OF ZWITTERIONIC RING INSERTED PRODUCTS

The formulation of the isocyanide insertion products was confirmed by a single-crystal X-ray diffraction study carried out on the mixed isocyanide complex (168).CHCl₃. The molecular structure of (168) is illustrated in Figure 14, together with the crystallographic numbering system, and important bond lengths and angles for (168) are presented in Table 6. The equation is that of the least-squares plane through Pt, C(1), C(2), C(3), and S, and deviations of relevant atoms from this plane are also given with Table 6.

The molecular structure consists of a five-membered ring containing a Pt(CNBu⁺XPh₃) moiety. The co-ordination about the platinum atom is effectively square-planar, with a small twist angle of 8.78(53)° between the P-Pt-C(6) and C(1)-Pt-C(3) planes. Overall, the geometry of (168) bears a very strong resemblance to that of the ketone analogue (143, L = Bu⁺NC, R' = OMe), prepared from the platinum oxodimethylenemethane complex (50, M = Pt, R = CO₂Me, L = PPh₃). Examination of the geometry around C(2) shows this carbon to be sp² hybridised, effectively lying in the plane formed by Pt, C(1), C(2), C(3), and S, deviating by only 0.027 Å from the least-squares plane through these atoms. The C(2)-C(5) and C(5)-O(4) bonds are respectively shorter and longer than C(1)-C(4) and C(4)-O(3),
TABLE 6a

Selected bond lengths and angles for the complex $\text{[Pt(CH(COPh)S(O)_2C(COPh)C:NHBu^t)(CNBu^t)(PPh_3)] (168).CHCl}_3$

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Bond angle</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-P</td>
<td>2.325 (4)</td>
<td>P-Pt-C(6)</td>
</tr>
<tr>
<td>Pt-C(6)</td>
<td>1.908 (11)</td>
<td>P-Pt-C(1)</td>
</tr>
<tr>
<td>Pt-C(1)</td>
<td>2.080 (10)</td>
<td>C(1)-Pt-C(3)</td>
</tr>
<tr>
<td>Pt-C(3)</td>
<td>2.060 (13)</td>
<td>C(3)-Pt-C(6)</td>
</tr>
<tr>
<td>C(6)-N(2)</td>
<td>1.197 (15)</td>
<td>C(6)-N(2)-C(7)</td>
</tr>
<tr>
<td>C(3)-N(1)</td>
<td>1.333 (17)</td>
<td>Pt-C(1)-S</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.396 (16)</td>
<td>C(1)-S-C(2)</td>
</tr>
<tr>
<td>C(1)-S</td>
<td>1.765 (13)</td>
<td>S-C(2)-C(3)</td>
</tr>
<tr>
<td>C(2)-S</td>
<td>1.741 (13)</td>
<td>S-C(2)-C(5)</td>
</tr>
<tr>
<td>S-O(1)</td>
<td>1.454 (8)</td>
<td>C(3)-C(2)-C(5)</td>
</tr>
<tr>
<td>S-O(2)</td>
<td>1.454 (11)</td>
<td>Pt-C(3)-C(2)</td>
</tr>
<tr>
<td>C(2)-C(5)</td>
<td>1.446 (19)</td>
<td>O(1)-S-O(2)</td>
</tr>
<tr>
<td>C(5)-O(4)</td>
<td>1.246 (17)</td>
<td>C(2)-C(5)-O(4)</td>
</tr>
<tr>
<td>C(1)-C(4)</td>
<td>1.547 (17)</td>
<td>O(4)-C(5)-C(51)</td>
</tr>
<tr>
<td>C(4)-O(3)</td>
<td>1.218 (17)</td>
<td>C(1)-C(4)-O(3)</td>
</tr>
<tr>
<td>N(1)-C(201)</td>
<td>1.510 (20)</td>
<td>C(3)-N(1)-C(201)</td>
</tr>
<tr>
<td>C(201)-C(202)</td>
<td>1.331 (27)</td>
<td>N(1)-C(201)-C(202)</td>
</tr>
<tr>
<td>C(202)-C(203)</td>
<td>1.50 (4)</td>
<td>N(1)-C(201)-C(202)</td>
</tr>
<tr>
<td>C(203)-C(204)</td>
<td>1.32 (4)</td>
<td>Twistb</td>
</tr>
</tbody>
</table>

Equation of least-squares plane through Pt, C(1), C(2), C(3), and S with deviations of relevant atoms:

$$13.3007 \times X + 8.4973 \times Y - 1.8440 \times Z = 3.7012$$

deviations: Pt -0.297; C(1) 0.387; C(2) 0.027; C(3) 0.194;
S -0.310 Å;
C(5) 0.261; O(4) 0.746; N(1) 0.729 Å.

a See Figure 14 for crystallographic numbering system;
b \( \angle \text{P-Pt-C(6)/C(1)-Pt-C(3)} \).
Molecular structure of [Pt(Ph(COPh)S)Cl_2(CNBu_H3)] with triphenylphosphine carbon atoms other than those bonded to phosphorus, and all hydrogen atoms omitted.
suggesting that there is a considerable delocalisation of the negative charge which is formally on C(2). The C(2)-C(3) bond appears normal [1.396(16) Å], but the C(2)-S bond is slightly shorter than the C(1)-S bond, suggesting a little stabilisation of the negative charge by the sulphone group. The short C(3)-N(1) bond of 1.333(17) Å is typical of a carbon-nitrogen double bond. It was not possible to locate the hydrogen atom on N(1) in the X-ray study, however this hydrogen would be expected to be directed towards the oxygen atom O(4), to form a weak, intramolecular hydrogen bond, as observed in the ketone analogue (143, L = Bu'TNC, R' = OMe), where the iminium proton was located in the X-ray study. The Pt-CH hydrogen atom could also not be located. Thus, on the basis of the X-ray data, complex (168) may be better represented as the delocalised enolate-type structure (169).

![Chemical structure](image)

3.7 MISCELLANEOUS REACTIONS OF METALLATHIETANE-3,3-DIOXIDE COMPLEXES

Pyrolysis studies on either cis- or trans-2,4-diphenylthietane-1,1-dioxide at 250°C have been shown to result in the elimination of sulphur dioxide from the strained four-membered ring system, yielding in each case, an equilibrium mixture of cis- and trans-1,2-diphenylcyclopropane. However, heating the platinathietane-3,3-dioxide complex (117) to 250°C did not effect the elimination of sulphur dioxide, and only unreacted (117) was isolated. This observation is consistent with both the reduced
ring strain in (117) (as a result of substitution of carbon by a substantially larger platinum atom), and with the presence of relatively shorter (and therefore stronger) carbon-sulphur bonds in the metalla-cycle, see Chapter 2.

The similarity in the behaviour of platinathietane-3,3-dioxide and platinaoxodimethylenemethane complexes towards isocyanide insertion, Sections 3.5 and 3.6, led to an investigation of the reactivity of the former towards hexafluoroacetone. The reaction of the oxodimethylene-methane complex (50, M = Pt, R = CO₂Me, L = PMePh₂) with hexafluoroacetone has been shown to result in ring expansion to afford the oxygen-bonded complex (170). No ring opening of a platinathietane-3,3-dioxide ring was observed, however, on treating the complex (117) with an excess of hexafluoroacetone, with only the solvated product (117).C(CF₃)₂(OH)₂ being isolated in high yield.

Treatment of (117) with one equivalent of (phenylsulphonyl)acetic acid in dichloromethane at room temperature resulted in the recovery of unreacted starting material (117), by ³¹P-{¹H} n.m.r. spectroscopy. On refluxing the mixture for 30 minutes, reaction occurred, resulting in the formation of a 1:1 mixture of unreacted (117) and the bis(carboxylato) complex cis-[Pt{OC(O)CH₂SO₂Ph}₂(PPh₃)₂](171). Complex (171) was identified in the mixture by comparison of its ³¹P-{¹H} n.m.r. spectrum
with that of an authentic sample of (171) prepared from cis-[PtCl₂(P₃Ph)₂],
(phenylsulphonyl)acetic acid, and silver(I) oxide in refluxing dichloro-
methane. The formation of this mixture indicates that cleavage of the
second platinum-carbon bond is much more rapid than the initial cleavage
of a metallacyclic platinum-carbon bond.

3.8 CONCLUSION

Ligand substitution reactions of the labile diethyl sulphide complex
[Pt(CHPhS(O)₂CHPh(SEt)₂] (111) afford a route into a range of mono- and
dinuclear platinathietane-3,3-dioxide complexes.

The reactions of platinathietane-3,3-dioxide complexes with alkyl
isocyanides have been investigated. In the case of phenyl substituted
complexes, simple ligand substitution occurs to give either mono- or
disubstituted isocyanide complexes. In contrast, platinathietane-3,3-
dioxide complexes containing electron-withdrawing benzoyl or methoxy-
carbonyl ring substituents readily undergo ring insertion to afford
zwitterionic five-membered ring products. A possible mechanism for isocyanide
insertion incorporates the formation of an intermediate
zwitterionic complex which contains a carbanionic centre, accounting for
the differing reactivity of the two series of platinathietane-3,3-dioxide
complexes. Selective insertion experiments with t-butyl isocyanide and
n-butyl isocyanide afford a single zwitterionic five-membered ring
product (168), which contains an inserted n-butyl isocyanide, together
with a co-ordinated t-butyl isocyanide ligand. A single-crystal X-ray
diffraction study carried out on this mixed isocyanide complex confirms
the zwitterionic formulation of these five-membered ring systems.
3.9 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. The $^{19}$P-$^{1}H$ n.m.r. spectrum was recorded in [${}^2H_2$]-chloroform on a JEOL JNM-PS 100 spectrometer, operating at 94.1 MHz, relative to external fluorotrichloromethane. The $^{13}$C-$^{1}H$ n.m.r. data for the aromatic region between $\delta$ 140 and 125 p.p.m. are omitted for clarity. The compounds 2,2'-bipyridine, n-butyl isocyanide, cyclo-octa-1,5-diene, iodomethane, trimethylphosphite, triphenylphosphite (Aldrich), bis-(diphenylphosphino)-methane (Alfa), silver(I) oxide (B.D.H.), carbon monoxide, chlorine (B.O.C.), trifluoriodomethane (Bristol Organics), t-butyl isocyanide (Fluka) and hexafluoroacetone (Koch-Light) were used as supplied from commercial sources. The compound (phenylsulphonyl)acetic acid was prepared from phenylthioacetic acid (Aldrich) by the literature procedure. The complex [Pd[$^{1}H$-CH$_2$C(O)CH(CO$_2$Me)]bipy] (166) was prepared via the literature method for the preparation of the ethyl ester analogue, and yielded comparable $^{1}H$ n.m.r. spectroscopic properties.

Attempted oxidative addition reactions to platinathietane-3,3-dioxide complexes

(i) With iodomethane

A solution of (119).CH$_2$Cl$_2$ (0.11 g) in dichloromethane (20 cm$^3$) with iodomethane (1 cm$^3$) was refluxed for 18h. The resulting colourless solution was evaporated to dryness under reduced pressure to afford an oily solid which was identified as containing unreacted (119) by its $^{31}$P-$^{1}H$ n.m.r. spectrum.

(ii) With trifluoriodomethane

An excess of trifluoriodomethane was condensed onto a frozen (-196°C) solution of (119).CH$_2$Cl$_2$ (0.12 g) in dichloromethane (30 cm$^3$) contained
in a Carius tube. The tube was sealed, heated to 50°C for 30 min., and left to stand for 48 h at room temperature. The tube was opened, and the contents evaporated to dryness under reduced pressure to afford white microcrystals which were identified as unreacted (119) by its $^{31}$P-$\{^1$H$\}$ n.m.r. spectrum.

(iii) With chlorine
A slow stream of chlorine was passed through a solution of (117).CH$_2$Cl$_2$. 0.5H$_2$O (0.10 g) in dichloromethane for 30 seconds. Evaporation to dryness under reduced pressure afforded white microcrystals which were identified as cis-[PtCl$_3$(PPh$_3$)$_2$] by comparison of its $^{31}$P-$\{^1$H$\}$ n.m.r. spectrum with that of an authentic sample.

Ligand substitution reactions of [Pt(CHPhS(O)$_2$CHPh)(SET$_2$)$_2$](III)

(i) With methyldiphenylphosphine
A solution of [Pt(CHPhS(O)$_2$CHPh)(SET$_2$)$_2$](III) (0.10 g, 0.16 mmol) in dichloromethane (20 cm$^3$) with methyldiphenylphosphine (0.10 g, 0.50 mmol) was refluxed for 1 h. 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(CHPhS(O)$_2$CHPh)-(PMePh$_2$)$_2$](144) (0.127 g, 94%) (Found: C, 57.5; H, 4.5. C$_{48}$H$_{38}$O$_2$P$_2$PtS requires C, 57.2; H, 4.6%), m.p. 139-141°C; $v$SO$_2$ at 1108vs and 1262s cm$^{-1}$. N.m.r. spectrum: $^1$H (300 MHz), $\delta$ 7.4-6.9 (m, 30H, Ph), 3.94 [d, second-order, 2H, Pt-CH, $^3$J(PH)$_{\text{trans}}$ $^3$J(PH)$_{\text{cis}}$] 11.65, $^2$J(PtH) 69.3], and 1.36 p.p.m. [d, second-order, 6H, Me, PMePh$_2$, $^2$J(PH) $^3$J(PtH) 29.8].

(ii) With trimethylphosphite
A solution of [Pt(CHPhS(O)$_2$CHPh)(SET$_2$)$_2$](III) (0.09 g, 0.14 mmol) in dichloromethane (20 cm$^3$) with trimethylphosphite (0.2 cm$^3$, 1.8 mmol) was
refluxed for 1h. The mixture was evaporated to dryness under reduced pressure to afford a colourless oil which was crystallised from dichloromethane-light petroleum to afford white microcrystals of

\[ \text{[Pt(CHPhS(O)\textsubscript{2}CHPh)(P(OMe)\textsubscript{3})\textsubscript{2}] (145)} \]

(0.083 g, 83%) (Found: C, 35.1; H, 4.4. \( \text{C}_{20}\text{H}_{39}\text{O}_{8}\text{P}_{2}\text{PtS}\) requires C, 34.9; H, 4.4%), m.p. 140-142°C; \( \nu_{\text{SO}_2} \) at 1108vs and 1273s cm\(^{-1}\). N.m.r. spectra: \( \text{^1H} \) (400 MHz), \( \delta \) 7.33-7.04 (m, 10H, Ph), 4.31 [d, second-order, 2H, Pt-CH, \( |3\text{J(PH)}\text{trans} + 3\text{J(PH)}\text{cis}| \) 11.0, \( 2\text{J(PtH)} \) 68.1], and 3.40 p.p.m. [d, second-order, \( ^{163} \) 18H, P(OMe)\textsubscript{3}], \( 3\text{J(PH)} \) 12.05]; \( 3\text{P} \{-\text{^1H}\} \) (162 MHz, \( \text{^2H}_1\)-chloroform), \( \delta \) 117.68 p.p.m. [s, \( \text{^1J(PtP)} \) 4099].

(iii) With triphenylphosphite

A solution of \[ \text{[Pt(CHPhS(O)\textsubscript{2}CHPh)(SEt\textsubscript{2})\textsubscript{2}] (111)} \]

(0.15g, 0.24 mmol) in dichloromethane (20 cm\(^3\)) with triphenylphosphite (0.2 cm\(^3\), 0.76 mmol) was refluxed for 2h. Work-up as in (ii) afforded white microcrystals of \[ \text{[Pt(CHPhS(O)\textsubscript{2}CHPh)(P(OMe)\textsubscript{3})\textsubscript{2}] (146)} \]

(0.19 g, 75%) (Found: C, 56.1; H, 4.0. \( \text{C}_{50}\text{H}_{42}\text{O}_{8}\text{P}_{2}\text{PtS}\) requires C, 56.6; H, 4.0%), m.p. 204-206°C; \( \nu_{\text{SO}_2} \) at 117vs and 1279m cm\(^{-1}\). N.m.r. spectra: \( \text{^1H} \) (400 MHz), \( \delta \) 7.19-6.67 (m, 40H, Ph), and 4.29 p.p.m. [d, second-order, 2H, Pt-CH, \( |3\text{J(PH)}\text{trans} + 3\text{J(PH)}\text{cis}| \) ca. 11, \( 2\text{J(PtH)} \) 71.8]; \( 3\text{P} \{-\text{^1H}\} \) (162 MHz, \( \text{^2H}_1\)-chloroform), \( \delta \) 100.55 p.p.m. [s, \( \text{^1J(PtP)} \) 4119].

(iv) With dpmm

A solution of \[ \text{[Pt(CHPhS(O)\textsubscript{2}CHPh)(SEt\textsubscript{2})\textsubscript{2}] (111)} \]

(0.10g, 0.16 mmol) in dichloromethane (20 cm\(^3\)) with dpmm (0.065 g, 0.17 mmol) was refluxed for 2h. Work-up as in (ii) afforded white microcrystals of \[ \text{[Pt(CHPhS(O)\textsubscript{2}CHPh)(dpmm)] (147)} \]

(0.11 g). Decomp. to black solid >220°C; \( \nu_{\text{SO}_2} \) at 1102vs and 1270m cm\(^{-1}\). N.m.r. spectra: \( \text{^1H} \) (300 MHz), \( \delta \) 7.8-6.7 (m, 30H, Ph), 4.91 [d, second-order, 2H, Pt-CH, \( |3\text{J(PH)}\text{trans} + 3\text{J(PH)}\text{cis}| \) ca. 10, \( 2\text{J(PtH)} \) 85.0], and 4.39 p.p.m. [t, 2H, CH\(_2\), dpmm, \( 2\text{J(PH)} \) 9.9, \( 3\text{J(PtH)} \) not
discernible]; $^{13}$C-{1'H} (75.5 MHz), δ 56.12 [dd, second-order, Pt-CH, $|^{2}$J(PTC)$_{\text{trans}} + ^{2}$J(PTC)$_{\text{cis}}| 91.8, ^{1}$J(PTC) 461.9], and 47.05 p.p.m. [t, CH$_{2}$, dppm, $^{1}$J(PTC) 28.3, $^{2}$J(PTC) not discernible]. The complex crystallised with CH$_{2}$Cl$_{2}$ and light petroleum and was not obtained analytically pure.

(v) With 2,2'-bipyridine
A solution of [Pt(CHPhS(O)$_{2}$CHPh)(SET$_{2}$)$_{2}$] (111) (0.10 g, 0.16 mmol) in dichloromethane (20 cm$^{3}$) with 2,2'-bipyridine (0.031 g, 0.20 mmol) was refluxed for 3h. The solution was evaporated to dryness under reduced pressure and the residue recrystallised from dichloromethane-diethyl ether to give yellow microcrystals of [[Pt(CHPhS(O)$_{2}$CHPh)(SET$_{2}$)$_{2}$]$_{2}$(μ-bipy)] (148) (0.09 g, 92%) (Found: C, 46.4; H, 4.0; N, 2.7. C$_{44}$H$_{52}$N$_{2}$O$_{4}$Pt$_{2}$S requires C, 45.5; H, 4.3; N, 2.3%), m.p. 230-240°C (decomp.); ν$_{SO_{2}}$ at 1109vs and 1268m cm$^{-1}$. N.m.r. spectra: $^{1}$H (400 MHz, [2H$_{2}$]-dichloromethane), δ 8.46-7.18 (m, 28H, aromatic CH), 4.94 [s, 2H, Pt-CH, $^{2}$J(PTH) 104.0], 4.36 [s, 2H, Pt-CH, $^{2}$J(PTH) 98.0], 2.49 (m, 4H, CH$_{2}$, Et$_{2}$S), 2.29 (m, 4H, CH$_{2}$, Et$_{2}$S), and 1.20 p.p.m. [t, 12H, CH$_{3}$, Et$_{2}$S, $^{3}$J(HT) 7.4]; $^{13}$C-{1'H} (100 MHz, [2H$_{2}$]-dichloromethane), δ 48.27 [s, Pt-CH, $^{1}$J(PTC) 624.0], 40.71 [s, Pt-CH, $^{1}$J(PTC) 614.0], 30.02 (s, CH$_{2}$, Et$_{2}$S) and 13.29 p.p.m. (s, CH$_{3}$, Et$_{2}$S).

(vi) With cyclo-octa-1,5-diene
A solution of [Pt(CHPhS(O)$_{2}$CHPh)(SET$_{2}$)$_{2}$] (111) (0.10 g, 0.16 mmol) in dichloromethane (20 cm$^{3}$) with COD (0.5 cm$^{3}$, 4.1 mmol) was refluxed for 12h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane-light petroleum to give white microcrystals of [[Pt(CHPhS(O)$_{2}$CHPh)(SET$_{2}$)$_{2}$]$_{2}$(μ-COD)] (149) (0.07 g, 74%) (Found: C, 44.8; H, 4.7. C$_{44}$H$_{56}$O$_{4}$Pt$_{2}$S$_{4}$ requires C, 45.3; H, 4.8%), m.p. 200-200°C (decomp.); ν$_{SO_{2}}$ at 1113vs and 1273m cm$^{-1}$. N.m.r. spectra:
\[ \text{H} (400 \text{ MHz}), \delta 7.56-6.96 \text{ (m, 2OH, Ph), 5.21 [m, 4H, CH=CH, J(PtH) ca. 19]}, 4.50 [s, 2H, Pt-CH, \text{J(PtH) 104.0}], 4.40 [s, 2H, Pt-CH, \text{J(PtH) 100.0}], 2.44 (m, 4H, CH\_2, Et\_2S), 2.21 (m, 8H, CH\_2, COD), 2.11 (m, 4H, CH\_2, Et\_2S), \] and 1.16 p.p.m. [t, 12H, CH\_3, Et\_2S, J(HH) 7.4]; \[ ^{13}\text{C}-\{^{1}\text{H}} \] (100 MHz), \delta 103.39 [s, C=C, J(PtC) 84.8], 101.38 [s, C=C, J(PtC) 70.5], 57.28 [s, Pt-CH, J(PtC) 586.1], 47.81 [s, Pt-CH, J(PtC) 604.3], 30.28 (s, CH\_2, COD), 29.57 (s, CH\_2, Et\_2S), 28.12 (s, CH\_2, COD), and 13.07 p.p.m. (s, CH\_3, Et\_2S).

