

**THE SYNTHESIS AND REACTIVITY OF FOUR-MEMBERED
PLATINACYCLES CONTAINING S AND/OR N BONDED LIGANDS**

A thesis submitted

by

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for the Degree of

Doctor of Philosophy

in the

Faculty of Science



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For My Parents

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ABSTRACT

Chapter 1 reviews the literature concerning transition metal η^3 -oxodimethylenemethane- (metallacyclobutan-3-one), metallathietane-3-oxide, metallathietane-3,3-dioxide and ureylene complexes. The review also briefly discusses the use of the oxodimethylenemethane metal fragment in organic synthesis.

The preparation and characterisation of platinathiazetidone-3-imine complexes $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}\text{L}_2]$ are described in Chapter 2. X-ray crystallographic studies on two of these derivatives ($\text{L} = \text{PPh}_3$ or PMePh_2) revealed the near-planarity of the four-membered ring. Both triphenylphosphine ligands in $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ are easily displaced by more basic phosphines or a chelating phosphine, and one is displaced by t-butyl isocyanide to give a monosubstituted derivative. The complex reacts with carbon monoxide to give a ring expansion product. Attempted ring expansions with small cumulenes were unsuccessful. Treatment of $[\text{Rh}(\text{Cl})(\text{CO})(\text{dppm})_2]$ with the dianion of N,N'-diphenylthiourea led to formation of the "A"-frame complex $[\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2]$.

Chapter 3 describes the synthesis and characterisation of platinathiadiazetidone-3,3-dioxide complexes of the type $[\text{Pt}\{\text{NRS}(\text{O})_2\text{NR}\}\text{L}_2]$ ($\text{R} = \text{H}$ or Ph). X-ray crystallographic studies on two of the derivatives ($\text{R} = \text{H}$, $\text{L} = \text{PMePh}_2$; $\text{R} = \text{Ph}$, $\text{L}_2 = \text{COD}$) showed the four-membered rings to be entirely flat, the molecules possessing a two-fold rotation axis about the platinum-sulphur vector. Efforts to insert small cumulene molecules into the N-H bonds of $[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ are described. Treatment of this complex with phenylacetylene gave *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMePh}_2)_2]$, whereas with dimethyl acetylenedicarboxylate the complex $[\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ was obtained, formally derived from insertion of the acetylene into a platinum-nitrogen bond. An X-ray crystallographic study revealed that the six-membered ring in this complex adopted a "pseudo-boat" conformation. Reaction of $[\text{PtCl}_2(\text{COD})]$ with sulphamide and excess silver(I) oxide in refluxing dichloromethane, followed by treatment of the filtrate from this reaction with an excess of t-butyl isocyanide afforded a complex which was formulated as $[\text{Pt}\{\text{C}(=\text{NBu}^t)\text{NHS}(\text{O})_2\text{NHC}(=\text{NBu}^t)\}(\text{CNBu}^t)_2]$. One phosphine ligand in $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PPh}_3)_2]$ can be replaced by t-butyl isocyanide to give a monosubstituted complex.

The final Chapter briefly describes attempts to synthesise further Pt(II) complexes from *cis*- $[\text{PtCl}_2\text{L}_2]$ and ligands possessing "activated" protons. The interaction of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with some p-tosylhydrazones in the presence of silver(I) oxide is investigated, and liquid ammonia as a synthetic reagent was also used in some of these reactions instead of silver(I) oxide. The complexes *cis*- $[\text{Pt}\{\text{NHS}(\text{O})_2\text{C}_6\text{H}_4\text{-p-R}\}_2\text{L}_2]$ ($\text{R} = \text{H}$ or Me) are obtained on reaction of *cis*- $[\text{PtCl}_2\text{L}_2]$ with the appropriate sulphonamide and an excess of silver(I) oxide in dichloromethane. The reaction of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with urea and silver(I) oxide in dichloromethane, or with urea in liquid ammonia, was investigated.

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 1986 and December 1989, under the supervision of Dr. R. D. W. Kemmitt.

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

Signed:*Mark Richard Moore*.....

Date:*12/06/91*.....

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Finally, I would like to thank my parents, without whose undying support and encouragement over the past years this thesis would not have been possible.

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ABBREVIATIONS AND SYMBOLS

General and Physical:

Å	- Angström unit
asym	- Asymmetric
br	- Broad
°C	- Centigrade
δ	- Chemical Shift
cm ³	- Cubic centimetres
d	- Doublet
g	- Gramme
Δ	- Heat
Hz	- Hertz
h	- Hour
i.r.	- Infrared
m	- Medium (i.r.); Multiplet (n.m.r.)
MHz	- Megahertz
m.p.	- Melting point
mmol	- Millimole
min	- Minute
n.m.r.	- Nuclear magnetic resonance
p.p.m.	- Parts per million
{ ¹ H}	- Proton decoupled
sh	- Shoulder
s	- Singlet (n.m.r.); Strong (i.r.)
sym	- Symmetric
t	- Triplet
vs	- Very strong
cm ⁻¹	- Wave number
w	- Weak

ABBREVIATIONS AND SYMBOLS (Continued)

Chemical:

Ac	- Acetyl
acac	- Anion of pentane-2,4-dione
bipy	- 2,2'-bipyridine
dppe	- 1,2-Bis-(diphenylphosphino)ethane
dpe	- Bis-(diphenylphosphino)ethylene
dppm	- Bis-(diphenylphosphino)methane
Bu ⁿ	- n-Butyl
Bu ^t	- t-Butyl
COD	- <u>cis, cis</u> -Cyclo-octa-1,5-diene
Cy	- Cyclohexyl
Cp	- Cyclopentadienyl anion
² H	- Deuterium
dba	- Dibenzylideneacetone
Et	- Ethyl
Me	- Methyl
mvk	- Methyl vinyl ketone
Cp*	- Pentamethylcyclopentadienyl anion
phenq	- Phenanthrene-9,10-quinone
phen	- 1,10-phenanthroline
Ph	- Phenyl
Pr ⁱ	- <u>iso</u> -Propyl
Pr ⁿ	- n-Propyl
THF	- Tetrahydrofuran
TMS	- Trimethylsilyl

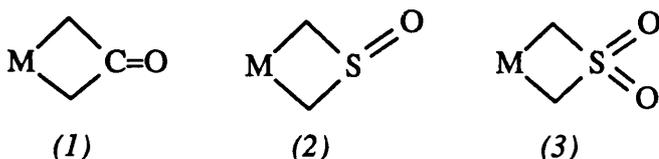
CHAPTER 1

**Oxodimethylenemethane, Metallathietane-3-oxide,
Metallathietane-3,3-dioxide and Ureylene
Complexes of Transition Metals**

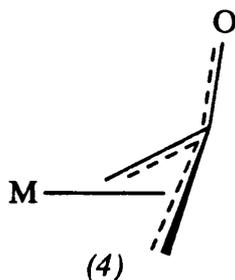
1.1 INTRODUCTION

There has been much recent interest in the development of four-membered ring systems containing transition metals. In particular, great attention has been paid to the synthesis and reactivity of metallacyclobutane complexes. Such complexes are now regarded as being key reaction intermediates in transition metal catalysed reactions, for example in the dimerisation and polymerisation of olefins and in olefin metathesis.¹

Metallacyclobutane complexes which possess a heteroatom, such as silicon,²⁻⁴ phosphorus,⁵ or oxygen⁶ in the 3-position of the ring have only recently received a measure of attention. The incorporation of a carbonyl group at the 3-position of a metallacyclobutane complex yields metallacyclobutan-3-ones (1), whereas when the heterogroup is a sulphoxide or sulphone moiety, metallathietane-3-oxide (2) or metallathietane-3,3-dioxide complexes (3) are obtained.

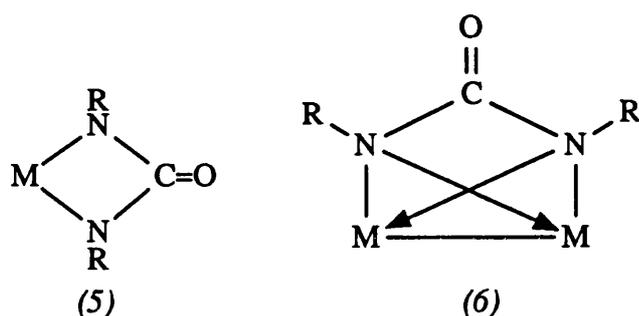


Metallacyclobutan-3-one complexes can also be regarded as "slipped" η^3 -oxodimethylenemethane species (4). The oxodimethylenemethane fragment has been used extensively as an intermediate in organic synthesis.



The use of organic isocyanates or azides in conjunction with certain transition metal complexes has been employed to give both monomeric (5) and dimeric (6) metal-ureylene derivatives.

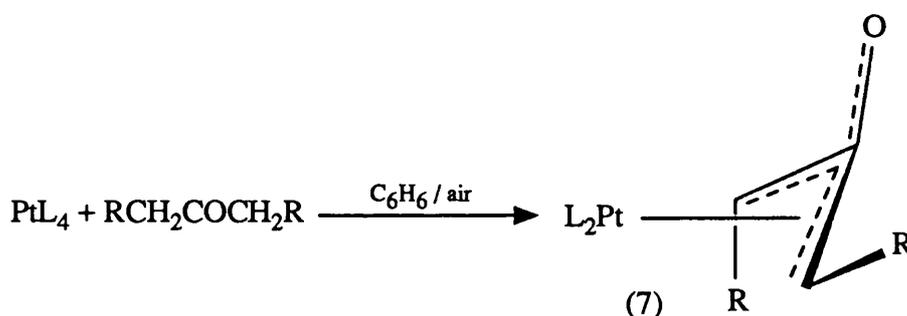
This first chapter summarises the literature concerning the synthesis and reactivity of oxodimethylenemethane, metallathietane-3-oxide, metallathietane-3,3-dioxide and metal-



ureylene complexes of transition metals. The rôle of oxodimethylenemethane metal complexes in organic synthesis is also briefly discussed.

1.2 SYNTHESIS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

The first examples of oxodimethylenemethane metal complexes (7, R = CO₂Me, L = PPh₃, PMePh₂, PMe₂Ph, or AsPh₃; R = CO₂Et, L = PPh₃ or AsPh₃) were prepared by the action of either the dimethyl or diethyl ester of 3-oxopentanedioic acid on a platinum(0) complex in benzene solution in the presence of air, Scheme 1.^{7,8}

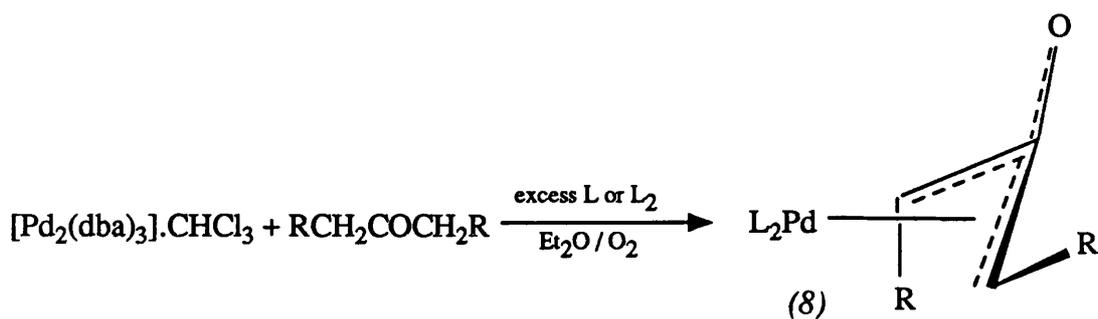


Scheme 1

The triphenylphosphine derivative (when R = CO₂Me) can also be synthesised from [Pt(trans-stilbene)(PPh₃)₂] under similar conditions.^{7,8}

Analogous palladium derivatives (8, R = CO₂Me, L = PPh₃, PMePh₂, PMe₂Ph, PEt₃, AsPh₃, or L₂ = bipy; R = CO₂Et, L = PPh₃, AsPh₃, or L₂ = bipy; R = CO₂Prⁿ, L₂ = bipy) can also be prepared via the reaction of [Pd₂(dba)₃].CHCl₃ with the appropriate donor ligands and the dialkyl esters of 3-oxopentanedioic acid in the presence of dioxygen, Scheme 2.⁹

The complexes (8, R = CO₂Me, R = CO₂Et, L = PPh₃ or AsPh₃) can also be prepared from reaction of [PdL₄] with the dialkyl ester of 3-oxopentanedioic acid in benzene in the presence

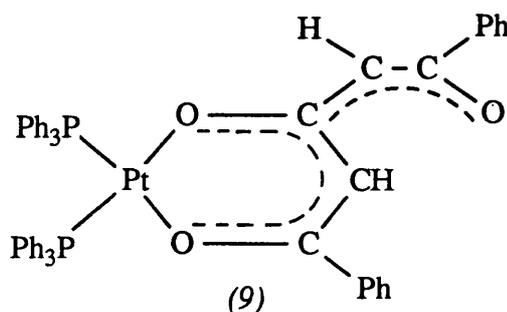


Scheme 2

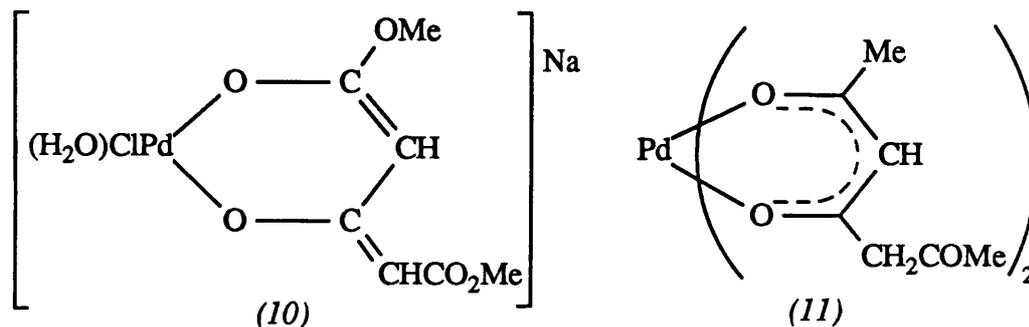
of dioxygen. The reaction of $[\text{Pd}(\text{OCO}_3)(\text{PPh}_3)_2]$ with the dimethyl or diethyl ester of 3-oxopentanedioic acid in ethanol gave the corresponding palladium oxodimethylenemethane complexes.⁹

Treatment of $[\text{Pd}(\text{O}_2)(\text{PPh}_3)_2]$ with the dimethyl ester of 3-oxopentanedioic acid in benzene under dioxygen gave the complex (8, R = CO₂Me, L = PPh₃).⁹ This result suggests that these reactions proceed via dioxygen complexes of the type $[\text{M}(\text{O}_2)\text{L}_2]$. In support of this contention is the observation that no reaction occurs between $[\text{Pt}(\text{PPh}_3)_4]$ and MeO₂CCH₂COCH₂CO₂Me in the absence of dioxygen.⁸

Reaction of the carbonate complexes $[\text{Pt}(\text{CO}_3)\text{L}_2]$ (where L = a phosphine or arsine donor ligand) with dialkyl esters of 3-oxopentanedioic acid in ethanol gave platinum oxodimethylenemethane complexes in good yield.⁸ Heptane-2,4,6-trione also reacts with the carbonate complexes $[\text{Pt}(\text{CO}_3)(\text{PPh}_3)_2]$ and $[\text{Pt}(\text{CO}_3)(\text{AsPh}_3)_2]$ to give the corresponding oxodimethylenemethane complexes (7, R = COMe, L = PPh₃ or AsPh₃).¹⁰ Interestingly, reaction of 1,5-diphenylpentane-1,3,5-trione with $[\text{Pt}(\text{CO}_3)(\text{PPh}_3)_2]$ did not give the expected oxodimethylenemethane complex, but a species containing a co-ordinated diene diolate group (9).¹⁰

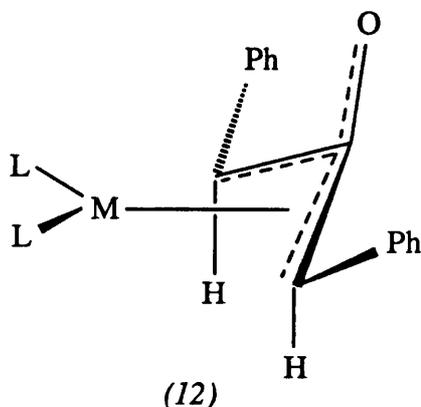


The reaction of $[\text{PdCl}_4]^{2-}$ with 3-oxopentanedioic acid dimethyl ester in water at room temperature gives (10), which, on treatment with triphenylphosphine yields (8, R = CO_2Me , L = PPh_3).¹¹ The reaction of PdCl_2 or $[\text{PdCl}_4]^{2-}$ with heptane-2,4,6-trione in water gives a palladium acetylacetonato complex (11) which can be converted into the complex (8, R = COMe , $\text{L}_2 = \text{bipy}$) by treatment with 2,2'-bipyridine.¹¹



Reaction of cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with dimethyl 3-oxopentanedioate or heptane-2,4,6-trione in refluxing 2-methoxyethanol containing triethylamine gave the complexes (7, R = CO_2Me or R = COMe , L = PPh_3).¹¹ The action of silver(I) oxide on cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ in refluxing dichloromethane with $\text{MeO}_2\text{CCH}_2\text{COCH}_2\text{CO}_2\text{Me}$, or refluxing an ethanolic suspension of cis- $[\text{Pt}(\text{OCOPh})_2(\text{PPh}_3)_2]$ with the same ester, gave (7, R = CO_2Me , L = PPh_3).⁸

Phenyl substituted derivatives (12) can be obtained from reaction of $\text{K}_2[\text{PhCHC}(\text{O})\text{CHPh}]$ with the complexes cis- $[\text{PtCl}_2\text{L}_2]$ (L = PPh_3 , AsPh_3 , or $\text{L}_2 = \text{COD}$) or trans- $[\text{PdCl}_2\text{L}_2]$ (L = PPh_3 or PEt_3) in a 1:1 ratio at low temperatures in tetrahydrofuran.¹²



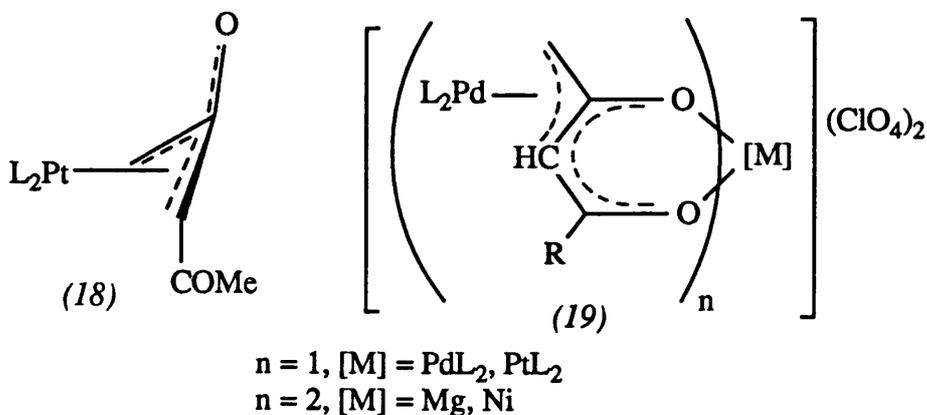
Interestingly, both phenyl groups occupy equatorial positions, in contrast to the normal

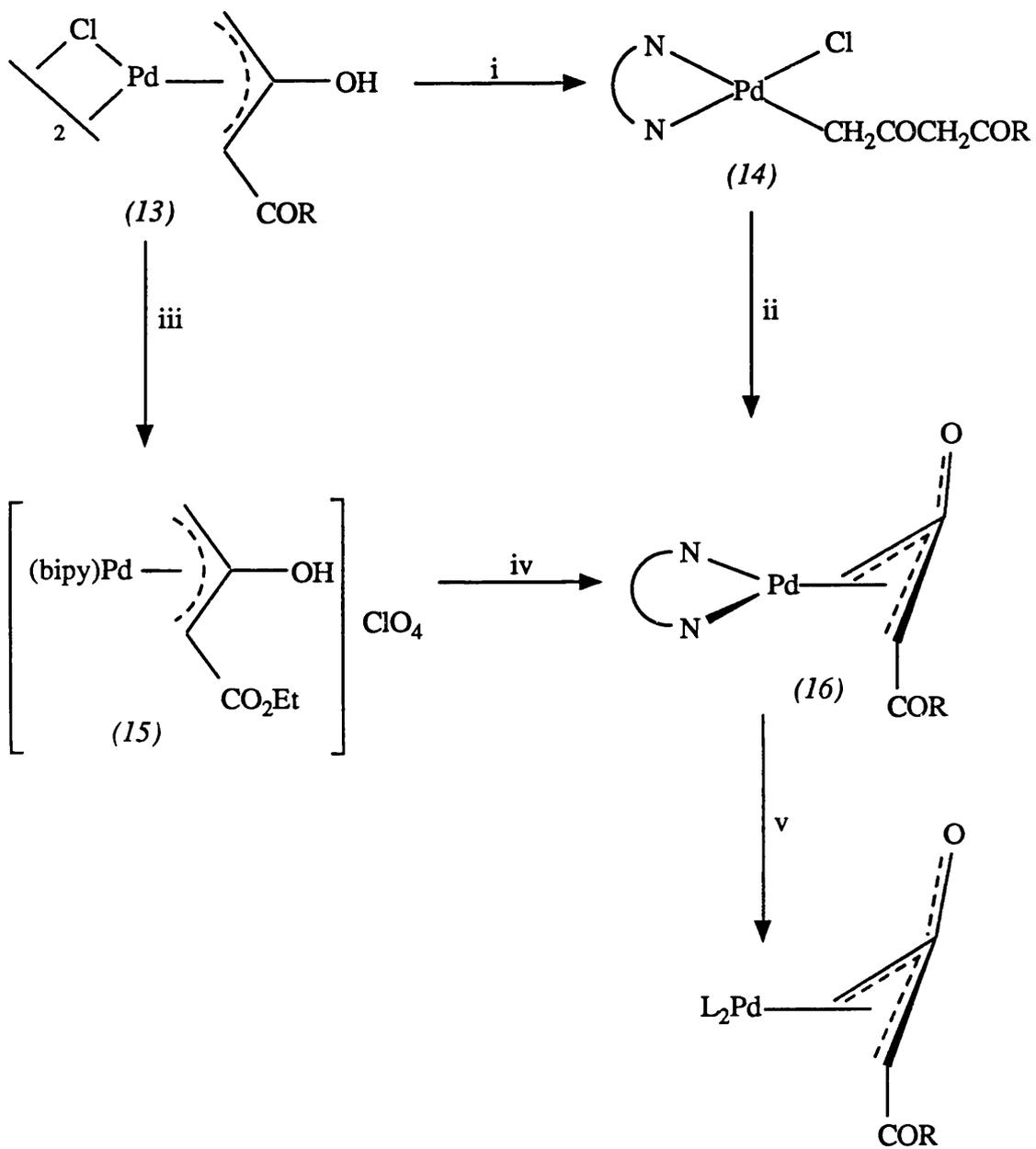
trans mode of substitution, as in (7) and (8). The complexes (12, M = Pt, L = PPh₃ or L₂ = dppe) may be prepared by replacement of the cyclo-octa-1,5-diene ligand in (12, M = Pt, L₂ = COD) by reaction with two mole equivalents of triphenylphosphine or one mole equivalent of 1,2-bis-(diphenylphosphino)ethane respectively.¹²

Monosubstituted complexes have also been prepared. Complexes such as (13, R = Me or OEt), on treatment with nitrogen donor ligands, such as 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine or 1,10-phenanthroline, undergo bridge-splitting reactions to afford complexes (14), which can be converted into (16) by treatment with thallium(I) acetylacetonate.¹³ The reaction of (13, R = OEt) with silver perchlorate, followed by treatment with 2,2'-bipyridine, gave complex (15), which afforded complex (16, R = OEt, $\overset{\curvearrowright}{\text{N}} \overset{\curvearrowright}{\text{N}} = 2,2'$ -bipyridine) on reaction with potassium acetylacetonate. The reaction of (16, R = Me or OEt, $\overset{\curvearrowright}{\text{N}} \overset{\curvearrowright}{\text{N}} = \text{bipy}$) with phosphines yields a variety of new oxodimethylenemethane complexes (17).^{14,15} All these reactions are summarised in Scheme 3.

[Pt(acac)₂], when treated with tri-*p*-chlorophenylphosphine, gave the complex (18, L = {(*p*-ClC₆H₄)₃P}).¹⁶ Interestingly, the reaction of [Pt(acac)₂] with triphenylphosphine and Al(OEt)Et₂ gave a complex, which, on recrystallisation from tetrahydrofuran, via elimination of ethane, yielded a product which may have been an oxodimethylenemethane species (18, L = PPh₃).¹⁷

The monosubstituted oxodimethylenemethane species may act as ligands towards other metal centres, such as in the complex (19).^{14,15}





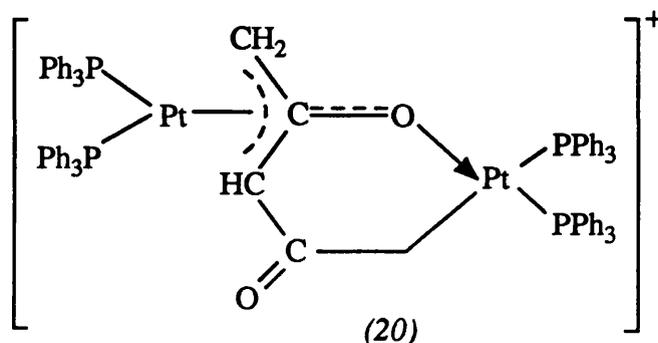
(17), R = Me, L₂ = dpe, dppe;
R = OEt, L = PPh₃, L₂ = dpe, dppe

i, bipy, Me₂bipy or phen
iii, AgClO₄, bipy iv, K(acac)

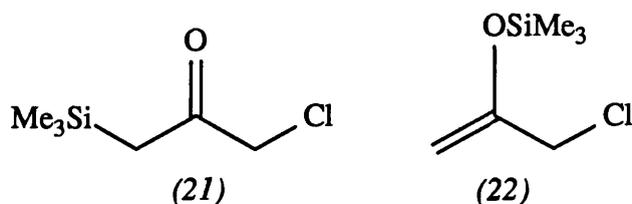
ii, Tl(acac)
v, phosphine

Scheme 3

More recently, it was reported that $[\text{Pt}(\text{acac})_2]$ and triphenylphosphine in hot methanol gave a complex $[\text{Pt}(\text{acac})(\text{PPh}_3)_2](\text{acac})$, and when the mixture was maintained at 60°C for more than four hours, a dinuclear species was obtained (20), with a small amount of (18, L = PPh_3) as a by-product.¹⁸ Complex (20) may be viewed as containing a bridging trianion of acetylacetonate, and can be isolated as either its acac^- or PF_6^- salts.



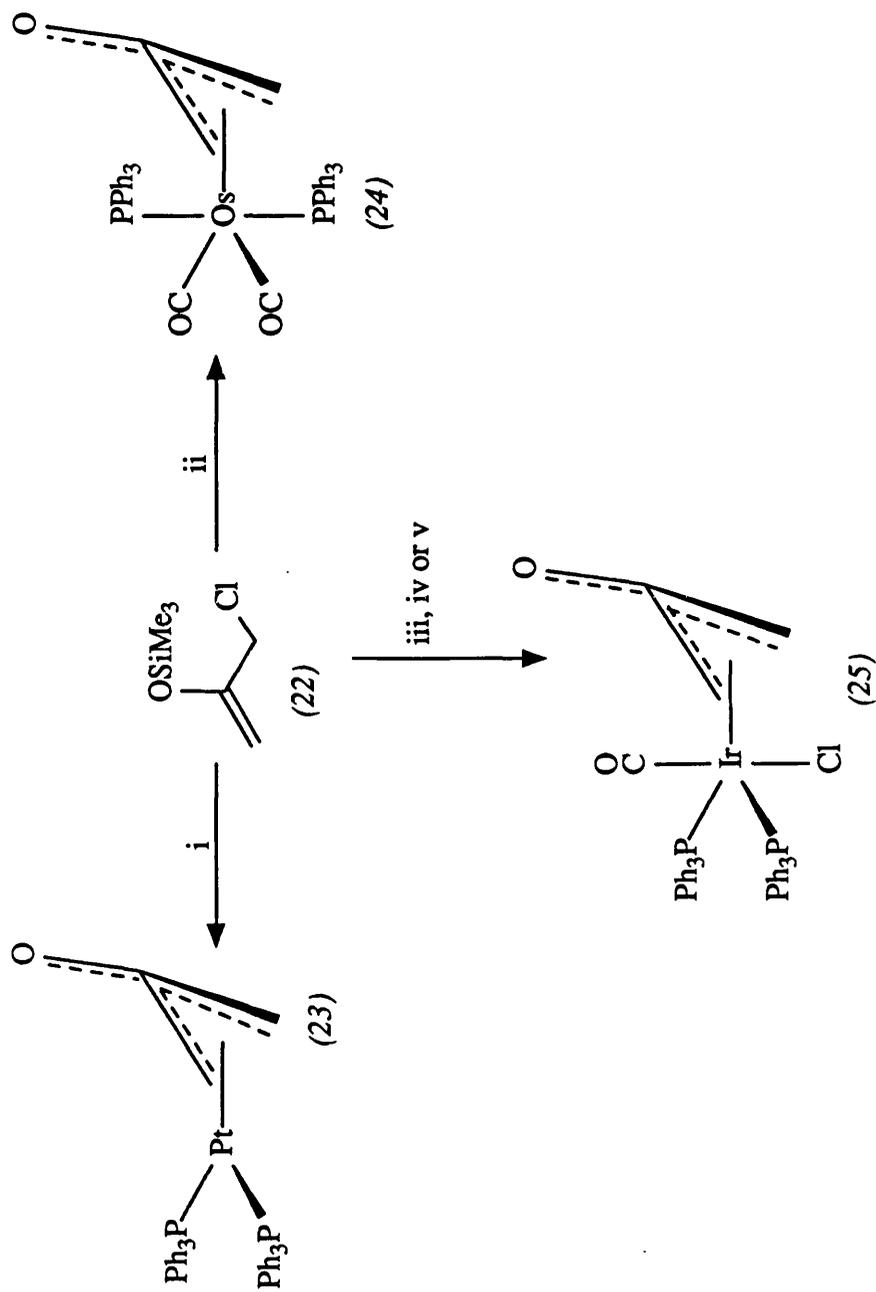
Unsubstituted oxodimethylenemethane complexes can also be synthesised. Reaction of $[\text{Pt}(\text{trans-stilbene})(\text{PPh}_3)_2]$ with an excess of 3-chloro-1-(trimethylsilyl)propan-2-one (21) gave the complex $[\text{Pt}\{\eta^3\text{-CH}_2\text{C}(\text{O})\text{CH}_2\}(\text{PPh}_3)_2]$ (23), together with 3-chloro-2-(trimethylsilyloxy)prop-1-ene (22), formed via a Broock rearrangement of (21).^{19,20}



Complex (23) can also be obtained via the action of an excess of sodium amalgam on $\text{cis-}[\text{PtCl}\{\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{Cl}\}(\text{PPh}_3)_2]$ in tetrahydrofuran.²⁰ The reaction of (22) with various metal complexes gave a range of oxodimethylenemethane complexes (23)-(25), as shown in Scheme 4.¹⁹

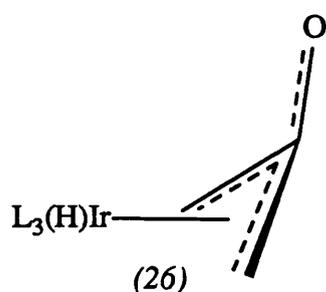
Complex (25) can also be synthesised via reaction of (21) with $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ and the isomerisation of $\text{Me}_3\text{SiCH}_2\text{COCH}_2\text{Cl}$ (21) to the silylenol ether (22) is also catalysed by $[\text{Pd}(\text{PPh}_3)_4]$.¹⁹

The complexes (26, L = PMe_3 or AsMe_3) can be produced by the treatment of $[\text{IrL}_4]\text{Cl}$ with the enolate salt of acetone.²¹

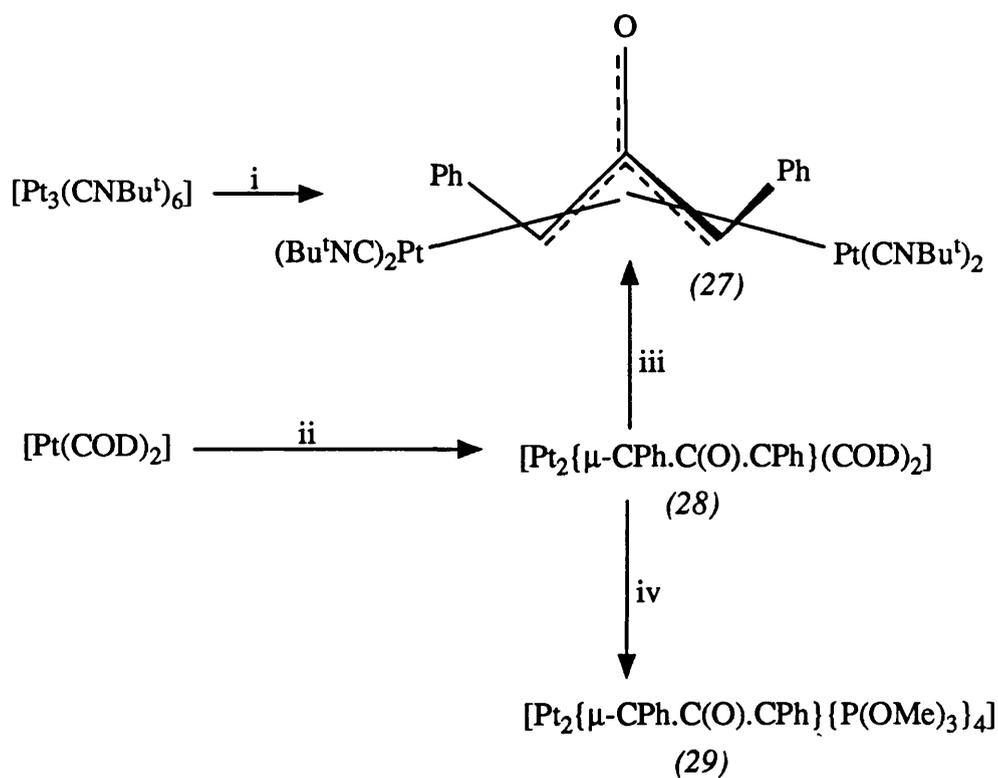


i, $[\text{Pt}(\text{trans-stilbene})(\text{PPh}_3)_2]$ ii, $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$
 iii, $\text{trans-}[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ iv, $[\text{IrH}(\text{CO})_2(\text{PPh}_3)_2]$ v, $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$

Scheme 4



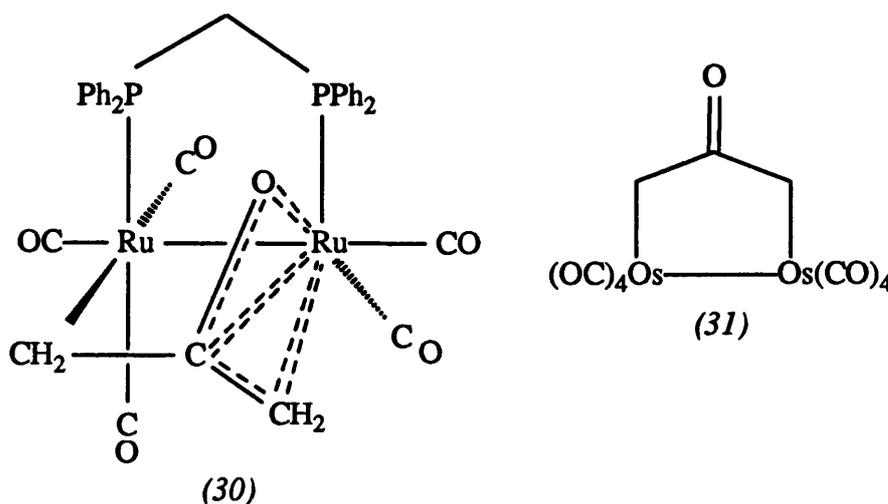
Interestingly, the reaction of $[\text{Pt}_3(\text{CNBu}^t)_6]$ with diphenylcyclopropenone gives a species which can be regarded as being a $\mu\text{-}\eta^3\text{:}\eta^3\text{'}$ -oxodimethylenemethane complex (27).²² A related complex (28) can be obtained via reaction of $[\text{Pt}(\text{COD})_2]$ with methylvinyl ketone, followed by addition of diphenylcyclopropenone.²² The initially formed species, $[\text{Pt}(\text{COD})(\text{mvk})_2]$ is suggested as being a source of "Pt(COD)". Replacement of the cycloocta-1,5-diene ligands in (28) by t-butyl isocyanide or trimethylphosphite gave (27) and (29) respectively. These reactions are summarised in Scheme 5.²²



i, diphenylcyclopropenone ii, mvk, diphenylcyclopropenone
 iii, t-butyl isocyanide iv, P(OMe)₃

Scheme 5

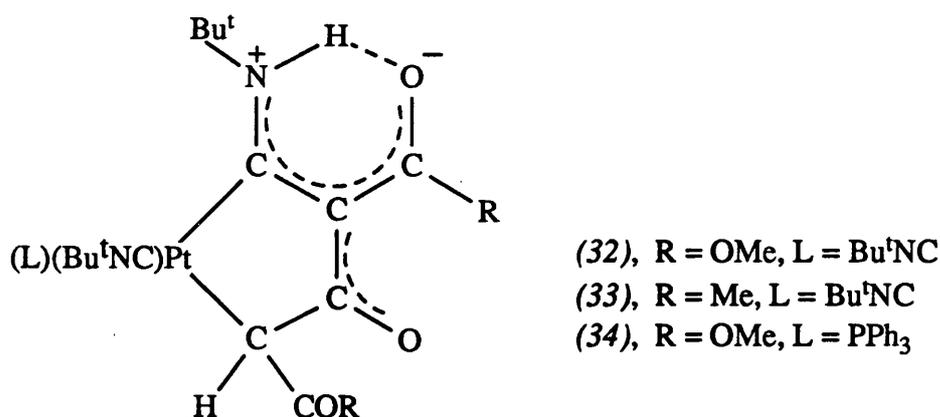
More recently, a diruthenium complex containing an oxodimethylenemethane ligand bonded in a η^4 -fashion has been reported (30), a crystallographic study confirming this co-ordination mode.²³ The dinuclear complex (31) can be synthesised from the treatment of $\text{Na}_2[\text{Os}_2(\text{CO})_8]$ with 1,3-dichloroacetone in tetrahydrofuran at 25°C.²⁴



1.3 REACTIONS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

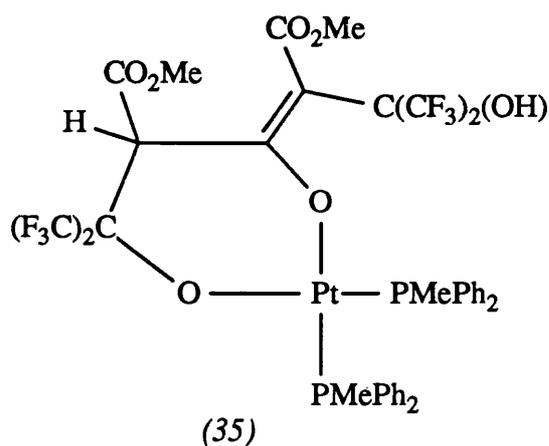
Ligand substitution reactions of oxodimethylenemethane metal complexes occur easily.²⁵ Triphenylarsine can be displaced from (7, R = CO₂Me, L = AsPh₃) and (8, R = CO₂Me, L = AsPh₃) with tertiary phosphines to afford the corresponding bis(phosphine) analogues. Treatment of the latter complex with 2,2'-bipyridine yields (8, R = CO₂Me, L₂ = bipy). When the complexes (7, R = CO₂Me, L = PPh₃ or AsPh₃) or (8, R = CO₂Me, L = PPh₃ or AsPh₃) are reacted with one mole equivalent of t-butyl isocyanide, a series of monosubstituted complexes are obtained. However, if complexes (7, R = CO₂Me, L = PPh₃ or AsPh₃) are treated with three mole equivalents of t-butyl isocyanide, then a zwitterionic complex (32) is formed which originates from insertion of a molecule of t-butyl isocyanide into a platinum-carbon bond, if the starting materials are regarded as metallacyclobutan-3-one complexes.

Complex (33) is prepared by a similar reaction with (7, R = COMe, L = AsPh₃). Treatment of complex (7, R = CO₂Me, L = PPh₃) with two mole equivalents of t-butyl



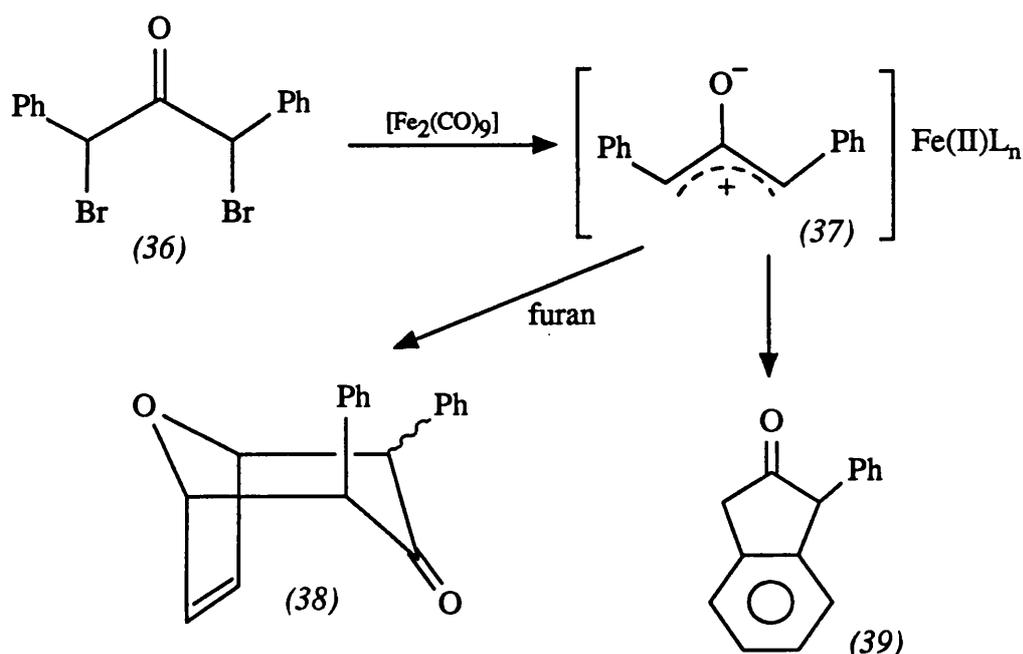
isocyanide, or $[\text{Pt}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{COCH}(\text{CO}_2\text{Me})\}(\text{CNBu}^t)(\text{PPh}_3)]$ with one mole equivalent of t-butyl isocyanide gave (34).