(vii) With carbon monoxide

Carbon monoxide was slowly bubbled through a solution of \([\text{Pt}(\text{CHPhS(O)}\_2\text{CH-Ph})\text{(SET\_2)}\_2]\) (111) (0.10 g, 0.16 mmol) in dichloromethane (10 cm\(^3\)) for 1h. The solution was reduced in volume to ca. 0.5 cm\(^3\), and addition of light petroleum (ca. 50 cm\(^3\)) gave white microcrystals of \([\text{Pt}(\text{CHPhS(O)}\_2\text{CHPh})\text{(CO)(SET\_2)}\_2]\) (150) (0.085 g, 94%) (Found: C, 41.1; H, 4.1. C\(_{19}\)H\(_{22}\)O\(_3\)PtS\(_2\) requires C, 40.9; H, 4.0%), m.p. decomp. >170°C; \(v\text{CO} \) at 2070s cm\(^{-1}\); \(v\text{SO}_2 \) at 1116vs and 1274s cm\(^{-1}\). N.m.r. spectrum: \(^{1}\text{H} \) (90 MHz), \delta 7.5-6.8 (m, 10H, Ph), 4.20 [s, 1H, Pt-CH, \text{J(PtH) 102}], 4.15 [s, 1H, Pt-CH, \text{J(PtH) 88}], 2.5-1.8 (m, 4H, CH\_2, Et\_2S), and 0.95 p.p.m. [t, 6H, CH\_3, Et\_2S, J(HH) 7.5].

Reaction of \([\text{Pt}(\text{CH(COPh)(S(O)}\_2\text{CH(COPh)})\text{(PMe\_2Ph)}\_2]\) (119).CH\(_2\)Cl\(_2\) with sulphur dioxide

An excess (ca. 1 cm\(^3\)) of liquid sulphur dioxide was condensed onto a frozen (-196°C) solution of \([\text{Pt}(\text{CH(COPh)(S(O)}\_2\text{CH(COPh)})\text{(PMe\_2Ph)}\_2]\) (119).CH\(_2\)Cl\(_2\) (0.12 g) in dichloromethane (30 cm\(^3\)) in a Carius tube. The tube was sealed, heated to 60°C for 2h, stood for a further 12h at room temperature, cooled to -196°C, opened, and the contents evaporated to dryness under reduced pressure to afford white microcrystals which were
identified as unreacted (119) from its $^{31}$P-{$^1$H} n.m.r. spectrum.

**Reactions of phenyl substituted metallathietane-3,3-dioxide complexes with alkyl isocyanides**

**(i) Preparation of $[\text{Pt}\{\text{CHPhS(O)}_2\text{CHPh}\}($CNBu$^t$)$]_2$ (152)**

A solution of $[\text{Pt}\{\text{CHPhS(O)}_2\text{CHPh}\}($AsPh$^3$)$_2$] (109).PhMe (0.18 g, 0.158 mmol) in dichloromethane (20 cm$^3$) with t-butyl isocyanide (0.2 cm$^3$, excess) was refluxed for 4h. The mixture was evaporated to dryness under reduced pressure to give a white solid which was recrystallised from dichloromethane-light petroleum to afford white microcrystals of the title complex (152) (0.065 g, 68%) (Found: C, 47.8; H, 4.9; N, 4.5.

C$_{24}$H$_{30}$N$_2$O$_2$PtS requires C, 47.6; H, 5.0; N, 4.6%), m.p. decomp. >200°C;

$\nu$CN at 2214 vs and 2188 vs cm$^{-1}$; $\nu$SO$_2$ at 1114 vs and 1277 m cm$^{-1}$. N.m.r.
spectra: $^1$H (400 MHz), $\delta$ 7.36-7.05 (m, 10H, Ph), 4.39 [s, 2H, Pt-CH, $^2$J(PtH) 79.9], and 1.19 p.p.m. (s, 18H, Bu$^t$); $^{13}$C-{$^1$H} (100 MHz), $\delta$ 57.58 (s, C, Bu$^t$), 50.01 [s, Pt-CH, $^1$J(PtC) 475.7], and 29.64 p.p.m. (s, Me, Bu$^t$); isocyanide carbons not observable.

**(ii) Preparation of $[\text{Pt}\{\text{CHPhS(O)}_2\text{CHPh}\}($CNBu$^n$)$_2$] (153)**

A solution of $[\text{Pt}\{\text{CHPhS(O)}_2\text{CHPh}\}($AsPh$_3$)$_2$] (109).PhMe (0.10 g, 0.087 mmol) in dichloromethane (20 cm$^3$) with n-butyl isocyanide (0.1 cm$^3$, 0.89 mmol) was refluxed for 2h. Work-up as for (152) afforded white microcrystals of the title complex (153) (0.038 g, 72%) (Found: C, 47.9; H, 4.7; N, 4.5. C$_{24}$H$_{30}$N$_2$O$_2$PtS requires C, 47.6; H, 5.0; N, 4.6%), m.p. 196-197°C;

$\nu$CN at 2248 s and 2232 s cm$^{-1}$; $\nu$SO$_2$ at 1111 vs and 1277 m cm$^{-1}$. N.m.r.
spectra: $^1$H (400 MHz), $\delta$ 7.36-6.98 (m, 10H, Ph), 4.40 [s, 2H, Pt-CH, $^2$J(PtH) 79.6], 3.32 [t, 4H, CH$_3$CH$_2$CH$_2$CH$_2$NC, $^3$J(HH) 6.6], 1.37 [quintet, 4H, CH$_3$CH$_2$CH$_2$CH$_2$NC, $^3$J(HH) 6.8], 1.13 [sextet, 4H, CH$_3$CH$_2$CH$_2$CH$_2$NC, $^3$J(HH) 7.4], and 0.80 [t, 6H, CH$_3$, $^3$J(HH) 7.4]; $^{13}$C-{$^1$H} (100 MHz),
δ 49.93 [s, Pt-CH, $^1J(PtC) = 481.4$], 43.52 (s, br, CH$_3$CH$_2$CH$_2$CH$_2$NC),
30.12 (s, br, CH$_3$CH$_2$CH$_2$CH$_2$NC), 19.14 (s, CH$_3$CH$_2$CH$_2$CH$_2$NC), and 12.91 p.p.m. (s, CH$_3$); isocyanide carbons not observable.

(iii) Preparation of $[\text{Pd}(\text{CHPhS}(O)_{2}\text{CHPh})(\text{CNBu}^t)(\text{PMe}_3)](154)$

A solution of $[\text{Pd}(\text{CHPhS}(O)_{2}\text{CHPh})(\text{PMe}_3)_2](113)$ (0.10 g, 0.20 mmol) in dichloromethane (20 cm$^3$) with t-butyl isocyanide (0.1 g, 1.2 mmol) was refluxed for 12 h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane-light petroleum to give white microcrystals of the title complex (154) (0.076 g, 75%) (Found: C, 52.0; H, 5.9; N, 2.9. C$_{22}$H$_{30}$NO$_2$PPdS requires C, 51.8; H, 5.9; N, 2.8%), m.p. 174-178°C (decomp.); $\nu_{CN}$ at 2185 s cm$^{-1}$; $\nu_{SO_2}$ at 1107 vs and 1270 m cm$^{-1}$. N.m.r. spectra: $^1H$ (400 MHz), δ 7.42-6.99 (m, 10H, Ph), 3.95 [d, 1H, Pd-CH, $^3J(PH) = 8.59$], 3.63 [d, 1H, Pd-CH, $^3J(PH) = 8.07$], 1.17 (s, 9H, Bu$^t$), and 1.03 p.p.m. [d, 9H, PMe$_3$, $^2J(PH) = 8.59$]; $^{31}P$-$^1H$ (162 MHz, $[^1H]$-chloroform), δ -20.0 p.p.m. (s).

(iv) Preparation of $[\text{Pt}(\text{CHPhS}(O)_{2}\text{CHPh})(\text{CNBu}^t)(\text{P(OMe})_3)](155)$

A solution of $[\text{Pt}(\text{CHPhS}(O)_{2}\text{CHPh})(\text{P(OMe)}_3)_2](145)$ (0.10 g, 0.145 mmol) in dichloromethane (20 cm$^3$) with t-butyl isocyanide (0.1 g, 1.2 mmol) was stirred for 1 h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane-light petroleum to afford white microcrystals of the title complex (155) (0.072 g, 77%) (Found: C, 41.3; H, 4.9; N, 2.1. C$_{22}$H$_{30}$NO$_3$P PtS requires C, 40.9; H, 4.7; N, 2.2%), m.p. 180-183°C; $\nu_{CN}$ at 2198 s cm$^{-1}$; $\nu_{SO_2}$ at 1110 vs and 1271 w cm$^{-1}$. N.m.r. spectra: $^1H$ (400 MHz), δ 7.47-7.03 (m, 10H, Ph), 4.40 [d, 1H, Pt-CH, $^3J(PH)^{\text{trans}} = 12.2$, $^2J(PtH) = 69.9$], 4.35 [d, 1H, Pt-CH, $^3J(PH)^{\text{cis}} = 8.34$, $^2J(PtH) = 77.8$], 3.42 [d, 9H, P(OMe)$_3$, $^3J(PH) = 12.35$], and 1.13 p.p.m. (s, 9H, Bu$^t$); $^{31}P$-$^1H$ (24 MHz), δ 118.19 p.p.m. [s, $^1J(PtP) = 4732$].
Reactions of benzoyl and methoxycarbonyl substituted metallathaeteane-
3,3-dioxide complexes with alkyl isocyanides

A With one equivalent of isocyanide

(i) Preparation of $\text{[Pt} (\text{CH(COPh)S(O)}_2\text{CH(COPh)}) \{\text{CNBu^t}(\text{PPh}_3)\}]$ (156)

t-Butyl isocyanide (0.015 g, 0.181 mmol) in dichloromethane (ca. 10 cm$^3$)
was added dropwise to a stirred solution of $\text{[Pt} (\text{CH(COPh)S(O)}_2\text{CH(COPh)}) -$
$(\text{PPh}_3)_2]$ (117).CH$_2$Cl$_2$.0.5H$_2$O (0.20 g, 0.18 mmol) in dichloromethane (20 cm$^3$),
and the mixture refluxed for 30 min. Evaporation to dryness under
reduced pressure afforded a pale yellow oil. Dissolution of the oil in
dichloromethane (ca. 2 cm$^3$) followed by addition of light petroleum
(50 cm$^3$) afforded white microcrystals of the title complex (156) (0.133 g,
88%) (Found: C, 55.1; H, 4.5; N, 1.5. C$_{39}$H$_{36}$NO$_8$PtS requires C, 55.7;
H, 4.3; N, 1.7%), m.p. 114-117°C; $\nu_{CN}$ at 2192 vs cm$^{-1}$; $\nu_{SO_2}$ at 1121 vs and
1302s cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz), $\delta$ 8.30-7.09 (m, 30H, Ph),
5.36 [d, 1H, Pt-CH, $^3$J(Pt)trans 9.32, $^2$J(PtH) 72.0], 4.80 [d, 1H, Pt-CH,
$^3$J(PH)cis 5.76, $^2$J(PtH) 66.3], and 6.69 p.p.m. (s, 9H, Bu$^t$); $^{13}$C-{$^1$H}
(75.5 MHz), $\delta$ 196.11 [s, CO, $^2$J(PtC) ca. 37], 193.41 [d, CO, $^2$J(PtC) 44.5,
$^3$J(PC) 3.9], 58.12 (s, C, Bu$^t$), 52.91 [d, Pt-CH, $^2$J(PC)cis 3.01, $^1$J(PtC)
47.17], 52.36 [d, Pt-CH, $^2$J(PC)trans 65.06, $^1$J(PtC) 324.9], and 28.85
p.p.m. (s, Bu$^t$); $^{31}$P-{$^1$H} (24 MHz), $\delta$ 12.71 p.p.m. [s, $^1$J(PtP) 2832].

(ii) Preparation of $\text{[Pt} (\text{CH(COPh)S(O)}_2\text{CH(COPh)}) \{\text{CNBu^t}(\text{PPh}_3)\}]$ (157)
n-Butyl isocyanide (0.015 g, 0.181 mmol) in dichloromethane (ca. 10 cm$^3$)
was added dropwise to a stirred solution of $\text{[Pt} (\text{CH(COPh)S(O)}_2\text{CH(COPh)}) -$
$(\text{PPh}_3)_2]$ (117).CH$_2$Cl$_2$.0.5H$_2$O (0.20 g, 0.18 mmol) in dichloromethane (20 cm$^3$),
and the solution evaporated to dryness under reduced pressure to afford a
pale yellow oil, which was shown to be a 1:1 mixture of the title complex
and liberated triphenylphosphine by $^{31}$P-{$^1$H} n.m.r. spectroscopy.
Dissolution of the oil in dichloromethane (0.5 cm$^3$) followed by addition
of light petroleum afforded white microcrystals of the title complex (157) (0.126 g, 85%). N.m.r. spectrum: $^{31}$P-$^1$H (24 MHz), δ 12.50 p.p.m. [s, $^1$J(PPt) 2822].

(iii) Preparation of $[\text{Pd}\{\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}\} \text{(CNBu}^\text{t})(\text{PET}_3)]$ (158). 0.5CH$_2$Cl$_2$

t-butyl isocyanide (0.008 g, 0.095 mmol) in dichloromethane (ca. 5 cm$^3$) was added dropwise to a stirred solution of $[\text{Pd}\{\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}\} \text{(PET}_3)_2]$ (128) (0.060 g, 0.095 mmol) in dichloromethane (20 cm$^3$), and the solution evaporated to dryness to afford a yellow oil. Dissolution of the oil in dichloromethane (2 cm$^3$) followed by addition of light petroleum (50 cm$^3$) afforded pale yellow microcrystals of the title complex (158). 0.5CH$_2$Cl$_2$ (0.044 g, 72%), m.p. 74-76°C; v$_{CN}$ at 2196 cm$^{-1}$; v$_{SO_2}$ at 1119 cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz), δ 8.29-7.27 (m, 10H, Ph), 5.30 (s, 1H, CH$_2$Cl$_2$), 4.88 [d, 1H, Pd-CH, $^3$J(PH)$_{\text{trans}}$ 8.51], 4.37 [d, 1H, Pd-CH, $^3$J(PH)$_{\text{cis}}$ 6.18], 1.74-1.41 (m, 6H, CH$_3$, PET$_3$), and 1.08 p.p.m. (s, 9H, Bu$^t$); $^{31}$P-$^1$H (24 MHz), δ 19.36 p.p.m. (s).

B With excess alkyl isocyanide

(i) Preparation of $[\text{Pt}\{\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}\} \text{C:NHBu}^\text{t}\} \text{(CNBu}^\text{t})(\text{PPh}_3)]$ (159). 0.5CH$_2$Cl$_2$

A solution of $[\text{Pt}\{\text{CH(COPh)}\text{S(O)}_2\text{CH(COPh)}\} \text{(PPh}_3)_2]$ (117).CH$_2$Cl$_2$.0.5H$_2$O (0.29 g, 0.26 mmol) in dichloromethane (25 cm$^3$) with t-butyl isocyanide (0.10 g, 1.2 mmol) was refluxed for 4h. The mixture was evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (2 cm$^3$) followed by addition of light petroleum (50 cm$^3$) afforded pale yellow microcrystals of the title complex (159).0.5CH$_2$Cl$_2$ (0.19 g, 76%). Slow recrystallisation from dichloromethane-light petroleum yielded pale yellow prisms. (Found: C, 55.4; H, 5.1; N, 2.9. $C_{44}H_{85}N_2O_4P$Pt$_3$.0.5CH$_2$Cl$_2$ requires C, 55.3; H, 4.8; N,
2.9%), m.p. 168-171°C with gas evolution; \( \nu_{\text{NH}} \) at 3054 cm\(^{-1} \); \( \nu_{\text{C=EN}} \) at 2186 vs cm\(^{-1} \); \( \nu_{\text{max}} \) (1700-1500 cm\(^{-1} \)) at 1660s, 1582s, 1570s, and 1526vs; \( \nu_{\text{SO}_2} \) at 1125s and 1307vs cm\(^{-1} \). N.m.r. spectra: \(^1\)H (400 MHz), \( \delta \) 13.33 [d, br, 1H, NH, \( ^3\)J(PtH) 93.6, \( ^4\)J(PH) 14.3, readily exchanged on shaking with \([^2\text{H}]_2\)-water containing a trace of \([^2\text{H}]_1\)-sodium hydroxide], 7.95-6.96 (m, 25H, Ph), 5.32 (s, 1H, CH\(_2\)Cl\(_2\)), 4.81 [d, 1H, Pt-CH, \( ^3\)J(PH) 11.2, \( ^2\)J(PtH) 80.0], 1.63 (s, 9H, Bu\(^t\)), and 0.92 p.p.m. (s, 9H, Bu\(^t\)); \(^{13}\)C-\(^1\)H (100 MHz), \( \delta \) 194.9 [s, CH-COPh, \( ^2\)J(PtC) not discernible], 188.1 [d, \( ^\circ\)COPh, \( ^3\)J(PtC) ca. 65.4, \( ^4\)J(PC) 3.4], 186.7 [d, C=\( ^\circ\)C, \( ^2\)J(PC) 113.2, \( ^1\)J(PtC) not discernible], 120.8 [s, \( ^\circ\)C, \( ^2\)J(PtC) and \( ^3\)J(PC) not discernible], 69.10 [d, Pt-CH, \( ^1\)J(PtC) 614.0, \( ^2\)J(PC) 3.83], 58.35 (s, C, Bu\(^t\)), 54.86 (s, C, Bu\(^t\)), 31.24 (s, Me, Bu\(^t\)), and 28.83 p.p.m. (s, Me, Bu\(^t\)); \(^{31}\)P-\(^1\)H (24 MHz), \( \delta \) 15.73 [s, \( ^1\)J(PtP) 1968].

(ii) Preparation of \([\text{Pt(CH(COPh)S(O)\(_2\))_2(C(COPh))C:NHBut}]\)(CNBut)(PMe\(_2\)Ph) (160).

A solution of \([\text{Pt(CH(COPh)S(O)\(_2\))CH(COPh)](PMe\(_2\)Ph)\(_2\)}\) (119).CH\(_2\)Cl\(_2\) (0.13 g, 0.152 mmol) in dichloromethane (15 cm\(^3\)) with t-butyl isocyanide (0.10 g, 1.2 mmol) was refluxed for 1h. The mixture was evaporated to dryness under reduced pressure to give a pale yellow oil. Dissolution of the oil in dichloromethane (ca. 2 cm\(^3\)) followed by addition of light petroleum (ca. 50 cm\(^3\)) afforded pale yellow microcrystals of the title complex (160). 0.5H\(_2\)O (0.101 g, 82%) (Found: C, 50.4; H, 5.2; N, 3.35. C\(_{34}\)H\(_{41}\)N\(_2\)O\(_4\)P\(_2\)S requires C, 51.1; H, 5.2; N, 3.5%), m.p. 139-140°C; \( \nu_{\text{NH}} \) at 3054w cm\(^{-1} \); \( \nu_{\text{C=EN}} \) at 2204vs cm\(^{-1} \); \( \nu_{\text{max}} \) (1700-1500 cm\(^{-1} \)) at 1661s, 1583s, 1568s, and 1527vs; \( \nu_{\text{SO}_2} \) at 1124s and 1308vs cm\(^{-1} \). N.m.r. spectra: \(^1\)H (400 MHz), \( \delta \) 13.24 [d, br, 1H, NH, \( ^3\)J(PtH) 85.5, \( ^4\)J(PH) 14.5], 7.95-7.13 (m, 15H, Ph), 5.01 [d, 1H, Pt-CH, \( ^3\)J(PH) 11.2, \( ^2\)J(PtH) 81.7], 1.83 (s, br, 1H, H\(_2\)O), 1.70 [d, 3H, Me, PMe\(_2\)Ph, \( ^2\)J(PH) 9.5], 1.57 [d, 3H, Me, PMe\(_2\)Ph, \( ^2\)J(PH)
9.5], 1.57 (s, 9H, Bu^), and 1.28 p.p.m. (s, 9H, Bu^); ^13C-{^1H} (75.5 MHz), δ 194.92 [s, CH-COPh, ^2J(PtC) 34.7], 189.45 [d, C=N, ^2J(Ph) 114.5, ^1J(PtC) 798.1], 188.51 [d, C=COPh, ^4J(Ph) ca. 1.9, ^3J(PtC) 62.3], 120.31 [s, C, ^2J(PtC) ca. 30], 66.81 [d, Pt-CH, ^2J(PC) 3.8, ^1J(PtC) 569.8], 58.88 [s, C, Bu^, ^3J(PtC) ca. 9.1], 54.85 [d, C, Bu^, ^4J(Ph) 3.8, ^3J(PtC) 24.5], 31.40 (s, Me, Bu^), 29.46 (s, Me, Bu^), 15.02 [d, Me, PMe_2Ph, ^1J(Ph) 34.4, ^2J(PtC) 28.3], and 14.38 p.p.m. [d, Me, PMe_2Ph, ^1J(Ph) 34.4, ^2J(PtC) 30.2]; ^31P-{^1H} (24 MHz), δ -14.92 p.p.m. [s, ^1J(PP) 1919].

(iii) Preparation of \([\text{Pt}\{(\text{COPh})\text{S}(\text{O})_2\text{C}(\text{COPh})\text{C}:\text{NHBu}^\text{t}\}]\{(\text{CNBu}^\text{t})(\text{PPh}_3)\}\) (161).

A solution of \([\text{Pt}\{(\text{COPh})\text{S}(\text{O})_2\text{CH}(\text{COPh})\}]\{(\text{PPh}_3)_2\}\) (117).CH_2Cl_2.0.5H_2O (0.30 g, 0.27 mmol) in dichloromethane (20 cm^3) with n-butyl isocyanide (0.1 cm^3, 0.96 mmol) was refluxed for 1 h. Work-up as in (ii) above afforded white microcrystals of the title complex (161).0.5CH_2Cl_2 (0.176 g, 68%) (Found: C, 55.5; H, 4.9; N, 2.9. C_{36}H_{41}N_{2}O_{6}PPtS.0.5CH_2Cl_2 requires C, 55.3; H, 4.8; N, 2.9%), m.p. 133-136°C. I.r.: ν_C=N at 2260vs; ν_C=N/C=O at 1686s and 1560vs(br); ν_SO_2 at 1124vs and 1306s cm^{-1}. N.m.r. spectra: ^1H (300 MHz), δ 12.55 [m, br, 1H, NH, ^2J(Ph) ca. 78, ^4J(Ph) and ^3J(Ph) not discernible], 5.25 (s, 1H, CH_2Cl_2), and 5.02 p.p.m. [d, 1H, Pt-CH, ^3J(Ph) 10.7, ^2J(Ph) 75.0]; ^31P-{^1H} (24 MHz), δ 14.52 p.p.m. [s, ^1J(PP) 1968].