Reaction of (7, R = CO₂Me, L = PMePh₂) with hexafluoroacetone led to formation of (35).⁷



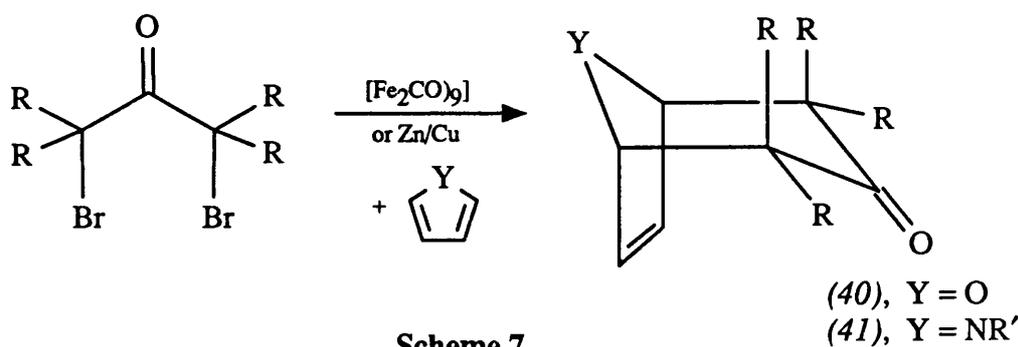
1.4 OXODIMETHYLENEMETHANE INTERMEDIATES IN ORGANIC SYNTHESIS

Non-isolated oxodimethylenemethane metal complexes have been extensively used in cycloaddition reactions with unsaturated molecules. For example, reaction of $[\text{Fe}_2(\text{CO})_9]$ with the α,α' -dibromoketone (36) generates an oxodimethylenemethane intermediate (37), which can react in the presence of furan to give (38) by a [3 + 4] cyclocoupling reaction.^{26,27} In the absence of a trapping agent, an intramolecular cycloaddition product is obtained (39), Scheme 6.^{26,27}



Scheme 6

The intermediacy of species such as (37) in the reduction of dibromoketones with $[\text{Fe}_2(\text{CO})_9]$ can be further supported, for example, by trapping with nucleophiles.^{26,27} Species similar to (37) can be obtained from α,α' -dibromoketones using an iron-graphite reagent.²⁸ The trapping of the intermediates, generated from treatment of α,α' -dibromoketones with $[\text{Fe}_2(\text{CO})_9]$ or a Zn/Cu couple, with furans, provides an efficient route to bridged ketonic systems (40), Scheme 7.²⁹⁻³¹



Scheme 7

Other reducing agents, such as Zn/Ag³² and Cu/NaI³³ have also been employed in similar cyclocoupling reactions of furans. An example of an intramolecular cycloaddition between an intermediate oxodimethylenemethane species and a furan moiety has been reported.³⁴

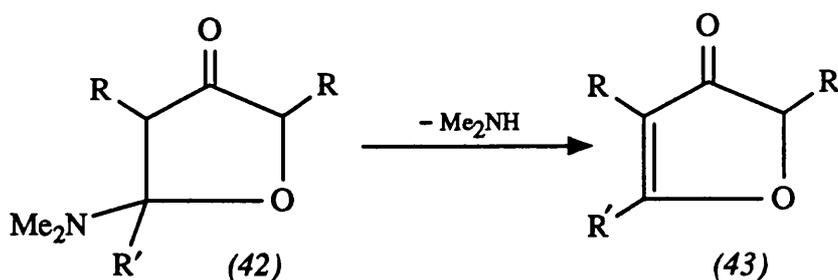
Attempts to obtain cycloadducts from thiophene led only to the formation of a substitution product.²⁹

Pyrrole derivatives possessing electron-withdrawing substituents on the nitrogen atom undergo [4 + 3] cycloadditions with α,α' -dibromoketones in the presence of $[\text{Fe}_2(\text{CO})_9]$ to give (41), Scheme 7.^{29,35} However, using the same reagents in conjunction with N-alkylated pyrroles gives ring substitution products.^{29,35} The use of a Cu/NaI reagent in acetonitrile alleviates this problem and cycloaddition products are obtained.³⁶

Aryl olefins react with oxodimethylenemethane fragments, generated from α,α' -dibromoketones and $[\text{Fe}_2(\text{CO})_9]$, to yield 3-arylcyclopentanones.³⁷⁻³⁹ 1,3-Dienes also combine with α,α' -dibromoketones in the presence of $[\text{Fe}_2(\text{CO})_9]$ to afford 4-cycloheptenones.²⁹ Increased yields are obtained when dieneirontricarbonyl complexes are employed instead of free dienes. Interestingly, reaction of η^1 -allyl(cyclopentadienyl)iron dicarbonyl with α,α' -dibromoketones and $[\text{Fe}_2(\text{CO})_9]$ gives substituted cyclohexanones after oxidative work-up.⁴⁰ 1,2-Dimethylenecyclohexanes react smoothly with oxodimethylenemethane intermediate species to afford further related products.⁴¹ Isoprene,⁴² isobutylene⁴³ and enamines^{40,44} have all been used as olefinic components in cycloaddition reactions with the oxodimethylenemethane metal species.

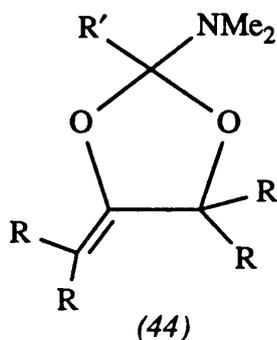
Cyclopentadiene undergoes [4 + 3] cycloaddition reactions with α,α' -dibromoketones in the presence of $[\text{Fe}_2(\text{CO})_9]$,^{29,42} a Zn/Cu couple,³¹ or Cu/NaI.⁴⁵ These reagents have been used more recently in the reaction of isodicyclopentadiene with dibromoketones.⁴⁶ The reactions of iron oxodimethylenemethane intermediates with a variety of cycloheptatriene systems have been studied.⁴⁷

Solvents can also engage in cycloaddition reactions. For example, treatment of α,α' -dibromoketones with N,N-dimethylated carboxamides in the presence of $[\text{Fe}_2(\text{CO})_9]$ gives species (42) which undergo elimination of dimethylamine to afford 3(2H)-furanones (43), Scheme 8.^{48,49}



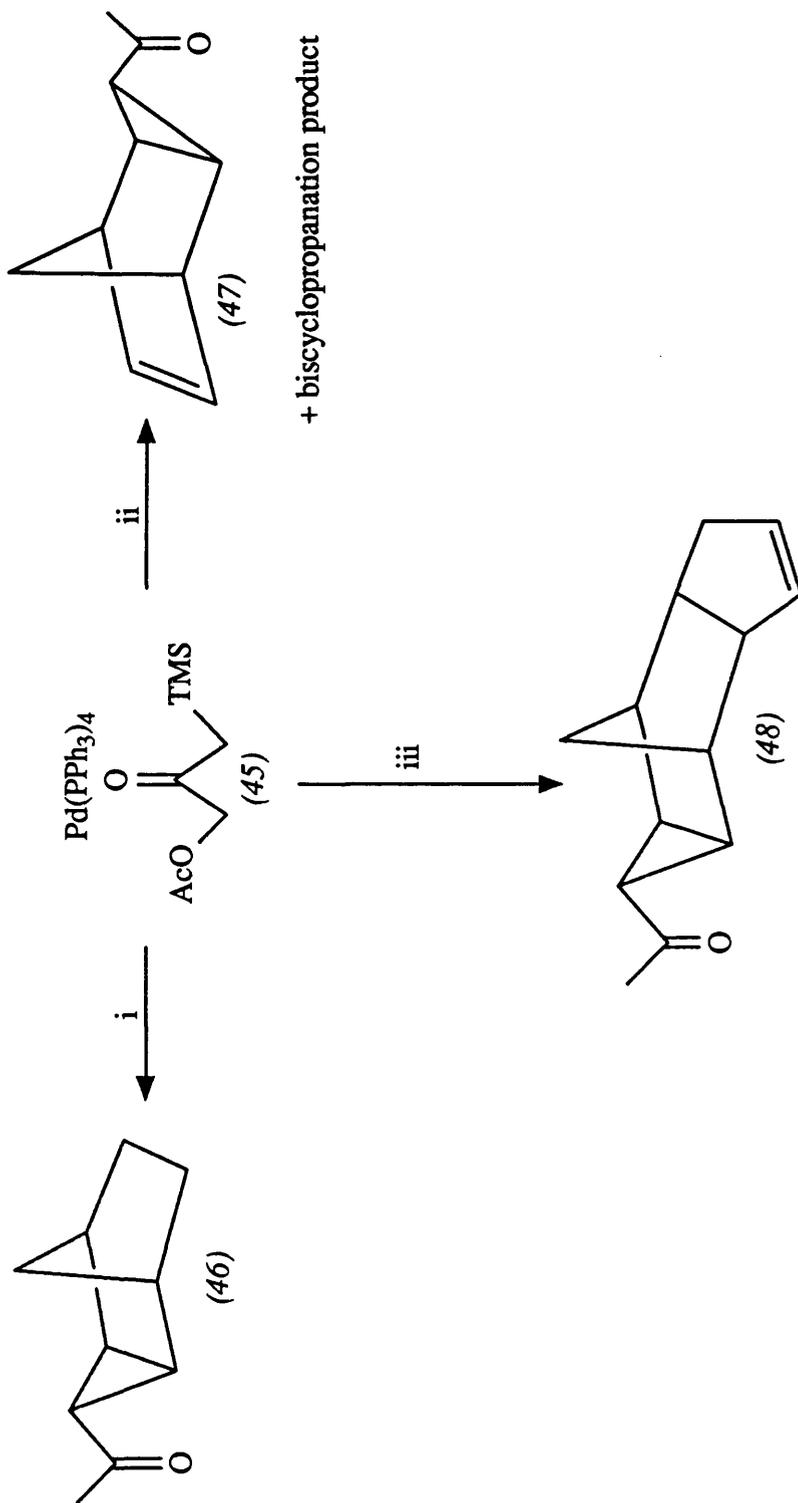
Scheme 8

In contrast, the Zn/Cu couple-mediated reduction of α,α' -dibromoketones in N,N-dimethylacetamide leads to formation of species (44).⁵⁰



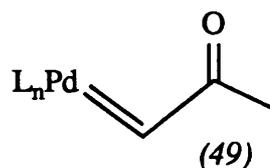
$\alpha,\alpha,\alpha',\alpha'$ -Tetrabromoacetone has also been employed in cycloaddition reactions.⁵¹ It should be noted that the above discussion is in no way an exhaustive study of cyclocoupling reactions involving oxodimethylenemethane metal intermediates, several extensive reviews having been published on the subject.^{52,53} The utility of many of the cycloaddition reactions described above in natural product synthesis has also been reviewed.⁵⁴

Recently, the palladium(0)-catalysed cyclopropanation of substrates containing strained double bonds with 1-acetoxy-3-(trimethylsilyl)-2-propanone (45) was studied. Norbornene, norbornadiene and dicyclopentadiene undergo such reactions to give (46), (47) and (48) respectively, Scheme 9.⁵⁵ Electron-deficient or simple alkenes did not react. These reactions could proceed via an oxodimethylenemethane palladium complex, or through an intermediate carbene species, such as (49), which could arise from rearrangement of the oxodimethylenemethane complex itself, or directly from (45).



i, norbornene ii, norbornadiene iii, dicyclopentadiene

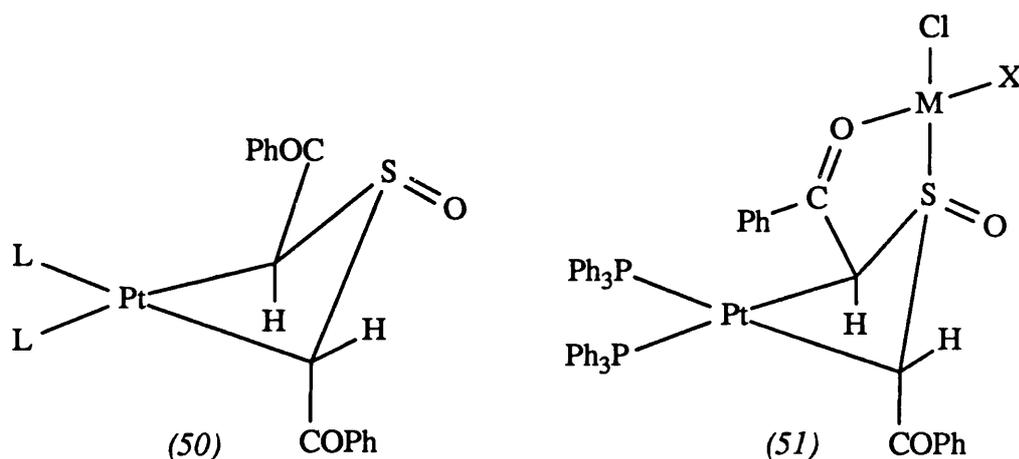
Scheme 9



1.5 SYNTHESIS AND REACTIVITY OF METALLATHIETANE-3-OXIDE AND METALLATHIETANE-3,3-DIOXIDE COMPLEXES

Related to the oxodimethylenemethane complexes described in Sections 1.2 and 1.3 are the metallathietane-3-oxide (2) and metallathietane-3,3-dioxide species (3).

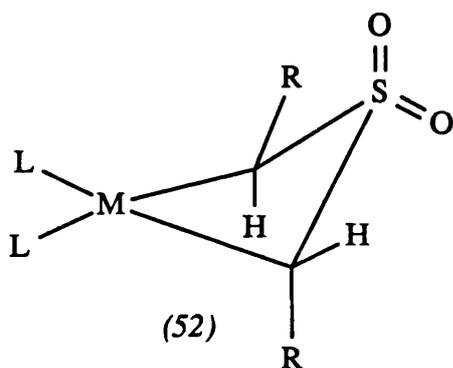
Platinathietane-3-oxide complexes (50) can be easily synthesised by refluxing a dichloromethane solution of cis-[PtCl₂L₂] (L = PPh₃, PMePh₂, or PMe₂Ph) with PhOCCH₂S(O)CH₂COPh in the presence of an excess of silver(I) oxide.⁵⁶



The oxygen atom in the sulphoxide group occupies an equatorial position. A novel complex (51, M = Rh, X = CO) can be obtained via reaction of (50, L = PPh₃) with [Rh₂Cl₂(CO)₄] in dichloromethane, the formation of this product clearly demonstrating the presence and ligand capacity of the lone pair possessed by the sulphur atom in the starting material. A similar compound (51, M = Pd, X = Cl) was obtained when (50, L = PPh₃) was treated with either one mole equivalent of trans-[PdCl₂(NCPPh)₂] or [PdCl₂(COD)] in dichloromethane.⁵⁷ Analogous complexes, where M = Pt, could not be synthesised.

Metallathietane-3,3-dioxide complexes (52, M = Pt or Pd, R = COPh, L = PPh₃, PMePh₂, PMe₂Ph, PMe₃, PEt₃, or PBuⁿ₃; M = Pt, R = COPh, L = P(OPh)₃) were obtained on reaction of either cis-[PtCl₂L₂] or trans-[PdCl₂L₂] with one mole equivalent of

PhOCCH₂S(O)₂CH₂COPh in the presence of an excess of silver(I) oxide in refluxing dichloromethane.^{56,58} The corresponding methyl ester derivatives (52, M = Pt or Pd, R = CO₂Me, L = PPh₃) were obtained from similar treatment of cis-[PtCl₂(PPh₃)₂] or trans-[PdCl₂(PPh₃)₂] with MeO₂CCH₂S(O)₂CH₂CO₂Me and silver(I) oxide.^{56,58}

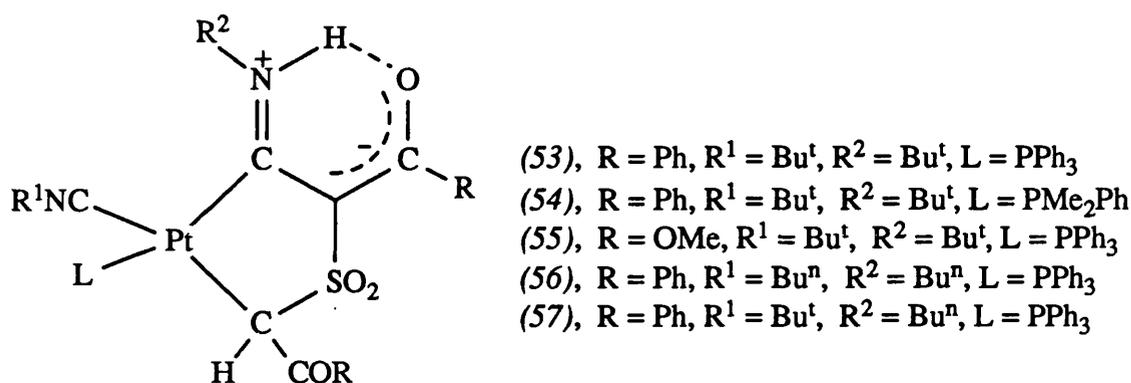


Phenyl substituted derivatives (52, M = Pt, R = Ph, L = PPh₃, AsPh₃, or SEt₂; M = Pd, R = Ph, L = PPh₃, PMe₃, or PEt₃; M = Ni, R = Ph, L = PMe₃ or L₂ = dppe) were synthesised by treatment of either cis- or trans-[MCl₂L₂] complexes with Li₂[PhCHS(O)₂CHPh] in tetrahydrofuran in a 1:1 ratio at low temperature.^{59,60} Reaction of the potassium salt of the 1,3-dianion of PhCH₂S(O)₂CH₂Ph with cis-[PtCl₂(AsPh₃)₂] or trans-[PdCl₂(PPh₃)₂] under identical conditions gave (52, M = Pt, R = Ph, L = AsPh₃) and (52, M = Pd, R = Ph, L = PPh₃) respectively.^{59,60} The complexes (52, M = Pd, R = Ph, L = PMe₃) and (52, M = Pd, R = Ph, L = PEt₃) were also prepared, respectively, via treatment of [Pd(O₂CMe)₂(PMe₃)₂], or [PdCl₂(NCPPh)₂] and triethylphosphine, with Li₂[PhCHS(O)₂CHPh].⁶⁰

Further platinathietane-3,3-dioxide complexes can be obtained via simple ligand displacement reactions. Thus, for example, treatment of (52, M = Pt, R = CPh, L = PPh₃) with one mole equivalent of either t-butyl or n-butyl isocyanide yielded the corresponding monosubstituted complexes, as did reaction of (52, M = Pd, R = CPh, L = PEt₃) with one mole equivalent of t-butyl isocyanide.⁶¹ The diethyl sulphide ligands in (52, M = Pt, R = Ph, L = SEt₂) can be readily displaced by methyldiphenylphosphine, trimethyl phosphite, triphenyl phosphite or bis(diphenylphosphino)methane to give new substituted derivatives.^{57,60} The replacement of one diethyl sulphide ligand in (52, M = Pt, R = Ph, L =

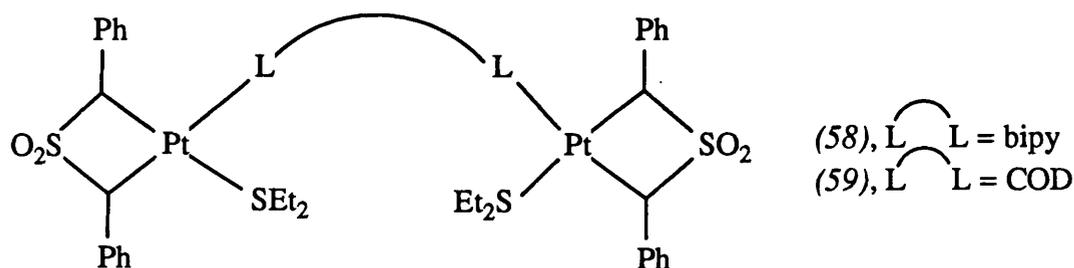
SEt₂) was accomplished by reaction with carbon monoxide at room temperature for 1 hour.^{59,60} Simple bis(isocyanide) complexes were obtained by reaction of (52, M = Pt, R = Ph, L = AsPh₃) with an excess of either t-butyl or n-butyl isocyanide in refluxing dichloromethane. No products derived from insertion of an isocyanide moiety into a platinum-carbon bond were observed.⁶⁰

However, ring insertion reactions did take place when (52, M = Pt, R = COPh, L = PPh₃ or PMe₂Ph; R = CO₂Me, L = PPh₃) were treated separately with an excess of either t-butyl or n-butyl isocyanide, to afford zwitterionic products (53)-(56).⁶¹



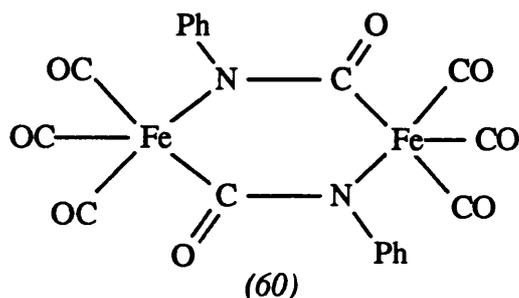
Interestingly, the complex (57) can be obtained either by reaction of one mole equivalent of t-butyl isocyanide with $[\text{Pt}\{\overline{\text{CH}(\text{COPh})\text{S}(\text{O})_2\text{CH}(\text{COPh})}\}(\text{CNBu}^n)(\text{PPh}_3)]$ or one mole equivalent of n-butyl isocyanide with $[\text{Pt}\{\overline{\text{CH}(\text{COPh})\text{S}(\text{O})_2\text{CH}(\text{COPh})}\}(\text{CNBu}^t)(\text{PPh}_3)]$ in refluxing dichloromethane.⁶¹

Binuclear complexes (58) and (59) were obtained via reaction of (52, M = Pt, R = Ph, L = SEt₂) with either an excess of 2,2'-bipyridine or cyclo-octa-1,5-diene in refluxing dichloromethane.^{59,60}

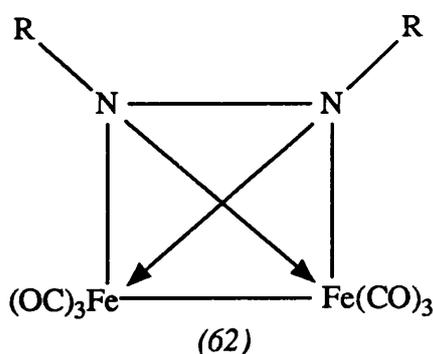
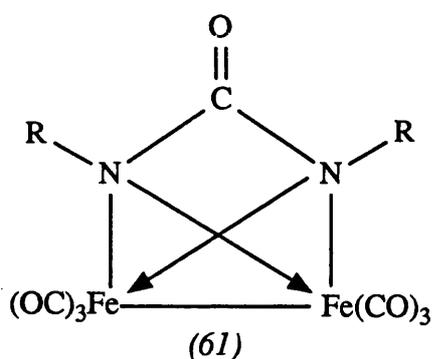


1.6 TRANSITION METAL-UREYLENE COMPLEXES

In 1964, Manuel described the reaction between $[\text{Fe}_3(\text{CO})_{12}]$ and phenyl isocyanate and formulated the major product as (60).⁶² The same product was isolated from a mixture of compounds obtained on reaction of $[\text{Fe}_3(\text{CO})_{12}]$ and phenyl azide. A product presumed to be analogous to (60) was isolated from reaction of $[\text{Fe}_3(\text{CO})_{12}]$ and n-butyl isocyanate.



Further investigations by other workers, including crystal structure studies, led to reformulation of the product (60) as being the ureylene-bridged species (61, R = Ph).⁶³⁻⁶⁵



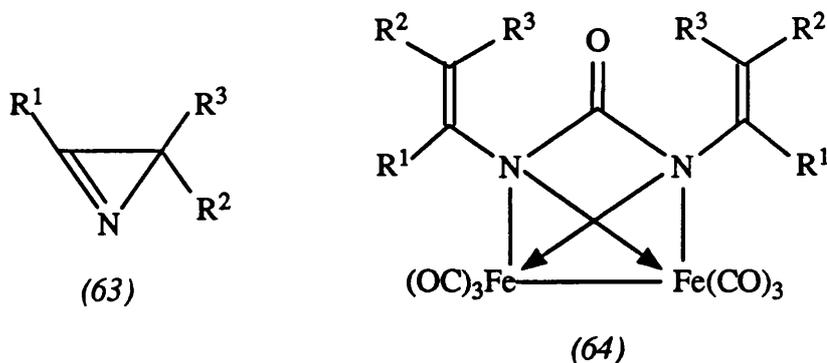
Reaction of $[\text{Fe}_2(\text{CO})_9]$ with phenyl azide in benzene solution at room temperature gave a mixture of compounds, one of which was (61, R = Ph).⁶⁶ The formation of this product in the reaction was proposed to proceed via spontaneous rearrangement of the complex (62, R = Ph), also formed in the same reaction. Reaction of $[\text{Fe}_2(\text{CO})_9]$ with methyl azide or methyl isocyanate led to formation, usually with other products, of (61, R = Me). The crystal structure of (61, R = Me) has been reported.⁶⁷ This compound was also obtained as one of the minor products isolated from the reaction between $[\text{Fe}_2(\text{CO})_9]$ and nitromethane.⁶⁶ The use of organic nitro compounds and iron-carbonyl complexes to yield derivatives of the type (61) was extended further by several groups. Reaction of $[\text{Fe}_2(\text{CO})_9]$ with 1-nitropropane in

anhydrous benzene at room temperature afforded, amongst other products, complex (61, R = n-C₃H₇), while (61, R = Bu^t) was isolated as the major product from the reaction of [Fe₂(CO)₉] with 2-methyl-2-nitropropane.⁶⁸ The ethyl substituted derivative (61, R = Et) was obtained from reaction of [Fe₂(CO)₉] with ethyl isocyanate⁶³ or from reaction of [Fe₃(CO)₁₂] and 1-nitroethane.^{69,70} Interestingly, this same complex was obtained in trace amounts from interaction of [Fe(CO)₃(C₈H₁₄)₂] and trans-azoethane.⁷¹ The treatment of [Fe(CO)₃(N₄Me₂)] with [Fe(CO)₅] under photolysis conditions led to formation of (61, R = Me).⁷² Compounds of the type (61) have been implicated as intermediates in a variety of metal-carbonyl catalysed reactions, for example in the decomposition of aryl azides to substituted ureas in the presence of [Fe(CO)₅] and acetic acid.⁷³ The ruthenium-catalysed reduction of nitrobenzene to aniline and N,N'-diphenylurea has been suggested to proceed via the ruthenium analogues of (61) and (62) (R = Ph).⁷⁴

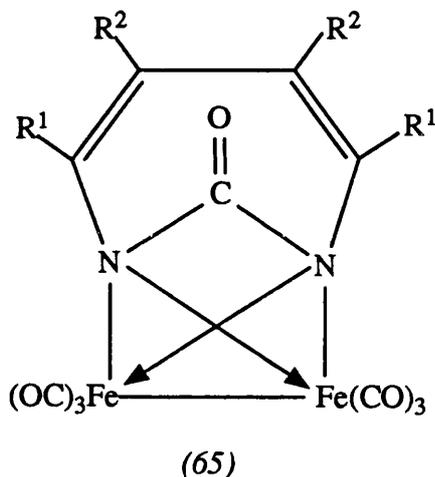
Reaction of [Fe₃(CO)₁₂] with p-methoxyphenyl azide gave the complex (61, R = p-C₆H₄OMe).⁷⁵ Treatment of (61, R = p-C₆H₄OMe or Ph) with a slight excess of either a phosphine or phosphite led to displacement of a terminal carbonyl group to afford monosubstituted derivatives.⁷⁵ Reaction of an excess of either methyl, phenyl or p-toluenesulphonyl azide, or p-toluenesulphonyl isocyanate, with [Fe(CO)₅] at 60-65°C or [Fe₂(CO)₉] at room temperature yields, amongst other products, an unidentified polymeric iron complex which may contain ureylene moieties, although this suggestion seems unlikely.⁷⁶

Azirines have been used to generate ureylene derivatives. Reaction of (63) with [Fe₂(CO)₉] in dry benzene led to the isolation of complexes (64, R¹ = Ph, R² = R³ = H; R¹ = p-MeC₆H₄, R² = R³ = H; R¹ = p-BrC₆H₄, R² = R³ = H; R¹ = Ph, R² = Me, R³ = H; R¹ = Ph, R² = Et, R³ = H; R¹ = Me, R² = CH{CH₃}₂, R³ = H, and R¹ = Ph, R² = R³ = Me), generally from a mixture of products.^{77,78}

The reaction of 1-phenyl-vinyl azide with [Fe₂(CO)₉] in benzene at 50°C for 4 hours, yielded, amongst other products (64, R¹ = Ph, R² = R³ = H).⁷⁷ Novel complexes of the type (65, R¹ = Ph, R² = H; R¹ = p-MeC₆H₄, R² = H, and R¹ = p-BrC₆H₄, R² = H)



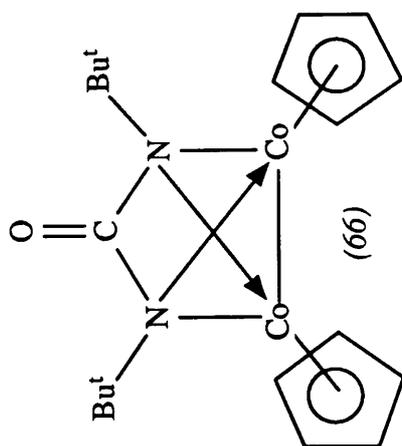
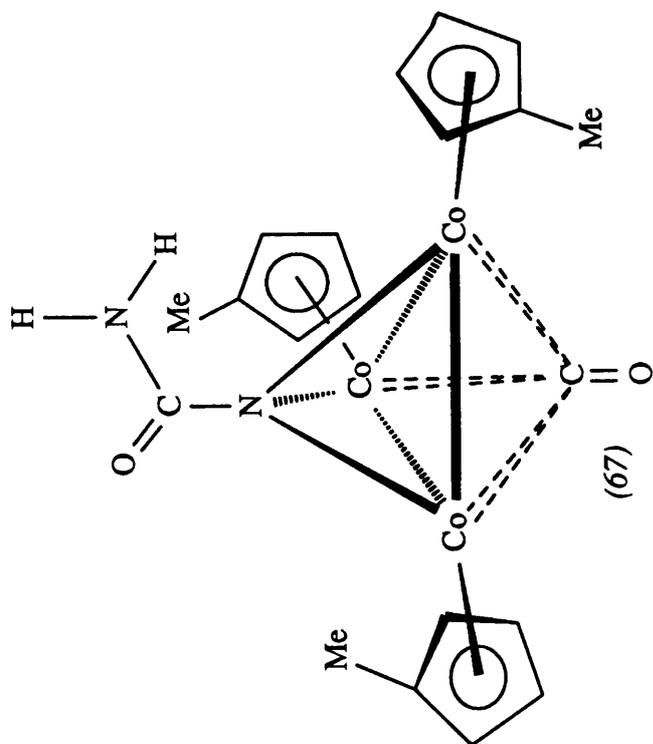
were also isolated from some reactions of the corresponding azirines (where $R^3 = H$) with $[\text{Fe}_2(\text{CO})_9]$.⁷⁷



The irradiation of 1-phenyl-vinyl azide with $[\text{Fe}(\text{CO})_5]$ in hexane or treatment of vinyl isocyanate with $[\text{Fe}_2(\text{CO})_9]$ at 40°C in benzene led to isolation of (64, $R^1 = \text{Ph}$, $R^2 = R^3 = \text{H}$) and (64, $R^1 = R^2 = R^3 = \text{H}$) respectively.⁷⁸ Complex (64, $R^1 = \text{Ph}$, $R^2 = R^3 = \text{Me}$) was also obtained as a side product from the treatment of 2,2-dimethyl-3-phenyl-2H-azirine (63, $R^1 = \text{Ph}$, $R^2 = R^3 = \text{Me}$) with $[\text{Fe}_2(\text{CO})_9]$ and dimethyl acetylenedicarboxylate.⁷⁸

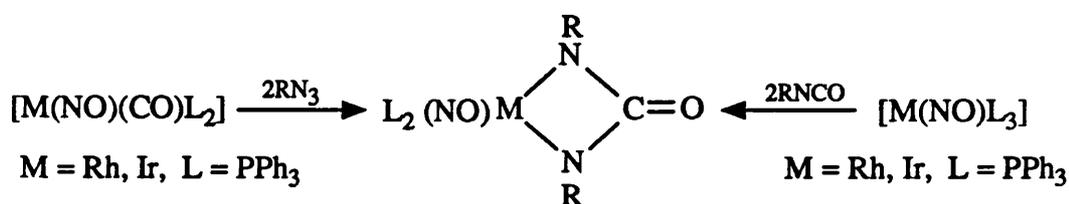
A bimetallic ureylene derivative of cobalt (66) was isolated from a mixture of products formed on treatment of $[\text{Co}(\text{Cp})(\text{CO})_2]$ with N-t-butyl-sulphurdiimide, its identity being confirmed by crystal structure investigations.⁷⁹⁻⁸¹

The formation of the formamidonitrene complex (67), as one of the products from the reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2]$ with Me_3SiN_3 , could proceed via initial formation of a

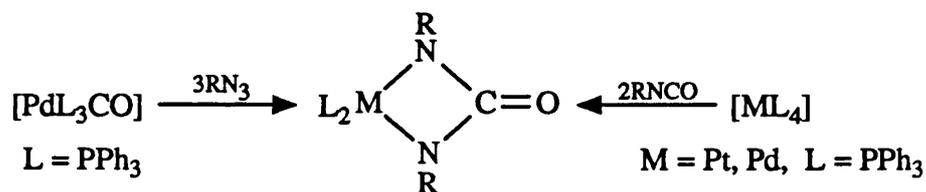


dimetallic ureylene-bridged species, $[\text{Co}_2\{\mu_2\text{-RNC(O)NR}\}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]$, similar to (66), where $\text{R} = \text{SiMe}_3$ or H .⁸²

Monometallic derivatives which contain chelating ureylene ligands are also known. The action in dry benzene of *p*-toluenesulphonyl azide on $[\text{M}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ or of *p*-toluenesulphonyl isocyanate on $[\text{M}(\text{NO})(\text{PPh}_3)_3]$ (where $\text{M} = \text{Rh}$ or Ir in both cases) gives complexes of the type (68), Scheme 10.⁸³ Platinum and palladium analogues (69) were derived via a similar methodology, Scheme 10.⁸³ The reactions involving the isocyanate species proceed with concomitant production of carbon monoxide, whereas those involving azides evolve nitrogen.



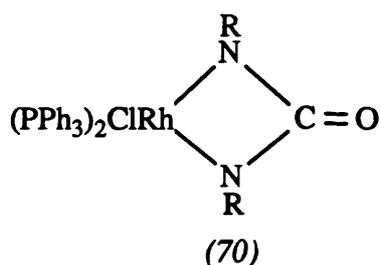
(68), $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$, $\text{L} = \text{PPh}_3$



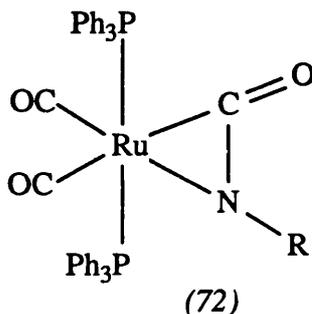
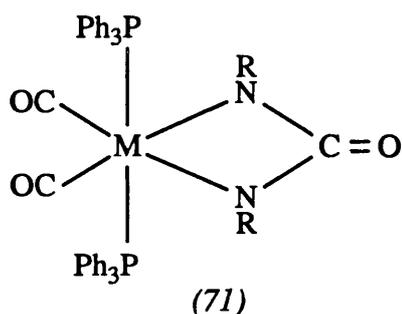
(69), $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$, $\text{L} = \text{PPh}_3$

Scheme 10

The complex $[\text{RhCl}(\text{PPh}_3)_3]$ also reacts in benzene with *p*-toluenesulphonyl isocyanate to afford (70, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$),⁸³ while trans- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ gives a corresponding ureylene derivative (70, $\text{R} = \text{P}(\text{O})\{\text{OPh}\}_2$) on treatment with diphenylphosphoryl azide in benzene for 14 days.⁸⁴ In the former reaction, trans- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ is also obtained as a by-product, whereas $[\text{RhCl}(\text{PPh}_3)_2]_2$ is the only species isolated as product if the latter reaction is carried out on a shorter time-scale.



Monomeric ureylene derivatives of ruthenium are also known, and are obtained from treatment of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ with either *p*-toluenesulphonyl azide or isocyanate at room temperature in benzene, leading to (71, $\text{M} = \text{Ru}$, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$),⁸⁵ or reaction of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ with *p*-tolyl isocyanate in refluxing toluene, yielding (71, $\text{M} = \text{Ru}$, $\text{R} = \text{p-MeC}_6\text{H}_4$).⁸⁶ The latter organic isocyanate can also be employed to prepare (71, $\text{M} = \text{Os}$, $\text{R} = \text{p-MeC}_6\text{H}_4$) from $[\text{OsH}_2(\text{CO})(\text{PPh}_3)_3]$.⁸⁶



(71, $\text{M} = \text{Ru}$, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$) can be formed from reaction of *p*-toluenesulphonyl azide in benzene with $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{RNC})]$ (72, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$), which is in turn synthesised on treatment of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ with *p*-toluenesulphonyl azide in benzene at 0-5°C.⁸⁵ Interestingly, the ruthenium cluster complex $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ affords (71, $\text{M} = \text{Ru}$, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$) on treatment with *p*-toluenesulphonyl azide.⁸⁵

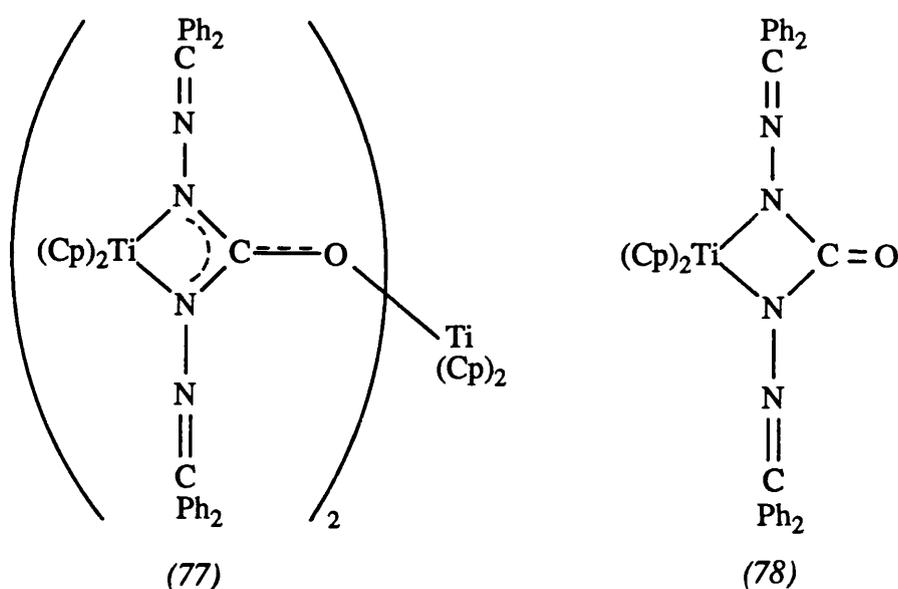
Oxidative addition of *N,N'*-ditoluene-*p*-sulphonylurea to $[\text{Pt}(\text{PPh}_3)_4]$, $[\text{RhCl}(\text{PPh}_3)_3]$ or $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ led to formation of (69, $\text{M} = \text{Pt}$, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$, $\text{L} = \text{PPh}_3$), (70, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$) or (71, $\text{M} = \text{Ru}$, $\text{R} = \text{p-MeC}_6\text{H}_4\text{SO}_2$) respectively.^{83,85}

A nickel-ureylene derivative (69, $\text{M} = \text{Ni}$, $\text{R} = \text{Ph}$, $\text{L} = \text{PEt}_3$) has been suggested as an intermediate in the reaction of phenyl isocyanate with $[\text{Ni}(\text{COD})_2]$ and triethylphosphine.⁸⁷

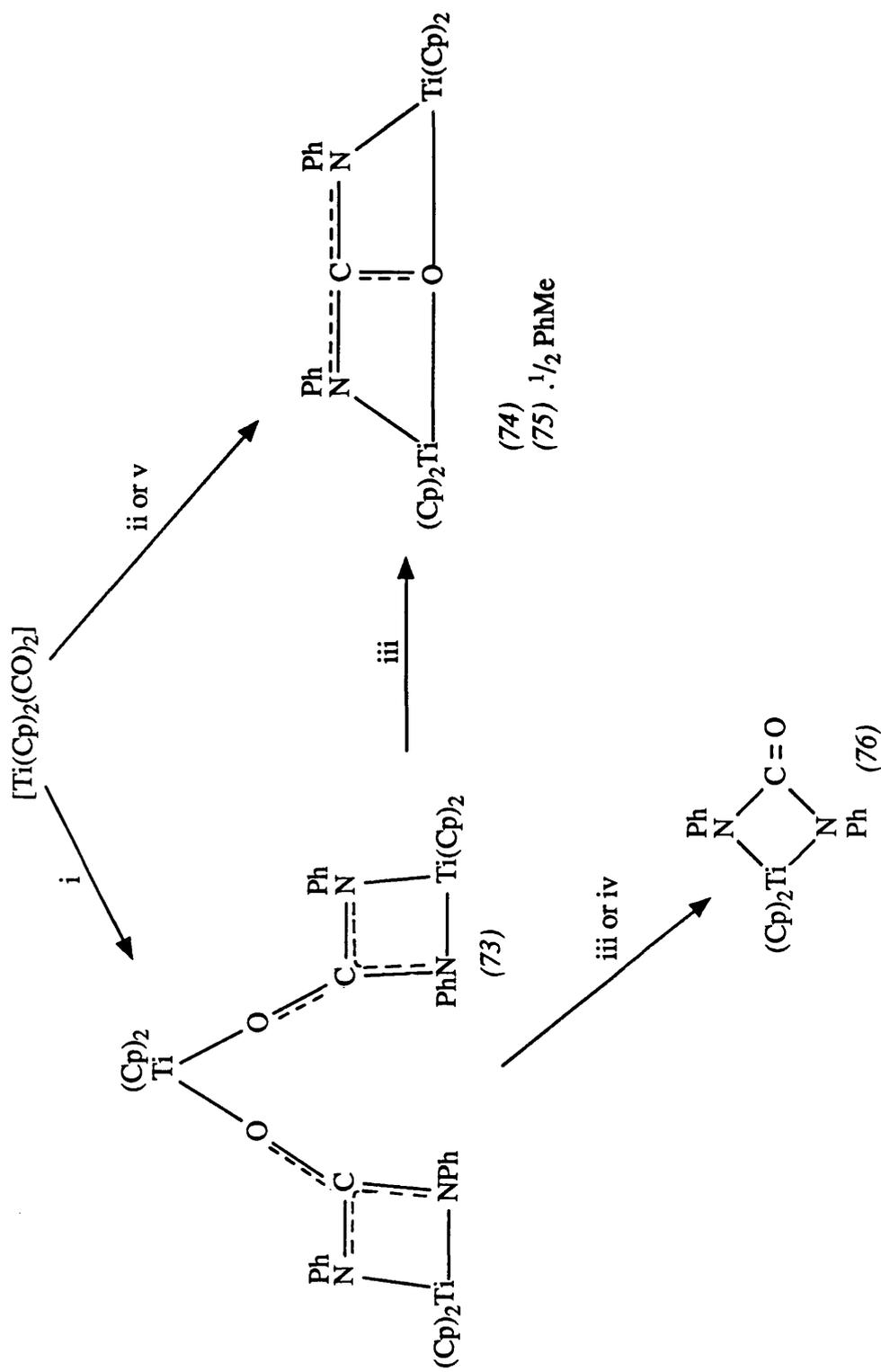
Early transition metal-ureylene complexes have been prepared. The room temperature

reaction of $[\text{Ti}(\text{Cp})_2(\text{CO})_2]$ with a large excess of phenyl isocyanate results in formation of (73), while on reaction of $[\text{Ti}(\text{Cp})_2(\text{CO})_2]$ with phenyl isocyanate in a 1:1 ratio at 60°C , the novel ditanium complex (74) is produced (75, 0.5 PhMe if the reaction is carried out in toluene).⁸⁸ A mononuclear complex (76) was prepared from (73) by heating in toluene, a process which also yielded (75), or by treatment with phenanthrene-9,10-quinone in tetrahydrofuran, leading to $[\text{Ti}(\text{Cp})_2(\text{phenq})]$ as a by-product. The crystal structure determinations of (73) and (75, 0.5 PhMe) revealed shortening of the C-N bonds and lengthening of the C-O bonds as compared to those in (61, R = Ph or Me), suggesting that the diphenylureylene moiety is acting as a delocalised ligand in both the titanium complexes. On treatment of $[\text{Ti}(\text{Cp})_2(\text{CO})_2]$ in tetrahydrofuran with (76) as a suspension in tetrahydrofuran, (74) is isolated. These reactions are summarised in Scheme 11.