(iv) Preparation of \([\text{Pt}\{(\text{CO}_2\text{Me})\text{S}(\text{O})_2\text{C}(\text{CO}_2\text{Me})\text{C}:\text{NHBu}^\text{t}\}]\{(\text{CNBu}^\text{t})(\text{PPh}_3)\}\) (162).

A solution of \([\text{Pt}\{(\text{CO}_2\text{Me})\text{S}(\text{O})_2\text{CH}(\text{CO}_2\text{Me})\}]\{(\text{PPh}_3)_2\}\) (130).CH_2Cl_2 (0.20 g, 0.197 mmol) in dichloromethane (20 cm^3) with t-butyl isocyanide (0.10 g, 1.2 mmol) was refluxed for 1 h. Work-up as in (ii) above afforded white microcrystals of the title complex (130).CH_2Cl_2 (0.163 g, 90%) (Found: C, 46.0; H, 5.0; N, 3.05. C_{24}H_{31}N_{2}O_{6}PPtS.CH_2Cl_2 requires C, 45.9; H, 4.7;
N, 3.1\%), m.p. 215-218°C (decomp.); \( \nu_{\text{C=N}} \) at 2084 vs cm\(^{-1}\); \( \nu_{\text{max}} \) (1700-1500 cm\(^{-1}\)) at 1672 vs, 1580 vs, and 1500 vs; \( \nu_{\text{SO}_2} \) at 1140 vs and 1297 vs cm\(^{-1}\).

N.m.r. spectra: \(^1\text{H}\) (90 MHz), \( \delta \) 10.5 [d, br, 1H, NH, \(^3\text{J(PtH)}\) ca. 95, \(^4\text{J(Ph)}\) ca. 14], 7.8-7.2 (m, 15H, Ph), 5.25 (s, 2H, CH\(_2\text{Cl}_2\)), 3.8 [d, 1H, Pt-CH, \(^2\text{J(PtH)}\) 84.0, \(^3\text{J(Ph)}\) 11.4], 3.75 (s, 3H, Me, CO\(_2\text{Me}\)), 3.4 [s, 3H, Me, CO\(_2\text{Me}\)], 1.5 (s, 9H, Bu\(^+\)), and 1.0 p.p.m. (s, 9H, Bu\(^+\)); \(^{31}\text{P}-\{^1\text{H}\} \) (24 MHz), \( \delta \) 16.34 p.p.m. [s, \(^1\text{J(PtP)}\) 1997].

Preparation of \([\text{Pd(CH}_2\text{C(O})\text{C}(\text{CO}_2\text{Me})\text{C(NH}Bu^+\})\text{(CN}Bu^+\)\text{)}\text{]}\text{]}\text{]}(167)\)

A solution of \([\text{Pd}\{\eta^3-\text{CH}_2\text{C(O})\text{CH}(\text{CO}_2\text{Me})}\}\text{bipy}\)](166) (0.182 g, 0.484 mmol) in dichloromethane (20 cm\(^3\)) with excess t-butyl isocyanide (0.2 cm\(^3\), 1.78 mmol) was refluxed for 1h. Evaporation to ca. 2 cm\(^3\) under reduced pressure followed by addition of light petroleum (50 cm\(^3\)) afforded pale yellow microcrystals of the title complex (167) (0.195 g, 86%). N.m.r. spectra: \(^1\text{H}\) (300 MHz), \( \delta \) 10.68 (s, br, 1H, NH), 3.69 (s, 3H, CO\(_2\text{Me}\)), 2.75 (s, 2H, Pd-CH\(_2\)), 1.54 (s, 9H, Bu\(^+\)), and 1.49 p.p.m. (s, 18H, Bu\(^+\)); \(^{13}\text{C}-\{^1\text{H}\} \) (75.5 MHz), \( \delta \) 206.73 [s, C=N, d in \(^{13}\text{C}\) spectrum, \(^2\text{J(CH)}\) 5.3], 199.46 (s, CO\(_2\text{Me}\)), 167.24 (s, CH\(_2\)-CO-C), 138.36 (s, br, Pd-CN), 136.09 (s, br, Pd-CN), 105.85 (s, C-CO\(_2\text{Me}\), apparent d in \(^{13}\text{C}\) spectrum but J(CH) not discernible), 56.78 (s, C, Bu\(^+\)), 56.50 (s, C, Bu\(^+\)), 52.43 (s, C, Bu\(^+\)), 49.11 [s, CO\(_2\text{Me}\), q in \(^{13}\text{C}\) spectrum, \(^1\text{J(CH)}\) 145.4], 37.44 [s, Pd-CH\(_2\), t in \(^{13}\text{C}\) spectrum, \(^1\text{J(CH)}\) 137.1], 29.90 (s, Me, Bu\(^+\)), 29.40 (s, Me, Bu\(^+\)), and 29.10 (s, Me, Bu\(^+\)). The complex decomposed quickly on standing, and could not be obtained analytically pure.

Reaction of \([\text{Pt(CH(COPh)}S(O})_{2}\text{CH(COPh)}\}\text{(CN}Bu^+\text{XPPh}_3\)\text{]}\text{]}(156) with n-butyl isocyanide

Complex (156) was prepared from (117).CH\(_2\text{Cl}_2\), 0.5H\(_2\text{O}\) (0.20 g) and n-butyl isocyanide (0.015 g) as described previously, and the solution evaporated to dryness under reduced pressure to afford a pale yellow oil which was
triturated with light petroleum (10 cm³) to remove triphenylphosphine.

The residual solid was dissolved in dichloromethane (25 cm³) and n-butyl
isocyanide (0.015 g, 0.181 mmol) in dichloromethane (10 cm³) was added.
The mixture was refluxed for 1 h and evaporated to ca. 1 cm³ under reduced
pressure. Addition of light petroleum gave pale yellow microcrystals of
\[
\text{[Pt(CH(COPh)S(O)\text{)}(COPh)C:NBu\text{}}^+\text{]}(\text{CNBu}^\text{t})(\text{PPh}_3)]\text{CH}_2\text{Cl}_2 \text{ (0.157 g, 88%).}
\]
Slow recrystallisation from dichloromethane-light petroleum gave colourless prisms. (Found: C, 53.4; H, 4.7; N, 2.75. C_{44}H_{45}N_{20}P_{2}PtS.CH_{2}Cl_{2}
requires C, 53.6; H, 4.7; N, 2.8%), m.p. 139-143°C; \nu_{NH} at 3040 cm⁻¹;
\nu_{CN} at 2186 vs; \nu_{\text{max}} (1700-1500 cm⁻¹) at 1650 s, and 1534 vs (br); \nu_{SO_2} at
1100 vs and 1284 s (br) cm⁻¹. N.m.r. spectra: \text{^1H (400 MHz), \delta 12.55 [m,}
br, 1H, NH, \text{^3J(PH) and } ^3\text{J(HH) not discernible, } ^3\text{J(PtH) 75.8}], 8.39-6.93
(m, 25H, Ph), 5.28 (s, 2H, \text{CH}_2\text{Cl}_2), 4.87 [d, 1H, Pt-CH, ^3\text{J(PH) 10.8,}
\text{^2J(PtH) 72.8}], 3.75 (m, 2H, \text{CH}_2, \text{Bu}^\text{n}), 3.53 (m, 2H, \text{CH}_2, \text{Bu}^\text{n}), 1.85 (m,
\text{2H, CH}_2, \text{Bu}^\text{n}), 1.56 (m, 2H, \text{CH}_2, \text{Bu}^\text{n}), 1.04 (s, 9H, \text{Bu}^\text{t}), and 1.01 p.p.m.
[t, 3H, Me, \text{Bu}^\text{n}, ^3\text{J(HH) 7.4]; } ^{31}\text{P-\{^1H} (24 MHz), \delta 14.52 p.p.m. [s,}
\text{^1J(PtP) 1972]. Crystals of (168).CHCl}_3 \text{ suitable for an X-ray study were}
obtained by slow diffusion of diethyl ether and hexane into a chloroform
solution of (168).

Reaction of \text{[Pt(CH(COPh)S(O)\text{)}(COPh)C:NBu\text{}}^+\text{]}(\text{CNBu}^\text{t})(\text{PPh}_3)]\text{CH}_2\text{Cl}_2 \text{ with t-butyl}
isocyanide

Complex (157) was prepared from (117).\text{CH}_2\text{Cl}_2.0.5\text{H}_2\text{O} \text{ (0.20 g) and t-butyl}
isocyanide (0.015 g) as described previously, and the solution evaporated
to dryness under reduced pressure to afford a pale yellow oil which was
triturated with light petroleum (10 cm³) to remove triphenylphosphine.
The residual solid was dissolved in dichloromethane (25 cm³) and t-butyl
isocyanide (0.015 g, 0.181 mmol) in dichloromethane (10 cm³) was added.
The mixture was refluxed for 1 h and evaporated to 1 cm³ under reduced
pressure. Addition of light petroleum afforded a pale yellow micro-
crystalline solid (0.196 g, 86%) which was identified as (168).CH₂Cl₂
from its ¹H and ³¹P-{¹H} n.m.r. spectra.

Miscellaneous reactions of metallathietane-3,3-dioxide complexes
Action of heat on \([\text{Pt}(\text{CH}(_2\text{COPh})\text{S}(_2\text{O})\text{CH}(_2\text{COPh}))\text{(PPh}(_3)_2\text{)}](117).\text{CH}_2\text{Cl}_2.0.5\text{H}_2\text{O}\)
A sample of (117).CH₂Cl₂.0.5H₂O was heated to 250°C in air for 10 min.,
to afford a brownish glass on cooling, which was shown to contain
unchanged (117) from its ³¹P-{¹H} n.m.r. spectrum.

Reaction of (117).CH₂Cl₂.0.5H₂O with hexafluoroacetone
An excess of hexafluoroacetone was condensed onto a frozen (-196°C)
solution of (117).CH₂Cl₂.0.5H₂O (0.20 g) in dichloromethane (20 cm³)
contained in a Carius tube. The tube was sealed, stirred at room
temperature for 48 h, cooled, opened, and the contents evaporated to dry-
ness under reduced pressure to afford a colourless oil. Recrystallisation
from dichloromethane-light petroleum afforded white needles of
\([\text{Pt}(\text{CH}(_2\text{COPh})\text{S}(_2\text{O})\text{CH}(_2\text{COPh}))\text{(PPh}(_3)_2\text{)}](117).\text{C}(_2\text{CF}(_3))\text{C(OH)}(_2\text{)}\) (0.201 g, 93%)
(Found: C, 54.5; H, 3.8. C₅₂H₄₂O₄P₂PtS.C(CF₃)₂(OH)₂ requires C, 54.9;
H, 3.7%), m.p. 172-176°C. Selected n.m.r. spectroscopic data: ¹H (400
MHz), δ 4.82 p.p.m. [d, second-order, 2H, Pt-CH, \(\frac{3}{2}J(\text{PH})\text{trans} + \frac{3}{2}J(\text{PH})\text{cis}\)]
9.49, ²J(PtH) 61.27]; ³¹P-{¹H} (24 MHz), δ 11.90 p.p.m. [s, ¹J(PtP) 2876];
¹⁹F-{¹H} (94 MHz), δ 1.4 p.p.m. (s).

Reaction of (117).CH₂Cl₂.0.5H₂O with (phenylsulphonyl)acetic acid
A solution of (phenylsulphonyl)acetic acid (0.013 g, 0.065 mmol) in
dichloromethane (10 cm³) was added to a stirred solution of (117).CH₂Cl₂.
0.5H₂O (0.070 g, 0.063 mmol) in dichloromethane (10 cm³). The solution
was stirred for 20 min., and evaporated to dryness under reduced pressure
to afford a white solid which was shown to contain unreacted (117) by
³¹P-{¹H} n.m.r. spectroscopy. The solid was dissolved in dichloromethane
(20 cm$^3$), refluxed for 30 min. and evaporated to dryness under reduced pressure to afford a white solid which was found to consist of a 1:1 mixture of unreacted (117) and the bis(carboxylate) complex $\text{cis-}[\text{Pt} \{\text{OC}(\text{O})\text{CH}_2\text{SO}_2\text{Ph}\}_2(\text{PPh}_3)_2]$(171) by comparison of its $^{31}\text{P}$-$^{1}\text{H}$ n.m.r. spectrum with those of authentic samples of (117) and (171) (see below).

**Preparation of [Pt(OC(O)CH$_2$SO$_2$Ph)$_2$(PPh$_3$)$_2$](171).CH$_2$Cl$_2$.H$_2$O**

Triphenylphosphine (0.14 g, 0.534 mmol), (phenylsulphonyl)acetic acid (0.107 g, 0.535 mmol), and silver(I) oxide (0.3 g, 1.3 mmol) were added in succession to a stirred solution of [PtCl$_2$(COD)] (0.10 g, 0.267 mmol) in dichloromethane (20 cm$^3$), and the mixture was refluxed for 30 min. The mixture was filtered to afford a pale yellow solution which was evaporated to dryness under reduced pressure to afford a pale yellow oil. Crystallisation of the oil from dichloromethane-light petroleum gave a pale yellow microcrystalline solid which was recrystallised from dichloromethane-light petroleum to afford white needles of the title complex (171).CH$_2$Cl$_2$.H$_2$O (0.201 g, 62%) (Found: C, 52.3; H, 4.2. C$_{52}$H$_{44}$O$_8$P$_2$PtS$_2$.CH$_2$Cl$_2$.H$_2$O requires C, 52.1; H, 4.0%), m.p. 132-134°C. N.m.r. spectra: $^{1}\text{H}$ (90 MHz), $\delta$ 7.9-7.1 (m, 40H, Ph), 5.3 (s, 2H, CH$_2$Cl$_2$), 3.36 (s, 4H, CH$_2$), and 1.8 p.p.m. (s, br, 2H, H$_2$O); $^{31}\text{P}$-$^{1}\text{H}$ (24 MHz), $\delta$ 5.0 p.p.m. [s, $^{1}\!$J(PtP) 3877].

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4.1 INTRODUCTION

The utility of silver(I) oxide in the synthesis of both metalla-thietane-3,3-dioxide ring systems (Chapter 2) and an \( \eta^3 \)-oxodimethylene-methane complex of platinum (50, \( R = \text{CO}_2\text{Me}, L = \text{PPh}_3 \))\(^{61,63} \) (Chapter 1), via the sulphones (107) or (108) and the dimethyl ester of 3-oxopentane-2,4-dioic acid respectively, led to an investigation of use of the related sulphoxide (172)\(^{104} \) in the synthesis of metalla-thietane-3-oxide ring systems (173). There has been much interest in the competing con-

\[
\text{PhOC} \quad \text{S} \quad \text{COPh}
\]

(172)

\[
\text{M} \quad \text{S} \quad \text{O}
\]

(173)

formational requirements of an oxygen atom and a non-bonding sulphur electron-pair in cyclic sulphoxides, and it has been shown that thietane-1-oxides (174) characteristically display a strong equatorial preference of the oxygen atom.\(^{106,112,164-169} \) The synthesis of metalla-thietane-3-oxide complexes would thus permit an examination of the effect of a metallacyclic metal atom on this equatorial preference, and would provide a comparison with the related metalla-thietane-3,3-dioxide complexes described in Chapter 2.

4.2 SYNTHESIS OF PLATINATHIETANE-3-OXIDE COMPLEXES

Treatment of the complexes cis-[PtCl\(_2\)L\(_2\)] (L = tertiary phosphine) with diphenacyl sulphoxide (172) and an excess of silver(I) oxide in refluxing dichloromethane affords, in high yields, the platinathietane-3-oxide complexes [Pt(CH(COPh)S(O)CH(COPh))L\(_2\)] (175, \( L = \text{PPh}_3 \)), (176, \( L = \text{PMePh}_2 \)),

-117-
and \((177, L = \text{PMe}_2\text{Ph})\), as illustrated in equation 41. Treatment of the
\[
\text{cis-}[\text{PtCl}_2] + (172) \\
\text{Ag}_2\text{O}, \text{CH}_2\text{Cl}_2, \Delta \\
\text{41}
\]
\[
(175) - (177)
\]
bromide-bridged dimeric complex \([\text{PtBr}_2(\text{PET}_3)]_2\) with one equivalent of triphenylarsine and one equivalent of \((172)\) per platinum, in the presence of excess silver(I) oxide afforded the mixed ligand complex
\[
[\text{Pt}(\text{CH}(\text{COPh})\text{S}(\text{O})\text{CH}(\text{COPh}))\text{(AsPh}_3)\text{(PET}_3))\] \((178)\) in good yield. Complexes \((175) - (178)\) are isolated as air-stable white to pale yellow micro-crystalline solids.

4.3 STRUCTURAL PROPERTIES OF PLATINATHETANE-3-OXIDE COMPLEXES

A single-crystal X-ray diffraction study has been carried out on the triphenylphosphine complex \((175)\), in order to compare the molecular structure of this sulphoxide complex with those of metallathietane-3,3-dioxide complexes, and in particular the analogous benzoyl substituted complex \((117)\), Chapter 2. Important bond lengths and angles are presented in Table 7, whilst the molecular structure is illustrated in Figure 15, together with the crystallographic numbering system. The complex crystallised with two molecules of dichloromethane per molecule of complex.

The overall geometry of \((175)\) bears resemblances to both the metallathietane-3,3-dioxide and thietane-1-oxide ring systems \((174)\). Thus, the
four-membered ring system of (175) is puckered by 36.65(46)°, this angle falling within the range of 27-41.9° observed for a number of thietane-1-oxide ring systems (174), for which some important structural data are presented in Table 8. The four-membered ring system of (175) is more puckered than both the related platinathietane-3,3-dioxide complex (117) [fold angle 15.25(56)°], and a number of platinacyclobutane complexes, where fold angles lie in the range 0-30°. Thietane-1-oxides are also typically more highly puckered than thietane-1,1-dioxides, as illustrated by a comparison of the data in Tables 3 and 8. The sulphoxide group of (175) adopts an equatorial position in the four-membered ring system, as is characteristic for thietane-1-oxide ring systems.

Hence, the structural properties of the parent organic four-membered ring system, in particular the strong equatorial preference of a sulphinyl oxygen, appear to be retained on incorporation of a metal atom into this four-membered ring system.

The C-S bonds and C-S-C bond angle of (175) are respectively shorter [average C-S 1.788(7) Å] and larger [C-S-C 90.4(3)°] than the corresponding values for thietane-1-oxide ring systems [average C-S ca. 1.84 Å; C-S-C ca. 76.5°] (Table 8). This would appear to indicate that the platinathietane-3-oxide ring in (175) is somewhat less ring strained than the thietane-1-oxide ring systems. The C-S-C bond angle for dimethyl sulfoxide, which possesses no ring strain, is 97.4°, suggesting that the platinathietane-3-oxide complex (175) contains a small amount of ring strain. Subsequently, C-S bond distances for (175) might be expected to be intermediate between those of dimethyl sulfoxide [average 1.798 Å] and thietane-1-oxides (Table 8). However, the C-S bond distances for (175) and dimethyl sulfoxide are essentially identical, suggesting that there is an additional C-S bond shortening in (175) to that which would be
### TABLE 7a,b

Selected bond lengths and angles for $\text{[Pt(CH(COPh)S(O)CH(COPh))(PPh_3)_2]}\cdot 175 \cdot 2\text{CH}_2\text{Cl}_2$

<table>
<thead>
<tr>
<th>Bond length</th>
<th>( \text{A} )</th>
<th>Angle</th>
<th>( \text{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt—P(1)</td>
<td>2.290 (2)</td>
<td>P(1)—Pt—P(2)</td>
<td>97.7 (1)</td>
</tr>
<tr>
<td>Pt—P(2)</td>
<td>2.319 (2)</td>
<td>P(1)—Pt—C(2)</td>
<td>94.8 (2)</td>
</tr>
<tr>
<td>Pt—C(1)</td>
<td>2.163 (7)</td>
<td>P(2)—Pt—C(1)</td>
<td>95.1 (2)</td>
</tr>
<tr>
<td>Pt—C(2)</td>
<td>2.123 (6)</td>
<td>C(1)—Pt—C(2)</td>
<td>72.6 (2)</td>
</tr>
<tr>
<td>Pt—S</td>
<td>2.840 (5)</td>
<td>Pt—C(1)—S</td>
<td>91.7 (3)</td>
</tr>
<tr>
<td>C(1)—S</td>
<td>1.779 (7)</td>
<td>Pt—C(2)—S</td>
<td>92.5 (3)</td>
</tr>
<tr>
<td>C(2)—S</td>
<td>1.797 (7)</td>
<td>C(1)—S—C(2)</td>
<td>90.4 (3)</td>
</tr>
<tr>
<td>S—O(1)</td>
<td>1.493 (6)</td>
<td>C(1)—S—O(1)</td>
<td>111.0 (4)</td>
</tr>
<tr>
<td>C(1)—C(3)</td>
<td>1.476 (10)</td>
<td>C(2)—S—O(1)</td>
<td>113.0 (3)</td>
</tr>
<tr>
<td>C(2)—C(4)</td>
<td>1.487 (11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3)—O(2)</td>
<td>1.221 (9)</td>
<td>Twist(^c)</td>
<td>9.16 (33)</td>
</tr>
<tr>
<td>C(4)—O(3)</td>
<td>1.218 (9)</td>
<td>Fold(^d)</td>
<td>36.65 (46)</td>
</tr>
</tbody>
</table>

\(^a\) See Figure 15 for crystallographic numbering system;
\(^b\) For comparison see Chapter 2, Tables 1 and 2;
\(^c\) \(\angle\text{P(1)—Pt—P(2)}\}/\text{C(1)—Pt—C(2)}\);
\(^d\) \(\angle\text{C(1)—S—C(2)/C(1)—Pt—C(2)}\).
FIGURE 15
Molecular structure of \([\text{Pt}(\text{CH(COOPh)}S(0)\text{CH(COOPh)})\{\text{PPPh}_3\}_2]\) (175), with only the attached carbon atoms of phenyl rings being illustrated.
TABLE 8
Selected structural data for thietane-1-oxide and metallathietane-3-oxide ring systems

<table>
<thead>
<tr>
<th>Ring</th>
<th>Fold angle (°)</th>
<th>C-S-C (°)</th>
<th>Mean bond distance (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-S</td>
<td>S=O</td>
</tr>
<tr>
<td>R</td>
<td>32</td>
<td>-</td>
<td>1.83(2)</td>
<td>1.492(19)</td>
</tr>
<tr>
<td>R = p-C₆H₄Br</td>
<td>33</td>
<td>-</td>
<td>1.84(1)</td>
<td>1.482(13)</td>
</tr>
<tr>
<td>CO₂H</td>
<td>27</td>
<td>76.6(5)</td>
<td>1.842(13)</td>
<td>1.526(10)</td>
</tr>
<tr>
<td>R'</td>
<td>29</td>
<td>76.5(3)</td>
<td>1.844(7)</td>
<td>1.502(4)</td>
</tr>
<tr>
<td>R' = n-C₆H₁₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>41.9</td>
<td>76.5(3)</td>
<td>1.847(4)</td>
<td>1.466(6)</td>
</tr>
<tr>
<td>L₂PPh₃</td>
<td>36.65</td>
<td>90.4(3)</td>
<td>1.788(7)</td>
<td>1.493(6)</td>
</tr>
</tbody>
</table>

*a* θC-C-C/C-S-C.
expected via a reduction in ring strain on going from a thietane-1-oxide to a less strained platinathietane-3-oxide ring system. An analogous shortening of the C-S bonds was observed in the metallathietane-3,3-dioxide ring systems (Chapter 2), and a similar contribution from the heteroallylic bonding representations (179) or (180) may be proposed to account for the C-S bond shortening in (175).