A similar compound to (73) was obtained via reaction of $[\text{Ti}(\text{Cp})_2(\text{CO})_2]$ with diphenyldiazomethane in toluene.⁸⁹ The isolated compound (77) can be reacted with phenanthrene-9,10-quinone to give a compound (78), related to (76).



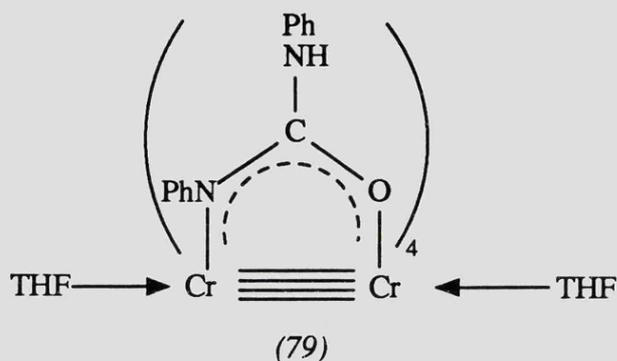
Treatment of μ -(η^1 : η^5 -cyclopentadienyl)-tris(η -cyclopentadienyl) ditanium (Ti-Ti) with at least a two-fold excess of urea led to formation of a number of products, one of which may have been a dimetallic ureylene derivative in which the ureylene moiety is bonded to the titanium atoms by both nitrogen and oxygen.⁹⁰



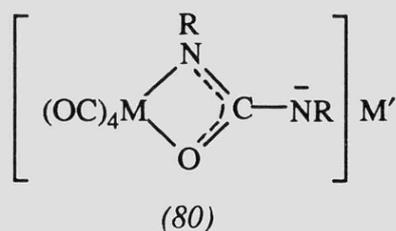
i, excess PhNCO **ii**, 1 eq. PhNCO, Δ **iii**, Δ , toluene **iv**, phenq **v**, (76), THF

Scheme 11

An interesting complex (79) has been synthesised by the reaction of the lithium salt of the monoanion of N,N'-diphenylurea with dichromium tetracetate in tetrahydrofuran. The organic ligands are attached to the two chromium atoms by one nitrogen atom and one oxygen atom.⁹¹



A series of compounds, formulated as ureadiide derivatives (80), have been obtained from the reaction of the potassium or lithium salts of the 1,3-dianions of substituted ureas with the complexes $[MBr(CO)_5]$ ($M = Mn$ or Re).⁹²



$M = Mn$ or Re , $M' = Li^+$, $R = Pr^i$ or $PhCH_2$
 $M = Mn$, $M' = Li^+$, $R = Et$, Cy , Ph or p -biphenyl
 $M = Mn$, $M' = K^+$, $R = Ph$ or p -biphenyl

Finally, the use of organic azides and isocyanates with transition metal complexes, leading to ureylene derivatives, has been reviewed.⁹³

This thesis describes the preparation and reactivity of more four-membered metallacycles, thus extending knowledge of such systems further.

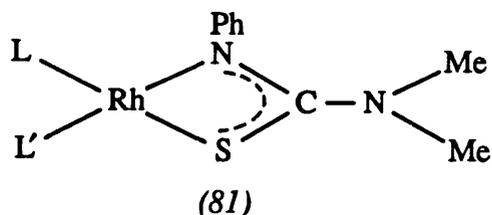
CHAPTER 2

Synthesis and Reactivity of Platinathiazetidine-3-imine Complexes

2.1 INTRODUCTION

There is much interest in the chemistry of ligands capable of bonding to metals via both nitrogen and sulphur atoms, and a vast number of metal complexes containing such ligands have been synthesised. However, simple thioureido complexes are not common in the literature, although the examples which are known span a variety of metals.

The reaction between $[\text{RhCl}(\text{PPh}_3)_3]$ and $\text{PhNHC}(\text{S})\text{NMe}_2$ in benzene is reported to proceed via oxidative addition of the N-H bond of the ligand to the metal centre to generate an intermediate hydrido-chlororhodium(III) complex, which on addition of triethylamine gives complex (81, $L = L' = \text{PPh}_3$).⁹⁴ Reaction of this species with carbon monoxide results in replacement of one phosphine ligand and formation of (81, $L = \text{CO}$, $L' = \text{PPh}_3$).

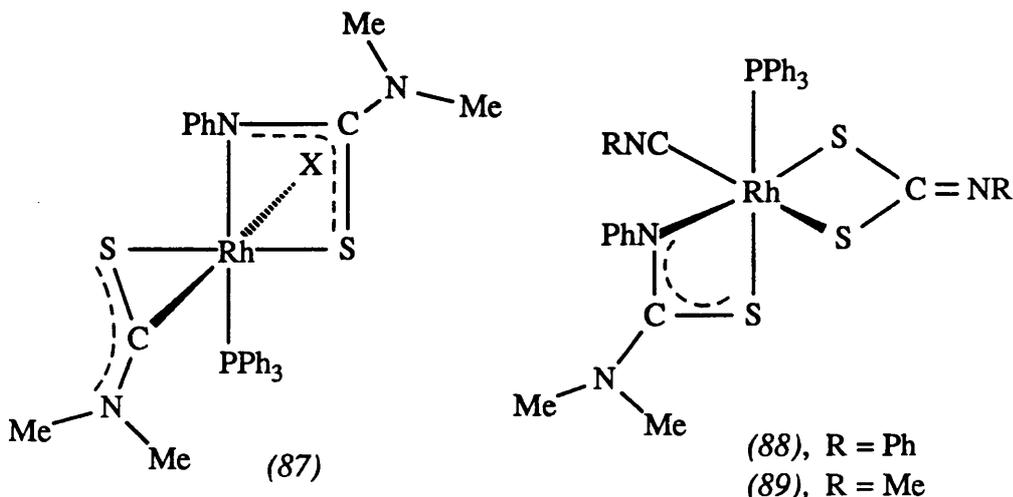


(81, $L = L' = \text{PPh}_3$) reacts with dioxygen to give $[\text{Rh}\{\overline{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}}\}(\text{O}_2)(\text{PPh}_3)_2]$ (82), and dihydrogen to yield $[\text{Rh}\{\overline{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}}\}\text{H}_2(\text{PPh}_3)_2]$ (83).⁹⁵ The thioureido ligands in both complexes bond to the metal as in (81). Interestingly, (81, $L = L' = \text{PPh}_3$) can be regenerated from (83) when the latter is treated with a mixture of benzene and cyclohexene saturated with ethylene. Complex (81, $L = L' = \text{CO}$) has also been reported, being obtainable from the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with $\text{PhNHC}(\text{S})\text{NMe}_2$ in toluene in the presence of triethylamine.⁹⁶

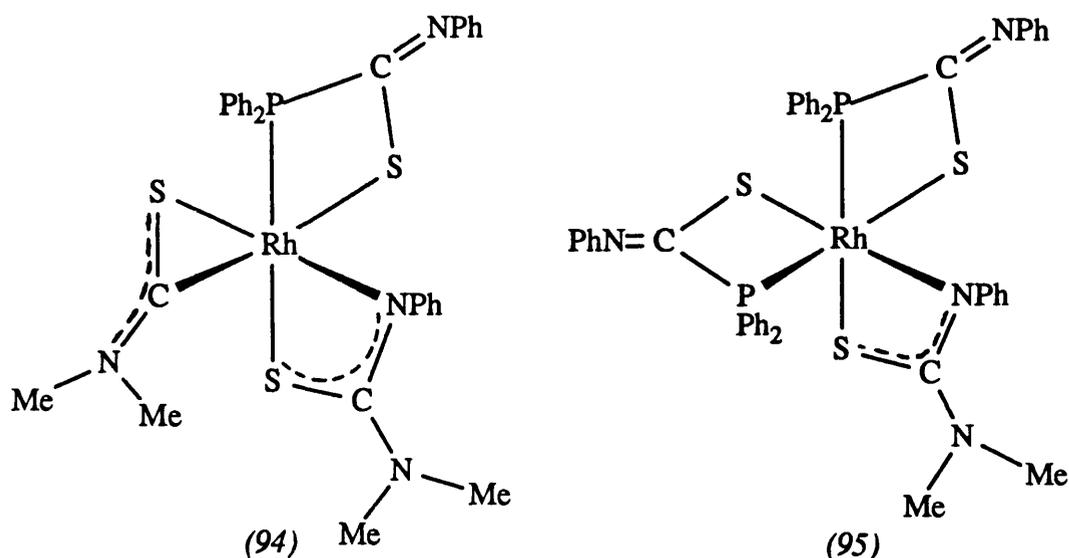
Treatment of (81, $L = L' = \text{PPh}_3$) with an excess of carbon disulphide in benzene or toluene yields a non-isolable species, formulated as $[\text{Rh}\{\overline{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}}\}(\eta^2\text{-CS}_2)(\text{PPh}_3)]$ (84).⁹⁷ Further reaction with carbon disulphide can occur, leading to $[\text{Rh}\{\overline{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}}\}(\text{CS})(\text{PPh}_3)]$ (85), together with a product tentatively assigned as $[\text{Rh}\{\overline{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}}\}(\text{CS}_3)(\text{PPh}_3)_2]$ (86). This latter stage of the reaction is proposed to proceed via a Rh(III)-thiocarbonyl-trithiocarbonato complex. However, if an excess of triphenylphosphine is added either to the initial reaction mixture or to the solution containing

(84), further reaction with carbon disulphide is prevented and (85) is formed directly, together with $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$, by sulphur abstraction from the $\eta^2\text{-CS}_2$ moiety in (84) by triphenylphosphine. In (85), the thioureido ligand is again bonded as in (81).

The complexes (87, X = Cl or Br) have been reported,⁹⁸ and an X-ray structure determination of the chlorine analogue has been completed.⁹⁹

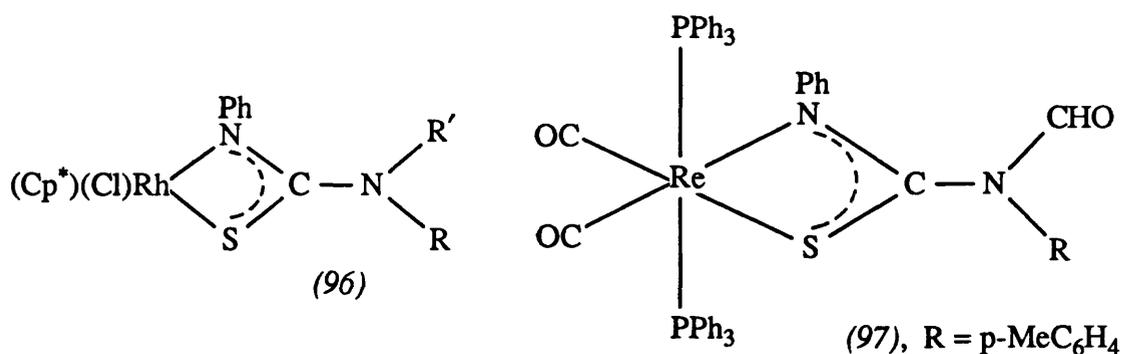


Species containing thioureido, together with dithiocarbonimidato ligands, have been synthesised (88,89).¹⁰⁰ A tris(thioureido) complex of rhodium, $[\text{Rh}\{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}\}_3]$ (90) can be prepared from the treatment of $[\text{RhCl}_3].3\text{H}_2\text{O}$ with $\text{PhNHC}(\text{S})\text{NMe}_2$ in methanol in the presence of triethylamine.¹⁰¹ Interestingly, both *mer* and *fac* isomers were isolated. The former can be irreversibly converted into the latter on heating in toluene for about 1 hour. The related complex, $[\text{Rh}\{\text{PhN}=\text{C}[\text{N}(\text{CH}_2)_5]=\text{S}\}_3]$ (91) is obtained via reaction of $[\text{RhCl}_3].3\text{H}_2\text{O}$ with $\text{PhNHC}(\text{S})\text{N}(\text{CH}_2)_5$ in ethanol with triethylamine. The dimeric complexes, $[\text{RhCl}\{\text{PhN}=\text{C}(\text{NR}_2)=\text{S}\}_2]_2$ (92, R = Me or $\text{R}_2 = (\text{CH}_2)_5$) can be synthesised by reaction of $[\text{RhCl}_3].3\text{H}_2\text{O}$ with $\text{PhNHC}(\text{S})\text{NMe}_2$ or $\text{PhNHC}(\text{S})\text{N}(\text{CH}_2)_5$ respectively in a methanol/toluene mixture, in the presence of an excess of triethylamine. $[\text{Rh}\{\text{PhN}=\text{C}(\text{NMe}_2)=\text{S}\}_2 (\text{Me}_2\text{NCS})]$ (93) exists as several isomers, while (94) is obtained as one isomer only from the reaction of $[\text{Rh}\{\text{PPh}_2\text{C}(\text{=NPh})\text{S}\}(\text{PPh}_3)_2]$ with $\text{Me}_2\text{NC}(\text{S})\text{N}(\text{Ph})\text{C}(\text{S})\text{NMe}_2$ in toluene, effectively an oxidative addition reaction of the ligand to the metal centre, with cleavage of one of the C(S)-NPh bonds.¹⁰¹



(95) was obtained from $[\text{Rh}\{\overline{\text{PPh}_2\text{C}(=\text{NPh})\text{S}}\}_2\text{Cl}]$ with $\text{PhNHC}(\text{S})\text{NMe}_2$ and triethylamine.¹⁰¹ A complex containing a thioureido ligand and a dithiocarbamate ligand was also reported.

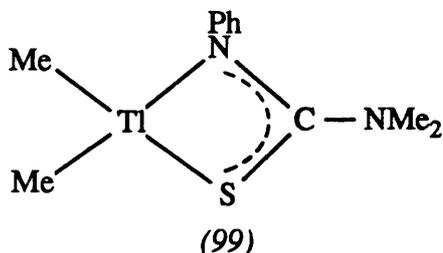
More recently, a thioureido complex of rhodium(III), containing a η^5 -bonded pentamethylcyclopentadienyl ligand, was reported (96, $\text{R} = \text{p-MeC}_6\text{H}_4$, $\text{R}' = -\text{CH} = \text{N-p-MeC}_6\text{H}_4$),¹⁰² and a six co-ordinate rhenium complex (97) has been synthesised.¹⁰³



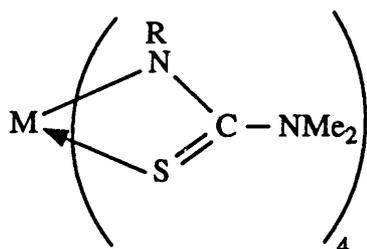
Thioureido complexes of molybdenum are also known. For instance, Brunner and Wachter prepared the molybdenum thioureido complex $[\text{Mo}\{\overline{\text{RN}=\text{C}(\text{R}')=\text{S}}\}(\text{Cp})(\text{CO})_2]$ (98, $\text{R} = \text{CH}(\text{Me})\text{Ph}$, $\text{R}' = \text{NHCH}(\text{Me})\text{Ph}$), which features a square-pyramidal geometry around the metal centre, and which can exist as a pair of diastereoisomers.¹⁰⁴

Nickel bis(thioureido) complexes have been obtained,¹⁰⁵ and copper(I), copper(II) and copper(III) derivatives are known,¹⁰⁶ although the latter were not isolated.

A thallium complex, obtained from the reaction of $\text{Me}_2\text{TlNMe}_2$ and phenyl isothiocyanate, was proposed to exist as the thioureido derivative (99) in benzene solution.¹⁰⁷



Early transition metal complexes which can be classed as thioureido derivatives are known. Reaction of phenyl isothiocyanate with $[\text{Ti}(\text{NMe}_2)_4]$ gave (100), while (101) and (102) resulted from treatment of $[\text{M}(\text{NMe}_2)_4]$ ($\text{M} = \text{Ti}$ or Zr) with methyl isothiocyanate respectively.¹⁰⁸



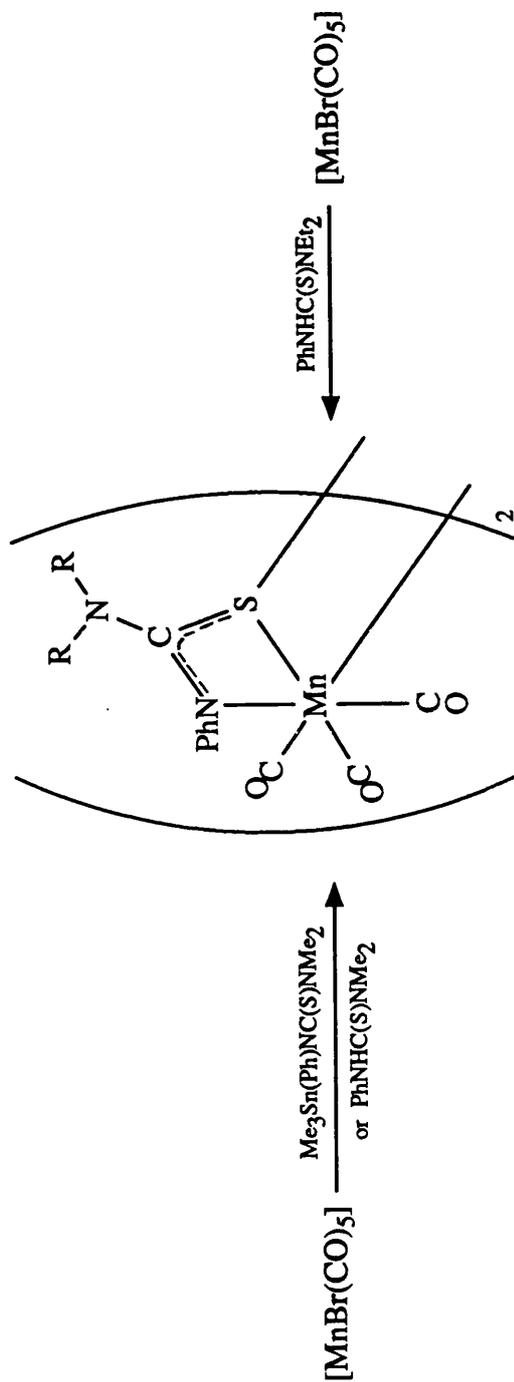
(100), $\text{M} = \text{Ti}$, $\text{R} = \text{Ph}$
 (101), $\text{M} = \text{Ti}$, $\text{R} = \text{Me}$
 (102), $\text{M} = \text{Zr}$, $\text{R} = \text{Me}$

Dimetallic manganese species containing thioureido ligands have been described.^{109,110} Reaction of N,N -dimethyl- N' -phenyl- N' -trimethylstannylthiourea¹⁰⁹ or $\text{PhNHC}(\text{S})\text{NMe}_2$ ¹¹⁰ with $[\text{MnBr}(\text{CO})_5]$ leads to formation of (103), the ethyl analogue (104) being produced on treatment of $[\text{MnBr}(\text{CO})_5]$ with $\text{PhNHC}(\text{S})\text{NEt}_2$.¹¹⁰ These reactions are summarised in Scheme 1.

Zinc thioureido species, including a bimetallic derivative, have been prepared.¹¹¹

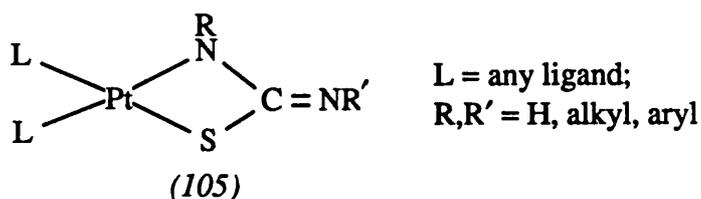
Interestingly, triiron octacarbonyl complexes containing thioureido ligands have been described, and are obtained from mixtures of products formed in the reactions of $[\text{Fe}_2(\text{CO})_9]$ with thioureas possessing N-H bonds.¹¹²

There are no reports in the literature concerning simple platinum compounds having the atomic framework (105), the four-membered ring bearing some relation to that in monometallic thioureido derivatives discussed above.

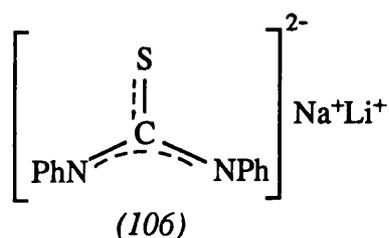


(103), R = Me
 (104), R = Et

Scheme 1



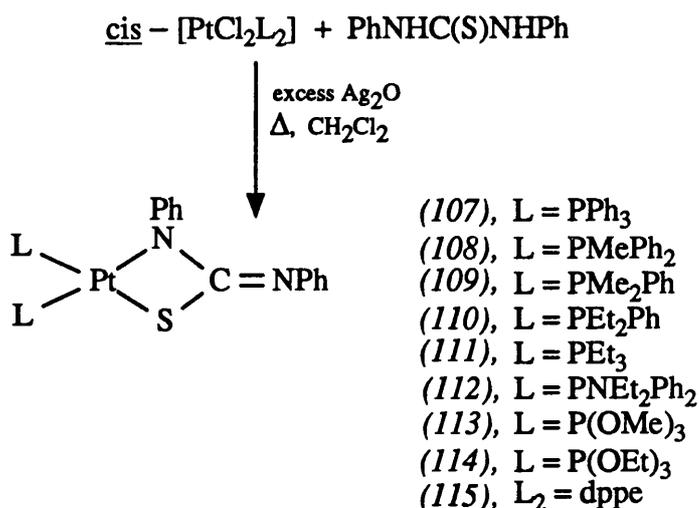
In Chapter 1 the use of silver(I) oxide in the preparation of some four-membered metallacycles from platinum(II) and palladium(II) dichloride complexes and various organic compounds was discussed. Other complexes containing Pt-C bonds can be obtained from reaction of *cis*-[PtCl₂(PEt₃)₂] and ligands possessing "acidic" C-H protons in the presence of silver(I) oxide.¹¹³ In all of these reactions, the rôle of silver(I) oxide is to act dually as a halide abstracting agent and a strong base.¹¹³ The ready availability of the thioureas (RNH)₂C=S (R = H, Ph), containing "activated" N-H protons, led to an investigation of their use, in conjunction with platinum(II) dichloride complexes and silver(I) oxide, in the synthesis of new four-membered ring complexes. Derivatives of the type (105) were obtained from N,N'-diphenylthiourea in such reactions, the results being presented as part of this Chapter. Studies on the use of sodium hydroxide in place of silver(I) oxide as a base, and of the preformed dianion (106) of N,N'-diphenylthiourea with *cis*-[PtCl₂L₂] species, in syntheses of derivatives of type (105), are also described.



The reactions of some of the new derivatives are described later in the Chapter.

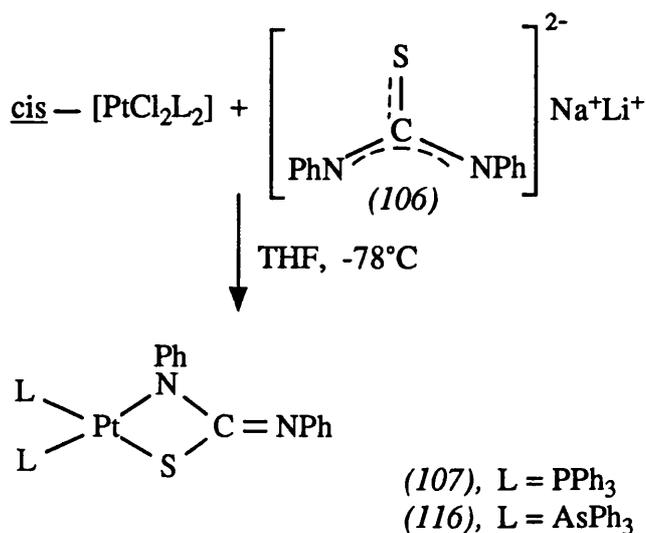
2.2 PREPARATION OF PLATINATHIAZETIDINE-3-IMINE COMPLEXES

Treatment of the complexes *cis*-[PtCl₂L₂] (L = PPh₃, PMePh₂, PMe₂Ph, PEt₂Ph, PEt₃, P(OMe)₃, or P(OEt)₃) (prepared *in situ* by reaction of [PtCl₂(COD)] with two mole equivalents of L) with one equivalent of N,N'-diphenylthiourea in refluxing dichloromethane in the presence of an excess of silver(I) oxide gave the complexes (107)-(111), (113) and (114), Scheme 2.



Scheme 2

Complexes (112) and (115) were synthesised by similar treatment of either $\text{cis} - [\text{PtCl}_2(\text{PNEt}_2\text{Ph}_2)_2]$ or $[\text{PtCl}_2(\text{dppe})]$ with one mole equivalent of N,N'-diphenylthiourea in refluxing dichloromethane in the presence of an excess of silver(I) oxide. The reaction of $\text{cis} - [\text{PtCl}_2(\text{PPh}_3)_2]$ with one equivalent of N,N'-diphenylthiourea and an excess of sodium hydroxide in a refluxing mixture of dichloromethane and THF led to production of complex (107) in moderate yield. Treatment of $\text{cis} - [\text{PtCl}_2\text{L}_2]$ (L = PPh_3 or AsPh_3) with one mole equivalent of the dianion of N,N'-diphenylthiourea in THF at low temperature gave the complexes (107) and (116) respectively, Scheme 3.



Scheme 3

All the complexes were isolated as pale to dark yellow air-stable solids, with the exceptions of (111), (113) and (114), which were obtained as dark yellow to brown oils. Attempts to obtain (111) as a solid product led to extensive decomposition. (113) and (114) were frequently obtained as the major components in a mixture of products from their respective syntheses. The formation of the complexes (107)-(116) with an N,S-bonded ligand as opposed to an N,N-bonded ligand is presumably associated with the preference for platinum(II) to bond to sulphur rather than nitrogen. However, dilithiated *N,N'*-diphenylthiourea exists as a dimer in the solid state, with monomeric units effectively formulated as "Ph \bar{N} -C(=NPh) \bar{S} " moieties.¹¹⁴ It is unlikely that such a species is formed in the silver(I) oxide or sodium hydroxide reactions, since the initial deprotonation of the organic substrate would lead to production of water, which would inhibit the formation of the dianion. Much more likely is formation of a monoanion, addition to platinum, and further deprotonation of the attached organic fragment and reaction in a similar fashion to yield the observed products.

Attempts to synthesise a complex unsubstituted at the two nitrogen atoms by reaction of *cis*-[PtCl₂(PPh₃)₂] with one mole equivalent of unsubstituted thiourea and an excess of silver(I) oxide in refluxing dichloromethane led to a mixture of products. Similarly, a mixture resulted on reaction of *cis*-[PtCl₂(PPh₃)₂] with one mole equivalent of *N*-phenylthiourea and excess silver(I) oxide in refluxing dichloromethane. Interestingly, the attempted synthesis of the palladium analogue of (107) by treatment of [PdCl₂(PPh₃)₂] with *N,N'*-diphenylthiourea and excess silver(I) oxide in refluxing dichloromethane gave only a mixture of products which could not be separated.

2.3 STRUCTURAL PROPERTIES OF PLATINATHIAZETIDINE-3-IMINE COMPLEXES

Single-crystal X-ray diffraction studies on two of the complexes have been carried out, to elucidate the molecular structure of the new derivatives. The complexes (107) and (108) have been studied, and summaries of important bond lengths and angles are given in Tables 1 and 2 respectively, with the molecular structure of (107) being shown in Figure 1, and that of

TABLE 1Selected bond lengths for the complexes $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}\text{L}_2]$

Bond Length (Å)	(107) ^a L = PPh ₃	(108).CH ₂ Cl ₂ ^b L = PMePh ₂
Pt — P(1)	2.308 (1)	2.274 (4)
Pt — P(2)	2.247 (1)	2.251 (5)
Pt — S	2.331 (1)	2.348 (4)
Pt — N(1)	2.054 (3)	2.037 (14)
C(1) — N(1)	1.348 (7)	1.369 (18)
C(1) — S	1.782 (5)	1.744 (16)
N(1) — C(21)	1.399 (5)	1.439 (15)
C(1) — N(2)	1.277 (6)	1.311 (19)
N(2) — C(11)	1.422 (7)	1.411 (15)

TABLE 2Selected bond angles for the complexes $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}\text{L}_2]$

Bond Angle (°)	(107) ^a L = PPh ₃	(108).CH ₂ Cl ₂ ^b L = PMePh ₂
P(1) — Pt — P(2)	97.5 (0)	95.5 (2)
P(1) — Pt — N(1)	97.4 (1)	97.6 (4)
P(2) — Pt — S	94.6 (0)	97.7 (2)
N(1) — Pt — S	70.5 (1)	70.0 (4)
N(1) — C(1) — S	107.7 (3)	107.9 (12)
Pt — S — C(1)	80.0 (2)	80.2 (6)
C(21) — N(1) — C(1)	117.3 (3)	121.9 (12)
C(21) — N(1) — Pt	138.1 (3)	135.0 (9)
N(1) — C(1) — N(2)	124.1 (5)	122.3 (14)
C(1) — N(2) — C(11)	121.7 (5)	122.7 (13)
N(2) — C(1) — S	128.2 (5)	129.8 (13)
Pt — N(1) — C(1)	101.7 (3)	101.7 (10)

^a See Figure 1 for crystallographic numbering system;^b See Figure 2 for crystallographic numbering system.

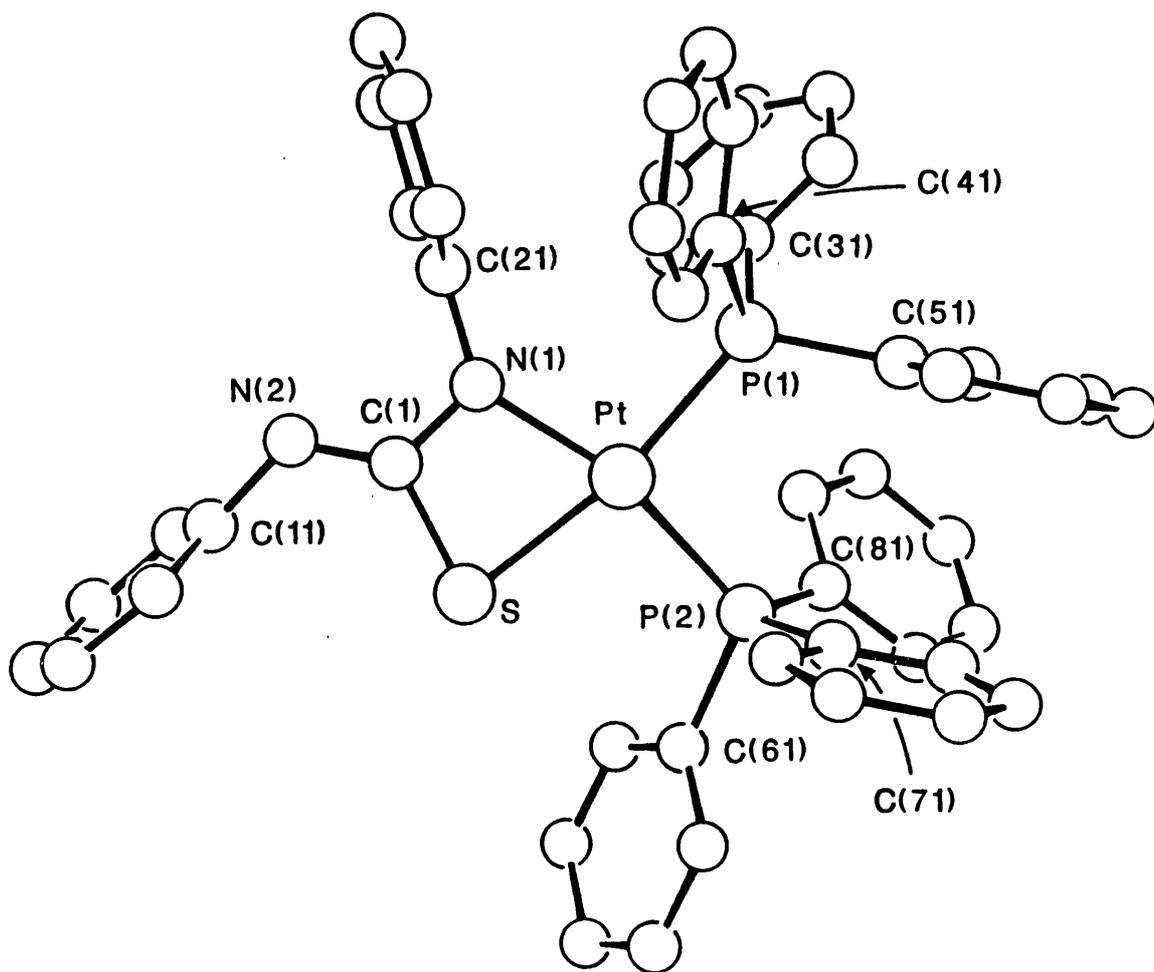


FIGURE 1

Molecular structure of $[\text{Pt}\{\text{NPhC}(\text{=NPh})\text{S}\}(\text{PPh}_3)_2]$ (107) with all hydrogens omitted.

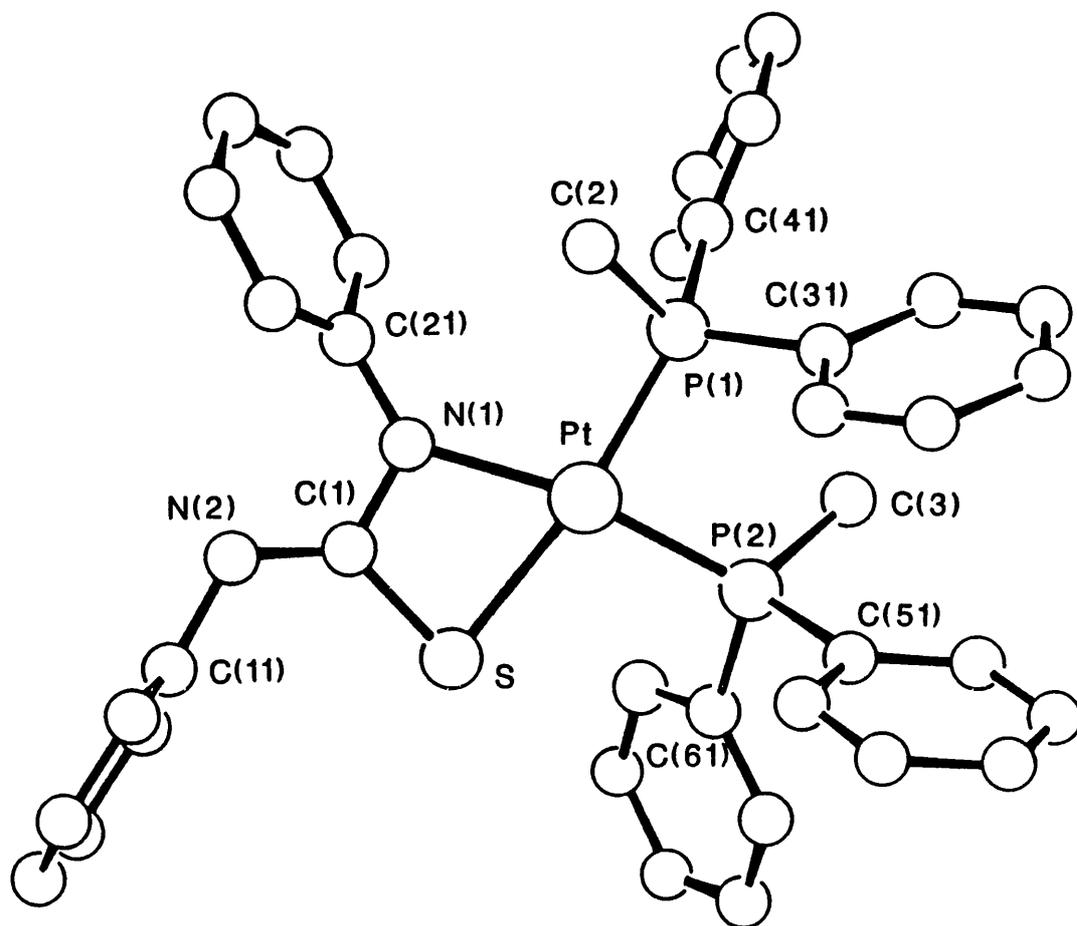
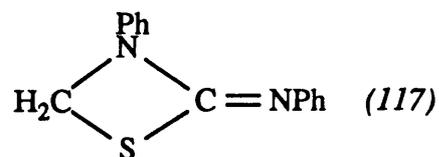


FIGURE 2

Molecular structure of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PMePh}_2)_2]$ (*108*) with all hydrogens omitted.

(108) in Figure 2, both diagrams showing the crystallographic numbering systems.

The coordination about the platinum atom in each complex is essentially square planar, the twist angle between the planes P(1)–Pt–P(2) and N(1)–Pt–S being 2.08° and 12.89° respectively for (107) and (108). The fold angle between the planes N(1)–Pt–S and N(1)–C(1)–S in (107) is 5.3°, whereas that in (108) is 5.4°. There is little deviation from planarity in the four-membered rings. Thus, (107) and (108) contrast with platinacyclobutan-3-one, platinathietane-3-oxide and platinathietane-3,3-dioxide complexes, which possess fold angles of 42.0-56.7°,^{8,10,12,20,25} 36.7°⁵⁶ and 15.3-24.2°^{56,58,60} respectively, showing the puckered nature of the four-membered rings in these systems. The "flatness" of the four-membered rings found in (107) and (108) can be compared with the thioureido ligands in (87, X = Cl)⁹⁹ and (96),¹⁰² which also show little deviation from planarity. Interestingly, the four-membered ring in 3-phenyl-2-phenylimino-1,3-thiazetidine (117), is almost flat.¹¹⁵



As expected, in both complexes the Pt–P(1) bond is longer than the Pt–P(2) bond, in accord with the greater trans influence of the sulphur atom as compared to the nitrogen atom N(1).

The values of the exocyclic bond lengths C(1)–N(2) in (107) and (108) are both indicative of significant double bond character, this comparing favourably with the observation of similar situations in other systems, for example in $[\text{Pt}\{\overline{\text{ON}(\text{Ph})\text{C}(\text{=NPh})\text{S}}\}(\text{PPh}_3)_2]$ ¹¹⁶ and in the thioureido ligand in (87, X = Cl).⁹⁹ The C–S bond in (107) has single bond character, with the corresponding bond in (108) being slightly shorter and comparable to the length of the C–S bond in (96) [1.741(6)Å],¹⁰² indicating some slight double bond character. Interestingly, the C–S bond length in (107) is almost identical with the corresponding bond length in (117).¹¹⁵

Double bond character is shown in the C(1)–N(1) bonds of both (107) and (108), an effect

also seen in the corresponding bond in (117). The amino-phenyl ring is rotated around the N(1)–C(21) bond out of the Pt–N(1)–C–S plane in both compounds, so that efficient π overlap of orbitals between N(1) and the attached aromatic system is prevented. This type of rotation has been observed in other systems, for example in (87, X = Cl),⁹⁹ (96),¹⁰² and in some technetium¹¹⁷ and rhenium^{103,118} thiazetidine systems. As a consequence, the N(1)–C(21) bonds in both (107) and (108) have single bond character. The reason for this rotation in (107) and (108) is not clear but it may occur to reduce unfavourable steric interactions between the amino-phenyl group and the phosphine moiety trans to the sulphur atom.

The four-membered ring in (117) exhibits a large degree of ring strain, as reflected in the C–S–C bond angle of 74.3(1)°.¹¹⁵ In the current complexes, the corresponding Pt–S–C angles are 80.0(2)° and 80.2(6)° for (107) and (108) respectively. It should also be noted that the N(1)–C(1)–S angles in (107) and (108) are considerably larger than the corresponding angle in (117) [95.0(1)°].¹¹⁵ These data indicate a reduction in ring strain in the platinum four-membered ring complexes with respect to (117), as a result of the replacement of the methylene group in (117) with a substantially larger platinum atom. Interestingly, the C(1)–N(2)–C(11) bond angle in both (107) and (108) is such as to direct the imino-phenyl group away from the amino-phenyl group.

2.4 N.M.R. SPECTRA OF PLATINATHIAZETIDINE-3-IMINE COMPLEXES

The new complexes were studied by ¹H n.m.r., ¹³C-{¹H} n.m.r. and ³¹P-{¹H} n.m.r. spectroscopic techniques.