![Diagram](image)

There is no discernible lengthening of the S=O bond of (175), compared to thietane-1-oxide rings (Table 8), as was the case for the metallathietane-3,3-dioxide complexes. A single-crystal X-ray diffraction study on the monolithiated sulphoxide [PhS(O)CHPhLi.TMEDA]$_2$ (181) has established the presence of a very short S-CH bond distance [1.63(1) Å], and some lengthening of the S=O bond, to 1.58(1) Å, is also observed.\textsuperscript{171}

As described for the metallathietane-3,3-dioxide complexes in Chapter 2, any contributions from the heteroallylic bonding representations (179) or (180) to the metallacyclic bonding would be expected to lengthen both the platinum-carbon and sulphur-oxygen bonds, and shorten the carbon-sulphur bonds. However, since the magnitude of C-S bond shortening in (181) is greater than the corresponding magnitude of S=O bond lengthening, a small amount of C-S bond shortening in (175) would be expected to be accompanied by a smaller, undetectable amount of S=O bond lengthening, and thus the S=O bond distance in (175) appears normal. The platinum-carbon and carbon-sulphur bonds of (175) are longer than the corresponding bonds for the sulphone analogue (117), presumably as a result of the more highly electronegative sulphur(VI) atom in (117).
The complex (175) exists as the trans-disubstituted isomer, with one benzoyl substituent in a pseudo-axial environment, and the other in a pseudo-equatorial environment, as is observed for all three metallathietane-3,3-dioxide complexes (109), (117), and (125), and a number of 1,3-disubstituted oxodimethylenemethane complexes of platinum\textsuperscript{61,63,64} and palladium.\textsuperscript{62,63} The twist angle between the P(1)-Pt-P(2) and C(1)-Pt-C(2) planes in (175) is 9.16°. This value is slightly larger than that for the related platinathietane-3,3-dioxide complex (117) [twist angle = 6.48°], possibly as a result of the larger fold angle in (175). Interestingly however, despite different fold angles and platinum-carbon and carbon-sulphur bond distances in the sulphone (117) and sulphoxide (175), the transannular platinum-sulphur distances are equal, at 2.840(5) Å. The trans substitution of the platinathietane-3-oxide ring in (175) results in this molecule being chiral, and an examination of the unit cell contents for (175) reveals that one molecule of each enantiomer co-crystallises in the unit cell.

4.4 N.M.R. AND I.R. STUDY OF PLATINATHIETANE-3-OXIDE COMPLEXES

The room temperature \textsuperscript{1}H n.m.r. spectra for the platinathietane-3-oxide complexes (175)-(177) are consistent with the puckered static structure, depicted in equation 41, and Figure 15. Two distinct resonances are observed for the axial and equatorial ring hydrogens H(1) and H(2) respectively, as illustrated for complex (175) in Figure 16. The magnitude of the coupling of H(1) and H(2) to their cis and trans phosphorus-31 nuclei indicate that the three-bond cis-P-Pt-C-H couplings are under dihedral angle control, as in the well-known Karplus relationships for vicinal H-C-C-H couplings in organic molecules.\textsuperscript{129} Thus, the higher field resonance due to the equatorial hydrogen H(2) shows coupling to
both the cis phosphorus atom [the P(1)-Pt-C(2)-H(2) torsion angle is -42.39°], and the trans phosphorus atom, to give a doublet of doublets.

The lower field resonance due to the axial ring hydrogen H(1) shows coupling to its trans phosphorus atom only, to give a doublet, see Figure 16. No coupling of H(1) to its cis phosphorus P(2) is observed, since the P(2)-Pt-C(1)-H(1) torsion angle is -88.25°.

The $^{31}$P-$^{1}$H n.m.r. spectra for (175)-(177) show the presence of two non-equivalent $^{31}$P nuclei, and second-order AB spectra are observed, to give a doublet of doublets with corresponding platinum-195 satellites. For example, for complex (175), resonances at 617.31 [d, P(1), $^{1}$J(PtP) 2920, $^{2}$J(PP) 19.5 Hz] and 12.58 p.p.m. [d, P(2), $^{1}$J(PtP) 2783, $^{2}$J(PP) 19.5 Hz] are observed.

The $^{1}$H-$^{31}$P broad-band decoupled n.m.r. spectrum of (175), measured at 360 MHz, consists of two single resonances at 65.03 [s, H(1), $^{2}$J(PtH) 77.3 Hz], and 4.63 p.p.m. [s, H(2), $^{2}$J(PtH) 48.8 Hz]. This indicates that there is no long-range proton-proton coupling between H(1) and H(2). Irradiation of the P(2) resonance leaves the H(1) resonance as a doublet, and collapses the H(2) resonance to a doublet. However, there is a reduction in the magnitude of the observed phosphorus-proton splittings $^{3}$P(1)H(1) and $^{3}$P(1)H(2) on irradiation of P(2). This may be due to some off-resonance decoupling of the P(1) nucleus occurring on irradiation of P(2), or due to the use of too much decoupling power.$^{172}$ Irradiation of the P(1) resonance collapses the H(1) resonance to a singlet, consistent with the trans assignment of P(1) and H(1), and collapses the H(2) resonance to a doublet, but again with a somewhat reduced splitting.

The magnitude of the coupling of H(2) to P(1) is greater than to P(2), the coupling constants being 10.05 and 2.06 Hz respectively, the two couplings being identified by the selective decoupling experiments.
FIGURE 16
$^1$H n.m.r. spectra of (175).
described above. Figure 16 illustrates the effect of selective
decoupling of the phosphorus nuclei on the $^1$H n.m.r. spectrum of
complex (175).

The $^1$H n.m.r. spectrum of (175) also reveals that the coupling of the
axial proton H(1) to the platinum-195 nucleus is greater than for the
equatorial proton H(2), with $^2J_{	ext{PtH}}(1) 77.3$ Hz, and $^2J_{	ext{PtH}}(2) 48.8$ Hz.
The value of $^2J_{(PH)}$ in cyclic organophosphorus compounds has been
observed to be greatest when the coupled proton lies close to the phos-
phorus lone-pair. Similar effects have also been observed in imines,
hyrazones, oximes, and aziridines, the magnitude of $^2J_{(15NH)}$ being
enhanced if the nitrogen lone-pair approaches the coupled hydrogen.

The C(1)-H(1) vector in (175), as determined from the X-ray study (Section
4.3), is aligned with the vector on platinum (defined as the $z$-direction)
which is perpendicular to the C(1)-Pt-C(3) plane, whereas the equatorial
C(2)-H(2) vector is not. Thus, the angles between the C(1)-H(1) and
C(2)-H(2) vectors and the vector on platinum perpendicular to the
C(1)-Pt C(3) plane are 17.75 and 124.68° respectively. The axial
hydrogen H(1) is subsequently closer to the platinum centre, as indicated
by the X-ray data [Pt---H(1) 2.528Å, Pt---H(2) 2.774Å]. It would there-
fore seem reasonable that the axial hydrogen H(1) experiences a greater
coupling to the platinum-195 nucleus since it lies closer to non-bonding
electron density on the platinum, which may possibly be an electron-
pair in a $d_{2z}+s+p_z$ hybrid orbital. This effect is also transmitted to
the trans phosphine ligands, since the values of $^3J_{(PH)}$ are greater
than the values of $^3J_{(PH)}$, for a given complex. Similarly in $\eta^3$-allyl
complexes of platinum(II), coupling of platinum-195 is greater to the
anti hydrogens than to the syn-hydrogens, these anti and syn
hydrogens being analogous to the axial and equatorial hydrogens respec-
tively of a platinathietane-3-oxide complex. Platinum oxadimethylene-
methane complexes similarly display a larger \( J(\text{PtH}) \) coupling to the axial
hydrogens than to the equatorial hydrogens.\(^{61,63,64}\) The values of \( J(\text{PH}) \)
in \( \eta^3 \)-allyl and oxadimethylene methane complexes of platinum and palladium
are also greater for the anti (equatorial) protons.\(^{61-64,175}\)

The n.m.r. data for (175)-(177) are consistent with the presence of a
static puckered isomer in solution, since rapid ring inversion would
effect coupling of the axial proton H(1) to its cis phosphine P(2).
However, it is not possible to discount a rapid equilibrium between the
highly predominant isomer with an equatorial sulphoxide group, and a small
undetectable amount of an isomer (182) formed by ring inversion, as
depicted in Figure 17. Sulphoxides characteristically retain their
stereochemical integrity at room temperature, and so inversion of the

\[
\begin{align*}
\text{COPh} & \quad \text{H(1)} \\
\text{COPh} & \quad \text{H(2)} \\
\text{COPh} & \quad \text{H(1)'} \\
\text{PhOC} & \quad \text{S}=\text{O} \\
\end{align*}
\]

\[182\]

Figure 17

sulphoxide group in these systems may be discounted. It is also not
possible, however, to discount an invertingomer such as (182) displaying
identical chemical shifts of its axial and equatorial ring protons to
those of the major isomer, Figure 17. Interestingly, complex (175)
displays a temperature-independent \(^1\text{H} \) n. m. r. spectrum in the range -90
to +60°C, and therefore, considering all of the n.m.r. data together,
it would seem likely that the platinathietane-3-oxide complexes are
indeed rigid in solution.
The chiral nature of the α-carbon atoms of the platinathietane-3-oxide ring may be demonstrated by the $^1$H n.m.r. spectrum of the dimethylphenylphosphine complex (177), in which all four methyl groups are non-equivalent (two pairs of diastereotopic methyl groups). This property has been described previously for the dimethylphenylphosphine-containing metallathietane-3,3-dioxide complexes.

The $^{13}$C-$^1$H n.m.r. spectra for the platinathietane-3-oxide complexes (175)-(177) show two distinct resonances for the Pt-CH ring carbons. Thus, for the methyldiphenylphosphine complex (176), resonances due to ring carbons C(1) and C(2) [atom numbering system is as for complex (175), see Figure 15] are observed at 644.76 and 49.98 p.p.m., each showing a large coupling to the trans phosphorus-31 atom [$^2J_{PtC}(1) 63.8$ and $^2J_{PtC}(2) 71.2$ Hz] as well as to the platinum-195 atom [$^1J_{PtC}(1) 391$ and $^1J_{PtC}(2) 398$ Hz]. These ring carbons also show a small coupling to the cis phosphorus-31 atom [$^2J_{PC}(2) 2.7$ and $^2J_{PC}(1) 2.25$ Hz].

The assignment of these carbon atoms is tentatively made by a consideration of the above coupling constants, together with the X-ray data for the triphenylphosphine complex. Thus, carbon atom C(1), which has the longer platinum-carbon bond when compared to C(2), may be expected to display smaller couplings to platinum-195 and trans phosphorus-31 atoms, as is observed. Furthermore, C(1) is trans to the phosphorus atom P(1), which has a shorter platinum-phosphorus bond, and has a larger value of $^1J(PtP)$ than the phosphorus P(2).

The carbonyl carbon atoms of the benzoyl substituents appear as two weak signals in the ranges 6202.35-203.51 and 196.06-199.15 p.p.m., with those of the PMe$_2$Ph complex (177) being sufficiently resolved to show coupling to both the platinum-195 atom [$^2J_{PtC} 30.2$ and 38.5 Hz], and the trans phosphorus-31 atom [$^3J_{PC} 3.9$ and 5.2 Hz]. Hence one of these
carbonyl carbon atoms displays a greater coupling to platinum-195 and phosphorus-31 than the other, again consistent with the presence of a static, puckered metalla-cycle in solution. The axial carbonyl group C(4)-O(3) is closer to the platinum centre and thus experiences a greater coupling to the platinum-195 and phosphorus-31 nuclei than the equatorial carbonyl group C(3)-O(2) [the distances Pt---C(4) and Pt---C(3) are 3.009 and 3.236 Å respectively]. This is identical to the greater phosphorus and platinum couplings displayed by an axial ring proton, as described previously.

The \(^{31}\)P--{\(^1\)H} n.m.r. spectrum of the initially isolated product of the mixed ligand complex (178) reveals the presence of two complexes, each displaying platinum-195 coupling on the single phosphorus resonance, with \(^{1}\)J(PtP) values of 2793 and 2756 Hz being observed for the major (76%) and minor (24%) isomers, (178a) and (178b) respectively. By means of \(^1\)H n.m.r. spectroscopy, relative configurations for these complexes may be assigned, on the basis of the magnitudes of the phosphorus-ring hydrogen coupling constants, which are under dihedral angle control, as described previously for the bis(phosphine) complex (175). The major isomer (178a) has the triphenylarsine ligand trans to the carbon bearing an axial benzoyl substituent, and the minor isomer (178b) has the triphenylarsine ligand trans to the carbon bearing an equatorial benzoyl substituent, Figure 18.
Thus, for complex (178a) the axial and equatorial ring protons both appear as doublets due to phosphorus coupling. However, the axial ring proton signal for the minor isomer (178b) appears as a singlet, since the cis-P-Pt-C-H torsion angle is expected to be around 90°, and therefore no phosphorus coupling would be expected. The magnitudes of platinum coupling on these ring protons are also consistent with their assignment as axial or equatorial, with the lower field axial protons showing the expected greater coupling to platinum-195. Thus, for example, the axial proton of (178a) shows a large \textit{trans} phosphorus coupling (10.0 Hz), together with a large platinum coupling (66.8 Hz), whereas the axial proton of (178b) shows a large platinum coupling of 86.3 Hz, but no phosphorus coupling. The equatorial proton of (178b) shows the expected smaller coupling to phosphorus of 3.0 Hz, together with a relatively small platinum coupling of 51.8 Hz.

Steric effects of the triphenylarsine and triethylphosphine ligands may influence the isomer distribution. The major isomer (178a) has the equatorial benzoyl substituent \textit{cis} to the triphenylarsine ligand, which, although somewhat bulkier than triethylphosphine, is bonded \textit{via} a longer platinum-ligand bond. The torsional strain between an equatorial benzoyl group and a \textit{cis} ligand might therefore be smaller for triphenylarsine than triethylphosphine, and this would account for the preferential formation of isomer (178a). Slow recrystallisation of the mixture of isomers of (178) from dichloromethane-light petroleum afforded pale yellow crystals of the major isomer (178a), but (178b) could not be obtained pure.

The i.r. spectrum of the dimethylphenylphosphine complex (177) has an intense band in the sulphoxide stretching region, at 1016 cm\(^{-1}\), assigned to \(v_{S=0}\). However, the i.r. spectra of the triphenylphosphine and methyl-
diphenylphosphine complexes (175) and (176) respectively contain several bands in the sulphoxide stretching region, however, the bands at 1023 cm$^{-1}$ for (175) and 1016 cm$^{-1}$ for (176) may be tentatively assigned to $\nu_{S=O}$. On going from diphenacyl sulphoxide (172) to the platinathietane-3-oxide (175) there is a decrease in $\nu_{S=O}$ of -9 cm$^{-1}$, and a similar, but larger decrease in $\nu_{S=O}$ is observed on going from diphenacyl sulphone$^{131}$ to the platinathietane-3,3-dioxide complex (117) of ca. -30 cm$^{-1}$. The benzoyl carbonyl groups appear as strong, somewhat broad bands around 1620 and 1630 cm$^{-1}$.

4.5 AN INITIAL STUDY OF THE CHEMISTRY OF PLATINATHIETANE-3-OXIDE COMPLEXES

4.5.1 Reactions with Metal Complexes containing Labile Ligands

Sulphoxide groups are capable of acting as ambidentate ligands, co-ordinating to specific metal centres via either oxygen or sulphur, and subsequently the co-ordination chemistry of sulphoxides is a much studied topic.$^{177-179}$ The reactions of the platinathietane-3-oxide complex (175) with a number of metal complexes containing labile ligands have therefore been investigated. Oxygen co-ordination of 3,3-dimethylthietane-1-oxide has previously been reported in the complex $[\text{Eu(dpm)}_3\{\text{(O)}\text{SCH}_2\text{CMe}_2\text{CH}_2\}]$.\textsuperscript{168}

The reaction of complex (175) with either one mole equivalent of the labile palladium complexes $[\text{PdCl}_2(\text{COD})]$ or $\text{trans-}[\text{PdCl}_2(\text{NCPh})_2]$, or with 0.5 mole equivalents of di-$\mu$-chlorotetracarbonyldirhodium(I), $[\text{Rh}_2(\mu-\text{Cl})_2(\text{CO})_4]$, in dichloromethane afforded crystalline products, characterised as the chelate ligand complexes (183) and (184) respectively, see equation 42, on the basis of their $^1$H and $^{31}$P-$^1$H n.m.r. and i.r. spectroscopic properties, and a single-crystal X-ray diffraction study carried out on the rhodium complex (184).

A summary of important bond lengths and angles for complex (184) is
given in Table 9, and the molecular structure is depicted in Figure 19, which also gives the crystallographic numbering system. The complex crystallised with two molecules of dichloromethane plus one molecule of water per molecule of complex.

The complex consists of a four-membered platinathietane-3-oxide ring system, in which the sulphur atom and the oxygen atom of the equatorial benzoyl substituent are co-ordinated to a rhodium-chloro-carbonyl moiety, to form a five-membered Rh-S-C-C-O chelate ring system. The structure of the platinathietane-3-oxide ring is similar to that of the uncomplexed molecule (175), see Section 4.3, but with several notable differences. The carbonyl group of the co-ordinated benzoyl substituent is somewhat longer [C(3)-O(2) 1.275(16) Å] than the unco-ordinated carbonyl group [C(4)-O(3) 1.221(9) Å], and is comparable with the C=O bond distance of 1.27 Å for the co-ordinated acetone ligand of the complex acetone(4-
### TABLE 9

Selected bond lengths and angles for

\[ \text{[Pt(\text{CH(COPh)S(O)CH(COPh)})_{2}\cdot\text{RhCl(CO)}]}_{2}\cdot\text{2CH}_{2}\text{Cl}_{2}\cdot\text{H}_{2}\text{O} \]

<table>
<thead>
<tr>
<th>Bond length</th>
<th>(Å)</th>
<th>Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–P(1)</td>
<td>2.262(3)</td>
<td>P(1)–Pt–P(2)</td>
<td>98.2(1)</td>
</tr>
<tr>
<td>Pt–P(2)</td>
<td>2.331(3)</td>
<td>P(1)–Pt–C(2)</td>
<td>93.4(4)</td>
</tr>
<tr>
<td>Pt–C(1)</td>
<td>2.173(12)</td>
<td>P(2)–Pt–C(1)</td>
<td>96.4(3)</td>
</tr>
<tr>
<td>Pt–C(2)</td>
<td>2.122(11)</td>
<td>C(1)–Pt–C(2)</td>
<td>71.8(5)</td>
</tr>
<tr>
<td>Pt–S</td>
<td>2.774(4)</td>
<td>Pt–C(1)–S</td>
<td>89.1(5)</td>
</tr>
<tr>
<td>C(1)–S</td>
<td>1.759(13)</td>
<td>Pt–C(2)–S</td>
<td>91.7(5)</td>
</tr>
<tr>
<td>C(2)–S</td>
<td>1.724(14)</td>
<td>C(1)–S–C(2)</td>
<td>92.6(6)</td>
</tr>
<tr>
<td>S–O(1)</td>
<td>1.481(9)</td>
<td>C(1)–S–O(1)</td>
<td>114.1(6)</td>
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<tr>
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<td>1.433(17)</td>
<td>C(2)–S–O(1)</td>
<td>113.0(6)</td>
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<tr>
<td>C(2)–C(4)</td>
<td>1.527(18)</td>
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<tr>
<td>C(3)–O(2)</td>
<td>1.275(16)</td>
<td>Rh–S–C(1)</td>
<td>97.9(5)</td>
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<tr>
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<td>1.201(16)</td>
<td>Rh–S–C(2)</td>
<td>113.6(4)</td>
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<td>2.185(4)</td>
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<td>81.9(3)</td>
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<td>Cl–Rh–O(2)</td>
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<td>1.792(16)</td>
<td>Cl–Rh–C(5)</td>
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<tr>
<td>C(5)–O(4)</td>
<td>1.149(16)</td>
<td>Rh–C(5)–O(4)</td>
<td>177.6(17)</td>
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<tr>
<td>Rh–Cl</td>
<td>2.327(4)</td>
<td>S–Rh–C(5)</td>
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<tr>
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<td>Rh–O(2)–C(3)</td>
<td>117.1(8)</td>
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- See Figure 19 for crystallographic numbering system;
- For comparison see Table 7 and Figure 15;
- \( \angle \text{P(1)–Pt–P(2)/C(1)–Pt–C(2)} \);
- \( \angle \text{C(5)–Rh–S/C1–Rh–O(2)} \);
- \( \angle \text{C(1)–S–C(2)/C(1)–Pt–C(2)} \).
Molecular structure of (184), with triphenylphosphine carbon atoms other than those bonded to phosphorus, and hydrogen atoms of phenyl rings being omitted.
hydroxy-4-methylpentan-2-one)-(η⁶-mesitylene)ruthenium bis(tetrafluoroborate). Furthermore, the co-ordinated ketone group is somewhat distorted from coplanarity with the attached phenyl ring, as demonstrated by the O(2)-C(3)-C(01)-C(06) torsion angle of -41.68°. The uncoordinated benzoyl group is effectively planar, since the O(3)-C(4)-C(11)-C(12) torsion angle is only 8.22°. The deviation of the co-ordinated benzoyl group from planarity is probably a consequence of steric interactions between this group and the phenyl rings of the triphenylphosphine ligands. The bond angles around the carbonyl carbon atoms of the co-ordinated and unco-ordinated benzoyl groups are fairly similar.

The geometry of the sulfoxide moiety is virtually unaffected by co-ordination to rhodium, with the C-S-O bond angles of the rhodium complex (184) being almost identical to those of the unco-ordinated complex (175). The most significant change in the structure of the sulfoxide moiety concerns the S=O bond length, which is shortened on co-ordination to rhodium, to 1.481(9) Å, as compared to 1.493(6) Å in (175). This S=O bond shortening is characteristic of co-ordination of a sulfoxide group via sulphur.¹⁷⁷

The P(2)-Pt bond, cis to the co-ordinated benzoyl substituent, is longer than the P(1)-Pt bond, with the P(2)-Pt and P(1)-Pt bond distances being 2.331(3) and 2.262(3) Å. The P(2)-Pt bond of the unco-ordinated complex (175) is also longer than the P(1)-Pt bond, although with the P(2)-Pt and P(1)-Pt bond distances being 2.319(2) and 2.290(2) Å in (175), the difference between the two bond distances is not as great as in (184). The co-ordination of the equatorial benzoyl substituent may have increased its effective steric bulk, causing an increased lengthening of the P(2)-Pt bond. The lengthening of platinum-phosphorus bonds via steric interactions with large cis ligands has been noted previously.⁶⁴,¹⁸¹,¹⁸²
The geometry about the rhodium atom is effectively square-planar, with the sulphur atom trans to the chloride ligand, and the rhodium-carbonyl trans to the co-ordinated benzoyl group. The twist angle between the C(5)-Rh-S and Cl-Rh-O(2) planes is 3.6°. The somewhat small S-Rh-O(2) angle of 81.9° is an indication of the reduced 'bite' of the chelating S,O-ligand, which is due to the donor atoms being part of, or attached to, a rigid metalla-cycle. The small Rh-S-C(1) bond angle of 97.9(5)° is also an indication of the small 'bite' angle of the ligand, since the Rh-S-C(2) bond angle is 113.6(4)°. The platinum-rhodium distance is 3.529 Å, and there is subsequently no significant Rh---Pt interaction [covalent radii: Pt 1.50; Rh 1.45 Å]. The remaining bond lengths and angles are unexceptional.

The ¹H, ¹³C-{¹H}, and ³¹P-{¹H} n.m.r. spectra of the co-ordinated platinathietane-3-oxide complexes (183) and (184) show the characteristic features for such a ring system. Thus, the axial and equatorial ring protons appear respectively as a doublet, and a doublet of doublets, with the axial proton showing, as expected, the larger coupling to platinum-195. An interesting comparison may be made between the ring proton signals for the palladium and rhodium complexes (183) and (184). The signals due to the axial ring protons of (183) and (184) are deshielded relative to the unco-ordinated molecule (175), appearing at 65.25 and 5.5 p.p.m. respectively. The axial ring proton of (175) appears at 65.05 p.p.m. However, on examining the chemical shifts for the equatorial protons, it may be observed that in the case of the palladium complex (183), this equatorial proton appears as the lower field ring proton resonance at 65.63 p.p.m., and is therefore experiencing a large deshielding effect. Deshielding of the sulfoxide ring protons is consistent with the co-ordination of the sulfoxide sulphur to an
electron-withdrawing metal centre. For the palladium complex (183), the greater deshielding of the equatorial ring proton is due to the greater proximity of this proton to the sulphur-co-ordinated PdCl₂ moiety. In the rhodium complex (184), only a slight deshielding of the equatorial ring proton is observed, from 64.65 p.p.m. in (175) to 64.95 p.p.m. in (184). This may be due in part to the rhodium(I) centre being less electron-withdrawing than a palladium(II) centre. Carbonyl double bonds characteristically exhibit anisotropic shielding and deshielding effects in organic systems and so it is possible that the rhodium-carbonyl group, which is approximately aligned with the C(2)-H(2) bond of (184), could be slightly shielding the equatorial proton. Metal-proton coupling is frequently observed in metal-sulphoxide systems, where the sulphoxide is sulphur-bonded, and the metal has non-zero spin. However, no coupling of either axial or equatorial ring protons of (184) to rhodium-103 was discernible, since this coupling is likely to be very small. For example, a number of S-bonded dimethyl sulphoxide complexes of rhodium(I) and rhodium(III) show no discernible coupling of the methyl protons to rhodium-103.

The \(^{13}\text{C}-(^1\text{H})\) n.m.r. spectrum of the palladium complex (183) shows the characteristic features for the platinathietane-3-oxide ring system, with each Pt-CH ring carbon appearing as a doublet due to coupling to the trans phosphorus-31 nucleus, with \(^2J\) values of 58.1 and 68.4 Hz being observed. No coupling of the ring carbons to their cis phosphines was discernible in the spectrum.

The \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectra for (183) and (184) show the characteristic second-order AB spectrum for the two non-equivalent phosphines of the platinathietane-3-oxide ring system. The value of \(^1J\) for one of the triphenylphosphine ligands is much larger than the other, for example, for
(184), values of $^1J(PtP)$ of 2803 and 3340 Hz are observed. The smaller value of $^1J(PtP)$ is assigned to the P(2) atom, as a result of the lengthening of the P(2)-Pt bond which is cis to the co-ordinated benzoyl group. The lengthening of the cis P(2)-Pt bond is accompanied by a shortening of the trans P(1)-Pt bond, with a concomitant increase in $JP(1)Pt$, when compared to the unco-ordinated complex (175).

The absence of any strong i.r. bands for the complexes (183) and (184) in the region 800-1030 cm$^{-1}$ is consistent with sulphur co-ordination in these complexes.$^{177,178}$ Co-ordination of a sulphone ligand via oxygen or sulphur is known to effect a decrease or increase respectively in the S=O stretching frequency.$^{177,178}$ The S=O stretch is tentatively assigned to the strong band at 1134 cm$^{-1}$ for (183) and 1119 cm$^{-1}$ for (184), these increased values of $v_{S=O}$ being comparable with the S=O stretching frequencies in the complexes $\{[\text{RhCl(S-Me}_2\text{SO)}_2]\}^{178}$ (1100 cm$^{-1}$) and trans-$[\text{PdCl}_2(\text{S-Me}_2\text{SO})_2]$ (1116 cm$^{-1}$).$^{184}$ The only other strong band in the co-ordinated sulphone stretching region, at around 1095 cm$^{-1}$, is also present in the unco-ordinated molecule (175). The palladium and rhodium complexes (183) and (184) show two strong ketone stretching bands due to the co-ordinated and unco-ordinated benzoyl substituents. The unco-ordinated benzoyl group exhibits a $v_{C=O}$ band at 1639 cm$^{-1}$ for (183) and 1642 cm$^{-1}$ for (184), these values being similar to those of (175). The co-ordinated benzoyl groups exhibit lower values of $v_{C=O}$, at 1490 cm$^{-1}$ for (183) and 1510 cm$^{-1}$ for (184). This carbonyl bond weakening is similar to that observed in the polymeric carbonyl-bridged complex $[\text{Pd(CH}_2\text{C(0)O)(PPh}_3)]_n$, for which a value of $v_{C=O}$ of 1545 cm$^{-1}$ is reported.$^{185}$ The rhodium-carbonyl group appears as an intense band in the i.r. spectrum, at 1982 cm$^{-1}$, typical of a rhodium(I) carbonyl.$^{186}$ Weak i.r. bands at 341 and 310 cm$^{-1}$ for (183), and 310 cm$^{-1}$ for (184) are
assigned as the metal-chloride stretching frequencies.

The mechanism of formation of (183) and (184) presumably involves initial co-ordination of the sulphur atom to the metal, followed by chelate ring formation. Consistent with this, no reaction is observed between the benzoyl substituents of the platinathietane-3,3-dioxide complex (117) and trans-[PdCl$_2$(NCPh)$_2$]. The reaction of trans-[PdCl$_2$(NCPh)$_2$] with two mole equivalents of the platinathietane-3-oxide (175) afforded a 1:1 mixture of the chelate complex (183) and unreacted (175), as evidenced by $^{31}$P-$^1$H n.m.r. spectroscopy. The platinathietane-3-oxide complex (175) is a sterically bulky ligand, and this, together with the expected stability of a five-membered chelate ring, accounts for the lack of reactivity between (175) and (183).

No reaction was observed between (175) and either of the two labile platinum complexes [PtCl$_2$(COD)] or cis-[PtCl$_2$(NCPh)$_2$]. Although platinum complexes are typically less labile than their palladium analogues, the absence of reaction of (175) with labile platinum complexes indicates that the sulphoxide ligand of (175) has only poor ligand properties. These poor ligand properties are further demonstrated by the absence of reaction between (175) and [Rh$_2$(μ-Br)$_2$(COD)$_2$] in refluxing dichloromethane.

Interestingly, in contrast to the platinathietane-3-oxide (175), no reaction was observed between diphenacyl sulphoxide (172) and [PdCl$_2$(COD)]. The enhanced ligand properties of the metallacycle probably arise as a result of the substitution of two hydrogen atoms of (172) by a more strongly electron-donating Pt(PPh$_3$)$_2$ moiety, although a contribution to the bonding from a heteroallylic bonding representation (179) or (180) may also be important.
4.5.2 Miscellaneous Reactions

Sulfoxides may react with alkylation agents, such as alkyl iodides, to afford $\ominus$-alkylated trialkylsulphonium ions, $[R_1R_2S-OR_3]^+$, which may be converted to the more stable $\ominus$-alkylated trialkyloxosulphonium ions $[R_1R_2S=O]^+$. However, no reaction was observed between either diphenacyl sulphoxide (172) or (175) and iodoethane, again illustrating the low basicity of the sulfoxide group in these systems. Interestingly, the palladium complex (94) (Chapter 1) may be considered to be an $\ominus$-methylated bis(phosphine)palladathietane-3-oxide complex. Attempts to oxidise the sulfoxide group of (175), to afford the platinathietane-3,3-dioxide complex (117) were also unsuccessful. Thus, shaking a dichloromethane solution of (117) with 30% hydrogen peroxide afforded only unreacted (117). Treatment of (117) with hydrogen peroxide in refluxing acetone resulted in the destruction of the complex, and no pure products could be isolated.

Ring-opening reactions of cyclopropanes by low-valent metal complexes have been shown to be a useful synthetic route into platinum- and palladacyclobutane complexes, see Chapter 1. However, treatment of thiirane-$\ominus$oxide (185) with $[\text{Pt}(n^2-C_2H_4)(\text{PPh}_3)_2]$ has been shown to result in isolation of an $\ominus$-co-ordinated zero-valent platinum complex, see equation 43, and no ring-opening of the three-membered ring was observed. However, it must be emphasised that platinum(0) will only ring-open cyclopropanes bearing electron-withdrawing substituents, and the use of Zeise's dimer (5) is required to effect the ring-opening of cyclopropanes which do not bear electron-withdrawing substituents.
4.6 CONCLUSION

The preparation of platinathietane-3-oxide complexes may be achieved in high yield via treatment of cis-[PtCl$_2$L$_2$] (L = tertiary phosphine ligand) with diphenacyl sulfoxide (172) and silver(I) oxide in refluxing dichloromethane.\textsuperscript{132} N.m.r. studies, together with a single-crystal X-ray diffraction study indicate that the four-membered platinathietane-3-oxide ring is puckered, both in solution and in the solid state, with the sulfoxide group adopting the expected equatorial environment. The X-ray data also suggest a heteroallylic contribution to the metallacyclic bonding, as was observed for the metallathietane-3,3-dioxide complexes described in Chapter 2.

Preliminary studies indicate that the sulphur atom of the platinathietane-3,3-dioxide complex (175) possesses limited ligand properties, and co-ordination of the sulphur atom and equatorial benzoyl substituent of this complex occurs on treatment of (175) with labile palladium or rhodium complexes, to afford five-membered chelate ring products. The formulation of these co-ordinated platinathietane-3-oxide complexes was confirmed by a single-crystal X-ray diffraction study carried out on the rhodium complex (184).

4.7 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. $^1$H-$^{31}$P n.m.r. spectra were recorded in $[^2]$H$_2$]-chloroform at room temperature, on a Bruker WH-360 spectrometer operating at 360.13 MHz. Phosphorus-31 hydrogen-1 splittings in the $^1$H-$^{31}$P n.m.r. spectra were reduced from the true coupling constant, but are reported as the coupling constants in order to illustrate the relative magnitudes of $J$(PH) couplings in the platinathietane-3-oxide ring systems. The $^{13}$C-$^1$H n.m.r. data for
the aromatic region between 6140 and 125 p.p.m. are omitted for clarity.

Iodoethane was used as supplied from Aldrich. The compounds diphenacyl sulfoxide (172),\textsuperscript{104} [PtCl\textsubscript{2}(COD)],\textsuperscript{99} [{\text{Br}}_2(PEt\textsubscript{3})\textsubscript{2}],\textsuperscript{188} [PtCl\textsubscript{2}(COD)],\textsuperscript{145} trans-[PtCl\textsubscript{2}(NCPh)]\textsubscript{2},\textsuperscript{142} [Rh\textsubscript{2}(\mu-Cl\textsubscript{2})(CO)\textsubscript{4}],\textsuperscript{189} cis-[PtCl\textsubscript{2}(NCPh)]\textsubscript{2},\textsuperscript{190} and [Rh\textsubscript{2}(\mu-Br\textsubscript{2})(COD)]\textsubscript{2}\textsuperscript{191} were prepared as described in the literature.

Preparation of platinathietane-3-oxide complexes

(i) Preparation of [Pt(CH(COPh)S(O)CH(COPh))\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (175)

Triphenylphosphine (0.28 g, 1.07 mmol), diphenacyl sulfoxide (0.153 g, 0.53 mmol), and silver(I) oxide (0.4 g, 1.7 mmol) were added in succession to a stirred solution of [PtCl\textsubscript{2}(COD)] (0.20 g, 0.53 mmol) in dichloromethane (25 cm\textsuperscript{3}), and the mixture was refluxed for 2 h. Filtration through 1 cm of celite gave a pale yellow solution which was evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (ca. 2 cm\textsuperscript{3}) followed by addition of light petroleum (ca. 50 cm\textsuperscript{3}) gave, on standing for 12 h, a pale yellow microcrystalline solid which was filtered off and dried in vacuo to give the title complex (175) (0.518 g, 97%) (Found: C, 62.5; H, 4.2.

C\textsubscript{52}H\textsubscript{42}O\textsubscript{3}P\textsubscript{2}PtS requires C, 62.2; H, 4.2%), m.p. softens 168-180°C, resolidifies 180-190°C, and decomp. >190°C; ν\textsubscript{C=O} at 1631vs(br) cm\textsuperscript{-1}; ν\textsubscript{S=O} at 1023s cm\textsuperscript{-1}. N.m.r. spectra: \textsuperscript{1}H (300 MHz), δ7.52-6.79 (m, 40H, Ph), 5.05 (d, 1H, H(1), \textsuperscript{3}J[PtH(1)] 10.31, \textsuperscript{2}J[PtH(1)] 77.3), and 4.65 p.p.m. (dd, 1H, H(2), \textsuperscript{3}J[PtH(2)] 10.05, \textsuperscript{2}J[PtH(2)] 2.06, \textsuperscript{2}J[PtH(2)] 48.8); \textsuperscript{1}H (400 MHz, -90°C, \textsuperscript{2}H\textsubscript{2}-dichloromethane or +60°C, \textsuperscript{2}H\textsubscript{6}-toluene), identical to room temperature spectrum; \textsuperscript{1}H-{\textsuperscript{31}P} (360 MHz, broad-band irradiation), δ5.03 {s, 1H, H(1), \textsuperscript{2}J[PtH(1)] 77.3}, and 4.63 p.p.m. {s, 1H, H(2), \textsuperscript{2}J[PtH(2)] 48.8}; \textsuperscript{1}H-{\textsuperscript{31}P} (360 MHz, irradiated at 145.787405
MHz \{\text{P}(1)\}, \delta 5.03 \{\text{s, H(1), }^2\text{J}[\text{PtH}(1)] 77.3\}, \text{and } 4.63 \text{ p.p.m.} \{\text{d, H(1), H(2), }^3\text{J}[\text{PtH}(2)] 2.06, \text{and }^2\text{J}[\text{PtH}(2)] 48.8\}; \text{ }^1\text{H-}{}^{31}\text{P} \text{ (360 MHz, irradiated at } 145.786752 \text{ MHz } \{\text{P}(2)\}, \delta 5.03 \{\text{d, H(1), H(2), }^3\text{J}[\text{PtH}(1)\text{H}(1)] 10.31, \text{and }^2\text{J}[\text{PtH}(2)] 77.3\}, \text{and } 4.63 \text{ p.p.m.} \{\text{d, H(1), H(2), }^3\text{J}[\text{PtH}(1)\text{H}(2)] 10.05, \text{and }^2\text{J}[\text{PtH}(2)] 48.8\}; \text{ }^{13}\text{C-}{\text{H}} \text{ (100 MHz), } \delta 202.35 \{\text{d, CO, }^2\text{J}(\text{PC}) 4.03, \text{and }^2\text{J}(\text{PtC}) \text{ not discernible}, \text{199.15 }\{\text{d, CO, }^3\text{J}(\text{PC}) 5.02, \text{and }^2\text{J}(\text{PtC}) \text{ not discernible}, \text{48.00 }\{\text{d, C(2), }^2\text{J}[\text{P}(2)\text{C}(2)] 71.48, \text{and }^2\text{J}[\text{P}(1)\text{C}(2)] \text{ not discernible, }^1\text{J}[\text{PtC}(2)] \text{ ca. 402}, \text{and } 45.05 \text{ p.p.m.} \{\text{d, C(1), }^2\text{J}[\text{P}(1)\text{C}(1)] 67.20, ^2\text{J}[\text{P}(2)\text{C}(1)] \text{ not discernible, }^1\text{J}[\text{PtC}(1)] \text{ ca. 410}; ^{31}\text{P-}{\text{H}} \text{ (24 MHz), second-order AB spin-system, } \delta 17.31 \{\text{d, P(1), }^1\text{J}[\text{PtP}(1)] 2920, \text{and }^2\text{J}[\text{P}(2)\text{P}(1)] 19.5\}, \text{and } 12.58 \text{ p.p.m.} \{\text{d, P(2), }^1\text{J}[\text{PtP}(2)] 2783, \text{and }^2\text{J}[\text{P}(1)\text{P}(2)] 19.5\}. \text{ See Figure 20. } ^{13}\text{C} \text{ quality crystals of (175).}

2\text{CH}_2\text{Cl}_2 \text{ were grown slowly from dichloromethane-light petroleum, in air.}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure20.png}
\caption{Figure 20}
\end{figure}

(ii) Preparation of [Pt\{CH(COPh)S(O)CH(COPh)\}(PMePh_2)_2](176).H_2O

Methylidiphenylphosphine (0.07 cm^3, 0.38 mmol), diphenacyl sulphoxide (0.077 g, 0.27 mmol) and silver(I) oxide (0.3 g, 1.3 mmol) were added in succession to a stirred solution of [PtCl_2(COD)] (0.10 g, 0.27 mmol) in dichloromethane (25 cm^3), and the mixture was refluxed for 2h. Work-up as in (i) above afforded pale yellow microcrystals of the title complex (176).H_2O (0.203 g, 85%) (Found: C, 55.2; H, 4.5. C_{42}H_{38}O_3P_2PtS.H_2O requires C, 56.2; H, 4.5%), m.p. 196-198°C (decomp.); \nu_C=O at 1631vs and
1620 vs cm$^{-1}$; $\nu_{s}=0$ at 1016 vs(br) cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz),
$\delta$7.60–6.95 (m, 30H, Ph), 5.36 {d, 1H, H(1), $^3$J[P(1)H(1)] 9.90, $^2$J[P(1)H(1)] 70.5}, 4.79 {dd, 1H, H(2), $^3$J[P(1)H(2)] 9.64, $^3$J[P(2)H(2)] 4.02,
$^2$J[P(2)H(2)] 54.03}, 2.09 (s, br, 2H, H$_2$O), 1.78 [d, 3H, Me, PMePh$_2$, $^2$J[PH]+$^4$J(PH) | 9.06, $^3$J[PtH(2) 28.5], and 1.39 p.p.m. [d, 3H, Me, PMePh$_2$, $^2$J[PH]+$^4$J(PH) | 9.98, $^3$J[PtH(2) 28.4]; $^{13}$C–{I[H]} (75.5 MHz), $\delta$203.0 [d, CO, $^3$J(PC) ca. 4, $^2$J(PtC) not discernible], 196.8 [d, CO, $^3$J(PC) ca. 5,
$^2$J(PtC) not discernible], 49.98 {dd, C(2), $^2$J[P(2)C(2)] 71.2, $^2$J[P(1)C(2)] 2.3, $^1$J[PtC(2)] ca. 398}, 44.76 {dd, C(1), $^2$J[P(1)C(1)] 63.8, $^2$J[P(2)C(1)] 2.7, $^1$J[PtC(1)] ca. 391}, 13.46 [d, Me, PMePh$_2$, $^1$J(PC)+$^3$J(PC) | 19.7,
$^2$J(PtC) not discernible], and 13.00 [d, Me, PMePh$_2$, $^1$J(PC)+$^3$J(PC) | 19.6,
$^2$J(PtC) not discernible]; $^{31}$P–{I[H]} (24 MHz), second-order AB spin-system,
$\delta$ -1.55 [d, P(2), $^1$J[PtP(2)] 2739, $^2$J[P(1)P(2)] 14.7], and -3.69 p.p.m.
{d, P(1), $^1$J[PtP(1)] 2822, $^2$J[P(2)P(1)] 14.7}. See Figure 20.