The room temperature ¹H n.m.r. spectrum of (108) shows two sets of second-order multiplets (with platinum-195 satellites) arising from the two non-equivalent methyl groups in the phosphorus moieties. Interestingly, only two sets of resonances are seen in the methyl region for (109) also, each having a relative integration of 6, suggesting that in each phosphine ligand the two methyl groups are equivalent to each other. This region is shown in Figure 3. Complex (110), containing diethylphenylphosphine ligands, appeared to decompose in n.m.r. solvents on standing, and so several attempts to obtain ¹H n.m.r. data for this compound proved unsuccessful (although a poor quality ¹³C-{¹H} n.m.r. spectrum was

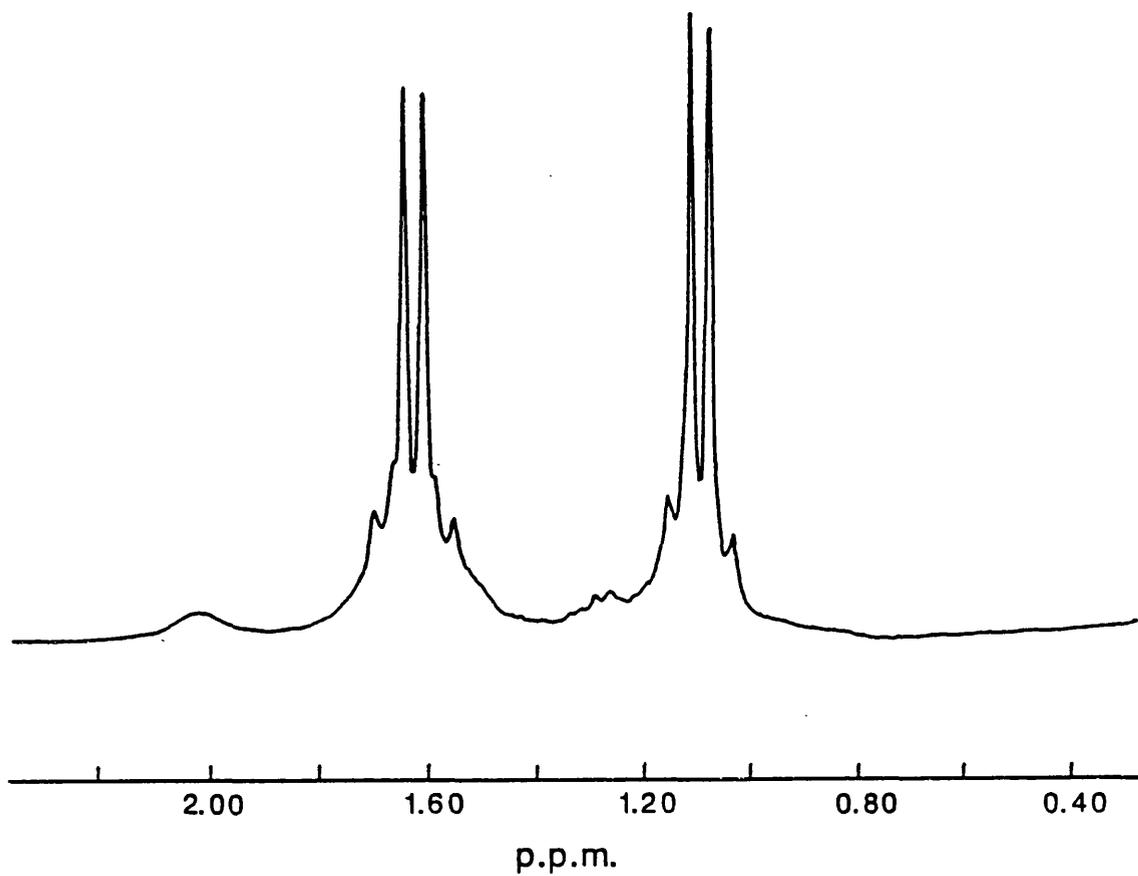


FIGURE 3

The methyl region in the room temperature 300 MHz ^1H n.m.r. spectrum of the complex $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PMe}_2\text{Ph})_2]$ (109).

recorded).

In the ^1H n.m.r. spectrum of complex (112), the methyl resonances are split into two cleanly separated triplets, with no observable platinum-195 or phosphorus-31 coupling, whereas the methylene signals appear as two different complex multiplets, from which no coupling constants can be obtained. The methylene region for complex (115) appears as a complicated multiplet in the ^1H n.m.r. spectrum in approximately the same position as has been observed for other four-membered metallacyclic ring systems containing chelating 1,2-bis-(diphenylphosphino)ethane ligands, such as nickelathietane-3,3-dioxide species.⁶⁰

The room temperature $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra of some of the new complexes were studied. The imino-carbon atom in the complexes (108)-(110) and (115) appears as a broad weak singlet, with no observable coupling to platinum-195 or phosphorus-31 nuclei, at a very similar position in each spectrum (see Experimental Section), indicating that the change in nature of the phosphines in these complexes has little effect on the chemical shift of these carbon atoms. The broadening of these signals is probably owing to the adjacent quadrupolar nitrogen nuclei. For complex (107), this signal is not observable, possibly owing to the extent of broadening in this case.

The carbon atoms of the methyl groups in (108) and (109) show up as two sets of second-order multiplets for each compound, each multiplet being a doublet of doublets with a small central feature. No platinum-195 satellites could be discerned in the spectra.

The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of all the new phosphorus-containing complexes were studied. The spectra indicate the presence of two chemically non-equivalent phosphorus nuclei in each complex, second-order AB patterns being observed with corresponding platinum-195 satellites. For example, complex $[\text{Pt}\{\overline{\text{NPhC(=NPh)S}}\}(\text{PPh}_3)_2]$ (107) shows resonances at δ 16.05 and 11.44 p.p.m., with $^1\text{J}(\text{PtP})$ being 3103 and 3261 Hz respectively. In all the spectra of the monodentate phosphine or phosphite complexes for which $^1\text{J}(\text{PtP})$ is discernible, the high-field components are associated with the greater $^1\text{J}(\text{PtP})$ values.

It should also be noted that the $^1\text{J}(\text{PtP})$ coupling constants for the derivative (112) are significantly greater than those seen for the other monodentate phosphine-containing

complexes. This effect has been observed in the value of $^1J(\text{PtP})$ in another platinum four-membered ring compound containing this phosphine, as compared to analogous compounds containing other monodentate phosphine ligands.¹¹⁹ The $^1J(\text{PtP})$ coupling constants for (114) are much larger than those for (107)-(112), as expected for monodentate phosphite ligands.

2.5 I.R. SPECTRA OF PLATINATHIAZETIDINE-3-IMINE COMPLEXES

The complexes obtained as solids all show a strong band in the i.r. spectrum in the range 1560-1547 cm^{-1} , attributed to the $\nu(\text{C}=\text{N})$ mode. $[\overline{\text{CH}_2\text{NPhC(=NPh)S}}]$ (117) exhibits a corresponding band at 1655 cm^{-1} .¹²⁰ Thus, there is a decrease of approximately 100 cm^{-1} in the $\nu(\text{C}=\text{N})$ frequency on going from the organic thiazetidine to the platinum analogues. Since the exocyclic C-N bond in (117) has more double bond character than the corresponding bonds in (107) and (108), as evidenced by the crystal structures of the compounds, it would be expected that lower $\nu(\text{C}=\text{N})$ values should be observed for (107) and (108) with respect to (117). Presumably a similar argument can be extended to the other i.r. spectra taken. It is also possible that the replacement of the methylene group in (117) with a larger platinum atom, resulting in a reduction in ring strain in the four-membered ring, would lead to a lowering in $\nu(\text{C}=\text{N})$ for the metal complexes.

2.6 REACTIONS OF PLATINATHIAZETIDINE-3-IMINE COMPLEXES

2.6.1 Attempted Oxidative Addition Reactions to $[\overline{\text{Pt}\{\text{NPhC(=NPh)S}\}}(\text{PPh}_3)_2]$ (107)

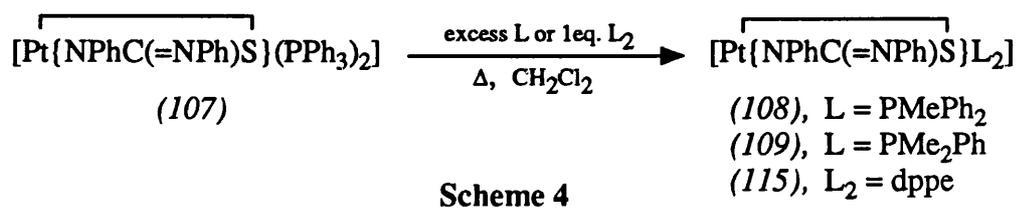
The treatment of (107) with gaseous hydrogen chloride in dichloromethane afforded the complex $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$, which was also obtained on reaction of (107) with one mole equivalent of mercuric chloride in acetone. Presumably, the organic product in the first of these reactions is N,N'-diphenylthiourea, although no attempts to confirm this were made.

The reaction of (107) with an excess of iodomethane in dichloromethane gave a number of phosphorus-containing products as seen in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the reaction residue. Attempts to obtain pure products from the residue were unsuccessful. It is in fact conceivable that products other than those originating from oxidative addition to the metal

centre could be formed in this reaction. The methylation of the sulphur or nitrogen atoms, with consequent formation of an iodide salt cannot be totally ruled out. However, owing to inability to isolate pure species from the reaction, the study was not pursued.

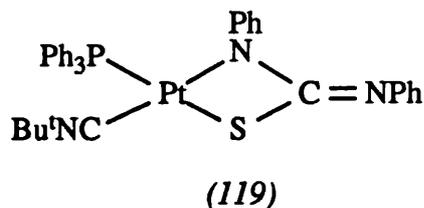
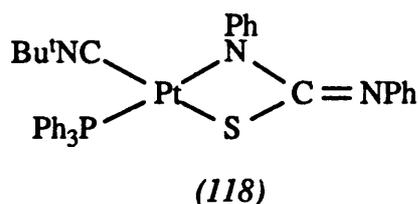
2.6.2 Ligand Substitution Reactions

The complex (107) undergoes simple phosphine displacement reactions with either more basic phosphines or a chelating phosphine. Thus, treatment of (107) with an excess of either methyldiphenylphosphine in refluxing dichloromethane for 1h, or dimethylphenylphosphine in refluxing dichloromethane for 0.5h, afforded the complexes (108) and (109) respectively, Scheme 4. Both compounds were obtained in surprisingly low yield. The treatment of (107) with one mole equivalent of 1,2-bis-(diphenylphosphino)ethane in refluxing dichloromethane for 0.5h gave the complex (115), Scheme 4, together with a small amount of unidentified decomposition product.



On reaction of (107) with an excess of t-butyl isocyanide in dichloromethane at room temperature, one phosphine ligand is replaced by isocyanide to give a monosubstituted species as the only product, $\overline{[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{CNBu}^t)(\text{PPh}_3)]}$. The bis(isocyanide) product was not obtained, and no evidence for insertion of an isocyanide moiety into either the platinum-nitrogen or platinum-sulphur bond of the starting material (107) was observed. Refluxing a similar reaction mixture led to decomposition. Unambiguous assignment of the substitution mode of the product [i.e. whether the isocyanide ligand is trans to sulphur, as in (118), or trans to nitrogen, as in (119)] on the basis of spectroscopic data is difficult, and it was not possible to grow crystals of the compound suitable for an X-ray structure determination to be carried out.

It is suggested, however, that (119) would be the preferred product, as the high trans



influence isocyanide ligand, in this isomer, is trans to the lowest trans influence atom, nitrogen, rather than trans to the alternative, but slightly higher trans influence sulphur atom, as in (118). The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of the complex consists of a single resonance with corresponding platinum-195 satellites, and in fact the value of $^1\text{J}(\text{PtP})$ [i.e. 2971 Hz] is consistent more with phosphorus trans to sulphur rather than with phosphorus trans to nitrogen. The room temperature ^1H n.m.r. spectrum of the product exhibits a resonance at δ 0.99 p.p.m., assigned to the protons in the t-butyl group, and an intense band at 2202 cm^{-1} is seen in the i.r. spectrum, arising from the terminal isocyanide ligand.

Finally, refluxing a solution of (116) with two mole equivalents of triphenylphosphine in dichloromethane results in replacement of the two triphenylarsine ligands and formation of (107) in moderate yield.

2.6.3 Reaction of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ (107) with Carbon Monoxide

In an attempt to replace either one or both phosphine ligands in (107), a slow stream of carbon monoxide was bubbled through a dichloromethane solution of the complex at room temperature, the reaction being monitored using ^{31}P - $\{^1\text{H}\}$ n.m.r. spectroscopy. Spectra taken during the course of the reaction are shown in Figure 4, the diminution of the resonances owing to the starting material and the concomitant increase in intensity of the resonances arising from the product being exhibited clearly. After 13.5h the reaction was complete. The final spectrum of the crude compound displayed an AB pattern, together with corresponding platinum-195 satellites (see spectrum labelled t = 13.5h, Figure 4). The i.r. spectrum of the compound in the solid state showed a strong band at 1578 cm^{-1} , indicative of a $\nu(\text{C}=\text{N})$ mode, and a strong band at 1647 cm^{-1} , assigned to a $\nu(\text{C}=\text{O})$ mode. No bands attributable to terminal metal-carbonyl ligands were observed, indicating that the product did not contain such ligands. These data suggested that (107) had undergone a ring expansion reaction with

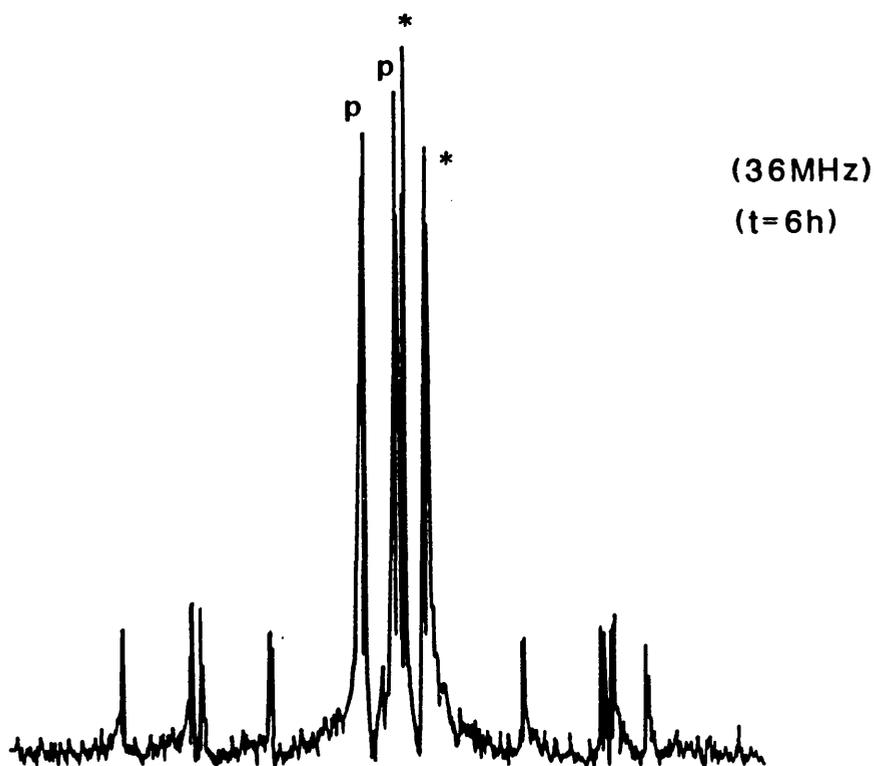
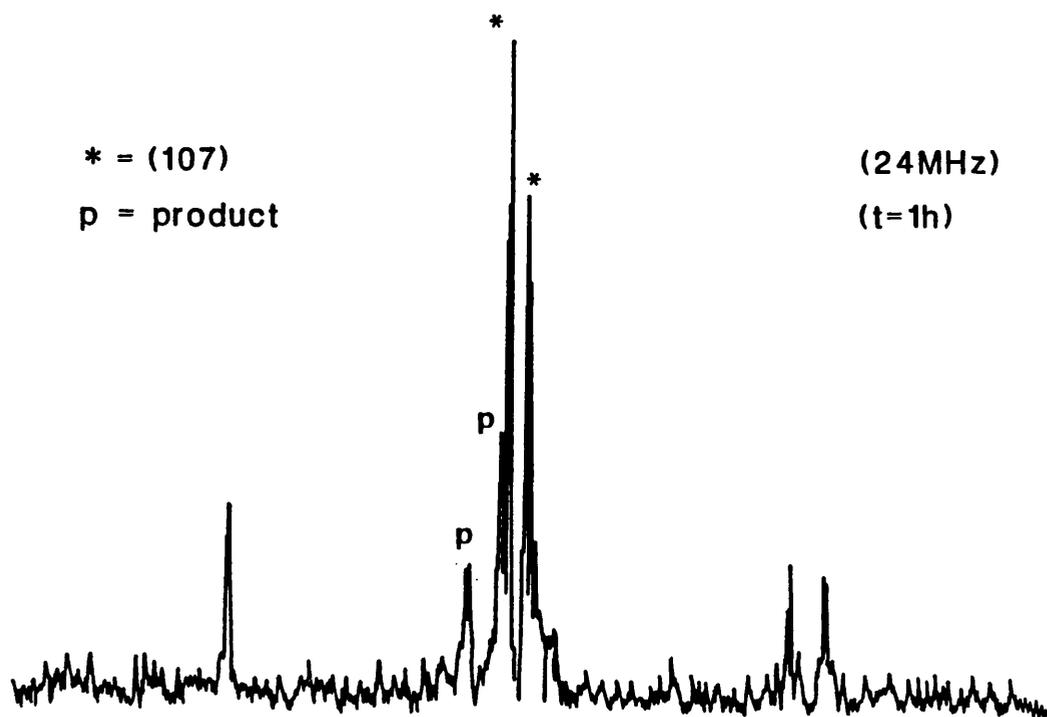
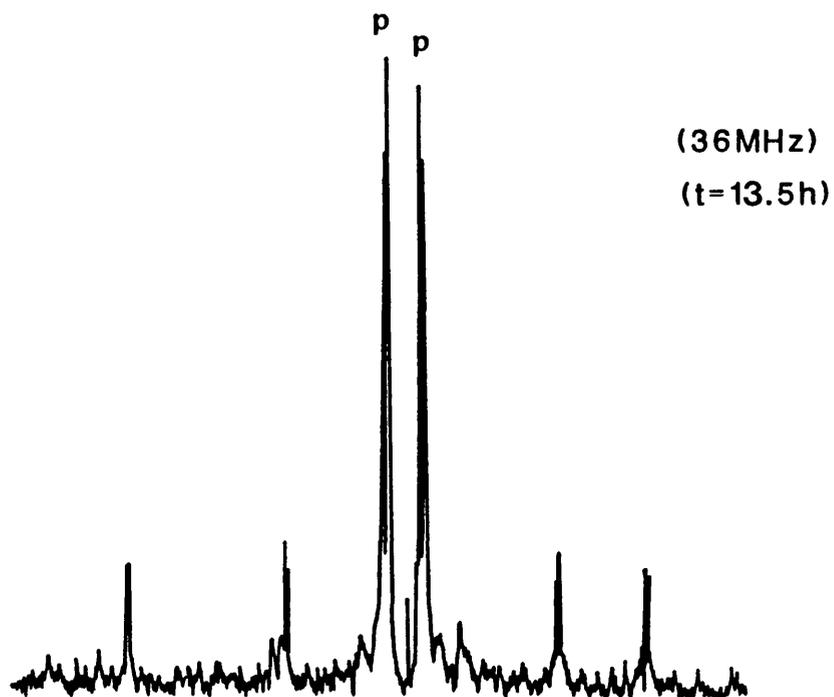
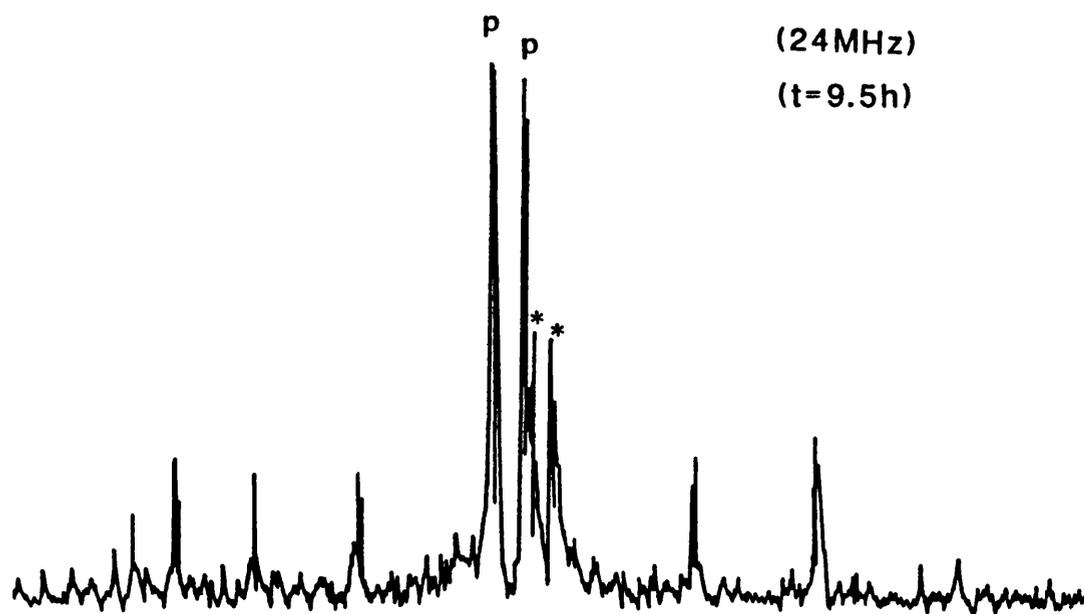


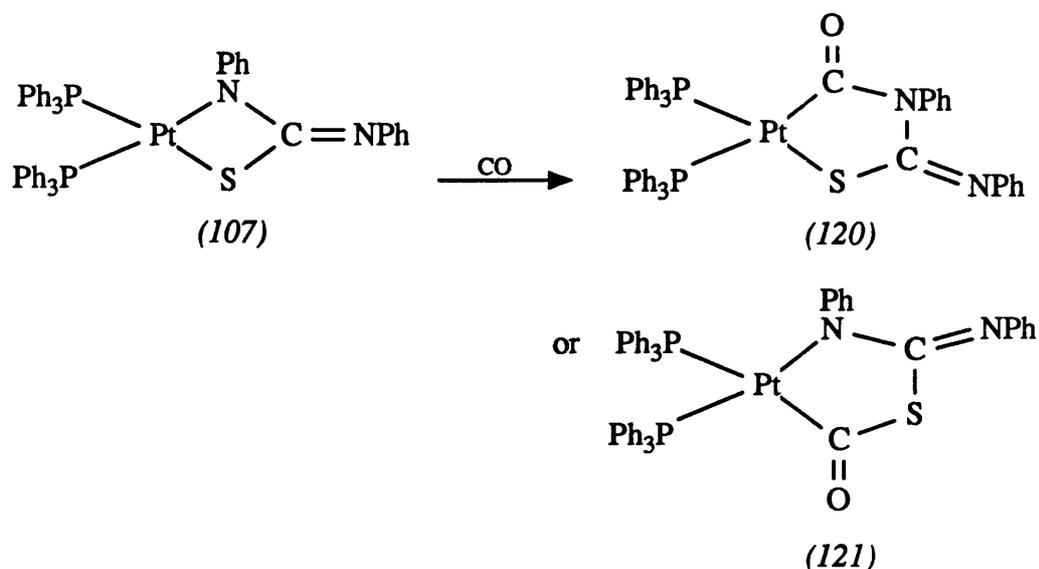
FIGURE 4

$^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra taken at intervals during the reaction of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ (107) with carbon monoxide.

FIGURE 4 (Continued)



carbon monoxide, Scheme 5.



Scheme 5

It can be seen that two products are possible, (120) arising from insertion of carbon monoxide into the platinum-nitrogen bond of (107), whereas the alternative (121) would be obtained on similar insertion into the platinum-sulphur bond of (107). It should be noted that insertion of carbon monoxide into transition metal-nitrogen bonds is rare, and only a few genuine examples have been reported [for examples, see Refs. 121 and 122]. Similarly, insertion of this species into metal-sulphur bonds is not well documented.¹²³ Unfortunately, crystals suitable for an X-ray structural investigation of the product could not be obtained, and after several recrystallisations it was found to be insufficiently soluble in common n.m.r. solvents to enable further n.m.r. studies to be conducted. The i.r. spectrum of the solid was the same after each recrystallisation. Further characterisation of the product is needed to ascertain its nature. Interestingly, an i.r. spectrum of the complex taken after it had been standing in air for several months was identical to those obtained previously, suggesting that the complex is stable to decarbonylation under such conditions.

The reaction of (107) with a slow stream of carbon monoxide in refluxing absolute ethanol for 6h also led to formation of the same compound, as indicated by the ³¹P-{¹H} n.m.r. spectrum of the crude reaction mixture.

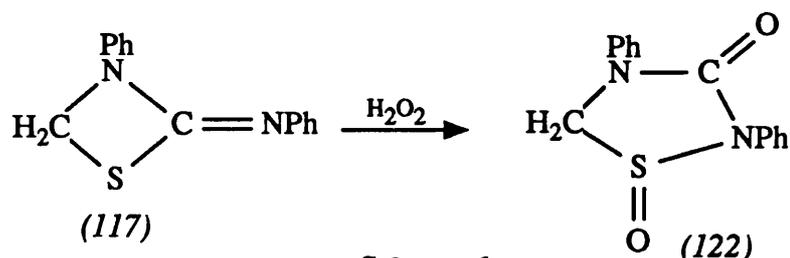
2.6.4 Reaction of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ (107) with Carbon Disulphide, Phenyl Isothiocyanate and Phenyl Isocyanate

It is known that transition metal complexes containing small ring systems in which the metal atom is included can undergo ring expansion reactions with cumulenes. For instance, carbon disulphide, phenyl isothiocyanate and phenyl isocyanate have been reported to give products derived from such reactions with $[\text{Pt}(\text{RNO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Ph}, \text{Bu}^t, \text{CF}_3$).^{124,125} It was hoped that these reagents could be used to effect ring expansion reactions of (107) and enable further ring systems to be obtained. However, treatment of (107) with an excess of carbon disulphide in dichloromethane at room temperature led only to the recovery of starting material. Similarly, refluxing a dichloromethane solution of (107) with an excess of phenyl isothiocyanate resulted in no reaction. Treatment of (107) with an excess of phenyl isocyanate in refluxing dichloromethane led to decomposition of the starting material.

2.6.5 Reaction of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ (107) with Hydrogen Peroxide

Treatment of (107) with an excess of 20% (v/v) hydrogen peroxide in a refluxing mixture of dichloromethane and acetone led only to the production of a mixture of compounds, the major phosphorus-containing species being triphenylphosphine oxide, as evidenced by the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the reaction residue. An AB pattern was also observed, with components at δ 15.18 and 10.53 p.p.m., possibly arising from a species different to the starting material. Unfortunately, attempts to isolate a pure sample of this species were unsuccessful. Attempted oxidation of the sulphur atom in (107) at room temperature using stronger hydrogen peroxide solution led only to the recovery of starting material. It should be noted that the oxidation of 3-phenyl-2-phenylimino-1,3-thiazetidine (117) by treatment with a mixture of glacial acetic acid and hydrogen peroxide did not yield the corresponding thiazetidine-1,1-dioxide species, but rather a product (122),¹²⁶ Scheme 6.

Attempts to oxidise the sulphoxide group in $[\text{Pt}\{\text{CH}(\text{COPh})\text{S}(\text{O})\text{CH}(\text{COPh})\}(\text{PPh}_3)_2]$ (50, $\text{L} = \text{PPh}_3$) with hydrogen peroxide under mild conditions were unsuccessful, whereas under more forcing conditions destruction of the complex was observed.⁵⁷ Interestingly, the attempted oxidation of the sulphur atom in the complex $[\text{Pt}_2(\mu\text{-S})(\text{CO})_2(\text{PBU}^t_2\text{Ph})_2]$ with 30%



Scheme 6

aqueous hydrogen peroxide resulted in the decomposition of the complex.¹²⁷

2.6.6 Miscellaneous Reactions of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ (107)

The behaviour of (107) with a variety of other reagents was studied, and the $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectral data for the products obtained are shown in Table 3. All the products displayed AB patterns, with corresponding platinum-195 satellites, in their $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra. The experimental details are presented in the Experimental Section.

TABLE 3

$^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. data^{a,b} for some miscellaneous reactions of $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PPh}_3)_2]$ (107)

Reagent ^d	δP_A ($^1\text{J}_{\text{PtP}_A}$)	δP_B ($^1\text{J}_{\text{PtP}_B}$)	$^2\text{J}(\text{P}_A\text{P}_B)$
NaIO_4	13.76 (3213)	9.12 (3479)	22.0
SO_2	13.93 (3208)	9.29 (3472)	24.4
SO_2^e	10.23 (3193)	5.62 (3438)	23.2
HBF_4	13.49 (3228)	9.02 (3489)	23.2
$\text{Me}_3\text{O}\cdot\text{BF}_4^c$	14.62 (3247)	9.18 (3433)	24.4

^a All spectra taken in CH_2Cl_2 solution at 25°C ; δ in p.p.m. relative to $[\text{P}(\text{OH})_4]^+$; J in Hz;

^b Recorded at 36 MHz unless stated otherwise;

^c Recorded at 24 MHz;

^d All reactions carried out at room temperature unless stated otherwise;

^e Reaction carried out under refluxing conditions.

When an excess of sodium periodate in water was added to a solution of (107) in THF at room temperature, an immediate decolourisation of the solution was observed. Work-up yielded a white solid which exhibited in its i.r. spectrum a strong band at 1557 cm^{-1} , attributed to a $\nu(\text{C}=\text{N})$ mode. The region $1200\text{-}1000\text{ cm}^{-1}$ contained a number of broad and ill-defined bands.

In an attempt to effect a ring expansion reaction of (107), a slow stream of sulphur dioxide was passed through a dichloromethane solution of the complex at room temperature, resulting in the isolation of a pale yellow solid after work-up. Carrying out the same reaction under extended refluxing conditions led to formation of a product showing in its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum an AB pattern with components centred at different chemical shifts than in the spectrum of the product obtained from the room temperature reaction. Again, as for the product from the sodium periodate reaction, the region $1200\text{-}1000\text{ cm}^{-1}$ in the i.r. spectrum was not well resolved.

The complex (107), when treated with HBF_4 , led to the isolation of a white solid, and attempts to methylate the sulphur atom of (107) by treatment with trimethyloxonium tetrafluoroborate in dichloromethane led to isolation of a highly crystalline solid.

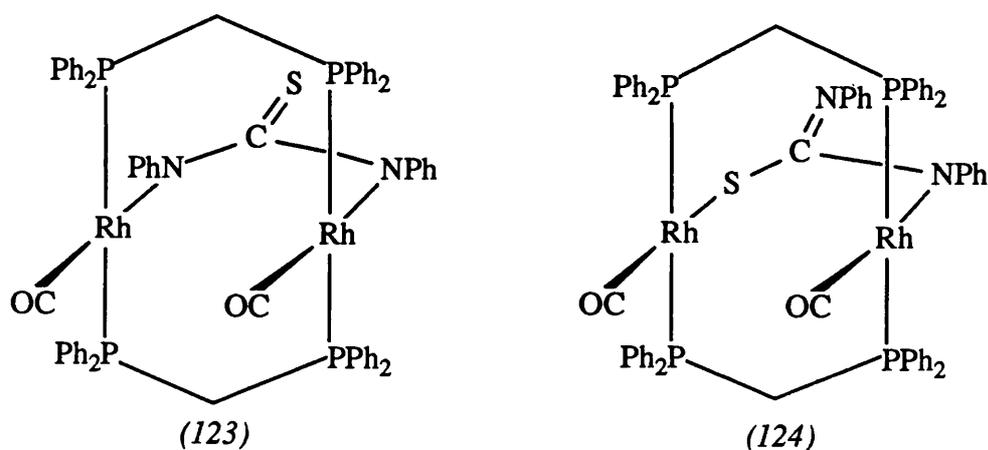
It can be seen from Table 3 that the chemical shifts of the low-field components of the AB patterns in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of the products are similar to each other on going from reaction to reaction (with the exception of the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum obtained from the product of the sulphur dioxide reaction in refluxing dichloromethane). This effect can also be seen with the corresponding high-field components for these same spectra. These results are rather surprising, taking into account the variety of reagents used in the reactions. Additionally, for all the spectra, the $^1\text{J}(\text{PtP})$ coupling constants associated with the low-field components fall within a relatively narrow range, as do the corresponding values for the high-field components.

The periodate ion is a powerful oxidising agent, and it was hoped that treatment of (107) with sodium periodate would result in formation of either the sulphoxide or sulphone derivative. It would be expected that treatment of (107) with fluoroboric acid would lead to

formation of a cationic species, with the BF_4^- moiety as a counterion. The three most likely sites for protonation in complex (107) are the sulphur atom and the two nitrogen atoms. Unfortunately, spectroscopic studies did not enable confident identification of any of the products, and no acceptable microanalytical data for any of the products were obtained. Further, it was not possible to obtain crystals of any of the products suitable for structural determinations to be carried out. In view of these results, the reactions were not studied further.

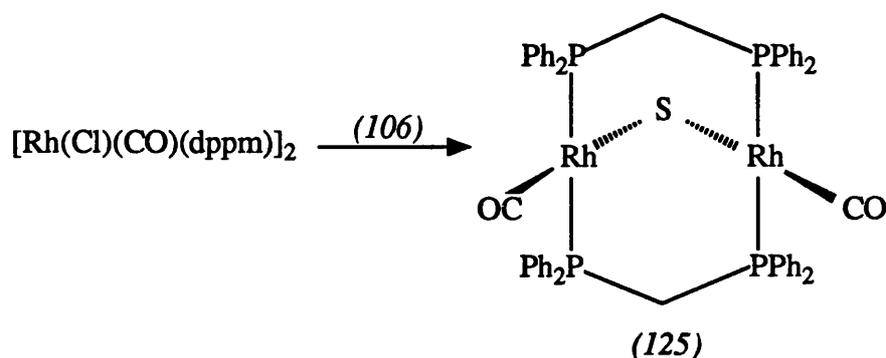
2.7 REACTION OF $[\text{Rh}(\text{Cl})(\text{CO})(\text{dppm})]_2$ WITH THE DIANION OF N,N'-DIPHENYLTHIOUREA

In an attempt to synthesise a dinuclear bridged species such as (123) or (124), the reaction of $[\text{Rh}(\text{Cl})(\text{CO})(\text{dppm})]_2$ with the dianion of N,N'-diphenylthiourea was investigated.



Thus, reaction of $[\text{Rh}(\text{Cl})(\text{CO})(\text{dppm})]_2$ with 1.45 mole equivalents of (106) in THF at room temperature gave reddy-orange crystals after work-up. The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of the crystals was identical to that taken of a sample of $[\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2]$ (125), made by the known literature method.¹²⁸ This suggested that the sulphur atom is abstracted from the dianion by the starting rhodium complex. The reaction is depicted in Scheme 7.

The carbodiimide, $\text{PhN}=\text{C}=\text{NPh}$, is presumed to be a by-product but no attempts to confirm this were made. It should be noted that C-S bond cleavage of species related to thioureas by transition metal complexes is known, for example in the formation of



Scheme 7

$[(\mu\text{-R}'\text{C}=\text{NPh})(\mu\text{-SR})\text{Fe}_2(\text{CO})_6]$ from $[\text{Fe}_3(\text{CO})_{12}]$ and $\text{RSC}(=\text{NPh})\text{R}'$ (R = Me, R' = Me, Et, Ph; R = Et, R' = Me),¹²⁹ and complexes $[\text{Co}_3(\text{CO})_7(\mu_3\text{-S})(\mu\text{-R}'\text{C}=\text{NR})]$ (R = C_6H_{11} , R' = Me, Ph) from $[\text{Co}_2(\text{CO})_8]$ and $\text{RNHC}(\text{S})\text{R}'$.¹³⁰

2.8 CONCLUSION

The preparation of platinathiazetidine-3-imine complexes may be achieved via treatment of the complexes $\text{cis-}[\text{PtCl}_2\text{L}_2]$ (L = donor ligand) with N,N'-diphenylthiourea in the presence of silver(I) oxide in refluxing dichloromethane. Sodium hydroxide, instead of silver(I) oxide, can also be used as a base in the case where L = PPh_3 . The dianion of N,N'-diphenylthiourea, in conjunction with $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ or $\text{cis-}[\text{PtCl}_2(\text{AsPh}_3)_2]$ in tetrahydrofuran at low temperature, also leads to formation of the corresponding platinathiazetidine-3-imines. Single-crystal X-ray diffraction studies on two derivatives have been carried out, establishing the near planarity of the four-membered ring in these systems.

Simple ligand displacement reactions can be carried out on some derivatives. Reaction of the triphenylphosphine analogue with carbon monoxide results in a ring expansion to yield a five-membered metallacycle containing an inserted carbon monoxide moiety.

The reaction of the dianion of N,N'-diphenylthiourea with $[\text{Rh}(\text{Cl})(\text{CO})(\text{dppm})]_2$ results in the formation of the "A"-frame complex, $[\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2]$.

2.9 EXPERIMENTAL

Microanalyses were carried out by C.H.N. Analysis Ltd., Alpha House, Countesthorpe Road, South Wigston, Leicester, LE8 2PJ, and by Butterworth Laboratories Ltd., 54-56 Waldegrave Road, Teddington, Middlesex, TW11 8LG. M.p.'s were recorded on a Reichert hot-stage apparatus, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer as KBr discs unless otherwise stated. The ^1H n.m.r. spectra were recorded at room temperature in $[\text{}^2\text{H}_1]\text{-chloroform}$, unless otherwise stated, on a Bruker AM 300 spectrometer operating at 300.13 MHz, or on a Varian EM 390 spectrometer operating at 90 MHz, with SiMe_4 (0.0 p.p.m.) as internal reference, positive values being to high frequency (low-field). Coupling constants J are in Hz. The $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectra were recorded in $[\text{}^2\text{H}_1]\text{-chloroform}$ at room temperature on a Bruker AM 300 spectrometer operating at 75.47 MHz, with SiMe_4 (0.0 p.p.m.) as internal reference. The $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra were recorded in dichloromethane, unless otherwise stated, either on a JEOL FX90Q spectrometer operating at 36.21 MHz, or on a JEOL JNM-FX60 spectrometer operating at 24.15 MHz, with $[\text{P}(\text{OH})_4]^+$ in $[\text{}^2\text{H}_2]\text{-water}$ (0.0 p.p.m.) as external reference, with positive values to high frequency (low-field). The low-field components in second-order AB spin system $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra are arbitrarily assigned as P_A . 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: acetone (potassium carbonate); 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. Absolute ethanol was used as supplied. The compounds 1,2-bis-(diphenylphosphino)ethane, carbon disulphide, dimethylphenylphosphine, iodomethane, mercuric chloride, methyldiphenylphosphine, n-butyl lithium (2.5 mol dm⁻³), N,N'-diphenylthiourea, N-phenylthiourea, phenyl isocyanate, phenyl isothiocyanate, sodium hydride, sodium periodate, thiourea, triethylphosphine, triethylphosphite, trimethyloxonium tetrafluoroborate, trimethylphosphite (Aldrich), silver(I) oxide, sulphur dioxide (BDH), carbon monoxide, hydrogen chloride (BOC), fluoroboric acid (54% solution in diethyl ether) and t-butyl isocyanide

(Fluka) were used as supplied from commercial sources. The compounds [PtCl₂(COD)],¹³¹ *cis*-[PtCl₂(PNEt₂Ph₂)₂],¹¹⁹ [PtCl₂(dppe)],¹³² *cis*-[PtCl₂(PPh₃)₂],¹⁸⁵ *cis*-[PtCl₂(AsPh₃)₂],¹³³ [PdCl₂(COD)],¹³⁴ [Rh(Cl)(CO)(dppm)]₂,¹²⁸ [Rh₂(μ-S)(CO)₂(dppm)]₂,¹²⁸ and PEt₂Ph¹³⁵ were prepared as described in the literature. Platinum metal salts were obtained on loan from Johnson Matthey plc.

2.9.1 Preparation of platinathiazetidine-3-imine complexes

(a) using silver(I) oxide; general method

Two equivalents of tertiary phosphine or tertiary phosphite, followed by one equivalent of N,N'-diphenylthiourea, and an excess of silver(I) oxide were added in succession to a stirred solution of [PtCl₂(COD)] in dichloromethane, and the mixture refluxed for 2.5h. The mixture was filtered through celite and the filtrate evaporated to dryness under reduced pressure. Dissolution of the residual oil in dichloromethane (ca. 2 cm³) followed by addition of light petroleum gave powdery solids which were recrystallised from dichloromethane - light petroleum, and dried in vacuo.

(i) [Pt{NPhC(=NPh)S}(PPh₃)₂] (107)

The complex [PtCl₂(COD)] (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and N,N'-diphenylthiourea (0.062g, 0.27 mmol) in dichloromethane (35 cm³) gave pale yellow crystals of the title complex (107) (0.20g, 78%) (Found: C, 61.4; H, 4.5; N, 2.8. C₄₉H₄₀N₂P₂PtS requires C, 62.2; H, 4.3; N, 3.0%), m.p. >230°C; ν_(C=N) at 1550vs cm⁻¹. N.m.r. spectra: ¹³C-¹H (75.5 MHz), C=N not observed, δ 134.85-120.61 p.p.m. (m, Ph); ³¹P-¹H (36 MHz), second-order AB spin-system, δ 16.05 {d, P_A, ¹J[PtP_A] 3103, ²J[P_BP_A] 22.0}, and 11.44 p.p.m. {d, P_B, ¹J[PtP_B] 3261, ²J[P_AP_B] 22.0}. These crystals were suitable for single-crystal X-ray diffraction.

(ii) [Pt{NPhC(=NPh)S}(PMePh₂)₂] (108).CH₂Cl₂

The complex [PtCl₂(COD)] (0.30g, 0.80 mmol) with methyldiphenylphosphine (0.34g, 1.70 mmol) and N,N'-diphenylthiourea (0.19g, 0.83 mmol) in dichloromethane (70 cm³) gave dark yellow crystals of (108).CH₂Cl₂ (0.39g, 54%) (Found: C, 52.9; H, 4.3; N, 3.2.

$C_{39}H_{36}N_2P_2PtS \cdot CH_2Cl_2$ requires C, 53.0; H, 4.2; N, 3.1%), m.p. 128-135°C; $\nu_{(C=N)}$ at 1547 vs cm^{-1} . N.m.r. spectra: 1H (300 MHz), δ 7.80-6.50 (m, 30H, Ph), 5.22 (s, 2H, CH_2Cl_2), 1.63 [d, second-order, 3H, Me, $PMePh_2$, $|^2J(PH) + ^4J(PH)|$ 9.96, $^3J(PtH)$ 29.7], and 1.27 p.p.m. [d, second-order, 3H, Me, $PMePh_2$, $|^2J(PH) + ^4J(PH)|$ 9.84, $^3J(PtH)$ 28.1]; ^{13}C - $\{^1H\}$ (75.5 MHz), δ 148.03 (s, C=N), 132.50-120.81 (m, Ph), 15.66 [dd, second-order, Me, $PMePh_2$, $|^1J(PC) + ^3J(PC)|$ not discernible, $^2J(PtC)$ not discernible], and 14.25 p.p.m. [dd, second-order, Me, $PMePh_2$, $|^1J(PC) + ^3J(PC)|$ not discernible, $^2J(PtC)$ not discernible]; ^{31}P - $\{^1H\}$ (24 MHz), second-order AB spin-system, δ 1.81 {d, P_A , $^1J[PtP_A]$ 3090, $^2J[P_BP_A]$ 22.0}, and -9.11 p.p.m. {d, P_B , $^1J[PtP_B]$ 3125, $^2J[P_AP_B]$ 22.0}. These crystals were suitable for single-crystal X-ray diffraction.