(iii) Preparation of $\left[\text{Pt}^{\left(CH(COPh)S(O)CH(COPh)\right)}\left(PMe_2Ph\right)\right]_2$ (177).0.5CH$_2$Cl$_2$
Dimethylphenylphosphine (0.15 g, 1.08 mmol), diphenacyl sulphoxide (0.153 g, 0.535 mmol), and silver(I) oxide (0.4 g, 1.7 mmol) were added in succession to a stirred solution of [PtCl$_2$(COD)] (0.20 g, 0.53 mmol) in dichloromethane (25 cm$^3$), and the mixture was refluxed for 1.5h. Work-up as in (i) above afforded pale yellow microcrystals of the title complex (177).

0.5CH$_2$Cl$_2$ (0.173 g, 40%) (Found: C, 48.7; H, 4.5. $\text{C}_{12}\text{H}_{34}\text{O}_{3}\text{P}_{2}\text{PtS.0.5}$
CH$_2$Cl$_2$ requires C, 48.9; H, 4.3%), m.p. 109-112°C; $\nu_{s}=0$ at 1636s and 1627s
cm$^{-1}$; $\nu_{s}=0$ at 1016s cm$^{-1}$. N.m.r. spectra: $^1$H (300 MHz), $\delta$8.00 7.16 (m,
20H, Ph), 5.31 (s, 1H, CH$_2$Cl$_2$), 5.26 {d, 1H, H(1), $^3$J[P(1)H(1)] 10.0,
$^2$J[PtH(1)] 68.4}, 5.21 {dd, 1H, H(2), $^3$J[P(1)H(2)] 8.7, $^3$J[P(2)H(2)] 4.7,
$^2$J[PtH(2)] 55.2}, 1.45 [d, 3H, Me, PMe$_2$Ph, $^2$J(PH)+$^4$J(PH) | 9.6, $^3$J(PtH)
ca. 30], 1.37 [d, 3H, Me, PMe$_2$Ph, $^2$J(PH)+$^4$J(PH) | 9.5, $^3$J(PtH) ca. 30],

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1.22 [d, 3H, Me, PMe₂Ph, |2J(PH) + 4J(PH)| 9.6, 3J(PtH) ca. 30], and
1.16 p.p.m. [d, 3H, Me, PMe₂Ph, |2J(PH) + 4J(PH)| 9.5, 3J(PtH) ca. 30];

13C-{1H} (75.5 MHz), δ203.51 [d, CO, 3J(PC) 3.9, 2J(PtC) 30.2], 196.06
[d, CO, 3J(PC) 5.2, 2J(PtC) 38.5], 50.38 {dd, C(2), 2J[P(2)C(2)] 68.9,
2J[P(2)C(2)] 2.2, 1J[PtC(2)] 378.7}, 43.44 {dd, C(1), 2J[P(1)C(1)] 62.1,
2J[P(1)C(1)] 2.6, 1J[PtC(1)] 355.3}, 15.79 [d, Me, PMe₂Ph, |1J(PC) + 3J(PC)|
17.3, 2J(PtC) not discernible], 15.33 [d, Me, PMe₂Ph, |1J(PC) + 3J(PC)|
17.4, 2J(PtC) not discernible], 15.20 [d, Me, PMe₂Ph, |1J(PC) + 3J(PC)|
12.8, 2J(PtC) not discernible], and 14.75 p.p.m. [d, Me, PMe₂Ph, |1J(PC) +
3J(PC)| 11.8, 2J(PtC) not discernible]; 31P-{1H} (24 MHz), second-order
AB spin-system, δ -16.26 {d, P(2), 1J[PtP(2)] 2734, 2J[P(2)P(2)] 19.5},
and -17.42 p.p.m. {d, P(1), 1J[PtP(1)] 2788, 2J[P(2)P(1)] 19.5}. See
Figure 20.

(iv) Preparation of [Pt{CH(COPh)S(O)CH(COPh)}(AsPh₃)(PET₃)] (178)
Triphenylarsine (0.065 g, 0.212 mmol), diphenacyl sulfoxide (0.062 g,
0.216 mmol) and silver(I) oxide (0.3 g, 1.3 mmol) were added in succession
to a stirred solution of the complex [{PtBr₂(PET₃)}₂] (0.10 g, 0.106 mmol)
in dichloromethane (25 cm³). The mixture was refluxed for 15h, filtered,
and the filtrate evaporated to dryness under reduced pressure to afford a
pale yellow oil, which was shown by 31P-{1H} and 1H n.m.r. spectroscopy
to consist of a mixture of isomers (178a) (76%) and (178b) (24%). Dissolu-
tion of the oil in dichloromethane (ca. 3 cm³) followed by addition of
light petroleum (ca. 70 cm³) afforded an off-white solid (0.319 g, 84%)
which contained the same ratio of isomers (178a) and (178b) as the oil.
Slow recrystallisation from dichloromethane-light petroleum afforded
pale yellow microcrystals of pure isomer (178a) (0.046 g, 12%).

Isomer (178a). (Found: C, 53.6; H, 4.6. C₉₆H₄₂AsO₃P₂PtS requires C,
53.2; H, 4.7%), m.p. 187-193°C (decomp.); vC=O at 1638vs and 1630vs

\( \text{cm}^{-1}; \) vS=O at 1030vs \( \text{cm}^{-1} \). N.m.r. spectra: \( ^1\text{H} \) (300 MHz), \( \delta \) 8.13-6.72 (m, 25H, Ph), 5.39 (d, 1H, H(2), \( ^3\text{J}[\text{PH}(2)]\) 8.45, \( ^2\text{J}[\text{PtH}(2)]\) 58.5), 4.99 (d, 1H, H(1), \( ^3\text{J}[\text{PH}(1)]\) 10.0, \( ^2\text{J}[\text{PtH}(1)]\) 66.8), 1.40-1.08 (m, 6H, CH\(_2\), PET\(_3\)), and 0.77 p.p.m. (m, 9H, CH\(_3\), PET\(_3\)); \( ^{13}\text{C}-\{^1\text{H}\} \) (75.5 MHz), \( \delta \) 201.19 [s, br, CO, \( ^2\text{J}(\text{PtC})\) ca. 32], 196.73 [s, CO, \( ^2\text{J}(\text{PtC})\) ca. 47], 49.04 [d, C(1), \( ^2\text{J}(\text{PC})\) 65.7, \( ^1\text{J}(\text{PtC})\) 345.2], 38.30 [s, br, C(2), \( ^1\text{J}(\text{PtC})\) 490.4], 16.20 [CH\(_2\), PET\(_3\), \( ^1\text{J}(\text{PC})\) 31.4, \( ^2\text{J}(\text{PtC})\) 8.5], and 7.97 p.p.m. (s, br, CH\(_3\), PET\(_3\), \( \text{J}(\text{PC})\) not discernible); \( ^{31}\text{P}-\{^1\text{H}\} \) (24 MHz), \( \delta \) 5.65 p.p.m. [s, \( ^1\text{J}(\text{PtP})\) 2793]. See Figure 18.

Isomer (178b). N.m.r. spectra: \( ^1\text{H} \) (300 MHz), platinathietane-3-oxide ring resonances at \( \delta \) 5.29 [s, 1H, H(1), \( ^2\text{J}(\text{PtH})\) 86.3], and 4.43 p.p.m. [d, 1H, H(2), \( ^3\text{J}(\text{PH})\) 3.0, \( ^2\text{J}(\text{PtH})\) 51.8]; \( ^{31}\text{P}-\{^1\text{H}\} \) (24 MHz), \( \delta \) 1.21 p.p.m. [s, \( ^1\text{J}(\text{PtP})\) 2759]. See Figure 18.

Reactions of \( \left[\text{Pt}\{\text{CH(\text{COPh})S(O)}\text{CH(\text{COPh})}\}\{\text{PPh}_3\}_2\right] \) (175) with labile metal complexes

(i) Preparation of \( \left[\text{Pt}\{\text{CH(\text{COPh})S(O)}\text{CH(\text{COPh})}\}\{\text{PPh}_3\}_2\cdot\text{PdCl}_2\right] \) (183). \( 2\text{CH}_2\text{Cl}_2 \)

(a) From trans-[PdCl\(_2\)(NCPh)\(_2\)]. A solution of trans-[PdCl\(_2\)(NCPh)\(_2\)] (0.038 g, 0.10 mmol) in dichloromethane (10 cm\(^3\)) was added to a solution of (175) (0.10 g, 0.10 mmol) in dichloromethane (25 cm\(^3\)) to afford an orange solution, which was examined by \( ^{31}\text{P}-\{^1\text{H}\} \) n.m.r. spectroscopy. This showed complete consumption of starting material, with formation of (183). The mixture was refluxed for 1h, and evaporation to dryness under reduced pressure afforded an orange oil. Dissolution of the oil in dichloromethane (2 cm\(^3\)) followed by addition of light petroleum (ca. 50 cm\(^3\)) afforded yellow microcrystals of the title complex (183). \( 2\text{CH}_2\text{Cl}_2 \) (0.103 g, 76%). Slow recrystallisation from dichloromethane-light petroleum
afforded fine bright yellow needles. (Found: C, 48.1; H, 3.5.
C_{32}H_{42}Cl_{2}O_{3}P_{2}PdPtS_{2}CH_{2}Cl_{2} requires C, 48.0; H, 3.4%), m.p. 207-210°C (decomp.); νC=O at 1639m and 1490s cm\(^{-1}\); νS=C at 341vw and 310vw cm\(^{-1}\). N.m.r. spectra: \(^1\)H (400 MHz), δ 7.68-6.68 (m, 40H, Ph), 5.63 \{d, 1H, H(2), \(^3\)J[P(1)H(2)] 9.8, \(^3\)J[P(2)H(2)] 3.0, \(^2\)J[PtH(2)] 44.8\}, 5.25 \{d, 1H, H(1), \(^3\)J[P(1)H(1)] 9.2, \(^2\)J[PtH(1)] 72.0\}, and 5.20 p.p.m. \(s, 4H, CH_2Cl_2\); \(^{13}\)C-{\(^1\)H} (100 MHz), δ 211.55 \[s, CO, \(^{31}\)J(PtC) ca. 28\], 196.41 \[s, CO, \(^{31}\)J(PtC) ca. 36\], 64.32 \{d, C(2), \(^{31}\)J[P(2)C(2)] 58.1, \(^{1}\)J[PtC(2)] 300.7\}, and 55.49 \{d, C(1), \(^{31}\)J[P(1)C(1)] 68.4, \(^{1}\)J[PtC(1)] 429.9\}; \(^{31}\)P-{\(^1\)H} (24 MHz, \[^2\]H\_\_\_hlorofo rm), second-order AB spin-system, δ 14.72 \{d, P(1), \(^1\)J[PtP(1)] 3408, \(^2\)J[P(2)P(1)] 19.5\}, and 10.08 p.p.m. \{d, P(2), \(^1\)J[PtP(2)] 2783, \(^2\)J[P(1)P(2)] 19.5\}. See Figure 21.

(b) From [PdCl\(_2\) (COD)]. A solution of [PdCl\(_2\) (COD)] (0.057g, 0.20 mmol) in dichloromethane (10 cm\(^3\)) was added to a solution of (175) (0.20g, 0.20 mmol) in dichloromethane (20 cm\(^3\)) to afford an orange solution which was refluxed for 1h. Work-up as in (i) above afforded fine bright yellow needles identified as (183).2CH\(_2\)Cl\(_2\) (0.133 g, 49%).

(ii) Preparation of [Pt(CH(COPh)S(O)CH(COPh))(PPh\(_3\))\(_2\).RhCl(CO)](184).
CH\(_2\)Cl\(_2\).2H\(_2\)O

A solution of the complex [Rh\(_2(\mu-Cl)_2\)(CO)_4] (0.039 g, 0.100 mmol) in dichloromethane (5 cm\(^3\)) was added to a stirred solution of (175) (0.20g, 0.20 mmol) in dichloromethane (25 cm\(^3\)) to afford an orange solution which was refluxed for 30 min. Evaporation to dryness under reduced pressure afforded an orange oil. Dissolution of the oil in dichloromethane (2 cm\(^3\)) followed by addition of light petroleum afforded yellow microcrystals of the title complex (184).CH\(_2\)Cl\(_2\).2H\(_2\)O (0.201 g, 78%). Slow recrystallisation from dichloromethane-light petroleum afforded
orange prisms of (184)·CH₂Cl₂·2H₂O suitable for an X-ray study. (Found: C, 49.8; H, 3.9. C₅₅H₄₂ClO₄P₂PtRhS·CH₂Cl₂·2H₂O requires C, 50.2; H, 3.7%), m.p. decompn. >200°C; νRHC≡O at 1982vs cm⁻¹; νC=O at 1642m and 1510m cm⁻¹; νS=O at 1119s cm⁻¹; νRh-Cl at 310vw cm⁻¹. N.m.r. spectra: 

$$^1$$H (300 MHz), δ 8.03-6.63 (m, 40H, Ph), 5.47 {d, 1H, H(1), $^3$J[PtH(1)] 9.5, $^2$J[PtH(1)] 73.5}, 5.28 (s, 2H, CH₂Cl₂), 4.95 {dd, 1H, H(2), $^3$J[PtH(2)] 10.05, $^2$J[PtH(2)] 3.5, $^2$J[PtH(2)] 48.0}, and 2.06 p.p.m. (s, br, 4H, H₂O); $^{31}$P-$^1$H (24 MHz), second-order AB spin-system, δ 15.73 (d, P(1), $^1$J[PtP(1)] 3340, $^2$J[PtP(1)] 19.5), and 9.88 p.p.m. (d, P(2), $^1$J[PtP(2)] 2803, $^2$J[PtP(2)] 19.5). See Figure 21.

![Figure 21](image_url)

Reaction of [Pt(CH(COPh)S(O)₂CH(COPh))(PPh₃)₂](117) with trans-[PdCl₂(NCPh₂)]

A mixture of (117)·CH₂Cl₂·0.5H₂O (0.128 g, 0.12 mmol) and trans-[PdCl₂-(NCPh₂)] (0.044 g, 0.11 mmol) in dichloromethane (20 cm³) was refluxed for 16h. Evaporation to dryness under reduced pressure afforded a pale yellow solid which was shown to contain unreacted (117) by $^{31}$P-$^1$H n.m.r. spectroscopy.
Reaction of trans-[PdCl₂(NCPh)₂] with two equivalents of (175)

A solution of trans-[PdCl₂(NCPh)₂] (0.019 g, 0.050 mmol) in dichloromethane (10 cm³) was added to a solution of (175) (0.10 g, 0.10 mmol) in dichloromethane (20 cm³), and the mixture was refluxed for 1 h. Evaporation to dryness under reduced pressure afforded a yellow oily solid, which was shown by ³¹P-¹H n.m.r. spectroscopy to consist of a 1:1 mixture of the chelate-ring product (183) and unreacted platinathietane-3-oxide (175).

Reaction of (175) with [PtCl₂(COD)]

A solution of [PtCl₂(COD)] (0.056 g, 0.149 mmol) in dichloromethane (5 cm³) was added to a solution of (175) (0.150 g, 0.149 mmol) in dichloromethane (20 cm³), and the mixture was refluxed for 1 h. Evaporation to dryness under reduced pressure afforded an off-white solid which was shown to contain unreacted (175) by ³¹P-¹H and ¹H n.m.r. spectroscopy.

Reaction of (175) with cis-[PtCl₂(NCPh)₂]

A solution of cis-[PtCl₂(NCPh)₂] (0.070 g, 0.149 mmol) in dichloromethane (5 cm³) was added to a solution of (175) (0.150 g, 0.149 mmol) in dichloromethane (20 cm³), and the mixture was refluxed for 12 h. Evaporation to dryness under reduced pressure afforded a pale yellow solid which was shown to contain unreacted (175) by ³¹P-¹H n.m.r. spectroscopy.

Reaction of (4) with [Rh₂(μ-Br)₂(COD)₂]

A solution of [Rh₂(μ-Br)₂(COD)₂] (0.044 g, 0.059 mmol) in dichloromethane (20 cm³) was added to a solution of (4) (0.12 g, 0.12 mmol) in dichloromethane (10 cm³), and the mixture was refluxed for 30 min. Evaporation to dryness under reduced pressure afforded an orange-yellow oil which was shown to contain unreacted (175) by ³¹P-¹H n.m.r. spectroscopy.
**Reaction of [PdCl₂(COD)] with diphenacyl sulfoxide (172)**

A solution of diphenacyl sulfoxide (172) (0.10 g, 0.35 mmol) in dichloromethane (10 cm³) was added to a solution of [PdCl₂(COD)] (0.10 g, 0.35 mmol) in dichloromethane, and the mixture was refluxed for 1h. Evaporation to dryness under reduced pressure afforded a yellow oily solid which was shown to contain unreacted (172) by ¹H n.m.r. spectroscopy.

**Miscellaneous Reactions**

**Reaction of (175) with iodoethane**

A solution of (175) (0.10 g) in dichloromethane (10 cm³) with iodoethane (ca. 2 cm³) was refluxed for 1.5h. Evaporation to dryness under reduced pressure afforded pale yellow microcrystals which were identified as unreacted (175) by ³¹P-{¹H} n.m.r. spectroscopy.

Similarly, a solution of diphenacyl sulfoxide (172) (0.10 g) in dichloromethane (10 cm³) with iodoethane (2 cm³) was refluxed for 1.5h. Evaporation to dryness under reduced pressure afforded a pale yellow oil, which was shown to be unreacted (172) by ¹H n.m.r. spectroscopy.

**Attempted oxidation of (175)**

A solution of (175) (0.10 g, 0.10 mmol) in dichloromethane contained in an n.m.r. tube was shaken vigorously with 10 drops of 30% (v/v) hydrogen peroxide for 10 min., and stood for a further 1h. ³¹P-{¹H} n.m.r. spectroscopy indicated the presence of unreacted (175). The mixture was transferred to a 100 cm³ flask, 10 cm³ of acetone and 0.4 cm³ 30% H₂O₂ added, and the mixture refluxed for 1h. Evaporation to dryness afforded a damp white solid which was extracted with dichloromethane, washed with water, dried (MgSO₄), and evaporated to dryness to afford a white solid. ³¹P-{¹H} n.m.r. spectroscopy showed a mixture of products, from which none could be isolated pure.
CHAPTER 5

Synthesis of $\eta^3$-Oxodimethylenemethane Complexes of Platinum and Palladium
5.1 INTRODUCTION

The utility of the 1,3-dianion of dibenzyl sulphone, (102) or (103) in the synthesis of metallathietane-3,3-dioxide complexes of platinum(II), palladium(II), and nickel(II) (105), as described in Chapter 2, led to an investigation into the use of other related 1,3-dianions in the synthesis of four-membered metallacyclic complexes.

The 1,3-dianion of dibenzyl ketone (1,3-diphenyl acetone) (104) (readily available as its di-potassium salt via the deprotonation of dibenzyl ketone by potassium amide in liquid ammonia\(^{(102)}\) can be viewed as a precursor for the synthesis of 1,3-diphenyl substituted \(\eta^3\)-oxodimethylene-methane complexes (106). A number of \(\eta^3\)-oxodimethylene-methane complexes of platinum(II), palladium(II), osmium(II), and iridium(III) have been synthesised previously, via a variety of routes, which are described in Chapter 1. These oxodimethylene-methane complexes may also be formulated as highly puckered metallacyclobutan-3-one systems (48).\(^{60-64,72,73}\)

5.2 SYNTHESIS OF OXODIMEYLENE-METHANE COMPLEXES

Treatment of either a suspension or solution of the complexes cis-[PtCl\(_2\)L\(_2\)] or trans-[PdCl\(_2\)L\(_2\)] with one equivalent of the 1,3-dianion of dibenzyl ketone (104) in THF at low temperature affords the oxodimethylene-methane complexes \([M(\eta^3-\text{CHPhC(O)CHPh})L_2]\) (186, \(M = \text{Pt}, L = \text{AsPh}_3\)), (187, \(M = \text{Pt}, L = \text{PPh}_3\)), (188, \(M = \text{Pt}, L_2 = \text{COD}\)), (189, \(M = \text{Pd}, L = \text{PPh}_3\)), and (190, \(M = \text{Pd}, L = \text{PET}_3\)), in moderate yields, as illustrated in equation 44. Two recrystallisations of the crude products afforded white to pale
yellow microcrystalline solids, which are air-stable in the solid state, but decompose in chloroform solutions exposed to air.

The labile COD ligand of (188) may be readily displaced at room temperature by either one equivalent of dppe or two equivalents of triphenylphosphine, to afford the complexes \([\text{Pt}(\eta^3-\text{CHPhC(O)CHPh})\text{dppe}]\) (191)\(\cdot\text{CH}_2\text{Cl}_2\) and (187) respectively.

Treatment of a THF solution of the \(\alpha\)-platinaketone complex cis-[Pt\(\text{Cl}(\text{CH}_2\text{COCH}_2\text{Cl})(\text{PPh}_3)_2\)] with an excess of 0.7% (w/w) sodium amalgam rapidly gave a quantitative yield of the known\(^{72,73}\) (see Chapter 1) unsubstituted oxodimethylenemethane complex (72), as depicted in equation 45.

\[
\begin{align*}
\text{cis-[Pt\(\text{Cl}(\text{CH}_2\text{COCH}_2\text{Cl})(\text{PPh}_3)_2\)]} & \quad \xrightarrow{\text{Na(Hg)}} \quad \text{THF} \\
\text{(72)} & \quad \xrightarrow{\text{THF}} \\
\text{(72)}
\end{align*}
\]

45. Complex (72) was identified by comparison of its \(^1\text{H}\) and \(^{31}\text{P}-{^1}\text{H}\) n.m.r. spectroscopic data with those reported in the literature.\(^{72,73}\)

This reaction may be loosely referred to as 'Wurtz-type' because of its
similarity to the true Wurtz reaction in which alkyl residues are
coupled via treatment of alkyl halides with sodium. This methodology
has previously been applied to the synthesis of organometallic complexes,
as in for example the synthesis of cyclic alkyne-platinum(0) complexes
from 1,2-dibromocycloalkenes. Treatment of the complexes [(OC)₄Mn(Br)-
(PPh₂(CH₂)ₙCH₂Cl)] (n = 1,4) with sodium amalgam has also recently been
shown to result in ring closure to afford the phosphometallacycloalkanes [(OC)₄Mn{PPh₂(CH₂)ₙCH₂}].