(iii) $[Pt\{NPhC(=NPh)S\}(PMe_2Ph)_2](109) \cdot 2CH_2Cl_2$

The complex $[PtCl_2(COD)]$ (0.10g, 0.27 mmol) with dimethylphenylphosphine (0.075g, 0.54 mmol) and N,N' -diphenylthiourea (0.062g, 0.27 mmol) in dichloromethane (35 cm^3) gave dark yellow crystals of $(109) \cdot 2CH_2Cl_2$ (0.16g, 68%) (Found: C, 42.8; H, 4.1; N, 3.3. $C_{29}H_{32}N_2P_2PtS \cdot 2CH_2Cl_2$ requires C, 42.9; H, 4.2; N, 3.2%), m.p. 190-200°C (decomp.); $\nu_{(C=N)}$ at 1555 vs cm^{-1} . N.m.r. spectra: 1H (300 MHz), δ 7.56-6.89 (m, 20H, Ph), 5.36 (s, 4H, CH_2Cl_2), 1.63 [d, second-order, 6H, Me, PMe_2Ph , $|^2J(PH) + ^4J(PH)|$ 10.38, $^3J(PtH)$ 33.2], and 1.09 p.p.m. [d, second-order, 6H, Me, PMe_2Ph , $|^2J(PH) + ^4J(PH)|$ 10.15, $^3J(PtH)$ 27.8]; ^{13}C - $\{^1H\}$ (75.5 MHz), δ 148.28 (s, C=N), 130.91-121.35 (m, Ph), 16.04 [dd, second-order, Me, PMe_2Ph , $|^1J(PC) + ^3J(PC)|$ not discernible, $^2J(PtC)$ not discernible], and 14.43 p.p.m. [dd, second-order, Me, PMe_2Ph , $|^1J(PC) + ^3J(PC)|$ 60.38, $^2J(PtC)$ not discernible]; ^{31}P - $\{^1H\}$ (24 MHz), second-order AB spin-system, δ -13.82 {d, P_A , $^1J[PtP_A]$ 3047, $^2J[P_BP_A]$ 24.4}, and -24.71 p.p.m. {d, P_B , $^1J[PtP_B]$ 3057, $^2J[P_AP_B]$ 24.4}.

(iv) $[Pt\{NPhC(=NPh)S\}(PEt_2Ph)_2](110)$

The complex $[PtCl_2(COD)]$ (0.10g, 0.27 mmol) with diethylphenylphosphine (0.093g, 0.56 mmol) and N,N' -diphenylthiourea (0.062g, 0.27 mmol) in dichloromethane (35 cm^3) gave pale yellow crystals of (110) (0.18g, 89%). Compound not obtained analytically pure;

m.p. semi-melts 142-155°C, complete melting 210-212°C (decomp.); $\nu_{(C=N)}$ at 1550 cm^{-1} . N.m.r. spectra: The ^1H n.m.r. spectrum (CD_2Cl_2) showed some decomposition of the compound. ^{13}C - $\{^1\text{H}\}$ (75.5 MHz, DEPT), δ 147.99 (s, C=N), 131.75-118.50 (m, Ph), 16.90-14.84 (m, CH_2 , PEt_2Ph), and 7.98-7.85 p.p.m. (m, Me, PEt_2Ph); ^{31}P - $\{^1\text{H}\}$ (24 MHz), second-order AB spin-system, δ 5.75 {d, P_A , $^1\text{J}[\text{PtP}_A]$ 3027, $^2\text{J}[\text{P}_B\text{P}_A]$ 24.4}, and -5.14 p.p.m. {d, P_B , $^1\text{J}[\text{PtP}_B]$ 3120, $^2\text{J}[\text{P}_A\text{P}_B]$ 24.4}.

(v) $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}(\text{PEt}_3)_2]$ (111)

The complex $[\text{PtCl}_2(\text{COD})]$ (0.15g, 0.40 mmol) with triethylphosphine (0.096g, 0.81 mmol) and *N,N'*-diphenylthiourea (0.093g, 0.41 mmol) in dichloromethane (40 cm^3) gave a dark brown oily product. N.m.r. spectrum: ^{31}P - $\{^1\text{H}\}$ (24 MHz), second-order AB spin-system, δ 8.47 {d, P_A , $^1\text{J}[\text{PtP}_A]$ 2988, $^2\text{J}[\text{P}_B\text{P}_A]$ 19.5}, and -2.62 p.p.m. {d, P_B , $^1\text{J}[\text{PtP}_B]$ 3081, $^2\text{J}[\text{P}_A\text{P}_B]$ 19.5}. Attempts to obtain a solid product led to decomposition.

(vi) $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}\{\text{P}(\text{OMe})_3\}_2]$ (113)

The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) with trimethylphosphite (0.066g, 0.54 mmol) and *N,N'*-diphenylthiourea (0.062g, 0.27 mmol) in dichloromethane (35 cm^3) gave a brown oily residue. N.m.r. spectra: ^1H (90 MHz), δ 7.30-6.30 (m, 10H, Ph), and 3.80-3.10 p.p.m. [m, 18H, Me, $\text{P}(\text{OMe})_3$]; ^{31}P - $\{^1\text{H}\}$ (24 MHz), second-order AB spin-system, δ 100.94 {d, P_A , $^1\text{J}[\text{PtP}_A]$ not discernible, $^2\text{J}[\text{P}_B\text{P}_A]$ 63.5}, and 90.86 p.p.m. {d, P_B , $^1\text{J}[\text{PtP}_B]$ not discernible, $^2\text{J}[\text{P}_A\text{P}_B]$ 63.5}. No solid product could be obtained from the reaction mixture. The ^1H n.m.r. spectrum of the crude product also contained peaks at approximately δ 5.45 and 2.25 p.p.m., arising from free COD ligand.

(vii) $[\text{Pt}\{\text{NPhC}(=\text{NPh})\text{S}\}\{\text{P}(\text{OEt})_3\}_2]$ (114)

The complex $[\text{PtCl}_2(\text{COD})]$ (0.13g, 0.35 mmol) with triethylphosphite (0.12g, 0.72 mmol) and *N,N'*-diphenylthiourea (0.081g, 0.35 mmol) in dichloromethane (45 cm^3) gave a dark yellow oily residue. N.m.r. spectra: The ^1H n.m.r. spectrum of the crude product showed resonances arising from the product, free COD ligand and other unidentified compounds; ^{31}P - $\{^1\text{H}\}$ (24 MHz), second-order AB spin-system, δ 95.60 {d, P_A , $^1\text{J}[\text{PtP}_A]$ 4844, $^2\text{J}[\text{P}_B\text{P}_A]$

58.6), and 84.71 p.p.m. {d, P_B, ¹J[PtP_B] 4878, ²J[P_AP_B] 58.6}.

Preparation of [Pt{NPhC(=NPh)S}(PNEt₂Ph₂)₂] (112)

N,N'-diphenylthiourea (0.062g, 0.27 mmol) and silver(I) oxide (0.38g, 1.64 mmol) were added in succession to a stirred solution of *cis*-[PtCl₂(PNEt₂Ph₂)₂] (0.20g, 0.26 mmol) in dichloromethane (70 cm³), and the mixture refluxed for 3h. The insoluble silver salts were filtered off on a pad of celite to yield a dark yellow solution, which was reduced in volume to ca. 3 cm³. Addition of light petroleum gave a pale yellow solid, which was recrystallised from dichloromethane - light petroleum, and dried in vacuo to give yellow microcrystals of [Pt{NPhC(=NPh)S}(PNEt₂Ph₂)₂] (112) (0.125g, 51%) (Found: C, 57.4; H, 5.4; N, 5.6. C₄₅H₅₀N₄P₂PtS requires C, 57.7; H, 5.4; N, 6.0%), m.p. semi-melts >100°C, complete melting 122°C (decomp.); $\nu_{(C=N)}$ at 1552s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.45-6.60 (m, 30H, Ph), 3.25-2.85 (m, 8H, CH₂, PNEt₂Ph₂), 1.03 [t, 6H, Me, PNEt₂Ph₂, ³J(HH) 6.80], and 0.85 p.p.m. [t, 6H, Me, PNEt₂Ph₂, ³J(HH) 6.37]; ³¹P-¹H (36 MHz), second-order AB spin-system, δ 61.85 {d, P_A, ¹J[PtP_A] 3408, ²J[P_BP_A] 24.4}, and 54.92 p.p.m. {d, P_B, ¹J[PtP_B] 3572, ²J[P_AP_B] 24.4}.

Preparation of [Pt{NPhC(=NPh)S}(dppe)] (115)

N,N'-diphenylthiourea (0.070g, 0.31 mmol) and silver(I) oxide (0.42g, 1.81 mmol) were added in succession to a stirred solution of [PtCl₂(dppe)] (0.186g, 0.28 mmol) in dichloromethane (50 cm³), and the mixture refluxed for 2.5h. The insoluble silver salts were removed by filtration through a pad of celite, the filtrate being reduced in volume to ca. 2 cm³ under reduced pressure. Addition of light petroleum afforded a pale yellow powdery solid, which was filtered off and washed with light petroleum and diethyl ether to give [Pt{NPhC(=NPh)S}(dppe)] (115) (0.163g, 71%) (Found: C, 56.3; H, 4.9; N, 2.5. C₃₉H₃₄N₂P₂PtS requires C, 57.1; H, 4.2; N, 3.4%), m.p. semi-melts 120°C, decomp. >150°C; $\nu_{(C=N)}$ at 1551s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.79-6.49 (m, 30H, Ph), and 2.27-2.13 p.p.m. (m, 4H, CH₂, dppe); ¹³C-¹H (75.5 MHz), δ 148.22 (s, C=N), 133.35-121.02 (m, Ph), and ca. 31-27 p.p.m. (m, CH₂, dppe); ³¹P-¹H (36 MHz), second-order AB spin-system, δ

43.41 {d, P_A, ¹J[PtP_A] 3091, ²J[P_BP_A] 9.8}, and 37.01 p.p.m. {d, P_B, ¹J[PtP_B] 3054, ²J[P_AP_B] 9.8}.

(b) using sodium hydroxide

Triphenylphosphine (0.15g, 0.57 mmol), N,N'-diphenylthiourea (0.062g, 0.27 mmol), and an excess of sodium hydroxide were added in succession to a stirred suspension of [PtCl₂(COD)] (0.10g, 0.27 mmol) in a mixture of dichloromethane (ca. 10 cm³) and THF (ca. 30 cm³), and the mixture refluxed for 1h, yielding a lemon yellow solution. The mixture was filtered to remove excess sodium hydroxide and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (ca. 20 cm³), and the solution washed with water (ca. 10 cm³). The dichloromethane layer was separated off and dried over anhydrous MgSO₄. The mixture was filtered and reduced to ca. 2 cm³ under reduced pressure, and addition of light petroleum yielded pale yellow microcrystals of (107) (0.162g, 63%), identified by comparison of their ³¹P-{¹H} n.m.r. spectrum with that of an authentic sample.

(c) using the dianion (106)

(i) Preparation of (106)

Sodium hydride (0.35g, 14.6 mmol) was placed in a schlenk and washed with two portions of light petroleum (ca. 2 x 20 cm³), the solid being dried under vacuum after each washing. THF (ca. 50 cm³) was then added, followed by N,N'-diphenylthiourea (1.00g, 4.38 mmol), with stirring, whereupon vigorous effervescence and formation of a pale green solution was observed. After stirring for 0.5h at room temperature, the mixture was cooled to -78°C and n-butyl lithium (1.75 cm³, 2.5 mol dm⁻³, 4.38 mmol) was added. The mixture was stirred at this temperature for 10 min and then allowed to warm slowly to room temperature. After stirring overnight the pale orangy-red mixture which had formed was filtered under nitrogen. 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.

(ii) Reaction of $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ with (106)

One mole equivalent of (106) was added to a stirred suspension of $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ (0.15g, 0.19 mmol) in THF (ca. 40 cm³) at -78°C. The mixture was stirred at -78°C for 15 min and then allowed to warm slowly to room temperature, whereupon it was stirred overnight, to give a pale yellow solution. The solution was evaporated to dryness under reduced pressure, and the residue extracted with toluene, the resulting solution being filtered. The filtrate was evaporated to dryness under reduced pressure, the residue dissolved in dichloromethane (ca. 5 cm³), and addition of light petroleum yielded a pale yellow solid which was filtered off and dried in vacuo to give (107) (0.10g, 56%), identified by comparison of its ³¹P-¹H} n.m.r. and i.r. spectra with those of an authentic sample.

(iii) Reaction of $\text{cis-}[\text{PtCl}_2(\text{AsPh}_3)_2]$ with (106)

Using a procedure similar to that described above, $\text{cis-}[\text{PtCl}_2(\text{AsPh}_3)_2]$ (0.50g, 0.57 mmol) and one mole equivalent of (106) in THF (ca. 50 cm³) gave yellow microcrystals of $[\text{Pt}\{\text{NPhC(=NPh)S}\}(\text{AsPh}_3)_2]$ (116) (0.309g, 52%). Compound not obtained analytically pure; m.p. 135-150°C; $\nu_{(\text{C}=\text{N})}$ at 1560s cm⁻¹. The identity of the compound is supported by its reaction with triphenylphosphine.

2.9.2 Reaction of $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ with thiourea in the presence of an excess of silver(I) oxide

The procedure used here is similar to that described in (a). The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol), triphenylphosphine (0.15g, 0.57 mmol), thiourea (0.021g, 0.28 mmol), and an excess of silver(I) oxide in dichloromethane (25 cm³) were refluxed for 2.5h. The mixture was filtered through celite and the filtrate evaporated to dryness under reduced pressure. The ³¹P-¹H} n.m.r. spectrum of the resulting oily residue showed the presence of a mixture of compounds, from which none could be isolated.

2.9.3 Reaction of $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ with N-phenylthiourea in the presence of an excess of silver(I) oxide

In a similar experiment to that described above, the complex $[\text{PtCl}_2(\text{COD})]$ (0.15g, 0.40

mmol), triphenylphosphine (0.225g, 0.86 mmol), N-phenylthiourea (0.055g, 0.40 mmol), and an excess of silver(I) oxide in dichloromethane (35 cm³) were refluxed for 2.5h. The mixture was filtered to yield a pale yellowy-green solution, which was evaporated to dryness under reduced pressure. The ³¹P-{¹H} n.m.r. spectrum of the resulting residue contained numerous peaks.

2.9.4 Reaction of [PdCl₂(PPh₃)₂] with N,N'-diphenylthiourea in the presence of an excess of silver(I) oxide

In a similar experiment to that described above, triphenylphosphine (0.393g, 1.5 mmol), N,N'-diphenylthiourea (0.163g, 0.71 mmol), and an excess of silver(I) oxide were added in succession to a stirred solution of [PdCl₂(COD)] (0.20g, 0.70 mmol) in dichloromethane (75 cm³), and the mixture refluxed for 2.5h. Filtering through celite gave a brown-black solution, which was evaporated to dryness under reduced pressure. The ³¹P-{¹H} n.m.r. spectrum of the resulting residue showed the presence of a mixture of compounds. Attempts to obtain pure products by column chromatography were unsuccessful.

2.9.5 Reactions of platinathiazetidine-3-imine complexes

(a) Attempted oxidative addition reactions to [Pt{NPhC(=NPh)S}(PPh₃)₂] (107)

(i) with hydrogen chloride

Dry hydrogen chloride gas was bubbled slowly through a solution of complex (107) (0.10g, 0.11 mmol) in dichloromethane (ca. 10 cm³) for 5 min, during which a colour change of pale yellow to colourless was observed. The solution was evaporated to dryness under reduced pressure. A ³¹P-{¹H} n.m.r. spectrum of the resulting residue showed only the presence of cis-[PtCl₂(PPh₃)₂].

(ii) with mercuric chloride

Mercuric chloride (0.017g, 0.063 mmol) was added to a stirred solution of (107) (0.06g, 0.063 mmol) in acetone (30 cm³), which resulted in the immediate formation of a milky white suspension. The mixture was stirred for a further 2h at room temperature and was then evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane and then filtered. The solution was evaporated to dryness, the ³¹P-{¹H} n.m.r. spectrum of

the resulting residue showing only the presence of cis-[PtCl₂(PPh₃)₂].

(iii) with iodomethane

Iodomethane (0.023g, 0.16 mmol) was added to a stirred solution of (107) (0.10g, 0.11 mmol) in dichloromethane (25 cm³) at -78°C, the mixture stirred at this temperature for 15 min, and then allowed to warm slowly to room temperature, whereupon it was stirred overnight. The mixture was evaporated to dryness under reduced pressure to give an oily residue, which contained a number of phosphorus-containing products as shown by its ³¹P-{¹H} n.m.r. spectrum.

(b) Ligand substitution reactions of [Pt{NPhC(=NPh)S}(PPh₃)₂] (107)

(i) with methyldiphenylphosphine

Methyldiphenylphosphine (0.11g, 0.55 mmol) was added to a stirred solution of (107) (0.10g, 0.11 mmol) in dichloromethane (25 cm³), and the mixture refluxed for 1h. The mixture was then evaporated to dryness under reduced pressure, and the residue recrystallised twice from dichloromethane - light petroleum to yield a pale yellow powdery solid which was filtered off and dried in vacuo to give (108).CH₂Cl₂ (0.02g, 20%), identified by comparison of its ³¹P-{¹H} n.m.r. spectrum with that of an authentic sample.

(ii) with dimethylphenylphosphine

Dimethylphenylphosphine (0.097g, 0.70 mmol) was added to a stirred solution of (107) (0.15g, 0.16 mmol) in dichloromethane (25 cm³), and the mixture refluxed for 0.5h. The mixture was reduced to ca. 0.5 cm³ under reduced pressure, the addition of light petroleum giving a pale yellow powdery solid which was filtered off and dried in vacuo to give (109).2CH₂Cl₂ (0.04g, 29%), identified by comparison of its ³¹P-{¹H} n.m.r. spectrum with that of an authentic sample.

(iii) with 1,2-bis-(diphenylphosphino)ethane

1,2-bis-(Diphenylphosphino)ethane (0.040g, 0.10 mmol) was added to a stirred solution of (107) (0.09g, 0.095 mmol) in dichloromethane (30 cm³), and the mixture refluxed for 0.5h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised

from dichloromethane - light petroleum to give a pale yellow solid, which was filtered off and dried in vacuo (0.04g). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the solid showed the formation of (115), along with some decomposition of (107) during the reaction.

(iv) with t-butyl isocyanide

t-Butyl isocyanide (0.147g, 1.77 mmol) was added to a solution of (107) (0.30g, 0.32 mmol) in dichloromethane (25 cm³), and the mixture stirred for 1h at room temperature. The mixture was then evaporated to dryness, and the residue stirred with diethyl ether for 1h. The mixture was allowed to settle and the diethyl ether was decanted off. The remaining solid was washed with diethyl ether and was then filtered off, washed with diethyl ether and light petroleum, and dried in vacuo. The solid was recrystallised from dichloromethane - diethyl ether to give yellow microcrystals of $[\text{Pt}\{\overline{\text{NPhC(=NPh)S}}\}(\text{CNBu}^t)(\text{PPh}_3)]$ (119).CH₂Cl₂ (0.120g, 44%) (Found: C, 52.2; H, 4.4; N, 4.7. C₃₆H₃₄N₃PPtS.CH₂Cl₂ requires C, 52.2; H, 4.3; N, 4.9%), m.p. semi-melts >122°C, complete melting 155-165°C; $\nu_{(\text{C}\equiv\text{N})}$ at 2202vs; ν_{max} at 1614-1548 cm⁻¹. N.m.r. spectra: ^1H (300 MHz), δ 7.62-6.84 (m, 25H, Ph), 5.30 (s, 2H, CH₂Cl₂), and 0.99 p.p.m. (s, 9H, Bu^t); $^{31}\text{P}\{-^1\text{H}\}$ (36 MHz), δ 7.61 p.p.m. [s, $^1\text{J}(\text{PtP})$ 2971]. Repeating the reaction under refluxing conditions led to decomposition.

Reaction of $[\text{Pt}\{\overline{\text{NPhC(=NPh)S}}\}(\text{AsPh}_3)_2]$ (116) with triphenylphosphine

Triphenylphosphine (0.045g, 0.172 mmol) was added to a stirred solution of (116) (0.088g, 0.085 mmol) in dichloromethane (30 cm³), and the mixture refluxed for 2.5h. The solution was reduced in volume to ca. 1 cm³, addition of light petroleum yielding a pale yellow solid, which was filtered off, washed with diethyl ether and light petroleum, and dried in vacuo, to give (107) (0.050g, 62%), identified by comparison of its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum with that of an authentic sample.

(c) Reaction of $[\text{Pt}\{\overline{\text{NPhC(=NPh)S}}\}(\text{PPh}_3)_2]$ (107) with carbon monoxide

(i) in dichloromethane

Carbon monoxide was bubbled through a solution of (107) (0.20g, 0.22 mmol) in dichloromethane (40 cm³) and the course of the reaction monitored by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r.

spectroscopy. After approximately 13.5h the reaction was complete and the flow of carbon monoxide was turned off. The mixture was reduced in volume to ca. 1 cm³ and addition of diethyl ether gave a dirty green microcrystalline solid, which was filtered off and dried in vacuo. The solid was recrystallised three times from dichloromethane - diethyl ether, to yield grey microcrystals (0.070g, 34%). The purified compound was found to be insoluble in all common organic solvents. Compound not obtained analytically pure; m.p. >230°C (decomp.); $\nu_{(C=O)}$ at 1647s cm⁻¹; $\nu_{(C=N)}$ at 1578s cm⁻¹. N.m.r. spectrum (crude): ³¹P-¹H (36 MHz), second-order AB spin-system, δ 24.06 {d, P_A, ¹J[PtP_A] 3547, ²J[P_BP_A] 22.0}, and 17.06 p.p.m. {d, P_B, ¹J[PtP_B] 1846, ²J[P_AP_B] 22.0}.

(ii) in ethanol

Carbon monoxide was bubbled through a refluxing suspension of (107) (0.20g, 0.22 mmol) in absolute ethanol (60 cm³) for 6h, after which time a brown solid was seen suspended in an almost colourless solution. The carbon monoxide flow was turned off and the mixture allowed to cool. The mixture was then evaporated to dryness under reduced pressure to give a dark brown solid, the ³¹P-¹H n.m.r. spectrum of which showed it to be the same compound as obtained from the reaction in dichloromethane (above). The n.m.r. solution was filtered and reduced in volume to ca. 1 cm³ under reduced pressure. Addition of light petroleum gave a dirty white solid, which was filtered off, washed with light petroleum and then dissolved in dichloromethane, the solution being treated with activated charcoal for 15 min. The mixture was filtered and evaporated to ca. 1 cm³ under reduced pressure, addition of light petroleum giving an off-white solid which was filtered off and dried in vacuo (0.13g, 63%). The compound was found to be insoluble in all common organic solvents.

(d) Reaction of [Pt{NPhC(=NPh)S}(PPh₃)₂] (107) with carbon disulphide

Carbon disulphide (0.13g, 1.70 mmol) was added to a solution of (107) (0.10g, 0.11 mmol) in dichloromethane (25 cm³), and the mixture stirred for 24h at room temperature. The mixture was evaporated to dryness under reduced pressure, a ³¹P-¹H n.m.r. spectrum

of the residue showing only the presence of starting material. Addition of light petroleum to the n.m.r. sample gave a pale yellow solid, which was filtered off and dried in vacuo to yield (107) (0.071g, 71%).

(e) Reaction of [Pt{NPhC(=NPh)S}(PPh₃)₂] (107) with phenyl isothiocyanate

An excess of phenyl isothiocyanate was added to a stirred solution of (107) (0.10g, 0.11 mmol) in dichloromethane (25 cm³), and the mixture refluxed for 1.5h. The mixture was evaporated to dryness under reduced pressure, a ³¹P-{¹H} n.m.r. spectrum of the residue showing only the presence of starting material. Addition of light petroleum to the n.m.r. sample gave a pale yellow solid, which was filtered off and dried in vacuo to give (107) (0.081g, 81%).

(f) Reaction of [Pt{NPhC(=NPh)S}(PPh₃)₂] (107) with phenyl isocyanate

An excess of phenyl isocyanate was added to a stirred solution of (107) (0.12g, 0.13 mmol) in dichloromethane (35 cm³), and the mixture refluxed for 4h. The mixture was evaporated to dryness, the ³¹P-{¹H} n.m.r. spectrum of the resulting residue showing that extensive decomposition of the starting material has occurred.

(g) Reaction of [Pt{NPhC(=NPh)S}(PPh₃)₂] (107) with hydrogen peroxide

Twenty drops of hydrogen peroxide (20% v/v) were added to a solution of (107) (0.10g, 0.11 mmol) in a mixture of dichloromethane (30 cm³) and acetone (10 cm³), and the mixture refluxed for 4h, during which time the solution slowly darkened. The mixture was evaporated to dryness under reduced pressure and the residue dissolved in dichloromethane. The resulting solution was washed with water, the organic layer being decanted off and dried over anhydrous MgSO₄. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The ³¹P-{¹H} n.m.r. spectrum of the residue indicated the presence of a number of phosphorus-containing compounds, one of which showed an AB pattern, with components at δ 15.18 and 10.53 p.p.m. The main compound in the mixture was triphenylphosphine oxide. Attempts to separate the various species in the mixture were unsuccessful.

Repeating the reaction with an excess of hydrogen peroxide (100% v/v) at room

temperature overnight in dichloromethane (35 cm³), led, after work-up as above, to a residue which showed only the presence of starting material in its ³¹P-¹H n.m.r. spectrum.

(h) Miscellaneous reactions of [Pt{NPhC(=NPh)S}(PPh₃)₂] (107)

The ³¹P-¹H n.m.r. data for the following reactions are summarised in Table 3. The products were also studied by other spectroscopic techniques but could not be identified.

(i) with sodium periodate

A solution of sodium periodate (0.039g, 0.18 mmol) in water (5 cm³) was added to a solution of (107) (0.07g, 0.074 mmol) in THF (30 cm³), and an immediate colour change of pale yellow to colourless was observed. The mixture was stirred for 2h at room temperature, and was then evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (30 cm³), and the solution washed with water (10 cm³). The organic layer was dried over anhydrous MgSO₄ and the mixture filtered. The filtrate was reduced in volume to ca. 1 cm³, addition of light petroleum affording a white microcrystalline solid (0.043g). I.r. $\nu_{(C=N)}$ at 1557s cm⁻¹.

(ii) with sulphur dioxide

Sulphur dioxide gas was bubbled slowly through a solution of (107) (0.20g, 0.22 mmol) in dichloromethane (40 cm³) at room temperature for 30 min (after 1 min, the solution had changed from yellow to almost colourless). The solution was evaporated to dryness under reduced pressure to leave an oily residue. The residue was dissolved in dichloromethane (ca. 2 cm³), and the solution filtered. Addition of diethyl ether yielded a pale yellow solid (0.123g).

Sulphur dioxide was bubbled slowly through a refluxing solution of (107) (0.15g, 0.16 mmol) in dichloromethane (35 cm³) for 6h. The mixture was filtered through celite to give a pale yellow solution, and the solution reduced to ca. 1 cm³ under reduced pressure. Addition of diethyl ether gave a yellow solid, which was filtered off, washed with light petroleum and diethyl ether, and dried in vacuo (0.080g).

(iii) with fluoroboric acid

Fluoroboric acid (0.10 cm³, 54% solution in diethyl ether) was added to a solution of (107) (0.15g, 0.16 mmol) in dichloromethane (25 cm³), and a colour change of yellow to almost colourless was observed immediately. The mixture was stirred overnight at room temperature to yield a slightly cloudy yellow solution. The mixture was filtered and the resulting solution evaporated to dryness under reduced pressure to give an off-white oily residue. Dissolution of the oil in dichloromethane (ca. 1 cm³), followed by addition of diethyl ether gave a white microcrystalline solid, which was filtered off and dried in vacuo (0.062g).

(iv) with trimethyloxonium tetrafluoroborate

Trimethyloxonium tetrafluoroborate (0.028g, 0.19 mmol) was added to a solution of (107) (0.15g, 0.16 mmol) in dichloromethane (30 cm³), and the mixture stirred for 2h at room temperature (after 15 min, an almost colourless solution was observed, after which time no change occurred). The mixture was filtered and the solution reduced in volume to ca. 1 cm³ under reduced pressure. Addition of light petroleum gave a white microcrystalline solid, which was recrystallised from dichloromethane - light petroleum to give a highly crystalline colourless solid (0.038g).

2.9.6 Reaction of [Rh(Cl)(CO)(dppm)]₂ with (106)

1.45 Mole equivalents of (106) were added to a stirred suspension of [Rh(Cl)(CO)(dppm)]₂ (0.270g, 0.245 mmol) in THF (40 cm³) at room temperature, and the mixture stirred for 3h, resulting in a deep red solution. The mixture was evaporated to dryness under reduced pressure, and the residue extracted with diethyl ether. The mixture was filtered, the dark red solution evaporated to dryness under reduced pressure, and the minimum quantity of dichloromethane added to dissolve the resulting residue. Light petroleum was slowly added until the solution started to cloud over, and the mixture was left to stand overnight, whereupon reddy-orange crystals were formed, which were filtered off and dried in vacuo (0.105g, 41%). The ³¹P-¹H} n.m.r. spectrum of the product was the

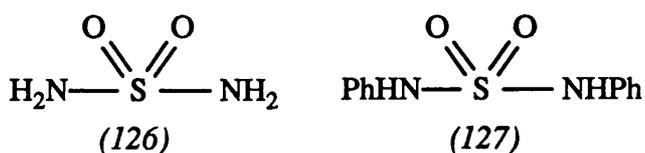
same as that of $[\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2]$ (125), as compared with the $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum of an authentic sample, made by the literature method.¹²⁸ $^{31}\text{P}\text{-}\{^1\text{H}\}$ (24 MHz) n.m.r. spectrum of $[\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2]$: δ 17.04 p.p.m. [d, $^1\text{J}(\text{RhP})$ 131.8].

CHAPTER 3

Synthesis and Reactivity of Platinathiadiazetidine-3,3-dioxide Complexes

3.1 INTRODUCTION

In Chapter 2 the use of silver(I) oxide as a powerful reagent in the synthesis of new four-membered platinacycles from platinum(II) dichloride complexes and *N,N'*-diphenylthiourea was described. These results and the availability of sulphamide (126) and *N,N'*-diphenylsulphamide (127)¹³⁶ led to an investigation into the synthesis of platinacycles containing the $[\overline{\text{Pt}\{\text{NRS}(\text{O})_2\text{NR}\}}]$ fragment (R = H or Ph) from these compounds and platinum(II) dichloride complexes using silver(I) oxide.



During the course of these studies Woollins *et al.* reported details of a different route to some of these complexes (i.e. $[\overline{\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}}]_2\text{L}_2$; L = PPh₃, PMePh₂, PMe₂Ph, PEt₃, or L₂ = dppe), from sulphamide or sulphuryl chloride in liquid ammonia in conjunction with platinum(II) dichloride complexes.^{137,138} However, a limited amount of data were reported in these references for the complexes, although a crystal structure of one of the derivatives (L = PMePh₂) was described.¹³⁷ Part of the work in this Chapter gives fuller data on some of the compounds also obtained in Refs. 137 and 138, as well as giving further examples of this type of compound. The crystal structure of the methyldiphenylphosphine derivative, also obtained during the current studies, is described and compared with that previously reported.¹³⁷ The synthesis of *N,N'*-diphenyl substituted complexes is also discussed here, the X-ray structure of one of these derivatives having been completed. Reactions of both the *N,N'*-unsubstituted and *N,N'*-diphenyl substituted complexes with a variety of reagents is discussed.

3.2 PREPARATION OF PLATINATHIADIAZETIDINE-3,3-DIOXIDE COMPLEXES

The complexes (128), (129), (131) and (134) were obtained from treatment of the corresponding *cis*-[PtCl₂L₂] complex (prepared *in situ* by reaction of [PtCl₂(COD)] with two mole equivalents of monodentate phosphine or one mole equivalent of bidentate phosphine)

All the complexes obtained from the reactions in the current study were isolated as air-stable solids, the N,N'-unsubstituted derivatives being white, whereas (135)-(140) ranged from white to yellow.

It was found that complexes (135), (137) and (140) could also be synthesised via treatment of the appropriate cis-phosphine platinum(II) dichloride complex with one mole equivalent of (127) in the presence of an excess of potassium hydroxide in a refluxing mixture of dichloromethane and THF.

3.3 STRUCTURAL PROPERTIES OF PLATINATHIA DIAZETIDINE-3,3-DIOXIDE COMPLEXES

Single-crystal X-ray diffraction studies were carried out on complexes (129) and $[\text{Pt}\{\overline{\text{NPhS(O)}_2\text{NPh}}\}(\text{COD})]$ (141) to establish the molecular geometry of platinathia-diazetidine-3,3-dioxide derivatives. The latter complex was isolated as a few crystals from a preparation of the bis(diphenylphosphino)ethane analogue. Selected bond lengths and angles for the complexes are shown in Tables 1 and 2, and the molecular structures of the complexes are depicted in Figures 1 and 2 with their crystallographic numbering systems. Complex (129) crystallises with two molecules of chloroform per molecule of complex.

It should be noted that in both compounds, there is a two-fold rotation axis about the Pt--S line, thus rendering all atoms on one side of the molecule exactly equivalent in relative position to the corresponding atoms on the other side of the molecule. For instance, in complex (129), N(1) is mapped exactly onto N(2), P(1) onto P(2) and so on. This effect is demonstrated in the tables of bond lengths and angles for the two complexes. Interestingly, this result for (129) contrasts with that found by Woollins et al. who observed no such rotation element about the Pt-S axis.¹³⁷ A consequence of the presence of this rotation element in the two molecules discussed here is that the four-membered rings are entirely flat, with no fold angles between the N(1)-Pt-N(2) and N(1)-S-N(2) planes. The crystal structure study previously reported by Woollins et al. shows that the four-membered ring in (129) is almost planar.¹³⁷ The complex $[\text{Rh}\{\text{S-t-Bu-N,N'-di-2,4,6-mesitylene-NSN}\}(\text{CO})_2]$ (142) possesses a four-membered RhN_2S ring in which the sulphur atom does not lie in the same plane as the

TABLE 1Selected bond lengths and angles for $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2] (129).2\text{CHCl}_3^a$

Bond Length	(Å)	Bond Angle	(°)
Pt – P(1), P(2)	2.243 (1)	P(1) – Pt – P(2)	98.0 (1)
Pt – N(1), N(2)	2.059 (5)	P(1) – Pt – N(1)	95.35
S – N(1), N(2)	1.615 (5)	P(2) – Pt – N(2)	95.35
S – O(1), O(2)	1.451 (4)	N(1) – Pt – N(2)	71.3 (3)
N(1) – H(1)	0.67 (4)	Pt – N(1) – S	96.3 (2)
N(2) – H(2)	0.67 (4)	Pt – N(2) – S	96.3 (2)
		N(1) – S – N(2)	96.0 (3)
		O(1) – S – O(2)	113.3 (4)
		Pt – N(1) – H(1)	115.0 (4)
		Pt – N(2) – H(2)	115.0 (4)
		H(1) – N(1) – S	107.0 (4)
		H(2) – N(2) – S	107.0 (4)

^a See Figure 1 for crystallographic numbering system.**TABLE 2**Selected bond lengths and angles for $[\text{Pt}\{\overline{\text{NPhS}(\text{O})_2\text{NPh}}\}(\text{COD})] (141)^a$

Bond Length	(Å)	Bond Angle	(°)
Pt – C(1), C(5)	2.162 (4)	C(1) – Pt – C(2)	37.3 (2)
Pt – C(2), C(6)	2.178 (4)	C(5) – Pt – C(6)	37.3 (2)
C(1) – C(2)	1.389 (8)	C(2) – Pt – C(6)	87.7 (2)
C(5) – C(6)	1.389 (8)	N(1) – Pt – N(2)	69.6 (2)
Pt – N(1), N(2)	2.020 (3)	Pt – N(1) – S	99.7 (2)
S – N(1), N(2)	1.617 (4)	Pt – N(2) – S	99.7 (2)
S – O(1), O(2)	1.435 (3)	N(1) – S – N(2)	91.0 (2)
N(1) – C(11)	1.408 (5)	O(1) – S – O(2)	112.3 (3)
N(2) – C(21)	1.408 (5)	Pt – N(1) – C(11)	137.1 (3)
		Pt – N(2) – C(21)	137.1 (3)
		C(11) – N(1) – S	122.3 (3)
		C(21) – N(2) – S	122.3 (3)

^a See Figure 2 for crystallographic numbering system.

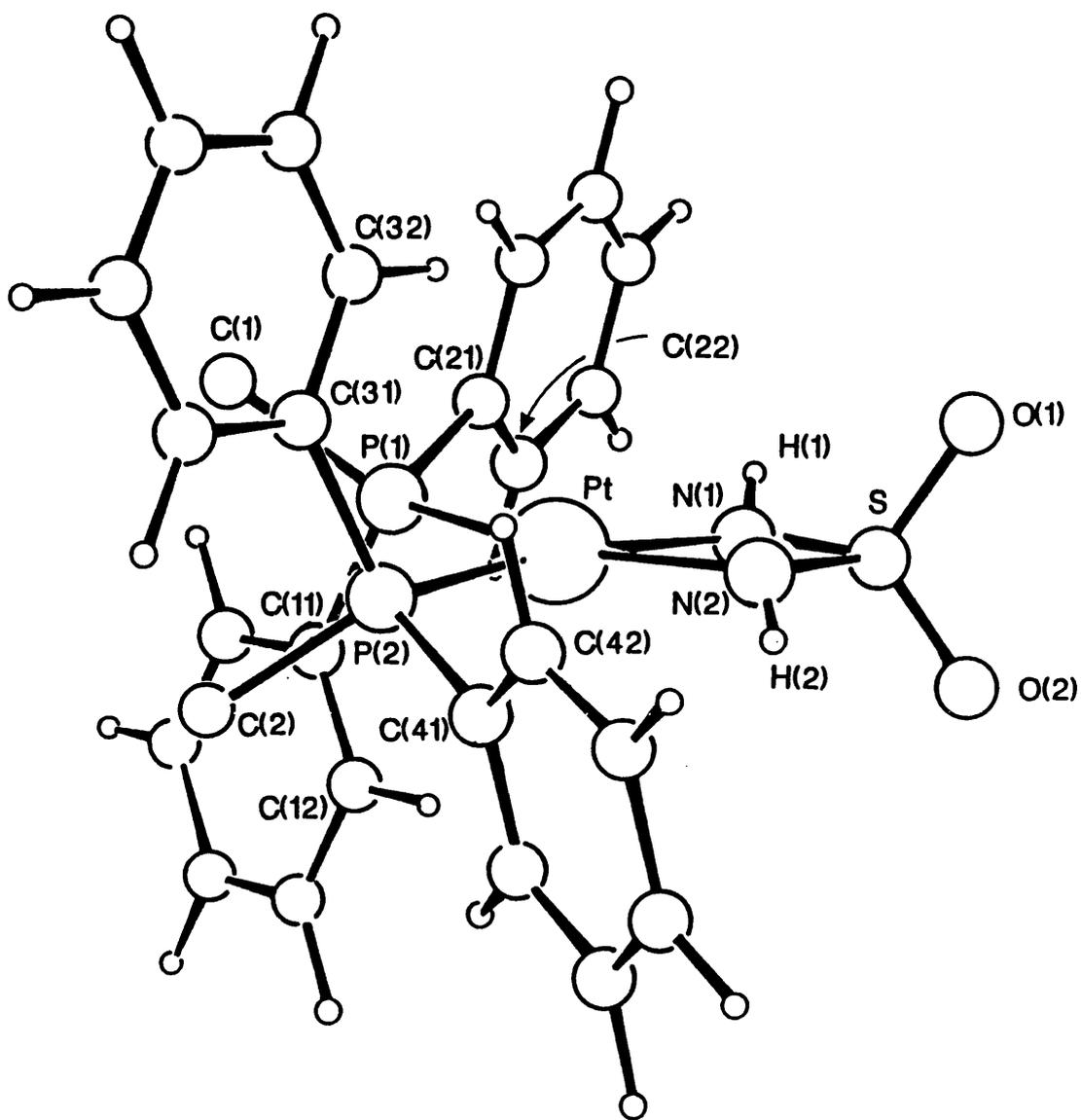


FIGURE 1

Molecular structure of $[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2] \cdot 2 \text{CHCl}_3$.