5.3 STRUCTURAL PROPERTIES OF DIPHENYL OXODIMETHYLENEMETHANE COMPLEXES

Single-crystal X-ray diffraction studies on a number of oxodimethylene-
methane complexes of platinum⁶¹,⁶³,⁶⁴,⁷³ and palladium⁶²,⁶³ have shown
that certain features of the molecular structure vary according to the
metal, ligands, and oxodimethylenemethane substituents. These structural
features are the degree of non-planarity of the metal-oxodimethylene-
methane system, and the degree of tipping of the oxygen atom, out of the
OCC plane, towards the metal atom. Accordingly, a single-crystal X-ray
diffraction study has been carried out on the triphenylarsine platinum
complex (186), in order to compare the molecular structure of (186) with
those of related platinum oxodimethylenemethane complexes, and with the
diphenyl substituted platinathietane-3,3-dioxide complex (109) (see
Chapter 2). Complex (186) crystallised with two molecules of dichloro-
methane per molecule of complex, and there are no short intermolecular
contacts between the platinum complex and the solvent molecules.

A summary of important bond lengths and angles is given in Table 10,
whilst the molecular structure of (186) is illustrated in Figure 22,
which also gives the crystallographic numbering system. The complex
consists of a 1,3-diphenyl substituted oxodimethylenemethane ligand co-
### TABLE 10a

Selected bond lengths and angles for [Pt(n^3-CHPhC(O)CHPh)(AsPh)_3]_2(186).2CH_2Cl_2

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Bond length (Å)</th>
<th>Angle</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt—As(1)</td>
<td>2.394(3)</td>
<td>As(1)—Pt—As(2)</td>
<td>96.9(1)</td>
</tr>
<tr>
<td>Pt—As(2)</td>
<td>2.391(3)</td>
<td>As(1)—Pt—C(3)</td>
<td>96.4(8)</td>
</tr>
<tr>
<td>Pt—C(1)</td>
<td>2.116(25)</td>
<td>As(2)—Pt—C(1)</td>
<td>97.5(6)</td>
</tr>
<tr>
<td>Pt····C(2)</td>
<td>2.350(26)</td>
<td>C(1)—Pt—C(3)</td>
<td>69.2(10)</td>
</tr>
<tr>
<td>Pt—C(3)</td>
<td>2.187(27)</td>
<td>Pt—C(1)—C(2)</td>
<td>79.0(16)</td>
</tr>
<tr>
<td>C(1)—C(2)</td>
<td>1.50(4)</td>
<td>Pt—C(1)—C(2)</td>
<td>77.2(16)</td>
</tr>
<tr>
<td>C(2)—C(3)</td>
<td>1.47(4)</td>
<td>C(1)—C(2)—C(3)</td>
<td>110.4(25)</td>
</tr>
<tr>
<td>C(2)—O</td>
<td>1.29(3)</td>
<td>C(1)—C(2)—O</td>
<td>116(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(3)—C(2)—O</td>
<td>133(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt—C(1)—C(11)</td>
<td>125.0(14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt—C(3)—C(01)</td>
<td>121.8(17)</td>
</tr>
</tbody>
</table>

| Twist | 12.0 | Fold | 56.7 | C(2)—O incline | 6.46 |

---

a See Figure 22 for crystallographic numbering system;
b $\angle$As(1)—Pt—As(2)/C(1)—Pt—C(3);
c $\angle$C(1)—C(2)—C(3)/C(1)—Pt—C(3);
d $\angle$C(1)—C(2)—C(3)/C(2)—O.
FIGURE 22
Molecular structure of $[\text{Pt(}n^3\text{-CHPhC}(O)\text{CHPh})\text{AsPh}_3]_2$ (186) with omission of triphenylarsine carbon atoms other than those bonded to arsenic, and all hydrogen atoms.
ordinated to a Pt(AsPh₃)₂ moiety, as depicted in equation 44. However, the complex may also be represented as a highly puckered platincyclobutane-3-one ring system, as in Figure 22. The bonding of the oxodimethyleneemethane ligand to the platinum atom is very different to the bonding observed in platincyclobutane complexes,¹ and in the platinnathetane-3,3-dioxide complex (109). The platinum-oxodimethyleneemethane system (186) is highly non-planar, with the fold angle between the C(1)-Pt-C(3) and C(1)-C(2)-C(3) planes being 56.7°. This value is slightly larger than the ranges of 48.0-51.0° and 51.3-53.3° observed in previous studies of oxodimethyleneemethane complexes of platinum⁶¹,⁶³,⁶⁴,⁷³ and palladium⁶²,⁶³ respectively. Such a large deviation from planarity is not a feature of saturated platincyclobutane complexes, where fold angles range from 0-30°.¹¹,²²,⁴⁷ Organic cyclobutanones are also slightly non-planar, for example, the fold angle in cis-1,3-di-t-butyl-1,3-dibromocyclobutane-2-one is 10°.¹⁹³ The platinnathetane-3,3-dioxide complex (109) is puckered by 24.56°. The bonding in oxodimethylenemethane complexes may be considered to contain contributions from both the metallacyclic (48) and η³-allylic type (49) representations.⁶¹-⁶⁴,⁷²,⁷³ The large degree of ring puckering in oxodimethylenemethane complexes is a consequence of the allylic contribution to the bonding, and this results in a relatively short transannular Pt---C(2) distance of 2.350(26) Å in (186). Furthermore, the Pt-C(1) and Pt-C(3) bond distances of (186) are somewhat longer, at an average of 2.152(26) Å,
than the platinum-carbon bond distances typically observed in platinacyclobutane and platinathietane-3,3-dioxide complexes (Chapter 2).

Thus, the average Pt-C distances in the platinacyclobutane complex \([\text{Pt}(\text{CH}_2\text{Me}_2\text{CH}_2)(\text{PET}_3)_2]\) (36)\(^\text{47}\) and the platinathietane-3,3-dioxide complex (109) are 2.083(6) and 2.073(21) Å respectively. The C(1)-C(2) and C(2)-C(3) bond distances of (186) also exhibit a significant shortening when compared to C-C bond distances in platinacyclobutanes. Thus, the C-C bond distances of (186) average 1.485(40) Å, whereas the C-C bond distances in the platinacyclobutane (36) are 1.535(10) Å.\(^\text{47}\) Metal \(\eta^3\)-allyl complexes typically contain long metal-carbon and short carbon-carbon bonds, the latter typically being around 1.40 Å.\(^\text{194-196}\) Hence the carbon-carbon bond distances for (186) are intermediate between those of platinacyclobutanes and \(\eta^3\)-allyl complexes, consistent with contributions to the bonding in (186) from both the metallacyclic (48) and \(\eta^3\)-allylic (49) bonding representations.

An interesting feature of the structure of (186) is that the C(2)-O bond is inclined by 6.46° out of the C(1)-C(2)-C(3) plane towards the platinum atom. This feature is also characteristic of other oxodimethylene- \(\text{enemethane and } \eta^3\)-allyl complexes, for example, in the dimeric \(\eta^3\)-2-methylallyl palladium chloride complex, the methyl group is inclined by 10.9° out of the \(\eta^3\)-allyl plane towards the metal.\(^\text{194}\) An important consequence of viewing the oxodimethylene-methane complex (186) in terms of the \(\eta^3\)-allylic representation (49) is that the bond order of the carbonyl group is less than two. Thus there is a lengthening of the C(2)-O bond in (186) to 1.29(3) Å, compared to 1.21 Å in \text{cis}-1,3-di-t-butyl-1,3-dibromocyclobutan-2-one.\(^\text{193}\) The weakening of the carbon-oxygen bond is also detected in the i.r. spectra of these oxodimethylene-methane complexes, and this is discussed in Section 5.5.
The co-ordination about the platinum atom in (186) is effectively square-planar, with the twist angle between the As(1)-Pt-As(2) and C(1)-Pt-C(3) planes being 12.0°. The Pt-As bonds of (186) are identical, at 2.394(3) and 2.391(3) Å, and are slightly shorter than the Pt-As bonds of the platinathietane-3,3-dioxide complex (109), where the average Pt-As bond distance is 2.413 Å. This reflects the somewhat lower trans influence of an oxodimethylenemethane ligand in (186) compared to a 1,3-diyl ligand in (109).

It is interesting to note that the oxodimethylenemethane complex (186) is the cis isomer, and has both phenyl substituents in equatorial environments, these being analogous to the syn positions of an η^3-allyl complex. In contrast however, ketone or ester 1,3-disubstituted oxodimethylenemethane complexes of platinum\(^{61,63,64}\) and palladium\(^{62,63}\) (50) have been shown to exclusively exhibit trans substitution, with the two substituents occupying axial and equatorial positions on the non-planar metal-oxodimethylenemethane system. Solution n.m.r. studies on a number of monosubstituted oxodimethylenemethane complexes (55)-(61) have established that the oxodimethylenemethane substituent occupies an axial position.\(^{65,67,68}\) Furthermore, trans substitution is also favoured for 2,4-disubstituted metallathietane-3,3-dioxide and platinathietane-3-oxide complexes, see Chapters 2 and 4 respectively. Although diequatorial substitution is favoured for a metallacycle of the type \([M(CHR^1CH_2CHR^2)-Cl_4]\),\(^{124}\) the presence of bulky ligands on the metal destabilises the diequatorial isomer, causing the observed axial-equatorial isomer to be formed. However, for η^3-allyl complexes which contain substituents on the outer allyl carbons, these substituents generally occupy syn (equatorial) rather than anti (axial) positions.\(^{196}\) Complex (186) is the most highly non-planar oxodimethylenemethane complex known [fold angle 56.7°],
and therefore has the greatest degree of η³-allylic character. This may partly account for the preference of complex (186) to contain two equatorial substituents. In platinum and palladium η³-allyl complexes the η³-allyl group lies at an angle of between 108 and 119° (equivalent to a fold angle between 61 and 72°) to the plane containing the metal and the donor atoms of the other ligands. However, since the fold angle of 56.7° for (186) is not significantly greater than the range of 48.0-53.3° observed for the other trans-1,3-disubstituted oxodimethylenemethane complexes of platinum and palladium, it is possible that conjugation of the oxodimethylenemethane ligand with the phenyl substituents is stabilising the diequatorial isomer.

With the oxodimethylenemethane ligand inclined at an angle of 56.7° to the C(1)-Pt-C(3) plane, conjugation of the π-system of this oxodimethylenemethane ligand with the π-systems of the phenyl substituents is possible if these phenyls adopt equatorial positions. This may be demonstrated by an examination of the C(1)-C(2)-C(3)-C(01) and C(3)-C(2)-C(1)-C(11) torsion angles for (186), which are -163.12(219) and 169.89(222)° respectively. These values indicate that the C-C-C plane of the oxodimethylenemethane ligand and the attached carbons of the phenyl substituents are effectively coplanar. Although the axially disposed oxodimethylenemethane hydrogen atoms of (186) could not be located in the X-ray study, examination of the C-C-C-H torsion angles for the axial H(1) and equatorial H(3) oxodimethylenemethane protons of the trans-1,3-disubstituted oxodimethylenemethane complex (50, M = Pt, R = CO₂Me, L = Ph₃) reveals that the equatorial hydrogen is almost coplanar with the oxodimethylenemethane ligand (being bent out of the CCC plane by approximately 19°), whereas the axial hydrogen is not, the torsion angles being C(3)-C(2)-C(1)-H(1) 53.65° and C(1)-C(2)-C(3)-H(3)
161.11°. *Ab initio* calculations by Albright\textsuperscript{197} on the complex 
[(H\textsubscript{3}P)\textsubscript{2}Pd(\eta\textsuperscript{3}-CH\textsubscript{2}C(O)CH\textsubscript{2})] have indicated that the stable geometry of 
this complex is puckered by 50.5°, the equatorial proton is bent by 
approximately 20° out of the C-C-C plane, whereas the axial proton is 
bent by 65° out of this plane. These values are in good agreement with 
those noted above for the related platinum complex (50, M = Pt, R = CO\textsubscript{2}Me, 
L = PPh\textsubscript{3}). Hence, little conjugation would be expected between an 
axially disposed phenyl substituent and the π-system of an oxodimethylene-
methane ligand.

The C-C-C-H torsion angle is an indicator of the relative contributions 
of \(\eta^3\)-allylic and metallacyclic character in an oxodimethylene-
methane complex.\textsuperscript{197} In an \(\eta^3\)-allylic representation (49), the C-C-C-H torsion 
angles for the syn (equatorial) and anti (axial) protons are approximately 
180 and 0° respectively. However, in a planar metallacyclobutan-3-one 
form both C-C-C-H torsion angles are approximately 120°. The C-C-C-H 
torsion angles of 53.65 and 161.11°, for the axial and equatorial protons 
respectively, of the oxodimethylene-methane complex (50, M = Pt, R = CO\textsubscript{2}Me, 
L = PPh\textsubscript{3}) therefore indicate that both the \(\eta^3\)-allylic and platinacyclo-
butan-3-one formulations contribute to the bonding in this complex.

It is worth noting that the phenyl substituents of (186) are somewhat 
twisted out of coplanarity with the oxodimethylene-methane ligand, 
possibly as a result of steric interactions with the phenyl rings of the 
triphenylarsine ligands. Thus, the torsion angles C(2)-C(3)-C(01)-C(02) 
and C(2)-C(1)-C(11)-C(16) are 19.00(46) and -53.48(65)° respectively, 
indicating that the phenyl groups are twisted towards the platinum, in 
the sense that the planes of the phenyl substituents are more nearly 
perpendicular to the platinum co-ordination plane.

A recent single-crystal X-ray diffraction study on the lithium
analogue of (104), \([\text{PhCHC(O)CHPh}Li_2 \cdot \text{ZIMEDA}]\) (192) has established that both phenyl groups adopt exo-positions, analogous to the equatorial substituents of (186). Interestingly, however, low temperature n.m.r. studies on (192) have demonstrated the presence of both the exo, endo-isomer (65%), and a symmetrical species (35%), which is presumably the exo, exo-isomer.

Overall, the geometry of (186) bears a resemblance to the \(\mu\)-2-oxo-1,3-diphenylpropanediylidine complex (193). In a similar fashion that \(\eta^1\)-oxodimethylenemethane complexes may be considered as metallacyclobutan-3-one complexes, the dinuclear complex (193) may also be considered as a diphenyl substituted 'oxodimethylenemethane' moiety bridging two metal centres, representation (193), or as a dimetallabicyclic complex, representation (194). A comparison of the X-ray data for the platinaoxo-dimethylenemethane complex (186) and the dinuclear complex (193), Table 11, illustrates the similarities in the molecular structures of these two complexes. The two dihedral (fold) angles of 52 and 55° between the C(1)-Pt-C(3) and C(1)-C(2)-C(3) planes in (193) are almost identical to the corresponding value in the mononuclear oxodimethylenemethane complex (186) of 56.7°. The bridging 'oxodimethylenemethane' ligand of (193) similarly contains short carbon-carbon bonds of 1.41(2) and 1.45(3) Å, together with a somewhat lengthened carbon-oxygen bond of 1.26(2) Å.
TABLE 11

A comparison of selected bond lengths and angles for the complexes [Pt(η³-CHPhC(O)CHPh)(AsPh₃)₂] (186) and [(Bu⁵NC)₂Pt(μ-CPhC(O)CPh)Pt(CNBu⁵)₂] (193) a

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>Complex</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(186)</td>
<td>(193)</td>
</tr>
<tr>
<td>Pt-C(1)</td>
<td>2.116(25)</td>
<td>2.11(2), 2.13(2)</td>
</tr>
<tr>
<td>Pt-C(3)</td>
<td>2.187(27)</td>
<td>2.10(2), 2.10(2)</td>
</tr>
<tr>
<td>Pt-C(2)</td>
<td>2.350(27)</td>
<td>2.48(2), 2.50(2)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.50(4)</td>
<td>1.41(2)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.47(4)</td>
<td>1.45(3)</td>
</tr>
<tr>
<td>C(2)-O</td>
<td>1.29(3)</td>
<td>1.26(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>Complex</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(186)</td>
<td>(193)</td>
</tr>
<tr>
<td>C(1)-Pt-C(3)</td>
<td>69.2(10)</td>
<td>62.4(7), 62.1(7)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>110.4(25)</td>
<td>99(1)</td>
</tr>
<tr>
<td>'Fold' b</td>
<td>56.7</td>
<td>55, 52</td>
</tr>
</tbody>
</table>

a See Reference 200;
b Dihedral angle between the planes C(1)-Pt-C(3) and C(1)-C(2)-C(3).
Although the oxodimethylenemethane complexes (186)-(191) are considered as complexes of platinum(II) or palladium(II), they may also, in principle, be formulated as an oxodimethylenemethane diradical coordinated to a metal(0) centre, as in representation (106), for example. The bonding of an unsubstituted oxodimethylenemethane ligand to a $d^{10}$-ML$_2$ metal centre has been considered in a qualitative fashion by considering the orbital interaction diagram for a $d^{10}$-ML$_2$ centre with an oxodimethylenemethane ligand, using symmetry labels for a $C_{2v}$ ML$_2$ group, as illustrated in Figure 23. This bonding picture of the oxodimethylenemethane fragment to a $d^{10}$-ML$_2$ centre is similar to that used to predict the mode of bonding of a trimethylenemethane ligand to a $d^{10}$-ML$_2$ centre.  

The four $\pi$-orbitals of the oxodimethylenemethane ligand are shown on the left of Figure 23, and are labelled $\pi_1-\pi_4$. There are four low energy metal orbitals labelled $1_a + a_2 + b_1 + 2a_1$, which are readily identifiable with the $e_g + b_2g + a_1g$ levels of a $D_{4h}$, square-planar metal complex. The $1a_1$, $3a_1$, and $\pi_1$ orbitals combine to form three molecular orbitals, the two lowest in energy, $1a'$ and $4a'$, being filled. The $a_2$ and $2a_1$ orbitals are essentially non-bonding. Of the remaining orbitals, $b_1$ and $\pi_2$ form a bonding combination, the resulting $2a'$ and $5a''$ levels being filled. The $b_2$ orbital is suitably hybridised towards the $\pi_3$ orbital, and strong overlap between these orbitals results in a bonding interaction between the metal centre and the oxodimethylenemethane ligand. The interaction between $b_2$ and $\pi_3$ is at a maximum when the dihedral angle between the L-M-L and oxodimethylenemethane planes is 90°, and when the ML$_2$ fragment is approximately below the two methylene carbons in an $\eta^3$-geometry. However, in the observed structures of oxodimethylenemethane complexes, the dihedral angles between the L-M-L and oxodimethylenemethane planes are always greater than 90° (i.e. fold angles less than 90°), and this
may be interpreted in terms of a contribution to the bonding scheme from a metallacyclobutan-3-one structure (48). Interestingly, however, a dihedral angle of 90° might also be expected in platinum and palladium \( \eta^3 \)-allyl complexes, however the \( \eta^3 \)-allyl group lies at an angle of between 108° and 119° to the plane containing the metal and the donor atoms of the other ligands.\(^{194,195}\)

The tipping of the oxodimethylenemethane oxygen atom towards the metal, for example by 6.46° in (186) is similar to the puckering of the \( \eta^n \)-tri-methylenemethane ligand in complexes of the type \([M(\eta^n-C(CH_2)\_3)\_L_3]\) (195), and a similar explanation may be used to account for this puckering.\(^{203}\)

An examination of Figure 23 reveals that there is a repulsive interaction between \( 1\_\alpha \) and \( \pi_1 \), although this repulsion is slightly moderated by the interaction of \( 3\_\alpha \). Puckering of the oxodimethylenemethane ligand re-

\[
\text{(195)}
\]

orientates the \( \pi_1 \) orbital, such that the oxygen and methylene orbitals now lie in the nodal region of \( d_{z^2} \). This bending also mixes \( s \)-character into the central carbon of the \( \pi_1 \) orbital, resulting in hybridisation of the \( \pi \)-component on the central carbon \( C(2) \) away from the metal atom, as shown in Figure 24. Furthermore, this reorientation results in mixing of the \( \pi_2 \) and \( \pi_3 \) levels with oxodimethylenemethane \( \sigma \)-bonding orbitals,
this process being forbidden in the planar ligand but allowed in the puckered ligand.\textsuperscript{203} As a consequence, the $\pi_3$ orbitals are more directed towards the $b_2$ orbital resulting in a better overlap.

It is important to note that the $\pi_3$ level of an oxodimethylenemethane ligand has both the same symmetry and energy as the $\pi_3$ level of a trimethylenemethane ligand,\textsuperscript{202} as well as the $\pi_2$ level of an $\eta^3$-allyl ligand,\textsuperscript{204} and therefore similarities in the structures of these complexes might be expected. For example, the substituent on the central carbon of an $\eta^3$-allyl complex is tipped towards the metal atom,\textsuperscript{194} similar to the tipping of the oxygen atom in oxodimethylenemethane complexes. The palladium-trimethylenemethane complex $[\text{Pd}(\text{C}(\text{CH}_2)_3)\text{L}_2]$ has been described in terms of an $\eta^3$-allylic structure (78),\textsuperscript{201,205,206} although interestingly, a metallacyclic representation (79) has also been considered.\textsuperscript{78,79}

Theoretical calculations on the $\eta^3$-trimethylenemethane complex (78, $\text{L} = \text{PH}_3$) have indicated that a dihedral angle of 96° between the P-Pd-P and trimethylenemethane planes (equivalent to a fold angle of 84°) gives the minimum energy geometry, with the ML$_2$ unit very near the axis formed by the two methylene carbons.\textsuperscript{201,205,206} In view of the tipping of the oxygen atom in oxodimethylenemethane complexes, which has also been recently predicted theoretically,\textsuperscript{197} it is surprising that theoretical studies on the $\eta^3$-trimethylenemethane-ML$_2$ system have been restricted to a planar trimethylenemethane ligand.\textsuperscript{201,205,206}

An $\eta^4$-oxodimethylenemethane complex (196) has recently been characterised by a crystallographic study.\textsuperscript{207} In this complex an oxodimethylenemethane ligand bridges two ruthenium atoms, with three atoms $\pi$-bonded to one ruthenium, and one methylene carbon $\sigma$-bonded to the other ruthenium. The carbon-oxygen and carbon-carbon bonds of (196) are respectively longer and shorter than the corresponding values for the unsubstituted
platinum \( \eta^2 \)-oxodimethylenemethane complex \((72)\),\(^{73}\) as would be expected for an \( \eta^1 \)-complex. This dinuclear complex illustrates that the oxodimethylenemethane ligand can co-ordinate to metals in an \( \eta^1 \)-type geometry, as well as via the more commonly observed \( \eta^2 \)-mode.