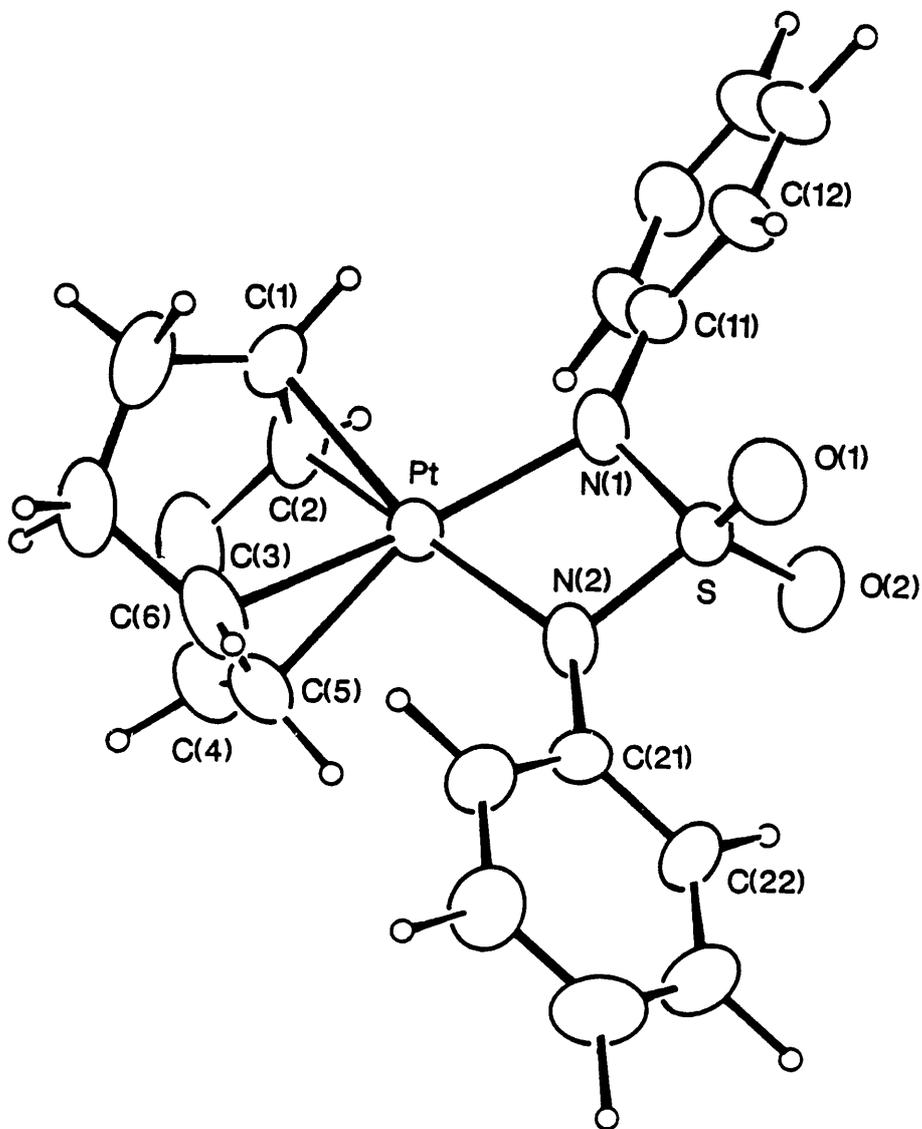
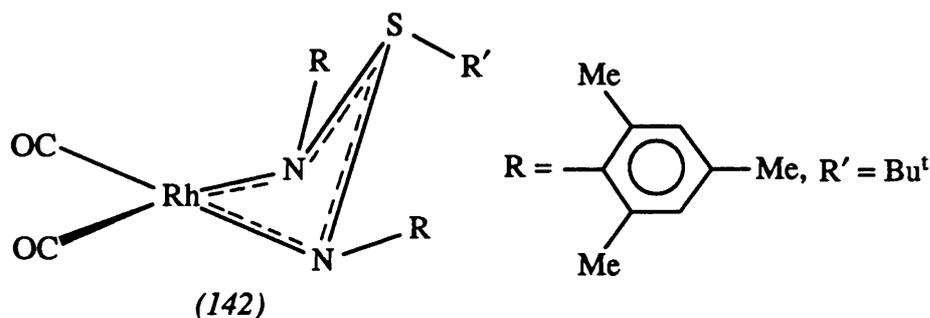


FIGURE 2
 Molecular structure of $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{COD})]$ (141).

rhodium and nitrogen atoms.^{139,140} The compound $[\text{Pt}\{\overline{\text{CH}(\text{COPh})\text{S}(\text{O})\text{CH}(\text{COPh})}\}(\text{PPh}_3)_2]$ (50, L = PPh₃) possesses a fold angle of 36.7°, the four-membered ring thus existing in a puckered conformation.⁵⁶



The bond lengths found for (129) here agree favourably with those reported by Woollins *et al.*¹³⁷ The S-O bonds are slightly longer than those reported for sulphamide [1.391Å,¹⁴¹ 1.429(1)Å¹⁴²] whereas the N-S bonds are very close in length to those in sulphamide.^{141,142} Interestingly, the S-O bond lengths are almost identical with those reported for disilver sulphamide [1.45(2)Å].¹⁴³

The S-O bond distances in (141) are slightly shorter than those observed for (129), whereas the N-S bond distances are surprisingly almost equal. The substitution of the hydrogen atoms on nitrogen in (129) by phenyl groups in (141) thus seems not to affect the N-S bond orders in the two complexes.

The N-H bond lengths in (129) found here are extremely short at 0.67(4)Å, the corresponding average value for sulphamide being of the order of 0.94Å.¹⁴² Woollins *et al.*¹³⁷ did not report the N-H bond distances. The phenyl rings attached to N(1) and N(2) in (141) are rotated somewhat out of the plane of the four-membered ring, and the N-phenyl bond lengths, at 1.408(5)Å, are of single bond character.

The two double bonds co-ordinated to the platinum atom in (141) have lengths similar to the corresponding bonds in [PtCl₂(COD)] [1.375(8) and 1.387(8)Å].¹⁴⁴ It should also be noted that the Pt-C(1) and Pt-C(2) bond lengths are not significantly different from each other and, in fact, are similar to the Pt-C bond lengths in [PtCl₂(COD)].¹⁴⁴ This situation also holds for the Pt-C(5) and Pt-C(6) bonds by virtue of the symmetry of (141). The similarity of

the Pt-C bond lengths to each other indicate that the cyclo-octa-1,5-diene ligand in (141) is essentially symmetrically co-ordinated to the platinum atom, as found for [PtCl₂(COD)] in Ref. 144. This latter observation contrasts with that found in an earlier structural study of [PtCl₂(COD)], in which a "slipping" of one of the double bonds attached to platinum was described, resulting in an unsymmetrically bound diene ligand.¹⁴⁵ It is strongly probable that this result is erroneous, however.¹⁴⁴

The N-S-N bond angles in the complexes (129) and (141) are considerably smaller than the corresponding angle seen in sulphamide [112.1(7)°,¹⁴¹ 111.45(8)°¹⁴²], this being a consequence of the presence of the four-membered rings in the two complexes. The N(1)-Pt-N(2) angle in (129) is slightly larger than that in (141).

Finally, the Pt---S non-bonding contact distances in (129) and (141) are 2.753(2)Å and 2.792(1)Å respectively, both values being outside the sum of the covalent radii (covalent radii : Pt 1.50; S 1.02Å¹⁴⁶), indicating no significant interaction between the platinum and sulphur atoms.

3.4 N.M.R. SPECTRA OF PLATINATHIADIAZETIDINE-3,3-DIOXIDE COMPLEXES

It was found that some of the derivatives synthesised via the silver(I) oxide methodology were insufficiently soluble to allow n.m.r. studies to be carried out. The complexes (128) and (134), synthesised by Woollins et al., were reported to be sufficiently soluble in organic solvents to enable such studies,¹³⁸ whereas the same compounds prepared here were found to be insoluble in all common solvents. The remaining N,N'-unsubstituted derivatives synthesised here and all the N,N'-diphenyl substituted derivatives were soluble in dichloromethane and chloroform.

The most interesting feature in the room temperature ¹H n.m.r. spectra of the soluble N,N'-unsubstituted derivatives studied here are the signals arising from the N-H protons, which are observed in the range δ 2.32-2.99 p.p.m. Unfortunately, although the general position of the resonances due to these protons (ca. δ 3 p.p.m.) is given for the same complexes in Ref. 138 by Woollins et al., no specific chemical shift data are reported. Thus a

direct comparison between coincident compounds obtained from the two different synthetic methods is not possible. No splitting of the N-H proton signals arising from possible coupling to platinum-195 or phosphorus-31 was observed at room temperature for the derivatives studied here.

A notable feature is seen in the ^1H n.m.r. spectrum of the methyldiphenylphosphine analogue (129). The methyl resonance region is observed as a filled-in doublet with corresponding platinum-195 satellites. Examples of bis(phosphine) metal complexes which show methyl groups as filled-in doublets in their ^1H n.m.r. spectra are known, for instance in the species $\text{cis-}[\text{PdL}_2(\text{N}_3)_2]$ ($\text{L} = \text{PMePh}_2$ or PMe_2Ph).¹⁴⁷ Figure 3 shows the region containing both the N-H and methyl resonances of (129).

The ^1H n.m.r. spectra of the N,N'-diphenyl substituted derivatives were unremarkable, as were the $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra of the derivatives studied by this method.

The room temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of all the soluble complexes consist of a single resonance with corresponding platinum-195 satellites. Chemical shifts and $^1\text{J}(\text{PtP})$ for the soluble derivatives (129) and (132) compare favourably with those quoted previously by Woollins *et al.* for the coincident complexes.¹³⁸ In the case of the complexes (133) and (139) containing aminophosphine ligands, the coupling constants $^1\text{J}(\text{PtP})$ are larger than those for the complexes containing other monodentate phosphines, a similar effect already having been noted in Chapter 2 for the platinathiazetidines. Interestingly, the chemical shift values for the soluble derivatives (129), (131), (132) and (133), and the corresponding N,N'-diphenyl substituted derivatives show the same variation with phosphine.

In several preparations of the complexes (135) and (137) small amounts of by-products were observed in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of the crude reaction residues, the quantities of which varied from reaction to reaction. These species exhibited single phosphorus resonances with corresponding platinum-195 satellites. They were removed by recrystallisation and were not isolated, thus their natures are unknown.

3.5 I.R. SPECTRA OF PLATINATHIAZETIDINE-3,3-DIOXIDE COMPLEXES

Table 3 shows the i.r. data for the asymmetric and symmetric stretching modes of the

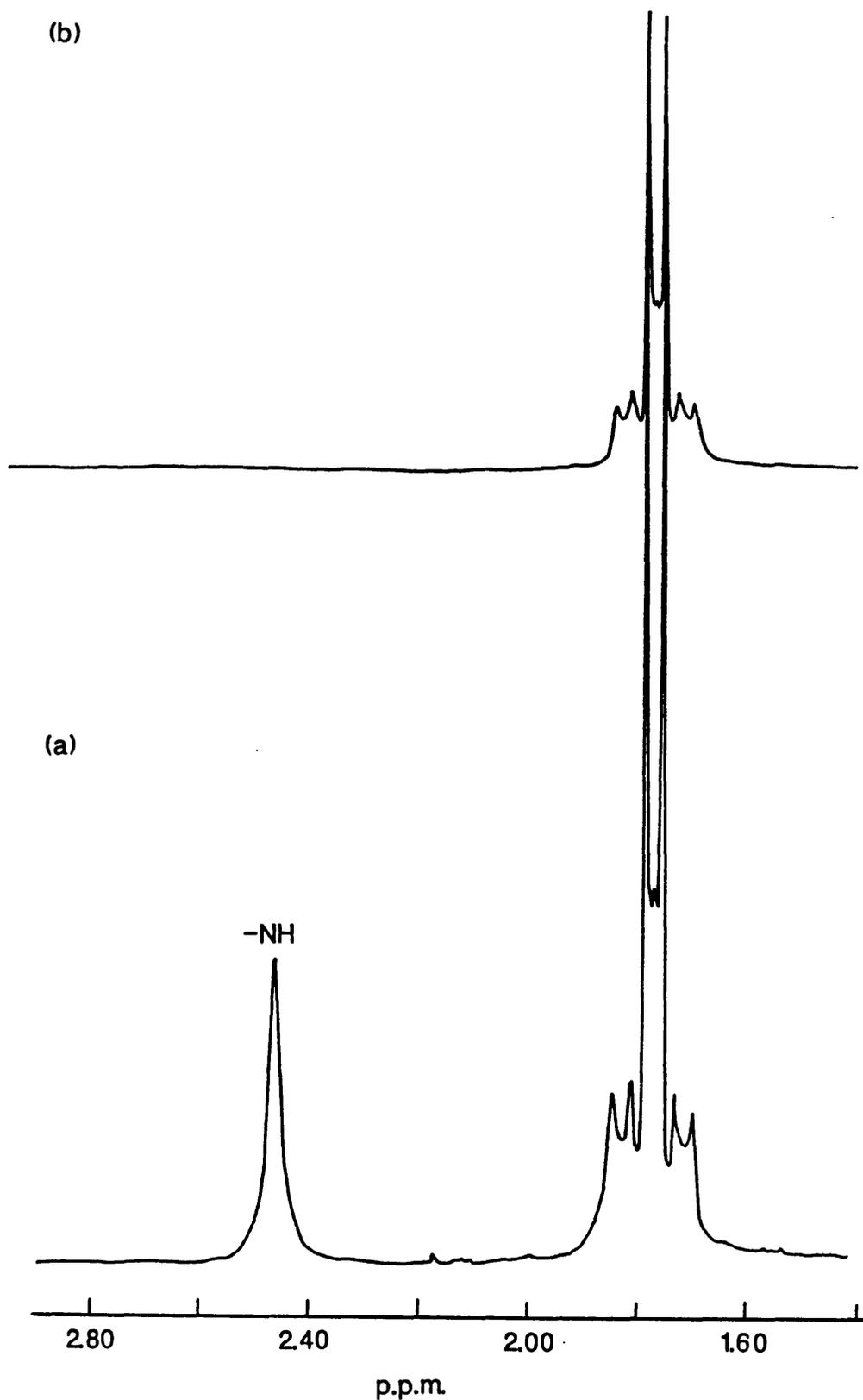


FIGURE 3

Room temperature ^1H n.m.r. spectrum at 300 MHz for the NH and methyl region of $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ (129) (a) before D_2O shake, (b) after D_2O shake.

TABLE 3

Asymmetric and symmetric $\nu(\text{SO})_2$ frequencies^a in the i.r. spectra of the complexes $[\text{Pt}\{\text{NRS}(\text{O})_2\text{NR}\}\text{L}_2]$, R = H or Ph

Complex	ν_{asym}^b	ν_{sym}^b	ν_{asym}^c	ν_{sym}^c
$[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PPh}_3)_2]$ (128)	1278 vs	1171 vs, 1158 vs, 1100 vs	1270 vs	1171 m, 1110 vs
$[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ (129)	1270 vs	1146 vs, 1114 vs	1261 vs	1137 vs, 1117 vs
$[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PEt}_2\text{Ph})_2]$ (131)	1274 vs	1170 vs, 1108 vs	–	–
$[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PEt}_3)_2]$ (132)	1261 vs(br)	1117 vs(br)	1262 vs	1170 m, 1115 vs
$[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PNEt}_2\text{Ph}_2)_2]$ (133)	1288 vs	1175 vs, 1108 vs	–	–
$[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{dppe})]$ (134)	1278 vs	1176 vs, 1116 vs	1272 vs	1113 vs
$[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PPh}_3)_2]$ (135)	1258 vs	1130 vs, 1100 vs	–	–
$[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PMePh}_2)_2]$ (136)	1260 vs	1135 vs, 1107 vs	–	–
$[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PEt}_2\text{Ph})_2]$ (137)	1245 vs	1142 vs, 1114 m	–	–
$[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PEt}_3)_2]$ (138)	1261 vs	1142 vs	–	–
$[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PNEt}_2\text{Ph}_2)_2]$ (139)	1260 vs	1132 vs, 1093 s	–	–
$[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{dppe})]$ (140)	1246 vs	1132 vs, 1114 vs	–	–

^a In cm^{-1} ; all spectra taken of samples as KBr discs; ^b Current study; ^c Values taken from Ref. 138 and reassigned.

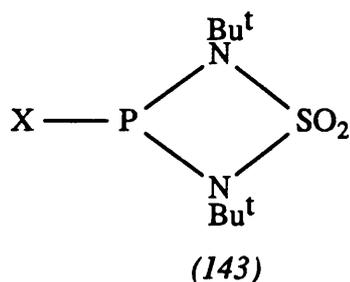
sulphonyl grouping for all the complexes [except (141)] obtained in this study, and several data are also included for the coincident N,N'-unsubstituted complexes synthesised in Refs. 137 and 138. It should be noted that in Ref. 138 asymmetric $\nu(\text{SO}_2)$ modes were incorrectly assigned as symmetric $\nu(\text{SO}_2)$ modes, and vice versa; the data has been correctly reassigned in Table 3.

Both the N,N'-unsubstituted and diphenyl substituted derivatives show very strong bands attributable to asymmetric and symmetric $\nu(\text{SO}_2)$ modes in their i.r. spectra. In both types of compound, except for the triethylphosphine derivatives, several bands are observed for the latter stretching mode. There is a favourable comparability between one of these bands reported in Ref. 138 and one of those observed for the coincident complexes in the present study (see Table 3). Additionally, there is a close correlation between one of the symmetric $\nu(\text{SO}_2)$ frequencies (or the only such frequency in the triethylphosphine case) of the N,N'-diphenyl substituted derivatives with the symmetric $\nu(\text{SO}_2)$ frequency reported for N,N'-diphenylsulphamide.¹⁴⁸ Only one band is seen for the asymmetric stretching mode for each complex. This band in the N,N'-unsubstituted complexes is, with the exception of the triethylphosphine derivative, observed at a slightly higher frequency than those bands in the corresponding N,N'-diphenyl substituted derivatives. In the triethylphosphine-containing complexes, the asymmetric modes appear at the same frequency. Again, the frequencies reported in Ref. 138 for the asymmetric stretching modes in the unsubstituted complexes are similar to those reported here for the coincident complexes.

Overall, the asymmetric stretching frequencies are lowered relative to that observed in sulphamide itself.¹⁴⁹ Such decreases have been observed in metal complexes containing O,O-bonded sulphamide anions (i.e. $[\text{CoX}_2] \cdot \text{H}_2\text{O}$, where $\text{X} = [\text{NH}_2\text{S}(\text{O})_2\text{NH}]^-$) or N,O-bonded dianions (i.e. $[\text{NiX}] \cdot \text{MeOH} \cdot \text{H}_2\text{O}$ or $[\text{CuX}] \cdot \text{MeOH}$, where $\text{X} = [\text{NHS}(\text{O})_2\text{NH}]^{2-}$).¹⁵⁰ In view of the crystal structure and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectral data reported here and by Woollins et al., this type of co-ordination of the sulphamide dianion is excluded in the present complexes. Interestingly, Woollins et al. made no specific reference to this observed decrease in the asymmetric stretching frequencies with respect to sulphamide.¹³⁸

The N,N'-unsubstituted derivatives also show either one or two bands arising from N-H stretching modes, in the range 3346-3165 cm⁻¹. In contrast, only one such band is reported for these type of complexes by Woollins *et al.*¹³⁸

Finally, it should be noted that phosphorus four-membered ring compounds of the type (143) are known (where X = Cl, F or NMe₂).¹⁵¹ In these systems, symmetric and asymmetric stretching sulphonyl frequencies are observed in the regions 1168-1178 and 1295-1330 cm⁻¹ respectively.



3.6 REACTIONS OF [Pt{NHS(O)₂NH}(PMePh₂)₂] (129)

3.6.1 Reaction of (129) with Hydrogen Chloride

The treatment of (129) with a slow stream of gaseous hydrogen chloride in dichloromethane at room temperature led only to the formation of *cis*-[PtCl₂(PMePh₂)₂], as evidenced by comparison of the ³¹P-¹H} n.m.r. spectrum of the reaction residue with that of an authentic sample.¹³²

3.6.2 Reaction of (129) with Carbon Monoxide

Reaction of complex [Pt{NHS(O)₂NH}(PMePh₂)₂] (129) with a slow stream of carbon monoxide in dichloromethane for 6h at room temperature yielded only starting material. The same result was observed when the reaction was carried out under refluxing conditions for 24h.

3.6.3 Reaction of (129) with Sulphur Dioxide

Sulphur dioxide was bubbled through a dichloromethane solution of (129) for 4h at room temperature, resulting in the formation of a mixture of several phosphorus-containing compounds as seen in the ³¹P-¹H} n.m.r. spectrum of the reaction residue. One of the

products present exhibited an AB pattern with components at δ 3.53 and -6.15 p.p.m., with corresponding platinum-195 satellites, the $^1\text{J}(\text{PtP})$ coupling constants being 2363 Hz and 4160 Hz respectively. However, several attempts to separate the various products and obtain pure species suitable for further characterisation were unsuccessful.

3.6.4 Attempted Deprotonation of (129) at Nitrogen

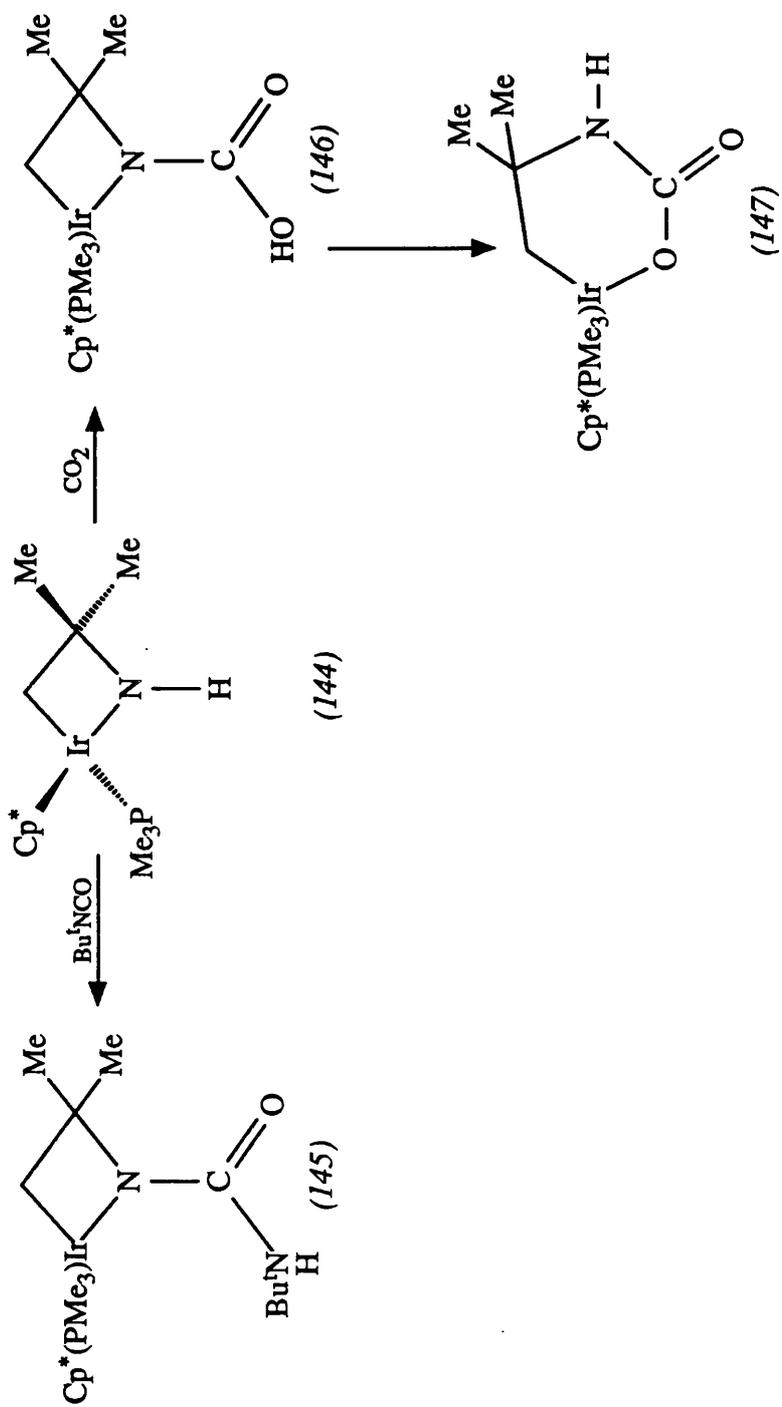
Attempts to remove the hydrogen atoms from the ring carbons in metallathietane-3,3-dioxide complexes have been reported. The use of an excess of either sodium hydride on $[\text{Pt}\{\overline{\text{CHPhS}(\text{O})_2\text{CHPh}}\}(\text{AsPh}_3)_2]$ (52, L = AsPh₃) or an excess of n-butyl lithium on $[\text{Pt}\{\overline{\text{CHPhS}(\text{O})_2\text{CHPh}}\}(\text{PPh}_3)_2]$ (52, L = PPh₃) were both unsuccessful and led to the recovery of the starting materials.⁵⁷ These reactions prompted an attempt to deprotonate the nitrogen atoms of (129), to allow comparison between the two types of systems. Thus, an excess of $\text{NaN}[(\text{SiMe}_3)_2]$ was added to a THF solution of (129) and the reaction stirred overnight at room temperature.

However, such treatment did not lead to deprotonation and only a signal from the starting platinum complex was seen in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the crude reaction residue. This result suggests that the N-H protons are not particularly acidic in $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ (129). However, it should be noted that shaking a sample of (129) with $[\text{}^2\text{H}_2]$ -water results in deuterium exchange at nitrogen.

3.6.5 Attempted Insertion Reactions into N-H Bonds of (129)

Recently, Bergman *et al.* described the insertion of small unsaturated molecules such as t-butyl isocyanate and carbon dioxide into the N-H bond of the azairidacyclobutane complex (144) to give (145) and (147) respectively, Scheme 3.¹⁵² The formation of complex (147) was suggested to proceed *via* the species (146) by slow rearrangement of the latter in solution. In view of these results, attempts were made to obtain new products derived from insertion of small molecules into the N-H bonds of complex (129).

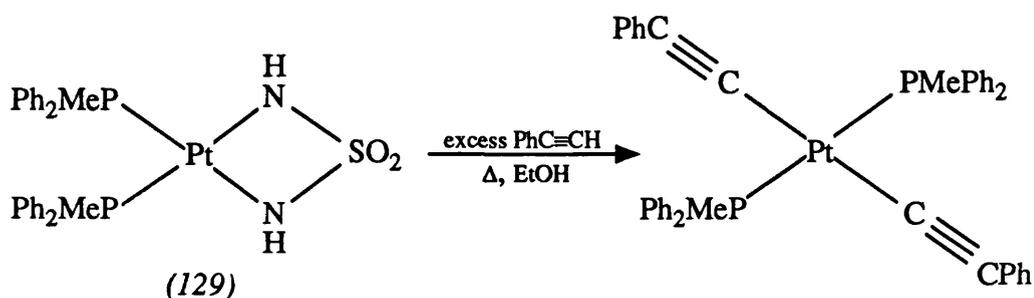
Treatment of $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ (129) with an excess of carbon disulphide in dichloromethane at room temperature resulted in no reaction. Treatment of (129) with an



Scheme 3

excess of phenyl isothiocyanate at room temperature in dichloromethane for 4h, followed by a short refluxing period, gave a mixture of mainly the starting complex (129) together with a small amount of another phosphorus-containing product, as seen in the $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum of the crude reaction residue. The minor product exhibited an AB pattern with resonances centred at δ 2.72 and -4.94 p.p.m. Interestingly, if the reaction is repeated under refluxing conditions (ca. 5h), the $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum of the reaction residue shows the same signals as before, the product giving rise to the AB pattern now being formed in smaller quantities relative to the starting material. Attempts to separate the two species from either of these reactions were unsuccessful. Treatment of complex (129) with an excess of phenyl isocyanate in dichloromethane at room temperature led to formation of a mixture of products.

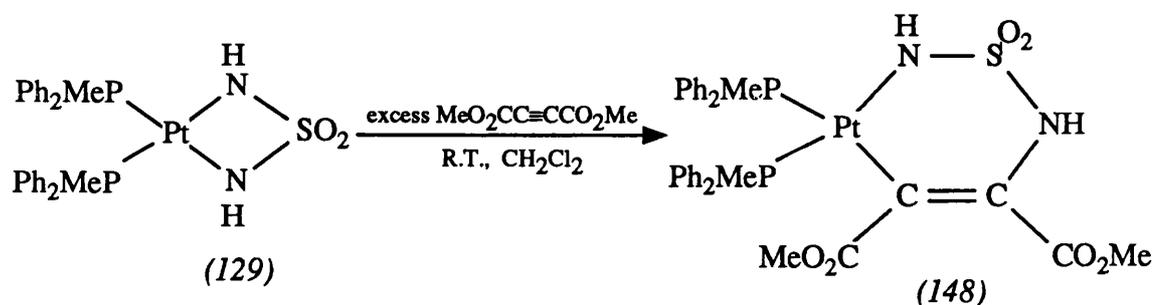
The behaviour of (129) with several acetylenes was also investigated. Thus, treatment of this complex with diphenylacetylene in refluxing absolute ethanol overnight resulted in no reaction taking place, whereas with the more reactive phenylacetylene under analogous conditions, a product was obtained showing in its $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum a singlet at δ 0.94 p.p.m. with corresponding platinum-195 satellites [$^1\text{J}(\text{PtP})$ 2522 Hz]. A very intense band at 2112 cm^{-1} was observed in the i.r. spectrum of the isolated solid product. The product is formulated as trans- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMePh}_2)_2]$, the data reported here comparing favourably with that reported for the same compound by Shaw *et al.*¹⁵³ The phenylacetylene reagent must be acting in this reaction as a weak acid, displacing the sulphamide moiety from the starting material. The reaction is depicted in Scheme 4.



Scheme 4

However, it is not known whether the cis-acetylide isomer is formed first, and then undergoes cis → trans isomerisation, or whether a species such as cis-[Pt(C≡CPh)(NHSO₂NH₂)(PMePh₂)₂] is produced initially, which then isomerises to the trans- form before reacting further with more phenylacetylene to give the observed product. It has been reported that cis-[Pt(C≡CPh)₂(PMePh₂)₂] is stable to isomerisation in organic solvents at room temperature and in refluxing chloroform.¹⁵⁴ Interestingly, isomerisation of the complexes cis-[PtX(C≡CPh)(PPh₃)₂] (X = Cl, Br, I) to their trans- analogues has been reported.¹⁵⁵

Reaction of an excess of dimethyl acetylenedicarboxylate with (129) in dichloromethane at room temperature for 6h gave a yellow solid, which was recrystallised to give mainly yellow crystals, accompanied by a small quantity of white crystals. The major product is formulated as (148), on the basis of its spectroscopic properties and a single-crystal X-ray diffraction study. The nature of the minor product is unknown. The formation of (148) is shown in Scheme 5.



Scheme 5

A summary of selected bond lengths and bond angles for (148) is presented in Table 4, and the molecular geometry is shown in Figures 4 and 5, together with the crystallographic numbering system. The complex features a six-membered ring, which exists in a "pseudo-boat" conformation, the fold angles between the best planes N(1)–S–C(2)–C(1) and either C(1)–Pt–N(1) or C(2)–N(2)–S (as defined in Figure 6) being 51.28° (θ^1) and 43.95° (θ^2) respectively. The plane N(1)–S–C(2)–C(1) possesses a slight twist element, the torsion angle from planarity being 8.8°. Normally, cyclohexenes exist in a half-chair conforma-

TABLE 4

Selected bond lengths and angles for $[\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ (148)^a

Bond Length	(Å)	Bond Angle	(°)
Pt – P(1)	2.183 (5)	P(1) – Pt – P(2)	101.6 (2)
Pt – P(2)	2.330 (4)	P(1) – Pt – C(1)	92.9 (6)
Pt – N(1)	2.033 (11)	C(1) – Pt – N(1)	82.7 (6)
Pt – C(1)	2.070 (15)	N(1) – Pt – P(2)	83.4 (3)
C(1) – C(3)	1.501 (19)	Pt – C(1) – C(2)	120.3 (11)
C(1) – C(2)	1.317 (21)	C(1) – C(2) – N(2)	118.0 (13)
C(2) – C(5)	1.475 (21)	C(2) – N(2) – S	112.9 (10)
C(2) – N(2)	1.468 (17)	N(1) – S – N(2)	108.4 (6)
N(2) – S	1.661 (14)	O(1) – S – O(2)	118.4 (8)
S – O(1)	1.457 (11)	N(1) – S – O(1)	111.8 (6)
S – O(2)	1.429 (14)	N(1) – S – O(2)	108.0 (7)
N(1) – S	1.654 (11)	N(2) – S – O(1)	102.0 (7)
		N(2) – S – O(2)	107.8 (7)
		S – N(1) – Pt	113.6 (6)

^a See Figures 4 and 5 for crystallographic numbering system.

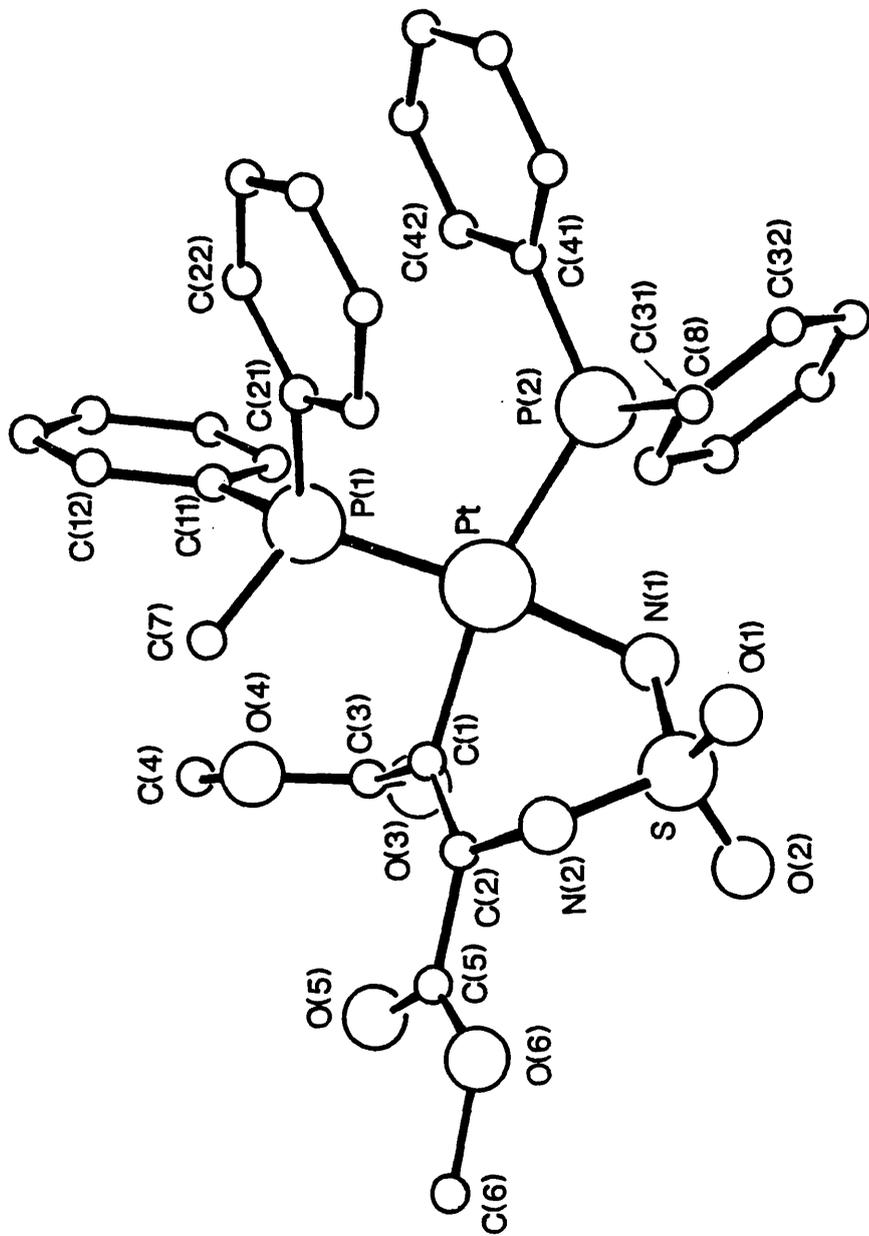


FIGURE 4
 Molecular structure of $[\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ (148),
 with all hydrogens omitted.

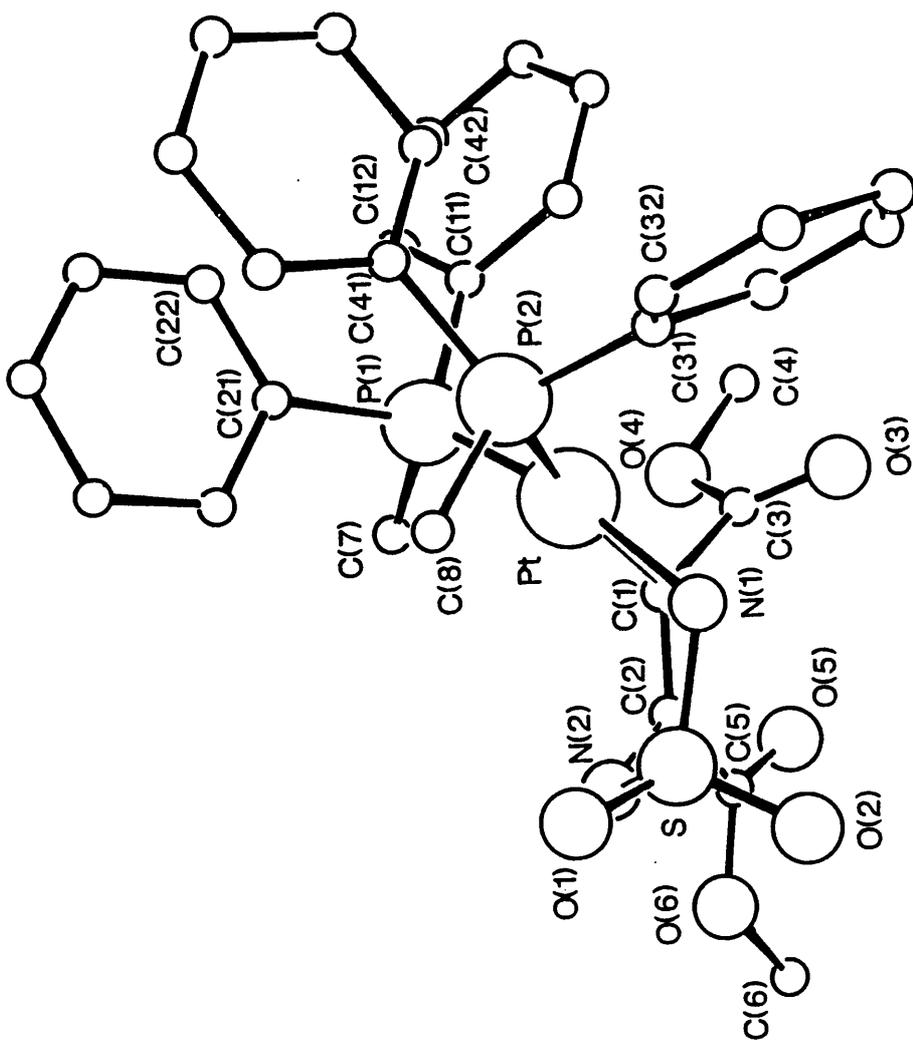


FIGURE 5
Molecular structure of $[\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ (148), with all hydrogens omitted.

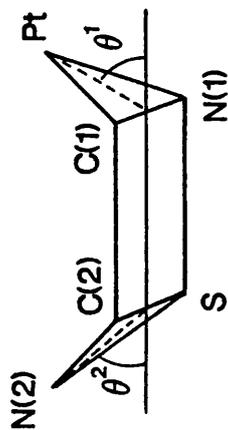


FIGURE 6
Fold angles θ^1 and θ^2 in (148), using the best plane through the atoms $\text{N}(1)\text{--S--C}(2)\text{--C}(1)$.

tion,¹⁵⁶ but here, in (148), the boat conformation may be preferred since in a half-chair conformation, unfavourable steric interactions between the phosphine ligand and the adjacent *cis*-C(CO₂Me) moiety would arise. Interestingly, the non-bonded contact distances Pt---S and Pt---N(2) are equal at 3.092Å.

The S-O bond lengths are comparable to those reported for the complex [Pt{ $\overline{\text{NHS(O)}_2\text{NH}}$ }(PMePh₂)₂] (129) by both Woollins *et al.*¹³⁷ and in this current study, whereas the N-S bond lengths are slightly longer in (148).

The C(1)–Pt–N(1) bond angle of 82.7(6)° in (148) is greater than the angle subtended at the platinum atom by the four-membered ring in (129) [i.e. N(1)–Pt–N(2) 71.3(3)°], this increase being a consequence of the relief of ring strain on going from a four-membered ring to a six-membered ring. Additionally, the angle subtended at the sulphur atom by the six-membered ring in (148) is greater than that subtended at the sulphur atom by the four-membered ring in (129).

The C(1)–C(2) bond, at 1.317(21)Å, is characteristic of a carbon-carbon double bond, and compares with the non-phenyl C=C bond distances in, for example, [Pt{ $\overline{\text{HC}=\text{C}(\text{H})\text{C}(\text{O})\text{O}}$ }(PPh₃)₂] [1.334(20)Å],¹⁵⁷ and [Pt{ $\overline{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{Cl})\text{C}(\text{O})\text{O}}$ }(CO)Cl][N(PPh₃)₂] [1.28(2)Å].¹⁵⁸

As expected, the Pt-P(2) bond is longer than the Pt-P(1) bond, owing to the greater *trans* influence of the olefinic carbon atom *trans* to P(2) compared to the nitrogen atom *trans* to P(1). It should be noted that the amino hydrogen atoms were not found in the crystal structure analysis.

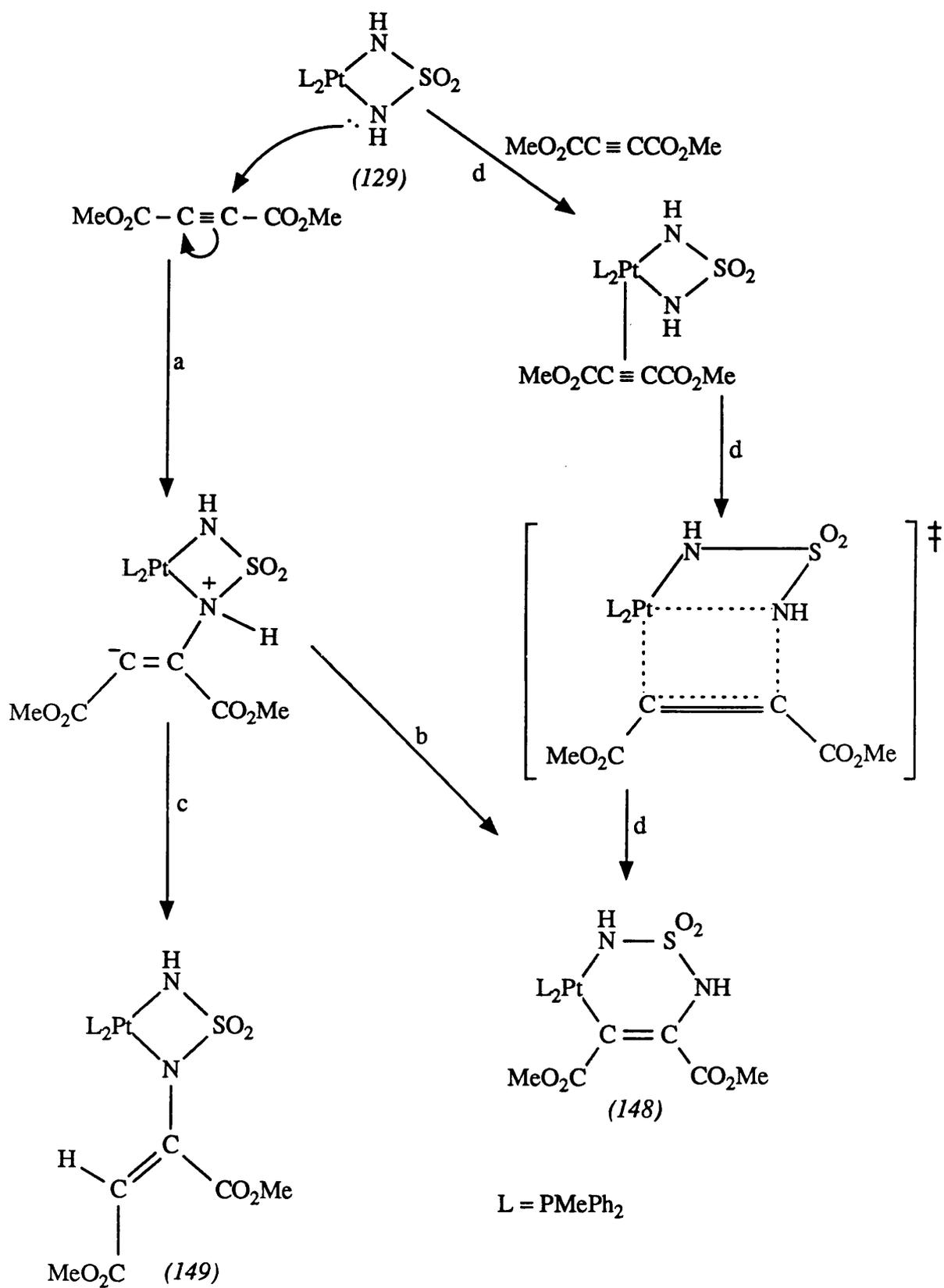
The ¹H n.m.r. spectrum of (148) shows resonances at δ 6.37 and 2.33 p.p.m. assigned to the two N-H protons. The high-field signal is split into two components of almost equal intensity, and is flanked by broad "shoulders" on the outer side of each component of the signal, these possibly being platinum-195 satellites. The low-field resonance shows no splitting and only slight broadening of its base. It seems most likely that the resonance at δ 2.33 p.p.m. arises from the N-H proton adjacent to the platinum, the low-field signal being assigned to the other N-H proton. The methyl groups in the ester moieties appear as two

resonances at δ 3.68 and 3.10 p.p.m., while the methyl groups in each of the phosphines exhibit second-order multiplets with corresponding platinum-195 satellites.

The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum shows two ester carbonyl group resonances, one a singlet at δ 173.39 p.p.m., the other being observed as a doublet centred at δ 162.82 p.p.m., owing to coupling with a phosphorus atom, no platinum-195 satellites being discernible. However, it is not possible to determine with confidence which carbonyl group gives rise to the high-field signal, and which gives rise to the low-field signal. The two ester methyl groups appear as single resonances, as expected, and the methyl groups in the phosphines show two sets of second-order resonances, although no platinum-195 satellites could be discerned in the spectrum. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the complex consisted of an AB pattern with corresponding platinum-195 satellites.

The i.r. spectrum of (*148*) shows one band arising from the N-H stretching modes, at 3245 cm^{-1} , and a very strong band at 1710 cm^{-1} , with a shoulder at 1726 cm^{-1} , attributable to the $\nu(\text{C}=\text{O})$ modes of the ester carbonyl groups. Bands arising from the asymmetric and symmetric $\nu(\text{SO}_2)$ modes are seen at 1285 and 1127 cm^{-1} respectively.

The formation of (*148*) from the reaction between (*129*) and dimethyl acetylenedicarboxylate can be viewed as a formal insertion of the activated alkyne into one of the platinum-nitrogen bonds of the starting metal complex. The mechanism of this reaction is not clear however. Initial attack by the lone pair of one of the nitrogen atoms on one of the carbon atoms of the electron-deficient carbon-carbon multiple bond system of the alkyne may occur [Path a, Scheme 6]. Subsequent attack of the carbanionic alkene moiety on platinum, and quenching of the positive charge on the quaternary nitrogen atom would then lead to the observed product [Path b, Scheme 6]. It should be noted that removal of the proton on the quaternary nitrogen atom by the carbanionic moiety [Path c, Scheme 6], rather than attack at platinum, would yield a species (*149*), formally derived from insertion of the acetylene into one of the N-H bonds of the starting complex (*129*). Since the dimethyl acetylenedicarboxylate is in excess, further reaction of the carbanionic moiety with more acetylene could be reasonably expected, to yield species containing more than one double



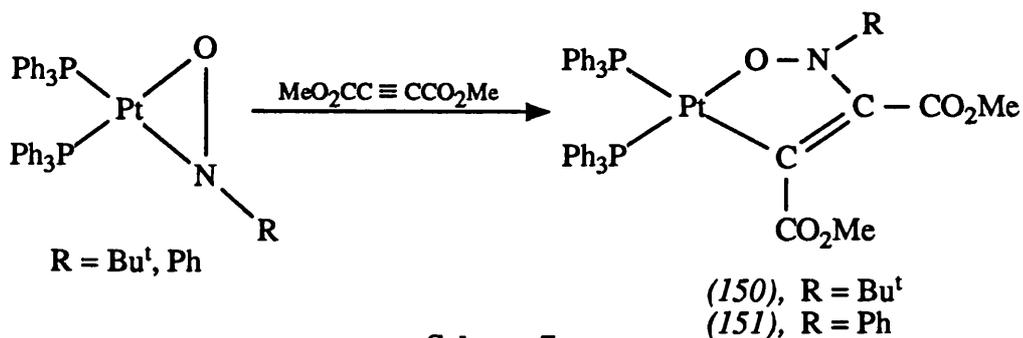
Scheme 6

bond. However, no evidence of such a species was observed, although as stated previously, a small amount of uncharacterised by-product was isolated from the reaction.

An alternative mechanism would involve the initial formation of a π -acetylene complex, followed by direct insertion of the co-ordinated acetylene into one of the platinum-nitrogen bonds [Path d, Scheme 6].

However, when the reaction was monitored by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy, no signals arising from possible reaction intermediates were observed, but only signals owing to the starting complex and the product.

Finally, it has been reported that (150) and (151) are formed on reaction of dimethyl acetylenedicarboxylate with the η^2 -nitroso complexes $[\text{Pt}(\text{RNO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Bu}^t, \text{Ph}$), Scheme 7.^{125,159} These reactions constitute a formal insertion of the acetylene into the platinum-nitrogen bond of the starting materials.



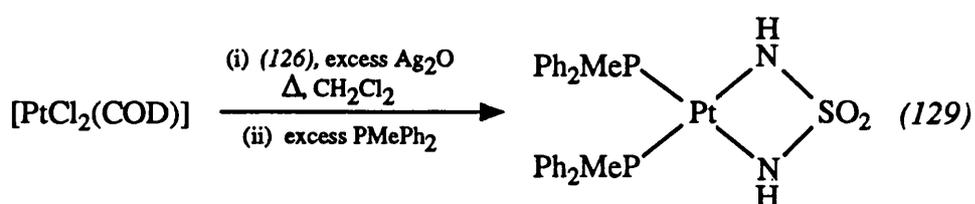
Scheme 7

Interestingly, the phenyl η^2 -nitroso derivative does not undergo any reaction with β -cyano- β -phenylstyrene, but requires the presence of more highly activated alkenes, such as β,β -dicyanostyrene or tetracyanoethylene for insertion into the platinum-nitrogen bond to take place.¹⁵⁹ Similarly, no reaction was observed with methylphenylacetylene. It appears that a highly electron-deficient multiple bond system with a strongly electrophilic carbon centre is necessary for insertion to occur. This may explain the inability of both diphenylacetylene and phenylacetylene to undergo insertion reactions with (129), possibly because they are not sufficiently activated to allow attack by the nitrogen lone pair. It should be noted that (135) does not react with dimethyl acetylenedicarboxylate under conditions

similar to those used in the reaction of (129) with this acetylene. The electron-withdrawing phenyl groups attached to the ring nitrogens may reduce the reactivity of the nitrogen lone pairs with electrophiles, and in addition the steric influence of these phenyl groups may also play a part in the failure of this reaction. The formation of products derived from insertion of carbon disulphide, phenyl isothiocyanate or phenyl isocyanate into the platinum-nitrogen bond of $[\text{Pt}(\text{RNO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Bu}^t, \text{CF}_3, \text{Ph}$) has been proposed to proceed via attack of the nitrogen lone pair of the η^2 -nitroso ligand on the electrophilic carbon atom of the incoming cumulenes.^{124,125} Such reactions can, however, also be regarded as direct insertion reactions, similar to Path d in Scheme 6.

3.6.6 Miscellaneous reactions of N,N'-unsubstituted platinathiadiazetidine-3,3-dioxide complexes

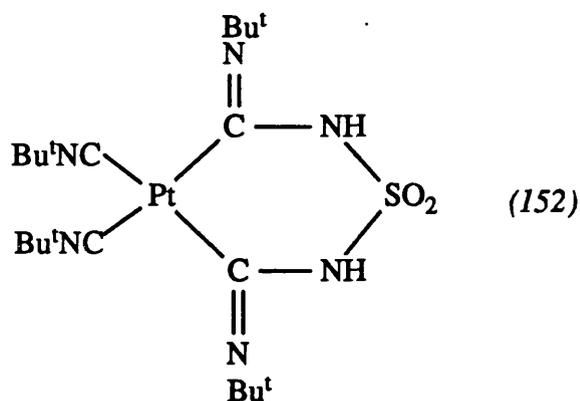
Treatment of $[\text{PtCl}_2(\text{COD})]$ with one mole equivalent of sulphamide (126) and an excess of silver(I) oxide in refluxing dichloromethane for 4h gave a pea-green filtrate after filtration. Stirring the filtrate in air with an excess of methyldiphenylphosphine at room temperature led to formation of a mixture of $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ (129) and methyldiphenylphosphine oxide, Scheme 8.



Scheme 8

If the silver(I) oxide reaction is repeated (refluxing period 6h) and the resulting filtrate treated with an excess of t-butyl isocyanide for 1h at room temperature, a very pale pink microcrystalline solid is obtained. The product is tentatively assigned as being (152), on the basis of spectroscopic and analytical data.

The ^1H n.m.r. spectrum of the solid shows resonances at δ 1.57 and 1.40 p.p.m., arising from two different types of t-butyl groups. Interestingly, a signal is also observed at δ 4.89 p.p.m., with corresponding platinum-195 satellites. On shaking with $[\text{}^2\text{H}_2]$ -water, the signal disappears, and is thus assigned to the N-H protons. The relative integrals of the signal at



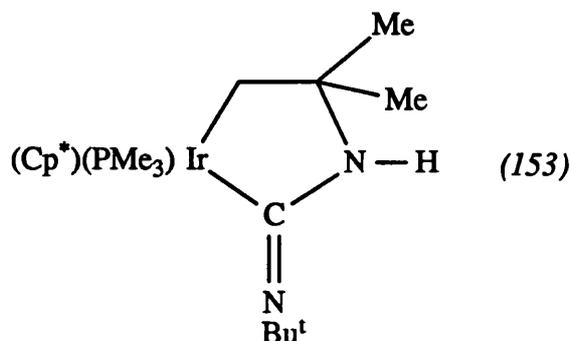
δ 4.89 p.p.m. and the t-butyl signals is 1:9:9. However, the microanalytical data indicated the presence of four t-butyl isocyanide moieties per molecule of compound, and thus two N-H groupings. The chemical shift of these latter protons exclude a zwitterionic structure similar to those found in complexes of the type (32)-(34)²⁵ and (53)-(55),⁶¹ in which the acidic N-H protons show a much lower field signal in the ¹H n.m.r. spectra than is observed for (152).

The i.r. spectrum of the compound shows strong bands at ca. 3450 and 3325 cm^{-1} , attributed to $\nu(\text{N-H})$ modes. Two intense bands at 2220 and 2185 cm^{-1} , consistent with $\nu(\text{C}\equiv\text{N})$ modes in a $\text{Pt}(\text{CNBu}^t)_2$ moiety, together with bands at ca. 1550 and 1530 cm^{-1} , assigned to $\nu(\text{C}=\text{N})$ modes of the inserted isocyanide groups are observed. Prominent bands corresponding to the asymmetric and symmetric $\nu(\text{SO}_2)$ modes are observed at 1267 and 1122 cm^{-1} respectively.

The formation of (129) in the reaction depicted in Scheme 8 suggests the intermediacy of a species such as $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{COD})]$ in the filtrate prior to treatment with methyl-diphenylphosphine. Several unsuccessful attempts were made to isolate the intermediate. The existence of such an intermediate is not unreasonable, however, in view of the isolation of the N,N'-diphenyl substituted analogue $[\text{Pt}\{\overline{\text{NPhS}(\text{O})_2\text{NPh}}\}(\text{COD})]$ (141), described earlier. Presumably the diene ligand is displaced by the incoming phosphine ligands. A similar displacement could occur when the intermediate is treated with the isocyanide, to yield a bis(isocyanide) platinum complex, which reacts further with more isocyanide to give the observed product (152). The formation of a six-membered ring fragment in (152) from the four-membered ring in the intermediate complex results from insertion of one isocyanide

molecule into each of the platinum-nitrogen bonds of the latter.

Finally, it is notable that the reaction of $[\text{Ir}(\overline{\text{CH}_2\text{CMe}_2\text{NH}})(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)]$ (144) with *t*-butyl isocyanide leads to insertion of one isocyanide molecule into the iridium-nitrogen bond of (144) and formation of (153).¹⁵²



3.7 MISCELLANEOUS REACTIONS OF $[\text{Pt}\{\overline{\text{NPhS(O)}_2\text{NPh}}\}(\text{PPh}_3)_2]$ (135)

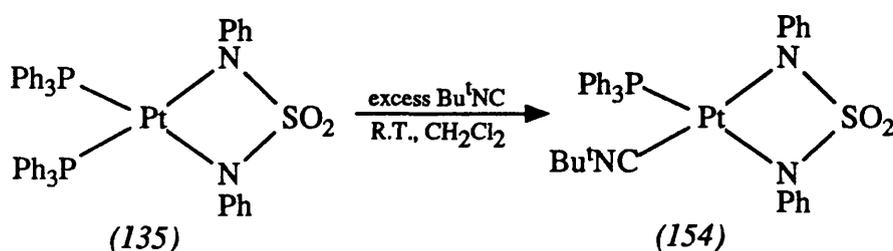
Passing a slow stream of gaseous hydrogen chloride through a dichloromethane solution of (135) resulted in formation of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$, whereas no reaction was observed on treatment of (135) with an excess of iodomethane in refluxing acetone for 2.5h.

Treatment of (135) in dichloromethane with a slow stream of carbon monoxide at room temperature for 3h resulted in no reaction. Similarly, carrying out the reaction under refluxing conditions for 6h led to the same result. More vigorous conditions were then used to try to effect reaction. Thus, bubbling carbon monoxide through a refluxing suspension of (135) in absolute ethanol for 6h gave a residue after work-up which showed in its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum mostly unreacted starting material, together with several minor peaks, one of which appeared to have platinum-195 satellites. However, repeating the reaction for 24h did not lead to further reaction, and in fact only starting material was detected in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the reaction residue. The reactions were not investigated further in view of the inconsistency of the results obtained.

Bubbling sulphur dioxide through a dichloromethane solution of (135) at room temperature for 1h resulted in isolation of a white powdery solid which was found to be insoluble in all common organic solvents after work-up. The i.r. spectrum of the solid

exhibited strong bands in the 1190-1065 cm^{-1} region, but no significantly strong bands between 1400 and 1250 cm^{-1} . Thus, the band attributable to the asymmetric $\nu(\text{SO}_2)$ mode seen in the starting material is absent in the current case. It seems that the ring fragment in (135) has been displaced or undergone some sort of rearrangement, although the nature of the final product is uncertain.

Treatment of a dichloromethane solution of (135) with an excess of t-butyl isocyanide at room temperature for 2h gave a creamy-white solid formulated as (154) on the basis of its spectroscopic and analytical data, the reaction being illustrated in Scheme 9.



Scheme 9

No evidence for insertion of an isocyanide molecule into a platinum- nitrogen bond was observed. The compound shows in its $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum a singlet with corresponding platinum-195 satellites, $^1\text{J}(\text{PtP})$ being 3262 Hz. The t-butyl protons appear at δ 1.01 p.p.m. in the ^1H n.m.r. spectrum, and the i.r. spectrum showed a very strong band at 2205 cm^{-1} arising from the $\nu(\text{C}\equiv\text{N})$ mode together with asymmetric and symmetric stretching bands of the sulphone group at 1260 and 1133 cm^{-1} respectively.

Refluxing a dichloromethane solution of (135) with an excess of 2.0M acetic acid gave, after work-up, a white microcrystalline solid, identified as cis- $[\text{Pt}\{\text{OC}(\text{O})\text{Me}\}_2(\text{PPh}_3)_2]$ by comparison of its $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. and i.r. spectra with those of a sample reported previously.¹⁶⁰

3.8 CONCLUSION

The treatment of cis- $[\text{PtCl}_2\text{L}_2]$ complexes with sulphamide or N,N'- diphenylsulphamide in the presence of an excess of silver(I) oxide leads to formation of complexes of the type

$[\text{Pt}\{\overline{\text{NRS}(\text{O})_2\text{NR}}\}\text{L}_2]$, where R = H or Ph. Potassium hydroxide, in place of silver(I) oxide, has been used to prepare some derivatives where R = Ph. Crystal structure determinations of two derivatives revealed the presence of totally flat four-membered ring fragments.

Attempted oxidative addition of hydrogen chloride to $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ (*129*) led to elimination of the organic ligand and formation of *cis*- $[\text{PtCl}_2(\text{PMePh}_2)_2]$. Reaction of the same complex (*129*) with carbon monoxide was unsuccessful, whereas with sulphur dioxide an unidentified product was obtained. An attempt to remove the protons from the nitrogen atoms in (*129*) was unsuccessful.

Several attempts were made to insert small unsaturated molecules into the N-H bonds of (*129*). Treatment with an excess of phenylacetylene led to formation of *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMePh}_2)_2]$, whereas with dimethyl acetylenedicarboxylate a complex containing a six-membered ring was isolated. The crystal structure of this new product established that the ring adopts a "pseudo-boat" conformation. A further complex containing a six-membered ring system was synthesised by treating *in situ* the species initially obtained from $[\text{PtCl}_2(\text{COD})]$, sulphamide and silver(I) oxide with *t*-butyl isocyanide.

Reaction of $[\text{Pt}\{\overline{\text{NPhS}(\text{O})_2\text{NPh}}\}(\text{PPh}_3)_2]$ (*135*) with gaseous hydrogen chloride leads to *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$, whereas no reaction was observed with iodomethane. Reaction with carbon monoxide gave inconsistent results, whereas with sulphur dioxide an insoluble product was obtained. One phosphine moiety can be replaced by an isocyanide ligand on reaction of (*135*) with an excess of *t*-butyl isocyanide. The organic ligand in (*135*) can be displaced by acetic acid, yielding a bis(acetato) complex.

3.9 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. The compounds 1,2-*bis*-(diphenylphosphino)ethane, carbon disulphide, dimethyl acetylenedicarboxylate, diphenylacetylene, iodomethane, methyldiphenylphosphine, phenylacetylene, phenyl isocyanate, phenyl isothiocyanate, sulphamide, triethylphosphine (Aldrich), silver(I) oxide, sulphur dioxide (BDH), carbon monoxide, hydrogen chloride (BOC), and *t*-butyl isocyanide (Fluka) were used as supplied from commercial sources. The compounds $[\text{PtCl}_2(\text{COD})]$,¹³¹

$\text{cis-}[\text{PtCl}_2(\text{PEt}_3)_2]$,¹⁶¹ $\text{cis-}[\text{PtCl}_2(\text{PNEt}_2\text{Ph}_2)_2]$,¹¹⁹ $\text{NaN}[(\text{SiMe}_3)_2]$,¹⁶² $\text{N,N}'$ -diphenylsulphamide,¹³⁶ and PEt_2Ph ¹³⁵ were prepared as described in the literature.

3.9.1 Preparation of $\text{N,N}'$ -unsubstituted platinathiadiazetidine-3,3-dioxide complexes using silver(I) oxide; general method

Two equivalents of tertiary monodentate phosphine or one equivalent of bidentate phosphine, followed by one equivalent of sulphamide (126) and an excess of silver(I) oxide were added in succession to a stirred solution of $[\text{PtCl}_2(\text{COD})]$ in dichloromethane, and the mixture refluxed for 4h. The mixture was filtered through celite and the filtrate evaporated to dryness under reduced pressure to afford a colourless oil. Dissolution of the oil in dichloromethane (ca. 2 cm³) followed by addition of light petroleum afforded a powdery solid which was recrystallised from dichloromethane - light petroleum, unless stated otherwise, and dried in vacuo.

(i) $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PPh}_3)_2]$ (128).0.5 CH_2Cl_2

The complex $[\text{PtCl}_2(\text{COD})]$ (0.15g, 0.40 mmol) with triphenylphosphine (0.225g, 0.86 mmol) and sulphamide (0.039g, 0.41 mmol) in dichloromethane (40 cm³) gave white microcrystals of (128).0.5 CH_2Cl_2 (0.281g, 82%) (Found: C, 51.3; H, 3.8; N, 3.5. $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_2\text{P}_2\text{PtS}.0.5 \text{CH}_2\text{Cl}_2$ requires C, 51.2; H, 3.9; N, 3.3%), m.p. >230°C; $\nu_{(\text{NH})}$ at 3335w and 3319w cm⁻¹; $\nu_{\text{asym}}(\text{SO}_2)$ at 1278vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1171vs, 1158vs and 1100vs cm⁻¹. The complex was found to be insoluble in all common organic solvents.

(ii) $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ (129).2 CHCl_3

The complex $[\text{PtCl}_2(\text{COD})]$ (0.15g, 0.40 mmol) with methyldiphenylphosphine (0.16g, 0.80 mmol) and sulphamide (0.040g, 0.42 mmol) in dichloromethane (40 cm³) gave white crystals of (129).2 CHCl_3 (0.123g, 33%) (Found: C, 36.8; H, 3.5; N, 3.2. $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_2\text{P}_2\text{PtS}.2\text{CHCl}_3$ requires C, 36.2; H, 3.3; N, 3.0%), m.p. semi-melts at 110°C, melts >230°C; $\nu_{(\text{NH})}$ at 3220w and 3165w cm⁻¹; $\nu_{\text{asym}}(\text{SO}_2)$ at 1270vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1146vs and 1114vs cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.50-7.31 (m, 22H, Ph + CHCl_3), 2.46 (s, br, 2H, NH, exchangeable with [²H₂]-water), and 1.77 p.p.m. {filled-in doublet, 6H,

Me, P_{Me}Ph₂, |²J(PH) + ⁴J(PH)| 9.80, ³J(PtH) 33.9]; ³¹P-{¹H} (24 MHz), δ -6.66 p.p.m. [s, ¹J(PtP) 3345]. These crystals were suitable for single-crystal X-ray diffraction studies.

(iii) [Pt{NHS(O)₂NH}(PEt₂Ph)₂] (131)

The complex [PtCl₂(COD)] (0.12g, 0.32 mmol) with diethylphenylphosphine (0.11g, 0.66 mmol) and sulphamide (0.031g, 0.32 mmol) in dichloromethane (40 cm³) gave white microcrystals of (131) (0.160g, 81%) (Found: C, 38.4; H, 4.9; N, 4.6. C₂₀H₃₂N₂O₂P₂PtS requires C, 38.6; H, 5.2; N, 4.5%), m.p. 218-221°C (decomp.); ν_(NH) at 3346w cm⁻¹; ν_{asym}(SO₂) at 1274vs cm⁻¹; ν_{sym}(SO₂) at 1170vs and 1108vs cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.47-7.28 (m, 10H, Ph), 2.99 (s, br, 2H, NH), 1.92 (m, 4H, CH₂, PEt₂Ph), 1.54 (m, 4H, CH₂, PEt₂Ph), and 0.85 p.p.m. (m, 12H, Me, PEt₂Ph); ¹³C-{¹H} (75.5 MHz), δ 133.05-128.45 (m, Ph), 14.63 (m, CH₂, PEt₂Ph), and 7.25 p.p.m. (m, Me, PEt₂Ph); ³¹P-{¹H} (24 MHz), δ -1.61 p.p.m. [s, ¹J(PtP) 3301].

(iv) [Pt{NHS(O)₂NH}(dppe)] (134)

The complex [PtCl₂(COD)] (0.10g, 0.27 mmol) with 1,2-bis-(diphenylphosphino)ethane (0.11g, 0.28 mmol) and sulphamide (0.026g, 0.27 mmol) in dichloromethane (30 cm³) gave white microcrystals of (134) (0.161g, 87%) (Found: C, 44.8; H, 3.7; N, 4.0. C₂₆H₂₆N₂O₂P₂PtS requires C, 45.4; H, 3.8; N, 4.0%), m.p. >230°C; ν_(NH) at 3238w cm⁻¹; ν_{asym}(SO₂) at 1278vs cm⁻¹; ν_{sym}(SO₂) at 1176vs and 1116vs cm⁻¹. The complex was found to be insoluble in all common organic solvents.

Preparation of [Pt{NHS(O)₂NH}(PEt₃)₂] (132)

Sulphamide (0.020g, 0.21 mmol) and silver(I) oxide (0.20g, 0.86 mmol) were added in succession to a stirred solution of the complex cis-[PtCl₂(PEt₃)₂] (0.10g, 0.20 mmol) in dichloromethane (30 cm³), and the mixture refluxed for 4h. The insoluble silver salts were removed by filtration to give a colourless solution, which was reduced in volume to ca. 2 cm³. Addition of diethyl ether afforded a white microcrystalline solid which was filtered off and dried in vacuo to give the title complex (132) (0.056g, 53%) (Found: C, 27.5; H, 6.1; N, 4.9. C₁₂H₃₂N₂O₂P₂PtS requires C, 27.4; H, 6.1; N, 5.3%), m.p. 173-178°C (decomp.); ν_(NH)

at 3245w cm^{-1} ; $\nu_{\text{asym}}(\text{SO}_2)$ at 1261vs(br) cm^{-1} ; $\nu_{\text{sym}}(\text{SO}_2)$ at 1117vs(br) cm^{-1} . N.m.r. spectra: ^1H (300 MHz), δ 2.72 (s, br, 2H, NH, exchangeable with [$^2\text{H}_2$]-water), 1.81 (m, 12H, CH_2 , PEt_3), and 1.14 p.p.m. (m, 18H, Me, PEt_3); $^{31}\text{P}\{-^1\text{H}\}$ (36 MHz), δ 1.14 p.p.m. [s, $^1\text{J}(\text{PtP})$ 3264].

Preparation of $[\text{Pt}\{\text{NHS}(\text{O})_2\text{NH}\}(\text{PNEt}_2\text{Ph}_2)_2]$ (133)

Sulphamide (0.015g, 0.16 mmol) and silver(I) oxide (0.28g, 1.21 mmol) were added in succession to a stirred solution of the complex cis- $[\text{PtCl}_2(\text{PNEt}_2\text{Ph}_2)_2]$ (0.12g, 0.15 mmol) in dichloromethane (30 cm^3), and the mixture refluxed for 4h. The insoluble silver salts were removed by filtration and the resulting colourless solution reduced in volume to ca. 2 cm^3 . Addition of light petroleum afforded white microcrystals which were filtered off and dried in vacuo to give the title complex (133) (0.060g, 50%) (Found: C, 47.5; H, 5.4; N, 6.8. $\text{C}_{32}\text{H}_{42}\text{N}_4\text{O}_2\text{P}_2\text{PtS}$ requires C, 47.8; H, 5.3; N, 7.0%), m.p. 202-204°C (decomp.); $\nu_{(\text{NH})}$ at 3336w cm^{-1} ; $\nu_{\text{asym}}(\text{SO}_2)$ at 1288vs cm^{-1} ; $\nu_{\text{sym}}(\text{SO}_2)$ at 1175vs and 1108vs cm^{-1} . N.m.r. spectra: ^1H (300 MHz), δ 7.35-7.25 (m, 20H, Ph), 3.26-3.20 (m, 8H, CH_2 , PNEt_2Ph_2), 2.32 (s, br, 2H, NH, exchangeable with [$^2\text{H}_2$]-water), and 1.02 p.p.m. [t, 12H, Me, PNEt_2Ph_2 , $^3\text{J}(\text{HH})$ 7.0]; $^{13}\text{C}\{-^1\text{H}\}$ (75.5 MHz), δ 132.24-127.97 (m, Ph), 43.36 (s, CH_2 , PNEt_2Ph_2), and 13.42 p.p.m. (s, Me, PNEt_2Ph_2); $^{31}\text{P}\{-^1\text{H}\}$ (24 MHz), δ 55.46 p.p.m. [s, $^1\text{J}(\text{PtP})$ 3735].

3.9.2 Preparation of N,N'-diphenyl substituted platinathiadiazetidene-3,3-dioxide complexes

(a) using silver(I) oxide; general method

Two equivalents of tertiary monodentate phosphine or one equivalent of bidentate phosphine, followed by one equivalent of N,N'-diphenylsulphamide (127) and an excess of silver(I) oxide were added in succession to a stirred solution of $[\text{PtCl}_2(\text{COD})]$ in dichloromethane, and the mixture refluxed for 3h. The mixture was filtered through celite and the filtrate evaporated to dryness under reduced pressure. Dissolution of the resulting oil in dichloromethane (ca. 1 cm^3) and addition of light petroleum gave a microcrystalline solid which was recrystallised from dichloromethane - light petroleum, unless stated otherwise, and dried in vacuo.

(i) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PPh}_3)_2]$ (*135*)

The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and *N,N'*-diphenylsulphamide (0.067g, 0.27 mmol) in dichloromethane (30 cm³) gave, on recrystallisation of the solid product from dichloromethane - diethyl ether, pale yellow crystals of the title complex (*135*) (0.154g, 59%) (Found: C, 59.9; H, 4.2; N, 2.9. $\text{C}_{48}\text{H}_{40}\text{N}_2\text{O}_2\text{P}_2\text{PtS}$ requires C, 59.7; H, 4.2; N, 2.9%), m.p. 205-211°C (decomp.); $\nu_{\text{asym}}(\text{SO}_2)$ at 1258 vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1130 vs and 1100 vs cm⁻¹. N.m.r. spectrum: ³¹P-¹H (36 MHz), δ 7.81 p.p.m. [s, ¹J(PtP) 3501].

(ii) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PMePh}_2)_2]$ (*136*)

The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) with methyl diphenylphosphine (0.108g, 0.54 mmol) and *N,N'*-diphenylsulphamide (0.067g, 0.27 mmol) in dichloromethane (35 cm³) gave, on recrystallisation of the solid product from dichloromethane - diethyl ether, white microcrystals of (*136*) (0.070g, 31%) (Found: C, 53.9; H, 4.3; N, 3.2. $\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_2\text{P}_2\text{PtS}$ requires C, 54.2; H, 4.3; N, 3.3%), m.p. 217-220°C (decomp.); $\nu_{\text{asym}}(\text{SO}_2)$ at 1260 vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1135 vs and 1107 vs cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.39-6.82 (m, 30H, Ph), and 1.62 p.p.m. (m, 6H, Me, PMePh₂); ³¹P-¹H (36 MHz), δ -8.21 p.p.m. [s, ¹J(PtP) 3394].

(iii) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PEt}_2\text{Ph})_2]$ (*137*).0.5 CH₂Cl₂

The complex $[\text{PtCl}_2(\text{COD})]$ (0.15g, 0.40 mmol) with diethylphenylphosphine (0.134g, 0.81 mmol) and *N,N'*-diphenylsulphamide (0.10g, 0.40 mmol) in dichloromethane (50 cm³) gave white microcrystals of (*137*).0.5 CH₂Cl₂ (0.050g, 15%) (Found: C, 47.8; H, 5.3; N, 3.5. $\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_2\text{P}_2\text{PtS}.0.5 \text{CH}_2\text{Cl}_2$ requires C, 47.8; H, 5.1; N, 3.4%), m.p. 218-220°C (decomp.); $\nu_{\text{asym}}(\text{SO}_2)$ at 1245 vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1142 vs and 1114 m cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.48-7.09 (m, 20H, Ph), 5.31 (s, 1H, CH₂Cl₂), 1.57 (m, 4H, CH₂, PEt₂Ph), 1.20 (m, 4H, CH₂, PEt₂Ph), and 0.69 p.p.m. (m, 12H, Me, PEt₂Ph); ³¹P-¹H (36 MHz), δ -4.58 p.p.m. [s, ¹J(PtP) 3313].

(iv) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PEt}_3)_2](138).0.5 \text{ H}_2\text{O}$

The complex $[\text{PtCl}_2(\text{COD})]$ (0.15g, 0.40 mmol) with triethylphosphine (0.096g, 0.81 mmol) and *N,N'*-diphenylsulphamide (0.101g, 0.407 mmol) in dichloromethane (35 cm³) gave, on stirring the initially obtained oil with light petroleum overnight, sandy-coloured microcrystals of $(138).0.5 \text{ H}_2\text{O}$ (0.21g, 78%) (Found: C, 40.0; H, 5.8; N, 4.2. $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}_2\text{P}_2\text{PtS}.0.5 \text{ H}_2\text{O}$ requires C, 40.4; H, 5.8; N, 3.9%), m.p. 222-224°C (decomp.); $\nu_{\text{asym}}(\text{SO}_2)$ at 1261 vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1142 vs cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.46-7.05 (m, 10H, Ph), 1.87 (s, br, 1H, H₂O), 1.52 (m, 12H, CH₂, PEt₃), and 1.05 p.p.m. (m, 18H, Me, PEt₃); ³¹P-¹H (36 MHz), δ -0.67 p.p.m. [s, ¹J(PtP) 3286].

(v) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{dppe})](140)$

The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) with 1,2-bis-(diphenylphosphino)ethane (0.11g, 0.28 mmol) and *N,N'*-diphenylsulphamide (0.067g, 0.27 mmol) in dichloromethane (30 cm³) gave yellow crystals of (140) (0.18g, 79%) (Found: C, 54.1; H, 4.1; N, 3.5. $\text{C}_{38}\text{H}_{34}\text{N}_2\text{O}_2\text{P}_2\text{PtS}$ requires C, 54.4; H, 4.1; N, 3.4%), m.p. >230°C; $\nu_{\text{asym}}(\text{SO}_2)$ at 1246 vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1132 vs and 1114 vs cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.59-6.60 (m, 30H, Ph), and 2.24-2.08 p.p.m. (m, 4H, CH₂, dppe); ³¹P-¹H (24 MHz), δ 37.92 p.p.m. [s, ¹J(PtP) 3384].

Several crystals of $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{COD})](141)$, one of which was suitable for a single-crystal X-ray diffraction study, were isolated from a subsequent preparation of the chelating phosphine analogue (140) .

Preparation of $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PNEt}_2\text{Ph}_2)_2](139)$

N,N'-Diphenylsulphamide (0.048g, 0.19 mmol) and silver(I) oxide (0.17g, 0.73 mmol) were added in succession to a stirred solution of cis- $[\text{PtCl}_2(\text{PNEt}_2\text{Ph}_2)_2]$ (0.15g, 0.19 mmol) in dichloromethane (35 cm³), and the mixture refluxed for 2.5h. The insoluble silver salts were removed by filtration, and the resulting solution evaporated to dryness under reduced pressure to afford a colourless oil. Dissolution of the oil in dichloromethane (ca. 2 cm³) and addition of light petroleum gave a pale yellow powdery solid which was recrystallised from

dichloromethane - light petroleum to give pale yellow microcrystals of the title complex (*139*) (0.12g, 66%) (Found: C, 55.3; H, 5.4; N, 5.8. $C_{44}H_{50}N_4O_2P_2PtS$ requires C, 55.3; H, 5.3; N, 5.9%), m.p. 175-176°C (decomp.); $\nu_{\text{asym}}(\text{SO}_2)$ at 1260 vs cm^{-1} ; $\nu_{\text{sym}}(\text{SO}_2)$ at 1132 vs and 1093 cm^{-1} . N.m.r. spectra: ^1H (300 MHz), δ 7.35-6.74 (m, 30H, Ph), 3.18-3.10 (m, 8H, CH_2 , PNEt_2Ph_2), and 0.97 p.p.m. [t, 12H, Me, PNEt_2Ph_2 , $^3\text{J}(\text{HH})$ 7.0]; ^{13}C - $\{^1\text{H}\}$ (75.5 MHz, DEPT), δ 132.96-122.64 (m, Ph), 43.46 (s, CH_2 , PNEt_2Ph_2), and 12.85 p.p.m. (s, Me, PNEt_2Ph_2); ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 52.03 p.p.m. [s, $^1\text{J}(\text{PtP})$ 3809].

(b) using potassium hydroxide; general method

Two equivalents of tertiary monodentate phosphine or one equivalent of bidentate phosphine, followed by one equivalent of *N,N'*-diphenylsulphamide (*127*) and an excess of potassium hydroxide were added in succession to a stirred suspension of $[\text{PtCl}_2(\text{COD})]$ in a mixture of dichloromethane (ca. 10 cm^3) and THF (ca. 30 cm^3), and the mixture refluxed for 1.5h. The mixture was filtered to remove excess potassium hydroxide and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (ca. 20 cm^3) and the solution washed with water (ca. 20 cm^3). The organic layer was separated off and dried over anhydrous MgSO_4 . The mixture was filtered and the solution reduced in volume to ca. 2 cm^3 , addition of diethyl ether yielding a microcrystalline solid which was filtered off and dried in vacuo.

(i) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PPh}_3)_2]$ (*135*)

The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) with triphenylphosphine (0.15g, 0.57 mmol) and *N,N'*-diphenylsulphamide (0.067g, 0.27 mmol) gave yellow microcrystals of the title complex (*135*) (0.09g, 35%), identified by comparison of their ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum with that of an authentic sample.

(ii) $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PEt}_2\text{Ph})_2]$ (*137*).0.5 CH_2Cl_2

The complex $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) with diethylphenylphosphine (0.091g, 0.55 mmol) and *N,N'*-diphenylsulphamide (0.067g, 0.27 mmol) gave white microcrystals of the title complex (*137*).0.5 CH_2Cl_2 (0.13g, 59%), identified by comparison of their ^{31}P - $\{^1\text{H}\}$

n.m.r. spectrum with that of an authentic sample.

(iii) [Pt{NPhS(O)₂NPh}(dppe)] (140)

The complex [PtCl₂(COD)] (0.10g, 0.27 mmol) with 1,2-bis-(diphenylphosphino)ethane (0.108g, 0.27 mmol) and N,N'-diphenylsulphamide (0.067g, 0.27 mmol) gave pale yellow microcrystals of the title complex (140) (0.163g, 72%), identified by comparison of their ³¹P-¹H} n.m.r. spectrum with that of an authentic sample.

3.9.3 Reactions of [Pt{NHS(O)₂NH}(PMePh₂)₂] (129).2CHCl₃

(i) with hydrogen chloride

Dry hydrogen chloride gas was bubbled slowly through a stirred solution of (129).2CHCl₃ (0.10g, 0.11 mmol) in dichloromethane (ca. 10 cm³) for 10 min. The solution was evaporated to dryness under reduced pressure to afford a colourless oil, the ³¹P-¹H} n.m.r. spectrum of which showed the presence of only cis-[PtCl₂(PMePh₂)₂], identified by comparison with the ³¹P-¹H} n.m.r. spectrum of an authentic sample.¹³²

(ii) with carbon monoxide

Carbon monoxide was bubbled slowly through a stirred solution of (129).2CHCl₃ (0.05g, 0.054 mmol) in dichloromethane (ca. 30 cm³) for 6h. The solution was evaporated to dryness under reduced pressure, the ³¹P-¹H} n.m.r. spectrum of the resulting residue showing only the presence of (129). Repeating the treatment under refluxing conditions (24h) again did not lead to any reaction.

(iii) with sulphur dioxide

Sulphur dioxide gas was bubbled slowly through a stirred solution of (129).2CHCl₃ (0.09g, 0.097 mmol) in dichloromethane (ca. 20 cm³) for 4h. A milky suspension was observed after 5 min, which remained during the course of the reaction. The mixture was filtered and the resulting solution evaporated to dryness under reduced pressure. The ³¹P-¹H} n.m.r. spectrum of the residue showed several phosphorus-containing compounds to be present, one of which displayed an AB pattern; ³¹P-¹H} n.m.r. spectrum (36 MHz),

second-order AB spin-system, δ 3.53 (d, P_A , $^1J[\text{Pt}P_A]$ 2363, $^2J[P_B P_A]$ 19.5), and -6.15 p.p.m. (d, P_B , $^1J[\text{Pt}P_B]$ 4160, $^2J[P_A P_B]$ 19.5). No pure complexes could be isolated from the reaction mixture.

Attempted deprotonation reaction at nitrogen

$\text{NaN}[(\text{SiMe}_3)_2]$ (0.058g, 0.32 mmol) was added to a solution of $(129).2\text{CHCl}_3$ (0.10g, 0.11 mmol) in THF (30 cm^3) and the mixture stirred at room temperature overnight, yielding a pale yellowish-orange solution and a white precipitate. The mixture was evaporated to dryness under reduced pressure, the residue extracted into dichloromethane (ca. 20 cm^3) and the mixture filtered under nitrogen. The filtrate was evaporated to dryness, a $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the residue showing only the presence of (129) .

Attempted insertion reactions into N-H bonds of $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}(\text{PMePh}_2)_2]$ $(129).2\text{CHCl}_3$

(i) with carbon disulphide

Carbon disulphide (0.063g, 0.83 mmol) was added to a solution of $(129).2\text{CHCl}_3$ (0.07g, 0.075 mmol) in dichloromethane (30 cm^3) and the mixture stirred at room temperature for 6h. The mixture was evaporated to dryness under reduced pressure, the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the residue showing only the presence of starting material (129) .

(ii) with phenyl isothiocyanate

Phenyl isothiocyanate (0.113g, 0.84 mmol) was added to a solution of $(129).2\text{CHCl}_3$ (0.07g, 0.075 mmol) in dichloromethane (25 cm^3) and the mixture stirred at room temperature for 4h. The mixture was then refluxed for 0.75h, and then reduced in volume to ca. 1 cm^3 under reduced pressure. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the solution showed a mixture of starting material (129) (major) and a species exhibiting an AB pattern, with components centred at δ 2.72 and -4.94 p.p.m. Repeating the reaction under refluxing conditions (5h) gave the same two species, but in a slightly different ratio.

(iii) with phenyl isocyanate

Phenyl isocyanate (0.16g, 1.34 mmol) was added to a solution of $(129).2\text{CHCl}_3$ (0.10g,

0.11 mmol) in dichloromethane (25 cm³) and the mixture stirred for 2h at room temperature. The mixture was reduced in volume to ca. 1 cm³, the ³¹P-{¹H} n.m.r. spectrum of the resulting solution showing the presence of a mixture of phosphorus-containing compounds.

(iv) with diphenylacetylene

Diphenylacetylene (0.065g, 0.36 mmol) was added to a stirred solution of (129).2CHCl₃ (0.12g, 0.13 mmol) in absolute ethanol (20 cm³), and the mixture refluxed for 20h. The mixture was then filtered to give a colourless solution which was evaporated to dryness under reduced pressure. The resulting residue was crystallised from dichloromethane - light petroleum, and the solid filtered off and dried in vacuo to give white microcrystals of the starting material (129), identified by comparison of their ³¹P-{¹H} n.m.r. spectrum with that of an authentic sample.

(v) with phenylacetylene

Phenylacetylene (0.093g, 0.91 mmol) was added to a stirred solution of (129).2CHCl₃ (0.10g, 0.11 mmol) in absolute ethanol (50 cm³), and the mixture refluxed for 20h. The mixture was evaporated to dryness under reduced pressure, the resulting pale yellow residue being dissolved in dichloromethane (ca. 1 cm³). Addition of light petroleum afforded a pale yellow solid, which was filtered off and dried in vacuo to give trans-[Pt(C≡CPh)₂(PMePh₂)₂] (0.062g, 71%), identified by comparison of its i.r. and ³¹P-{¹H} n.m.r. spectra with those of an authentic sample.¹⁵³ The data obtained here is included for completeness; $\nu_{(\text{C}\equiv\text{C})}$ at 2112s cm⁻¹. N.m.r. spectrum: ³¹P-{¹H} (24 MHz), δ 0.94 p.p.m. [s, ¹J(PtP) 2522].