5.4 N.M.R. STUDY OF DIPHENYL OXODIMETHYLENEMETHANE COMPLEXES

The room temperature \( ^1H \) n.m.r. spectra of the oxodimethylenemethane complexes (187) and (189)-(191) containing phosphine ligands are consistent with the presence of a static, highly puckered metal-oxodimethylenemethane system, with both phenyl substituents occupying equatorial positions, as observed in the X-ray study of (186). However, it is also not possible to rule out an equilibrium between this major diequatorial isomer and a small, undetectable amount of a diaxially substituted isomer formed by inversion of the oxodimethylenemethane ligand. Thus, the oxodimethylenemethane protons of (187) and (189)-(191) appear as a simple doublet, showing coupling to the trans phosphorus-31 nucleus only, with \( ^3J(\text{PH}) \) in the range 9.45-11.1 Hz, and corresponding platinum-195 satellites are observed where appropriate. The absence of coupling of the oxodimethylenemethane hydrogens to their cis phosphines arises as a result of dihedral angle control of the three-bond cis-P-Pt-C-H couplings. This relationship is also observed in puckered platinathetane-3-oxide complexes (Chapter 4), and in trans-1,3-disubstituted oxodimethylen-
methane complexes of platinum and palladium (50), which are static at low temperature, with one hydrogen in an axial environment.\textsuperscript{61-64} The cis-P-Pt-C-H axial torsion angles in these \textit{trans}-1,3-disubstituted oxodimethylenemethane complexes lie in the range 80-100°,\textsuperscript{61-64} and so no coupling of an axial hydrogen to its cis phosphine is observed. The large $^2J$(PtH) couplings for all of the oxodimethylenemethane complexes (186)-(191) are also consistent with the presence of axial hydrogens. This property has been discussed previously in Chapter 4. The values of $^2J$(PtH) for the complexes (186)-(188) vary according to the \textit{trans} influence of the accompanying ligand, with an increase in \textit{trans} influence from COD to AsPh$_3$ to PPh$_3$ effecting a decrease in $^2J$(PtH) from 104.4 Hz to 84.2 Hz.

Interestingly, no change in the $^1$H n.m.r. spectrum of (190) was observed on cooling to -90°C, and similarly there was no change on warming a solution of (187) to 80°C. These observations suggest that the oxodimethylenemethane complexes are rigid in solution, and that the barrier to inversion is large. A number of \textit{trans}-1,3-disubstituted oxodimethylenemethane complexes of platinum and palladium (50),\textsuperscript{61-64} and the unsubstituted complex (72) are fluxional in solution at room temperature, whereas the monosubstituted oxodimethylenemethane complexes (55)-(61)\textsuperscript{65,67,68} are rigid at room temperature with the oxodimethylenemethane substituent in an axial environment. An oxodimethylenemethane complex containing two axial phenyl substituents would not possess any conjugation between the π-systems of the oxodimethylenemethane ligand and these phenyl substituents, as described in Section 5.3, and therefore inversion of a diequatorially substituted oxodimethylenemethane ligand (which would generate such a diaxially substituted complex) is an unfavoured process. In contrast, the inversion of a \textit{trans} disubstituted oxodimethylenemethane
complex generates an identical trans isomer, and therefore a much smaller barrier to inversion is involved, and these complexes are subsequently fluxional at room temperature.

The $^{13}$C-$^{1}$H n.m.r. spectra for (186)-(188) show features characteristic of an oxodimethylenemethane ligand.\textsuperscript{61-64,73} Thus, for the triphenylphosphine complex (187), the Pt-CH carbons appear as the A part of an AMXX spin system ($M=^{195}$Pt, $X=^{31}$P),\textsuperscript{126,127} giving a second-order doublet of doublets with a small central resonance. Satellite features due to coupling to platinum-195 are also observed, the values of $^1$J(PtC) increasing in the order PPh$_3$ < AsPh$_3$ < COD, consistent with the expected decrease in trans influence of these ligands. The central oxodimethylenemethane carbon of (187) appears as a weak signal at $6173.2$ p.p.m., showing coupling to both phosphorus nuclei to give a triplet with $^3$J(PC) $5.5$ Hz. Coupling of this carbon to platinum-195 is also observed, with $^2$J(PtC) $155$ Hz, these values of $^3$J(PC) and $^2$J(PtC) being similar to values in other platinum oxodimethylenemethane complexes.\textsuperscript{61,63,64,73} The olefinic and methylene groups of the COD ligand of (188) both appear as two distinct resonances in the $^1$H and $^{13}$C-$^{1}$H n.m.r. spectra, as a result of the presence of a rigid, disubstituted oxodimethylenemethane ligand.

In the synthesis of (186) and (188)-(190) only a single cis-diequatorial isomer was observed in the initially isolated products. However, the cis-diequatorial platinum complex (187) was always initially contaminated with a small variable amount, around $10-20\%$, of the trans-disubstituted isomer (197), identified by $^1$H and $^{31}$P-$^{1}$H n.m.r. spectroscopy. A typical $^1$H n.m.r. spectrum of a mixture of (187) and (197) is shown in Figure 25. In contrast to the cis-disubstituted isomer (187), the trans-disubstituted complex is fluxional at room temperature, Figure 26, giving
FIGURE 25

$^1$H n.m.r. spectrum of the Pt-CH region for a mixture of cis- and trans-diphenyl oxodimethylenemethane complexes (187) and (197) respectively.
the expected AA'XX' pattern of a second-order doublet of doublets with platinum-195 satellites, similar to the spectra observed for other trans-disubstituted platinum oxodimethylenemethane complexes.\(^\text{61,63,64}\)

Two recrystallisations of the mixture afforded pure (187), but (197) could not be obtained pure. Thus, the mode of substitution of an oxodimethylenemethane ligand bears a strong influence on the behaviour of the complex in solution, with trans-disubstituted complexes being fluxional at room temperature, and cis-diequatorial substituted complexes being rigid.

![Figure 26](image)

The values of \(^1J(\text{PtP})\) in the \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectrum of the cis- and trans-diphenyl substituted oxodimethylenemethane complexes (187) and (197) are 3152 and 2993 Hz respectively, these values being characteristic for triphenylphosphine ligands trans to an oxodimethylenemethane moiety.\(^\text{61,64,73}\)

5.5 I.R. SPECTRA OF OXODIMETHYLENEETHANE COMPLEXES

The i.r. spectra of the oxodimethylenemethane complexes (186)-(191) show the typically low values of \(\nu_{\text{C}=\text{O}}\) found in these systems,\(^\text{61-64,72,73}\) the values for the platinum and palladium complexes lying in the ranges 1599-1609 cm\(^{-1}\) and 1593-1594 cm\(^{-1}\) respectively. The lowering of the carbonyl bond order may be attributed to a contribution to the bonding from the \(\eta^3\)-allylic representation (49). The values of \(\nu_{\text{C}=\text{O}}\) are consider-
ably lower than those of both 1,3-diphenyl acetone (1720 cm$^{-1}$)\textsuperscript{199} and cyclobutanones (ca. 1780 cm$^{-1}$)\textsuperscript{129} indicating that the contribution from (49) to the bonding in the oxodimethylenemethane complexes is considerable.

The value of $\nu_{C=O}$ is dependent on the metal and the ligand, as has been observed in other oxodimethylenemethane complexes of platinum,\textsuperscript{61,63,64,68,72,73} palladium,\textsuperscript{62,63,65,67} iridium,\textsuperscript{71-73} and osmium.\textsuperscript{72,73} A correlation between the fold angle and the value of $\nu_{C=O}$ for the oxodimethylenemethane ligand has been observed in trans-disubstituted oxodimethylenemethane complexes of platinum and palladium.\textsuperscript{61-64} In the complexes (186)-(191), on changing the metal from platinum to palladium, there is an increase in allylic character (49), with a concomitant decrease in $\nu_{C=O}$. Similarly, values of $\nu_{C=O}$ decrease on increasing the trans influence of the ancillary ligands of the platinum complexes (186)-(188) from COD to AsPh$_3$ to PPh$_3$.

5.6 CONCLUSION

The preparation of diphenyl substituted oxodimethylenemethane complexes of platinum and palladium may be achieved via the 1,3-dianion of 1,3-diphenyl acetone (104). A single crystal X-ray diffraction study establishes the presence of a diequatorially substituted $\eta^3$-oxodimethylenemethane ligand which suggests an allylic contribution to the bonding of the ligand to the metal centre. The carbon-oxygen bond of the oxodimethylenemethane fragment is tipped out of the C-C-C plane towards the metal, this being a consequence of the allylic type of bonding.

In the synthesis of the cis-diequatorially substituted oxodimethylenemethane complex (187) the initially isolated product was always con-
taminated with the trans-isomer (197). $^1$H n.m.r. studies indicate that these cis and trans isomers are respectively static and fluxional in solution at room temperature.

In summary, the 1,3-dianions of dibenzyl sulphone (102) and dibenzyl ketone (104) are reagents for the synthesis of metallathietane-3,3-dioxide and $\eta^3$-oxodimethylene methane complexes respectively. Since the syntheses of these complexes represent a general reaction in organo-metallic chemistry, the use of these, and other 1,3-dianionic reagents may find application in the synthesis of other new and interesting metallacyclic complexes.

5.7 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. The $^{13}$C-$^1$H n.m.r. data for the aromatic region between 6140 and 125 p.p.m. are omitted. 1,2-Bis(diphenylphosphino)ethane was used as supplied from Fluka. The compounds cis-[PtCl$_2$(AsPh$_3$)$_2$],$^{135}$ cis-[PtCl$_2$(PPh$_3$)$_2$],$^{136}$ [PtCl$_2$(COD)],$^{99}$ trans-[PdCl$_2$(PPh$_3$)$_2$],$^{138}$ trans-[PdCl$_2$(NCPh)$_2$],$^{142}$ and cis-[PtCl(CH$_2$COCH$_2$Cl)(PPh$_3$)$_2$]$^{63}$ were prepared as described in the literature.

The dianion K$_2$[PhCHC(O)CHPh](104) was prepared in liquid ammonia solution as described in the literature.$^{102}$ The ammonia was allowed to boil away, and the residual red solid dissolved in THF to give a solution of ca. 0.2 mol. dm$^{-3}$, which 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.
Preparation of oxodimethylenemethane complexes using K₂[PhCHC(O)CHPh] (104); general method

One equivalent of a THF solution of K₂[PhCHC(O)CHPh] (104), prepared as above, was added to stirred suspension or solution of cis-[PtCl₂L₂] (L = AsPh₃, PPh₃; L₂ = COD) or trans-[PdCl₂L₂] (L = PPh₃ or PE₃) in THF (ca. 40 cm³) at -78°C. The mixture was stirred for 10 min. at -78°C, allowed to warm to room temperature and stirred for 14 h to give a clear yellow-brown to brown solution. Evaporation to dryness under reduced pressure gave an oil which was extracted into toluene (ca. 30 cm³), and filtered. The volume of the filtrate was reduced to ca. 2-3 cm³, and light petroleum (ca. 60 cm³) was added to precipitate out the complex as an off-white to yellowish-brown solid which was filtered off, dried, and examined by ³¹P-{¹H} and/or ¹H n.m.r. spectroscopy. Two recrystallisations from either toluene-light petroleum and/or dichloromethane-light petroleum afforded microcrystals of the pure oxodimethylenemethane complex.

(i) [Pt{n⁺-CHPhC(O)CHPh}₂(AsPh₃)] (186).PhMe. The compound cis-[PtCl₂-(AsPh₃)₂] (0.40 g, 0.46 mmol) gave a yellowish solid which, after two recrystallisations from toluene-light petroleum at -20°C afforded white microcrystals of (186).PhMe (0.21 g, 42%) (Found: C, 63.2; H, 4.7. C₅₁H₄₂As₂OPT. C₇H₈ requires C, 62.9; H, 4.6%), m.p. 210-212°C (decomp.); νC=O at 1602 cm⁻¹. N.m.r. spectra: ¹H (400 MHz), 67.28-6.57 (m, 4 H, Ph), 4.14 [s, 2H, Pt-CH, ²J(PtH) 100.3], and 2.35 p.p.m. (s, 3H, Me, PhMe); ¹³C-{¹H} (100 MHz), 6174.39 [s, CO, ²J(PtC) not discernible], 61.52 [s, Pt-CH, ¹J(PtC) 308.4], and 21.3 p.p.m. (s, Me, PhMe). X-ray quality crystals of (186).2CH₂Cl₂ were grown slowly from dichloromethane-light petroleum.
(ii) \([\text{Pt}(\eta^3-\text{CHPhC(O)CHPh})\text{(PPh)_2}] (187)\) and (197). The compound \(\text{cis-[PtCl}_2\text{(PPh}_2\text{)]}(0.40 \text{ g}, 0.506 \text{ mmol})\) gave a pale yellow solid (0.48 g, ca. 93%) from toluene-light petroleum, which was shown to be a mixture of (187) (ca. 80-90%) and (197) (10-20%, varying from reaction to reaction), by \(^{31}\text{P}-\{^1\text{H}\}\) and \(^1\text{H}\) n.m.r. spectroscopy. Two recrystallisations from toluene-light petroleum yielded white microcrystals of pure (187).PhMe (0.238 g, 46%).

\text{Cis-isomer (187).PhMe.} (\text{Found: C, 67.5; H, 5.0. C}_{51}\text{H}_{42}\text{OP}_{2}\text{Pt.C}_7\text{H}_8}\) requires C, 68.2; H, 4.9%), m.p. 210-212°C (decomp.); \(\nu_{\text{C}=\text{O}}\) at 1600s cm\(^{-1}\).

\text{N.m.r. spectra:} \(^1\text{H}\) (400 MHz), \(\delta 7.4-6.6\) (m, 45H, Ph), 4.01 [d, 2H, Pt-CH, \(^3\text{J(PH)}\) 10.3, \(^2\text{J(PtH)}\) 84.2], and 2.35 p.p.m. (s, 3H, Me, PhMe); \(^1\text{H}\) (300 MHz, \([^2\text{H}_8]\)-toluene, 80°C), oxodimethylenemethane spectral features identical to room temperature spectrum; \(^{13}\text{C}-\{^1\text{H}\}\) (75.5 MHz), \(\delta 173.2\) [t, CO, \(^3\text{J(PC)}\) 5.5, \(^2\text{J(PC)}\) 155], 67.07 [dd, second-order, Pt-CH, \(|^2\text{J(PC)}\text{trans} + ^3\text{J(PC)}\text{cis}| 57.8, \(^1\text{J(PC)}\) 242.4], and 20.2 p.p.m. (s, Me, PhMe);

\(^{31}\text{P}-\{^1\text{H}\}\) (162 MHz), \(\delta 21.50\) p.p.m. [s, \(^1\text{J(PtP)}\) 3152].

\text{Trans isomer (197): Selected n.m.r. spectroscopic data:} \(^1\text{H}\) (400 MHz), \(\delta 4.32\) p.p.m. [dd, second-order, Pt-CH, \(|^3\text{J(PH)}\text{trans} + ^3\text{J(PH)}\text{cis}| 4.5, \(^2\text{J(PtH)}\) 50.0]; \(^{31}\text{P}-\{^1\text{H}\}\) (162 MHz), \(\delta 20.33\) p.p.m. [s, \(^1\text{J(PtP)}\) 2993].

(iii) \([\text{Pt}[\eta^3-\text{CHPhC(O)CHPh}]\text{(COD)}]\) (188). The compound \([\text{PtCl}_2\text{(COD)}]\) (0.25 g, 0.67 mmol) gave a yellowish solid which was recrystallised firstly from toluene-light petroleum and then from dichloromethane-light petroleum to give white microcrystals of (188) (0.16 g, 47%) (Found: C, 53.6; H, 4.8. \(\text{C}_{23}\text{H}_{24}\text{OPt}\) requires C, 54.0; H, 4.7%), m.p. decomp. at 185-195°C to a black solid; \(\nu_{\text{C}=\text{O}}\) at 1609vs cm\(^{-1}\). \text{N.m.r. spectra:} \(^1\text{H}\) (300 MHz), \(\delta 7.58-7.08\) (m, 10H, Ph), 5.00 [m, 2H, CH=CH, COD, \(^1\text{J(PtH)}\) 56.1], 4.35 [m, 2H,
CH=CH, COD, J(PtH) 49.2], 3.99 [s, 2H, Pt-CH, \(^2 J(PtH)\) 104.4], 2.35-2.20 (m, 4H, CH\(_2\), COD), and 2.20-2.01 p.p.m. (m, 4H, CH\(_2\), COD); \(^{13}\)C-{\(^1\)H} (75.5 MHz), \(\delta\)178.36 [s, CO, \(^2 J(PtC)\) not discernible], 104.30 [s, C=C, COD, \(^1 J(PtC)\) 99.4], 98.34 [s, C=C, COD, \(^1 J(PtC)\) 78.0], 63.28 [s, Pt-CHPh, \(^1 J(PtC)\) 351.7], 30.27 (s, CH\(_2\), COD), and 29.45 p.p.m. (s, CH\(_2\), COD).

(iv) [Pd\(n^2\)-CHPhC(O)CHPh](PPh\(_3\))\(_2\)](189).0.5 CH\(_2\)Cl\(_2\). The compound trans-[PdCl\(_2\)(PPh\(_3\))\(_2\)] (0.38 g, 0.58 mmol) gave a brownish solid which was recrystallised from toluene-light petroleum and then dichloromethane-light petroleum to give pale yellow microcrystals of (189).0.5 CH\(_2\)Cl\(_2\) (0.28 g, 56%) (Found: C, 69.8; H, 5.0. C\(_{51}\)H\(_{42}\)OP\(_2\)Pd.0.5 CH\(_2\)Cl\(_2\) requires C, 70.2; H, 4.9%), m.p. 138-140°C (decomp.); \(\nu_{C=O}\) at 1594s cm\(^{-1}\). N.m.r. spectra: \(^1\)H (400 MHz), \(6\)7.71-6.52 (m, 40H, Ph), 5.22 (s, 1H, CH\(_2\)Cl\(_2\)), and 4.15 p.p.m. [d, 2H, Pd-CH, \(^3 J(PH)\) 9.45]; \(^{31}\)P-{\(^1\)H} (162 MHz), \(\delta\)29.65 p.p.m. (s).

(v) [Pd\(n^2\)-CHPhC(O)CHPh](PET\(_3\))\(_2\)](190). Triethylphospine (0.15 g, 1.26 mmol) was added to a stirred suspension of trans-[PdCl\(_2\)(NCPh)\(_2\)] (0.217 g, 0.566 mmol) in toluene (20 cm\(^3\)), and the mixture stirred for 1h. Evaporation to dryness under reduced pressure gave a pale yellow oil which was stirred with light petroleum (ca. 10 cm\(^3\)), to give a pale yellow solid. This solid, with K\(_2\)[PhCHC(O)CHPh] (104) gave a yellowish-brown solid which was recrystallised from toluene-light petroleum and then from dichloromethane-light petroleum to give pale yellow microcrystals of (190) (0.215 g, 69%) (Found: C, 58.8; H, 7.7. C\(_{27}\)H\(_{42}\)OP\(_2\)Pd requires C, 58.9; H, 7.7%), m.p. 162-164°C (decomp.); \(\nu_{C=O}\) at 1593s cm\(^{-1}\). N.m.r. spectra: \(^1\)H (400 MHz, \([\^2\text{H}_2]\)-dichloromethane), \(6\)7.27-7.14 (m, 10H, Ph), 3.87 [d, 2H, Pd-CH, \(^3 J(PH)\) 9.64], 1.40-1.11 (m, 12H, CH\(_2\), PET\(_3\)), and 1.02-0.94 p.p.m. (m, 18H, CH\(_3\), PET\(_3\)); \(^{31}\)P-{\(^1\)H} (162 MHz, \([\^2\text{H}_2]\)-dichloromethane),
\( \delta 15.62 \text{ p.p.m. (s)}. \)

**Reaction of (188) with dppe**

A solution of (188) (0.053 g, 0.10 mmol) and dppe (0.090 g, 0.23 mmol) in dichloromethane (20 cm\(^3\)) was stirred for 1 h. Evaporation to dryness under reduced pressure afforded a white solid which was recrystallised from dichloromethane-diethyl ether, and dried in vacuo to give white microcrystals of (191).\( \text{CH}_2\text{Cl}_2 \) (0.065 g, 71\%) (Found: C, 57.0; H, 4.6. \( \text{C}_{41}\text{H}_{36}\text{OP}_{2}\text{Pt}\text{CH}_2\text{Cl}_2 \) requires C, 56.9; H, 4.3\%), m.p. 236-239°C (decomp.); \( \nu_{\text{C=O}} \) at 1599 s cm\(^{-1}\). N.m.r. spectra: \( ^1\text{H} \) (300 MHz), \( \delta 7.64-6.72 \) (m, 30H, Ph), 5.32 (s, 2H, \( \text{CH}_2\text{Cl}_2 \)), 3.99 [d, 2H, Pt-CH, \(^3\text{J}(\text{PtH}) \) 11.1, \(^2\text{J}(\text{PtH}) \) 85], and 2.38-1.94 p.p.m. (m, 4H, \( \text{CH}_2 \), dppe).

**Reaction of (188) with triphenylphosphine**

A solution of (188) (0.10 g, 0.196 mmol) and triphenylphosphine (0.105 g, 0.40 mmol) in dichloromethane (20 cm\(^3\)) was stirred for 1 h. Evaporation to dryness under reduced pressure afforded a white solid which was washed with light petroleum (5 cm\(^3\)) and identified as (187) from its \( ^1\text{H} \) and \(^3\text{P}-[\text{\( ^1\text{H} \)}] \) n.m.r. spectra.

**Preparation of \([\text{Pt}(\eta^3-\text{CH}_2\text{C}(\text{O})\text{CH}_2)](\text{PPh}_3)_2\) (72)**

To a sodium amalgam prepared from 2 cm\(^3\) mercury and 0.2 g sodium was added a solution of the complex cis-[PtCl(\( \text{CH}_2\text{COCH}_2\text{Cl} \))(PPh\(_3\))\(_2\)] (0.19 g, 0.225 mmol) in THF (30 cm\(^3\)). The mixture was swirled for 15 min., whereupon the colourless solution turned deep yellow. The solution was decanted from the amalgam, filtered, and evaporated to dryness under reduced pressure to afford a brownish oil. Dissolution of the oil in dichloromethane (2 cm\(^3\)) followed by addition of light petroleum (50 cm\(^3\)) gave a pale yellow microcrystalline solid which was identified as the
title complex (72) (0.152 g, 87%) by comparison of its $^1$H and $^{31}$P-$^1$H n.m.r. spectra with those of an authentic sample.\textsuperscript{72,73}
REFERENCES