(vi) with dimethyl acetylenedicarboxylate

An excess of dimethyl acetylenedicarboxylate was added to a solution of (129).2CHCl₃ (0.145g, 0.156 mmol) in dichloromethane (50 cm³) and the mixture stirred for 6h at room temperature, to give a dark orange solution. The mixture was evaporated to dryness under reduced pressure to yield a greenish-orange solid, which was dissolved in dichloromethane (ca. 8 cm³), the resulting solution being filtered. Addition of light petroleum afforded a yellow solid, which was recrystallised from dichloromethane - light petroleum to give a

mixture of yellow (major) and white (minor) crystals.

Yellow crystals - Formulated as $[\text{Pt}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{NHS}(\text{O})_2\text{NH}\}(\text{PMePh}_2)_2]$ (*148*), m.p. 185-189°C (decomp.); $\nu_{(\text{NH})}$ at 3245w cm^{-1} ; $\nu_{(\text{C}=\text{O})}$ at 1726(sh) and 1710vs cm^{-1} ; $\nu_{\text{asym}}(\text{SO}_2)$ at 1285vs cm^{-1} ; $\nu_{\text{sym}}(\text{SO}_2)$ at 1127vs cm^{-1} . N.m.r. spectra: ^1H (300 MHz), δ 7.42-7.18 (m, 20H, Ph), 6.37 (s, br, 1H, NH), 3.68 (s, 3H, Me, CO_2Me), 3.10 (s, 3H, Me, CO_2Me), 2.33 (m, 1H, NH), 2.18 [d, second-order, 3H, Me, PMePh_2 , $|^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})|$ 10.74, $^3\text{J}(\text{PtH})$ not discernible], and 1.76 p.p.m. [d, second-order, 3H, Me, PMePh_2 , $|^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})|$ 9.42, $^3\text{J}(\text{PtH})$ not discernible]; ^{13}C - $\{^1\text{H}\}$ (75.5 MHz), δ 173.39 (s, CO, CO_2Me), 162.82 [d, CO, CO_2Me , $\text{J}(\text{PC})$ 10.62], 132.47-128.39 (m, Ph), C=C not observed, 52.46 (s, Me, CO_2Me), 50.62 (s, Me, CO_2Me), 17.70 [dd, second-order, Me, PMePh_2 , $|^1\text{J}(\text{PC}) + ^3\text{J}(\text{PC})|$ not discernible, $^2\text{J}(\text{PtC})$ not discernible], and 10.22 p.p.m. [dd, second-order, Me, PMePh_2 , $|^1\text{J}(\text{PC}) + ^3\text{J}(\text{PC})|$ not discernible, $^2\text{J}(\text{PtC})$ not discernible]; ^{31}P - $\{^1\text{H}\}$ (36 MHz), second-order AB spin-system, δ 3.30 {d, P_A , $^1\text{J}[\text{PtP}_\text{A}]$ 2198, $^2\text{J}[\text{P}_\text{B}\text{P}_\text{A}]$ 19.5}, and -0.81 p.p.m. {d, P_B , $^1\text{J}[\text{PtP}_\text{B}]$ 3569, $^2\text{J}[\text{P}_\text{A}\text{P}_\text{B}]$ 19.5}.

3.9.4 Miscellaneous reactions of N,N'-unsubstituted platinathiadiazetidene-3,3-dioxide complexes

(i) Reaction of $[\text{PtCl}_2(\text{COD})]$ with sulphamide, silver(I) oxide and methyldiphenylphosphine

Sulphamide (0.026g, 0.27 mmol) and silver(I) oxide (0.40g, 1.72 mmol) were added in succession to a stirred solution of $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) in dichloromethane (35 cm^3), and the mixture refluxed for 4h. The insoluble silver salts were removed by filtration to afford a pea-green solution. Methyldiphenylphosphine (0.54g, 2.70 mmol) was added to the filtrate and the mixture stirred in air at room temperature for 30 min. The mixture was then evaporated to dryness under reduced pressure, the residue being washed with light petroleum. A ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of the resulting gummy solid showed the presence of (*129*) and methyldiphenylphosphine oxide.

(ii) Reaction of $[\text{PtCl}_2(\text{COD})]$ with sulphamide, silver(I) oxide and t-butyl isocyanide

Sulphamide (0.065g, 0.68 mmol) and silver(I) oxide (1.00g, 4.3 mmol) were added in succession to a stirred solution of $[\text{PtCl}_2(\text{COD})]$ (0.25g, 0.67 mmol) in dichloromethane (60

cm³), and the mixture refluxed for 6h. The insoluble silver salts were removed by filtration, and t-butyl isocyanide (0.28g, 3.37 mmol) was added to the filtrate, the mixture being stirred at room temperature for 1h. The mixture was evaporated to dryness under reduced pressure, and the residue stirred with diethyl ether at room temperature for 1h, whereupon a pale yellowish-brown solid was formed. The solvent was decanted off and the solid stirred with a fresh portion of diethyl ether for a further hour. The solid was filtered off and dissolved in dichloromethane (ca. 5 cm³), the solution being filtered. Addition of diethyl ether gave a microcrystalline solid which was recrystallised from dichloromethane - diethyl ether to yield pale pink microcrystals of $[\text{Pt}\{\text{C}(=\text{NBu}^t)\text{NHS}(\text{O})_2\text{NHC}(=\text{NBu}^t)\}(\text{CNBu}^t)_2]$ (*152*) (0.062g, 15%) (Found: C, 38.6; H, 6.2; N, 13.6. C₂₀H₃₈N₆O₂PtS requires C, 38.6; H, 6.2; N, 13.5%), m.p. >230°C (decomp.); $\nu_{(\text{NH})}$ at 3450m and 3325m cm⁻¹; $\nu_{(\text{C}=\text{N})}$ at 2220vs and 2185vs cm⁻¹; $\nu_{(\text{C}=\text{N})}$ at 1550vs and 1530vs cm⁻¹; $\nu_{\text{asym}}(\text{SO}_2)$ at 1267vs cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1122vs cm⁻¹. N.m.r. spectrum: ¹H (300 MHz), δ 4.89 [s, 2H, NH, exchangeable with [²H₂]-water, ³J(PtH) 30.7], 1.57 (s, 18H, Bu^t), and 1.40 p.p.m. (s, 18H, Bu^t).

3.9.5 Reactions of $[\text{Pt}\{\text{NPhS}(\text{O})_2\text{NPh}\}(\text{PPh}_3)_2]$ (*135*)

(i) with hydrogen chloride

Dry hydrogen chloride gas was bubbled slowly through a stirred solution of (*135*) (0.10g, 0.104 mmol) in dichloromethane (ca. 10 cm³) for 10 min, resulting in a colour change of pale yellow to colourless. The solution was evaporated to dryness under reduced pressure, the ³¹P-¹H n.m.r. spectrum of the remaining residue showing the presence of cis-[PtCl₂(PPh₃)₂], by comparison with that of an authentic sample.

(ii) with iodomethane

Iodomethane (0.228g, 1.61 mmol) was added to a stirred solution of (*135*) (0.10g, 0.104 mmol) in acetone (30 cm³), and the mixture refluxed for 2.5h. The mixture was filtered hot and the filtrate evaporated to dryness under reduced pressure. A ³¹P-¹H n.m.r. spectrum of the residue showed only the presence of unreacted (*135*).

(iii) Reaction of [Pt{NPhS(O)₂NPh}(PPh₃)₂] (I35) with carbon monoxide

(a) in dichloromethane

Carbon monoxide was bubbled slowly through a stirred solution of (I35) (0.10g, 0.104 mmol) in dichloromethane (ca. 40 cm³) for 3h at room temperature. The solution was reduced in volume to ca. 1 cm³ under reduced pressure, a ³¹P-{¹H} n.m.r. spectrum of the residue showing only the presence of starting material. Repeating the reaction under refluxing conditions (6h) had no effect.

(b) in ethanol

Carbon monoxide was bubbled slowly through a refluxing suspension of (I35) (0.10g, 0.104 mmol) in absolute ethanol (60 cm³) for 6h. During the course of the reaction the suspension dissolved, and the resulting solution darkened. The solution was filtered hot, and the deep orange filtrate was evaporated to dryness under reduced pressure. The ³¹P-{¹H} n.m.r. spectrum of the residue showed the presence of several phosphorus-containing species, starting material (I35) being the major component. Repeating the treatment under extended refluxing conditions (24h) did not lead to any reaction whatsoever.

(iv) Reaction of [Pt{NPhS(O)₂NPh}(PPh₃)₂] (I35) with sulphur dioxide

Sulphur dioxide was bubbled slowly through a stirred solution of (I35) (0.10g, 0.104 mmol) in dichloromethane (30 cm³) for 1h at room temperature, a colour change of pale yellow to colourless being observed after 15 min. The solution was reduced in volume to ca. 1 cm³ under reduced pressure, addition of light petroleum yielding a white solid which was then found to be insoluble in all common organic solvents. The i.r. spectrum showed ν_{\max} in the region 1190-1065 cm⁻¹.

(v) Reaction of [Pt{NPhS(O)₂NPh}(PPh₃)₂] (I35) with t-butyl isocyanide

t-Butyl isocyanide (0.07g, 0.84 mmol) was added to a solution of (I35) (0.20g, 0.21 mmol) in dichloromethane (40 cm³) and the mixture stirred for 2h at room temperature. The mixture was reduced in volume to ca. 2 cm³ under reduced pressure, and diethyl ether was added to precipitate a white solid. The mixture was evaporated to dryness, the solid being

stirred with diethyl ether for 1h. The mother liquor was decanted off, the solid dissolved in dichloromethane (ca. 1 cm³) and addition of light petroleum afforded a creamy-white powder which was filtered off and dried in vacuo to give $[\text{Pt}\{\overline{\text{NPhS}(\text{O})_2\text{NPh}}\}(\text{CNBu}^t)(\text{PPh}_3)]$ (*154*) (0.073g, 44%), m.p. >230°C; $\nu_{(\text{C}\equiv\text{N})}$ at 2205 vs cm⁻¹; $\nu_{\text{asym}}(\text{SO}_2)$ at 1260 s cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1133 s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.59-6.71 (m, 25H, Ph), and 1.01 p.p.m. (s, 9H, Bu^t); ³¹P-¹H (36 MHz), δ 5.99 p.p.m. [s, ¹J(PtP) 3262]. Compound not obtained analytically pure.

(vi) Reaction of $[\text{Pt}\{\overline{\text{NPhS}(\text{O})_2\text{NPh}}\}(\text{PPh}_3)_2]$ (*135*) with acetic acid

Acetic acid (0.2 cm³, 2.0 mol dm⁻³, 0.4 mmol) was added to a stirred solution of (*135*) (0.10g, 0.104 mmol) in dichloromethane (30 cm³), and the mixture refluxed for 4h. The resulting colourless solution was filtered hot and evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (20 cm³) and the solution washed with water (10 cm³), the organic layer being separated off and dried over anhydrous MgSO₄. The mixture was filtered and reduced in volume to ca. 1 cm³, addition of light petroleum affording white microcrystals of $[\text{Pt}\{\text{OC}(\text{O})\text{Me}\}_2(\text{PPh}_3)_2]$ (0.07g, 80%), identified by comparison of its ³¹P-¹H n.m.r. and i.r. spectra with those of an authentic sample.¹⁶⁰

(vii) Reaction of $[\text{Pt}\{\overline{\text{NPhS}(\text{O})_2\text{NPh}}\}(\text{PPh}_3)_2]$ (*135*) with dimethyl acetylenedicarboxylate

Dimethyl acetylenedicarboxylate (0.034g, 0.24 mmol) was added to a solution of (*135*) (0.09g, 0.093 mmol) in dichloromethane (30 cm³) and the mixture stirred at room temperature for 3h. The mixture was evaporated to dryness under reduced pressure, the ³¹P-¹H n.m.r. spectrum of the resulting residue showing only the presence of (*135*).

CHAPTER 4

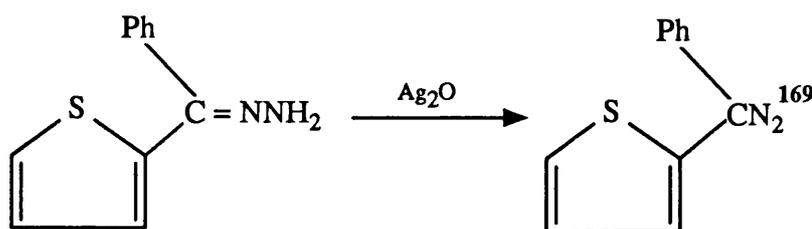
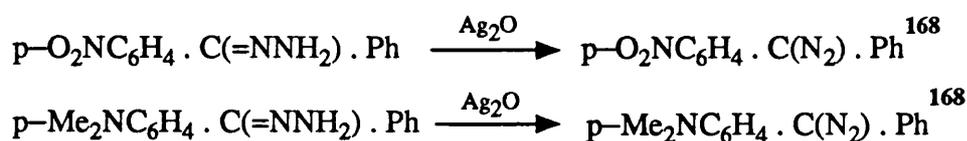
Miscellaneous Reactions of Bis(phosphine)Pt(II) Dichloride Complexes

4.1 INTRODUCTION

The preparation of four-membered platinacycles from *cis*-[PtCl₂L₂] complexes and ligands containing "activated" N-H protons in the presence of silver(I) oxide was discussed in Chapters 2 and 3. This Chapter describes attempts to extend the silver(I) oxide methodology to the synthesis of further platinum(II) complexes from *cis*-[PtCl₂L₂] species and other molecules containing "activated" protons. The use of liquid ammonia as a synthetic reagent in place of silver(I) oxide in some of these reactions is also discussed.

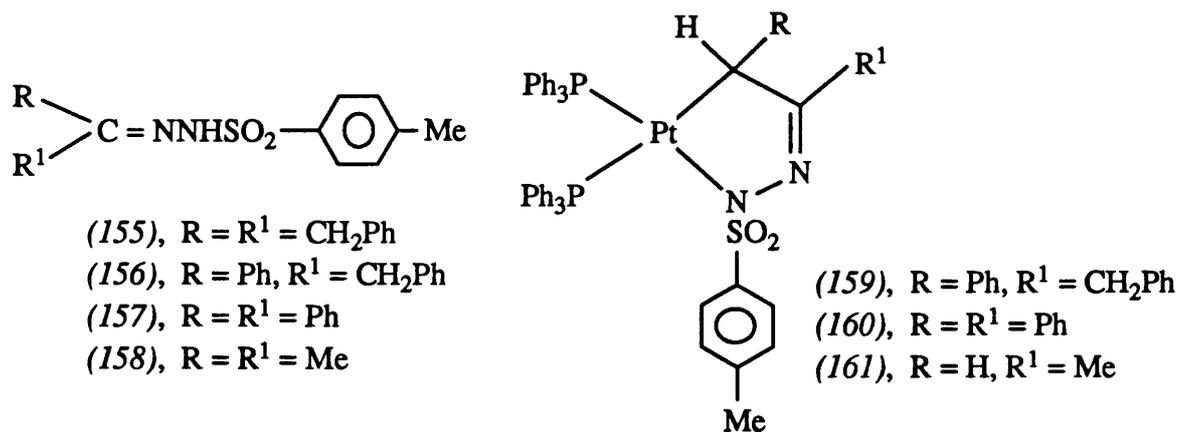
4.2 REACTION OF *cis*-[PtCl₂(PPh₃)₂] WITH p-TOSYLHYDRAZONES IN THE PRESENCE OF SILVER(I) OXIDE OR IN LIQUID AMMONIA

p-Tosylhydrazones are known to react with bases, such as sodium hydroxide to give the corresponding diazocompounds,¹⁶³ and sodium in ethylene glycol, sodium hydride or sodamide, to give mainly 1-olefins.¹⁶⁴ Interestingly, the formation of diazocompounds from their corresponding hydrazones using silver(I) oxide has also been reported,¹⁶⁵⁻¹⁶⁹ and some examples are shown in Scheme 1.



Scheme 1

It was considered of interest therefore to investigate the interaction of *cis*-[PtCl₂(PPh₃)₂] with p-tosylhydrazones in the presence of silver(I) oxide in refluxing dichloromethane. 1,3-Diphenylacetone p-tosylhydrazone (155), deoxybenzoin p-tosylhydrazone (156), benzophenone p-tosylhydrazone (157), and acetone p-tosylhydrazone (158) were used in these studies.



It was hoped that it would be possible, in the cases of (155), (156) and (158), to form five-membered platinacycles of the type (159)-(161) respectively, with silver(I) oxide acting as a base (to deprotonate the nitrogen atom and a carbon atom α - to the C=N moiety) and a halide abstracting agent (to remove chloride ions from the starting metal complex).

Thus, treatment of cis-[PtCl₂(PPh₃)₂] (prepared in situ by reaction of [PtCl₂(COD)] with two mole equivalents of triphenylphosphine in dichloromethane) with one mole equivalent of either (155) or (156) in refluxing dichloromethane in the presence of an excess of silver(I) oxide led, after work-up, to isolation of small quantities of pale yellow solids. Paradoxically, during the work-up procedure, it was necessary to remove all traces of dichloromethane from the initial crude reaction residues, as it was found that the products reacted slowly with this solvent at room temperature to give cis-[PtCl₂(PPh₃)₂] as the main phosphorus-containing product, and the starting p-tosylhydrazones, as shown by ³¹P-¹H} n.m.r., ¹H n.m.r., and ¹³C-¹H} n.m.r. spectroscopy. An attempted recrystallisation of some of the solid obtained from the reaction involving (155), using a dichloromethane - diethyl ether mixture, over several days, resulted in formation of cis-[PtCl₂(PPh₃)₂] along with other phosphorus-containing compounds, as shown by ³¹P-¹H} n.m.r. spectroscopy. The solids were found to react with every other solvent in which they were soluble, with the exception of toluene. Unfortunately, attempts to obtain ¹H n.m.r. and ¹³C-¹H} n.m.r. spectra using toluene-d₈ were unsuccessful, since, owing to the presence of a large amount of undeuterated toluene in the toluene-d₈ sample used, only resonances arising from undeuterated toluene were observed, which effectively "swamped" the signals arising from the product. ¹H n.m.r. and ¹³C-¹H}

n.m.r. spectra were therefore run rapidly in chloroform- d_1 , but some reaction with the solvent to give small amounts of the respective starting p-tosylhydrazones was observed. However, these spectra were readily compared with those of the organic starting materials, and so resonances owing to the metal complexes could be assigned to the spectra of the solids obtained here.

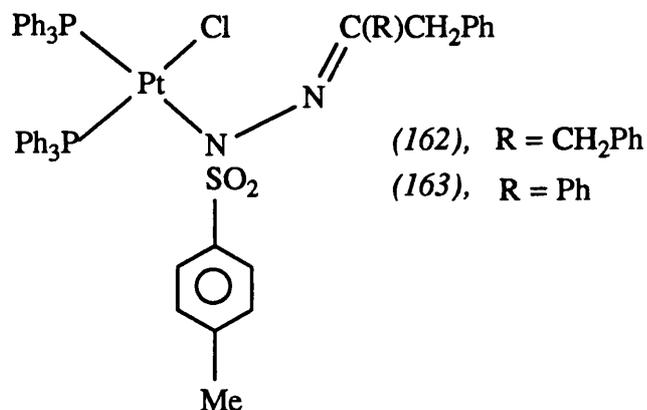
The ^1H n.m.r. spectrum of the solid derived from (155), when taken in chloroform- d_1 , contained several notable features. Together with signals corresponding to (155) were two doublets, centred at δ 6.23 and 3.73 p.p.m., the distance between the two lines in each doublet being ca. 16 Hz. Further, a very distorted second-order AB spin pattern was observed, centred at δ 3.30 p.p.m., the coupling constant between the components of each doublet in the multiplet being ca. 14 Hz. The complex also exhibited what was presumably a methyl resonance at δ 2.27 p.p.m. [cf. δ 2.47 p.p.m. in the ^1H n.m.r. spectrum of an authentic sample of (155)]. The ^1H n.m.r. spectrum of the solid derived from (156) consisted, aside from signals corresponding to (156), of doublets centred at δ 6.70 and 4.51 p.p.m., the coupling constants being 16 Hz in each case. Interesting is the absence of an AB type spin pattern similar to that observed previously at δ 3.30 p.p.m. in the ^1H n.m.r. spectrum of the solid obtained from (155). This is presumably related to the presence of only one benzyl group in (156) as opposed to two such groupings in (155). The spectrum also shows a methyl resonance at δ 2.28 p.p.m. [cf. δ 2.38 p.p.m. for the methyl resonance in the ^1H n.m.r. spectrum of (156)]. Reliable integration values for either of these spectra could not be obtained.

The ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum of the solid obtained from (155) showed two signals arising from methylene groups, at δ 42.86 and 38.09 p.p.m., and a methyl resonance at δ 21.40 p.p.m. In contrast, the ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum of that derived from (156) exhibited only one methylene resonance, at δ 36.06 p.p.m., although a signal corresponding to a methyl group was observed at δ 21.12 p.p.m. Interestingly, no signal corresponding to an imino-carbon atom was observed in either spectrum. It should be noted however that such carbon atoms often have long relaxation times and are thus sometimes not observed.

The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra (in toluene) of the products obtained after recrystallisation from

toluene - light petroleum were very similar, both consisting of AB spin-system patterns with corresponding platinum-195 satellites. One of the $^1\text{J}(\text{PtP})$ coupling constants in each spectrum is ca. 3200 Hz, indicative of phosphorus trans to nitrogen, the other being of the order of 4000 Hz. I.r. spectra of the solids (as KBr discs; spectral regions between $400\text{-}200\text{ cm}^{-1}$ were taken additionally as Nujol mulls between polythene sheets) showed one weak band for each product at ca. 315 cm^{-1} , possibly arising from $\nu(\text{Pt-Cl})$ modes. No bands attributable to $\nu(\text{NH})$ modes were observed in either spectrum, although bands typical of asymmetric and symmetric $\nu(\text{SO}_2)$ vibrations were seen in both spectra.

The data discussed above precludes the formation of complexes such as (159) and (160) in these two reactions. For instance, a signal arising from a methine carbon atom is not observed in either $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectrum, and the $^1\text{J}(\text{PtP})$ coupling constants in both $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra are not consistent with such formulations. Further, no bands arising from $\nu(\text{Pt-Cl})$ modes would be expected for (159) and (160). The data are more in agreement with species (162) and (163), although the ^1H n.m.r. data is not totally consistent with these formulations.



The ^1H n.m.r. data for the solid derived from (156) would partially fit with the metal complex being (163), assuming the two benzylic protons were inequivalent, although if this were the case then there is no apparent reason why these protons would have significantly different chemical shift values. This also applies to one set of benzylic protons in (162), an additional problem being an explanation for the very similar chemical shift values of the two protons in the other benzylic group.

The thermal decomposition of diazocompounds (formed in situ from p-tosylhydrazones and bases) in high boiling aprotic solvents normally leads to products derived from carbenoid species.¹⁷⁰ It should be noted however that treatment of p-chlorobenzophenone hydrazone with silver(I) oxide in either diethyl ether or benzene at ca. 30°C gives the corresponding diazocompound, p-chlorodiphenyldiazomethane, which does not decompose at this temperature (decomposition occurs above 35°C).¹⁶⁵ In contrast, 2-diazopropane decomposes at -20°C in diethyl ether.¹⁶⁶ Although dichloromethane is regarded as an aprotic solvent, it is highly unlikely that carbenes are formed in the silver(I) oxide reactions discussed above involving cis-[PtCl₂(PPh₃)₂] and either (155) or (156). Whatever the metal complexes obtained here, no significant structural changes must occur to the p-tosylhydrazones during these reactions, since the latter are regenerated on reaction of the metal complexes with chlorinated solvents at room temperature. It is hoped the above discussion can form the basis of further studies on these systems.

Treatment of cis-[PtCl₂(PPh₃)₂] with one mole equivalent of benzophenone p-tosylhydrazone (157) in the presence of an excess of silver(I) oxide in refluxing dichloromethane resulted only in the recovery of the starting materials. Treatment of cis-[PtCl₂(PPh₃)₂] with one mole equivalent of acetone p-tosylhydrazone (158) in the presence of an excess of silver(I) oxide in refluxing dichloromethane yielded a mixture of phosphorus-containing products, from which no pure species could be isolated.

In an effort to gain further insight into these systems, some of the above reactions were conducted in liquid ammonia instead of with silver(I) oxide in refluxing dichloromethane. However, treatment of either 1,3-diphenylacetone p-tosylhydrazone (155) or acetone p-tosylhydrazone (158) with an equimolar amount of cis-[PtCl₂(PPh₃)₂] in liquid ammonia at -78°C resulted only in the recovery of cis-[PtCl₂(PPh₃)₂], as shown by ³¹P-¹H} n.m.r. spectroscopy. It is noteworthy that both p-tosylhydrazones are soluble in liquid ammonia at -78°C, no colour change occurring on dissolution in either case. In contrast to the corresponding reactions employing silver(I) oxide, the solids isolated from the reactions carried out in liquid ammonia were found to be insoluble in toluene. The ³¹P-¹H} n.m.r. spectra were therefore taken in

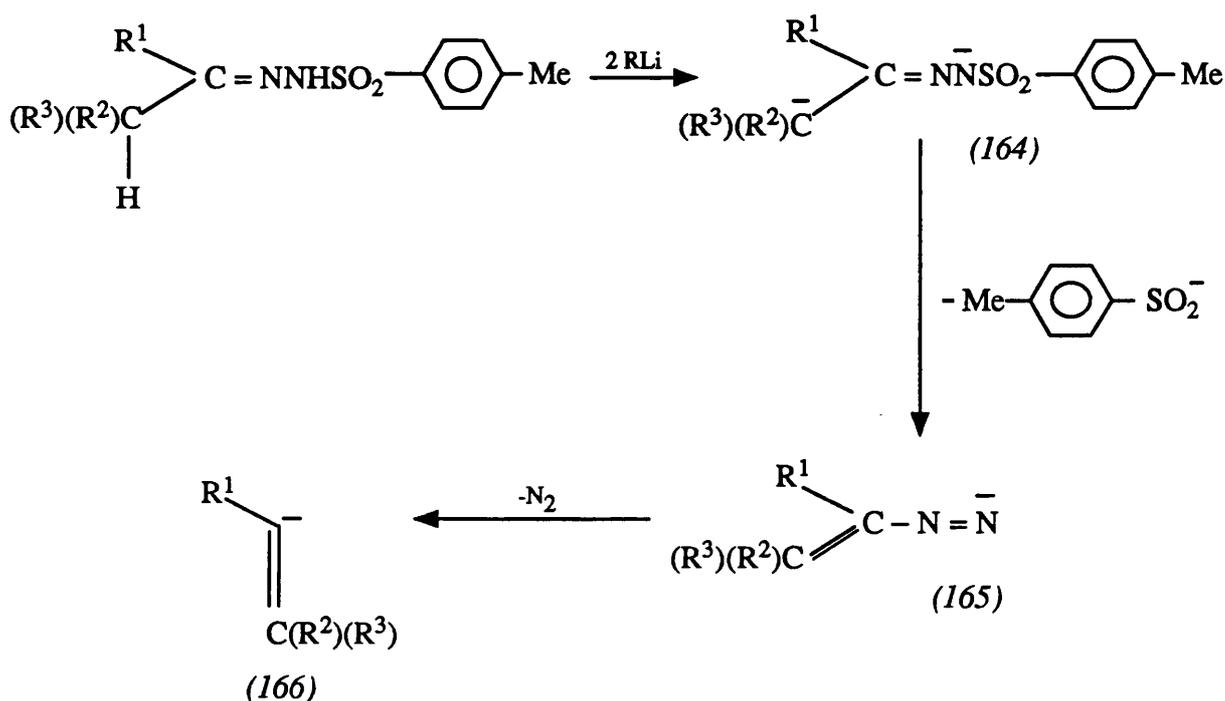
dichloromethane immediately upon work-up. There was no evidence for initial phosphorus-containing metal complexes which could have decomposed in this n.m.r. solvent to give back cis-[PtCl₂(PPh₃)₂], and unless instantaneous reaction with this solvent takes place, it is unlikely that any species other than cis-[PtCl₂(PPh₃)₂] were present in the reaction mixture before work-up.

These reactions employ a methodology similar to that used by Woollins et al. in reactions of [MCl₂L₂] complexes with simple nitrogen- and sulphur-containing molecules.^{137,138} Both mono- and dipotassium salts of some phenylhydrazones have been prepared by treatment of the organic compound with potassium amide in liquid ammonia,¹⁷¹⁻¹⁷³ sodamide also having been used to form monosodium salts under similar conditions.¹⁷¹ The salts can then be reacted further with, for example, organic chlorides and bromides to yield mono- or di-alkylated products. Thus, in future studies it may be advantageous to use potassium amide or sodamide in liquid ammonia to form salts of p-tosylhydrazones, and then to react these species in situ with cis-[PtCl₂L₂] complexes.

4.3 REACTION OF cis-[PtCl₂(PPh₃)₂] WITH THE 1,4-DIANION OF 1,3-DIPHENYL-ACETONE p-TOSYLHYDRAZONE

Alkylolithium reagents have been used extensively as bases in reactions with p-tosylhydrazones. For example, reaction of a wide range of p-tosylhydrazones with two equivalents of methylithium at -78°C generates a dianion (164), which can be trapped with electrophiles, such as iodomethane.¹⁷⁴ If no electrophile is added at -78°C, and the mixture containing the dianion allowed to warm to room temperature, then a vinyl anion (166) is formed via elimination of tosylate anion and loss of nitrogen. Addition of electrophiles, at intermediate temperatures, before complete loss of nitrogen has occurred, can lead to capture of both the species (165) and (166). These reactions are summarised in Scheme 2.¹⁷⁴

The reaction of cis-[PtCl₂(PPh₃)₂] with the 1,4-dianion of 1,3-diphenylacetone p-tosylhydrazone (164, R¹ = CH₂Ph, R² = H, R³ = Ph) at low temperature was studied to enable comparison with the silver(I) oxide and liquid ammonia reactions discussed previously. Thus, treatment of cis-[PtCl₂(PPh₃)₂] with one mole equivalent of this dianion (prepared by an



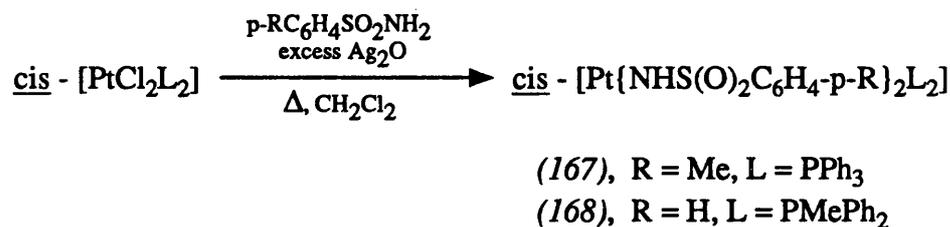
Scheme 2

adaptation of the literature procedure;¹⁷⁵ see Experimental Section) in THF at -78°C resulted in the instantaneous formation of a white precipitate. Further stirring at 0°C did not result in any change. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the final reaction residue after work-up showed only the presence of *cis*-[PtCl₂(PPh₃)₂]. The dianion is stable at 0°C , and so warming the mixture from -78°C to this temperature would not lead to decomposition as in Scheme 2. Although *cis*-[PtCl₂(PPh₃)₂] has a low solubility in THF, it would be expected that some reaction would occur at -78°C or temperatures intermediate between -78°C and 0°C with the dianion. The final $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum was taken in dichloromethane, but as previously, no evidence for products which decompose slowly in this solvent was seen.

4.4 REACTION OF PLATINUM(II) DICHLORIDE COMPLEXES WITH SULPHONAMIDES IN THE PRESENCE OF SILVER(I) OXIDE

Treatment of *cis*-[PtCl₂(PPh₃)₂] with two mole equivalents of p-toluenesulphonamide in the presence of an excess of silver(I) oxide in refluxing dichloromethane afforded the compound (167). Similarly, (168) was prepared by refluxing a mixture of *cis*-[PtCl₂(PMePh₂)₂] and two mole equivalents of benzenesulphonamide with an excess of silver(I) oxide in dichloro-

methane. The reactions are depicted in Scheme 3.



Scheme 3

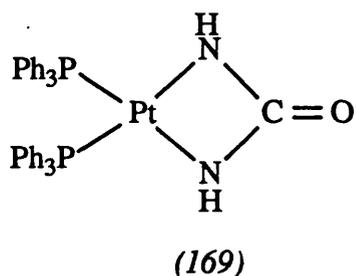
Compound (167) had previously been prepared¹⁷⁶ via reaction of the platinum(0) complex [Pt(PPh₃)₄] with p-MeC₆H₄SO₂N.NaCl.3H₂O in benzene for 60h, or by reacting [Pt(PPh₃)₄] with p-toluenesulphonyl azide in benzene containing a small amount of water for 20 minutes, followed by stirring the filtrate from this reaction for a further 17 hours. Either route is time-consuming. Compound (168) can also be obtained by treatment of cis-[PtCl₂(PMePh₂)₂] with benzenesulphonamide in liquid ammonia,¹³⁸ albeit in lower yield than the alternative route described in this Section. Thus, the reactions employing silver(I) oxide provide a convenient method for the synthesis of such species in good yield.

It is noteworthy that the ¹H n.m.r. spectrum at 90 MHz of a crude sample of (167) before purification exhibited a signal at ca. δ 3.20 p.p.m. which was assigned to the N-H protons, in agreement with the result reported previously.¹⁷⁶ However, the signal seen in the spectrum obtained here also possessed platinum-195 satellites [²J(PtH) ca. 21 Hz], which were not observed previously. There is no evidence of further splitting of the signal by possible coupling to phosphorus-31. At 300 MHz, the chemical shift of the -NH protons remains the same but the satellites are not visible. The compounds cis-[Pt{NHS(O)₂C₆H₄-p-Me}₂L₂] (L = PMe₂Ph or PEt₃) have also been reported,¹³⁸ although no ¹H n.m.r. data is available.

4.5 REACTION OF cis-[PtCl₂(PPh₃)₂] WITH UREA IN THE PRESENCE OF SILVER(I) OXIDE OR IN LIQUID AMMONIA

The success of the silver(I) oxide methodology in the synthesis of compounds of type [Pt{NHS(O)₂NH}L₂] from the corresponding cis-[PtCl₂L₂] species and sulphamide, as described in Chapter 3, prompted an investigation into the analogous reaction of

cis-[PtCl₂(PPh₃)₂] with urea and silver(I) oxide. It was hoped that the product of this reaction would be the monometallic ureylene derivative (169).



Thus, refluxing a mixture of cis-[PtCl₂(PPh₃)₂] and one mole equivalent of unsubstituted urea with an excess of silver(I) oxide in dichloromethane for 3h gave, after work-up, a white powdery solid. The ¹H n.m.r. spectrum of the solid exhibited no observable features attributable to N-H protons, the spectrum being identical before and after shaking the n.m.r. sample with [²H₂]-water. The ¹³C-¹H n.m.r. spectrum was uninformative, there being no readily discernible signals other than those owing to phenyl carbon atoms. The ³¹P-¹H n.m.r. spectrum consisted of a single resonance, at δ 12.50 p.p.m., with corresponding platinum-195 satellites [¹J(PtP) 3286 Hz]. A signal of small intensity was also seen at δ 7.46 p.p.m., although no platinum-195 satellites could be discerned. Further, the i.r. spectrum of the solid showed no bands arising from ν(NH) modes, but an intense band at 2230 cm⁻¹ and a broad, very strong band at 1637 cm⁻¹ were observed. Interestingly, the former band corresponds well with the position of the asymmetric ν(NCO) band in cis-[Pt(NCO)₂(PPh₃)₂] (2227, 2180 cm⁻¹; ¹⁷⁶ 2234 cm⁻¹; ¹⁷⁷ 2230, 2200 cm⁻¹ as a Nujol mull or 2258 cm⁻¹ as a solution in nitromethane¹⁷⁸). Bands arising from a symmetrical ν(NCO) mode in cis-[Pt(NCO)₂(PPh₃)₂] have been reported (1313 cm⁻¹; ¹⁷⁷ 1355, 1312 cm⁻¹ ¹⁷⁸), and a weak band at 1318 cm⁻¹ was seen in the i.r. spectrum of the solid obtained here. To obtain definitive i.r. data for cis-[Pt(NCO)₂(PPh₃)₂], an authentic sample was prepared by a simple metathesis reaction involving cis-[PtCl₂(PPh₃)₂] and silver(I) cyanate in the absence of light¹⁷⁸ (refluxing a similar mixture for a shorter time in light also gave cis-[Pt(NCO)₂(PPh₃)₂]). The ³¹P-¹H n.m.r. spectrum of the sample prepared consisted of a single resonance at δ 7.68 p.p.m., with corresponding platinum-195 satellites [¹J(PtP) 3564 Hz] [cf. absolute value of δ 7.20 p.p.m.;¹⁷⁹

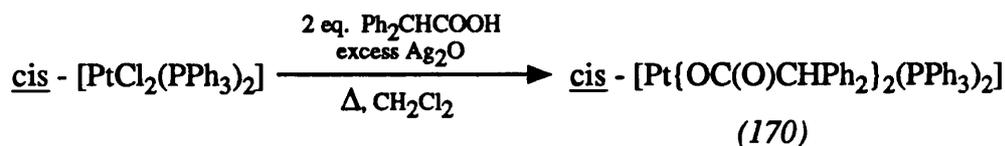
no $^1J(\text{PtP})$ value quoted]. The i.r. spectrum showed intense absorptions at 2246 and 2230 cm^{-1} , but no significantly strong band was observed in the region 1700-1600 cm^{-1} . The small intensity signal seen in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the solid obtained from the silver(I) oxide reaction is thus possibly owing to the presence of a small amount of cis- $[\text{Pt}(\text{NCO})_2(\text{PPh}_3)_2]$ in the solid, and this would also account for the intense absorption at 2230 cm^{-1} observed in the i.r. spectrum. The band at 1637 cm^{-1} seen in the same spectrum is tentatively assigned to a $\nu(\text{C}=\text{O})$ vibration, but direct comparison of the position of this band with the $\nu(\text{C}=\text{O})$ band in unsubstituted free urea is difficult, since there is much controversy surrounding the exact position of such a band in authentic samples of the latter compound.¹⁸⁰⁻¹⁸⁴ The species giving rise to the major peak at δ 12.50 p.p.m. in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum is possibly a carbonyl-containing compound, but without further investigation the compounds in the solid cannot be assigned structures with confidence. Particularly disappointing is the inability to grow crystals of the solid or one of its constituents suitable for X-ray crystallographic studies.

The rôle of silver(I) oxide in the reaction is crucial, however, since treatment of cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with one mole equivalent of unsubstituted urea in refluxing dichloromethane for 3h in the absence of silver(I) oxide led only to the recovery of the starting platinum compound, no resonances arising from other species being observed in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the crude reaction mixture.

In view of the successful syntheses of complexes of the type $[\text{Pt}\{\overline{\text{NHS}(\text{O})_2\text{NH}}\}\text{L}_2]$ by reaction of the corresponding cis- $[\text{PtCl}_2\text{L}_2]$ compounds and sulphamide in liquid ammonia,^{137,138} an attempt was made to apply this methodology to an analogous reaction with urea in an effort to prepare (169). However, treatment of unsubstituted urea with one mole equivalent of cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ in liquid ammonia at -78°C led only to the recovery of starting platinum compound, as shown by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy.

4.6 REACTION OF *cis*-[PtCl₂(PPh₃)₂] WITH DIPHENYLACETIC ACID IN THE PRESENCE OF SILVER(I) OXIDE

Treatment of *cis*-[PtCl₂(PPh₃)₂] with two mole equivalents of diphenylacetic acid in the presence of an excess of silver(I) oxide in refluxing dichloromethane afforded (170), Scheme 4.



Scheme 4

The spectroscopic and analytical data are in accord with the proposed identity of the product. Thus, the ¹H n.m.r. spectrum showed the expected phenyl resonances and a singlet at δ 4.23 p.p.m., assigned to the two protons adjacent to the carbonyl groups. The ³¹P-¹H n.m.r. spectrum consisted of a single resonance with platinum-195 satellites [¹J(PtP) 3848 Hz] and the i.r. spectrum exhibited strong bands at 1650 and 1639 cm⁻¹, arising from ν(C=O) vibrations.

4.7 CONCLUSION

Treatment of *cis*-[PtCl₂(PPh₃)₂] with either 1,3-diphenylacetone p-tosylhydrazone or deoxybenzoin p-tosylhydrazone in the presence of an excess of silver(I) oxide in refluxing dichloromethane gave small amounts of solids which were not identified with confidence. These products were found to react with most solvents in which they were soluble. Benzophenone p-tosylhydrazone and acetone p-tosylhydrazone were used in similar experiments, the former leading to no observed reaction, whereas the latter resulted in formation of a mixture of products. There was no observed reaction between *cis*-[PtCl₂(PPh₃)₂] and either 1,3-diphenylacetone p-tosylhydrazone or acetone p-tosylhydrazone in liquid ammonia, this also being the case when *cis*-[PtCl₂(PPh₃)₂] was treated with the 1,4-dianion of 1,3-diphenylacetone p-tosylhydrazone.

Good yields of compounds of the type *cis*-[Pt{NHS(O)₂C₆H₄-p-R}₂L₂] were obtained on

treatment of the corresponding cis-[PtCl₂L₂] complexes with two mole equivalents of the appropriate sulphonamide and an excess of silver(I) oxide in refluxing dichloromethane.

The reaction of cis-[PtCl₂(PPh₃)₂] with urea and excess silver(I) oxide in refluxing dichloromethane afforded a mixture of unidentified products, whilst no reaction was observed on treatment of urea with cis-[PtCl₂(PPh₃)₂] in liquid ammonia.

The silver(I) oxide methodology was successfully extended to the synthesis of a bis(carboxylato) complex from cis-[PtCl₂(PPh₃)₂] and diphenylacetic acid, in the presence of this reagent.

4.8 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. The compounds diphenylacetic acid, p-toluenesulphonamide, urea (Aldrich), benzenesulphonamide, silver(I) cyanate and silver(I) oxide (BDH) were used as supplied from commercial sources. Anhydrous ammonia was used as supplied (BOC). The compounds [PtCl₂(COD)],¹³¹ cis-[PtCl₂(PPh₃)₂],¹⁸⁵ acetone p-tosylhydrazone,¹⁸⁶ and 1,3-diphenylacetone p-tosylhydrazone¹⁷⁵ were prepared as described in the literature. Benzophenone p-tosylhydrazone and deoxybenzoin p-tosylhydrazone were synthesised by an adaptation of the literature method.¹⁸⁶

4.8.1 Reaction of cis-[PtCl₂(PPh₃)₂] with p-tosylhydrazones

(a) in the presence of silver(I) oxide

(i) with 1,3-diphenylacetone p-tosylhydrazone (155)

Triphenylphosphine (0.15g, 0.57 mmol), 1,3-diphenylacetone p-tosylhydrazone (155), (0.103g, 0.27 mmol) and silver(I) oxide (0.40g, 1.72 mmol) were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (35 cm³), and the mixture refluxed for 4h. The insoluble silver salts were filtered off, and the filtrate evaporated to dryness under reduced pressure. The residue was pumped dry on a vacuum-line for several minutes and then dissolved in toluene (ca. 5 cm³), the resulting solution being filtered. Addition of light petroleum precipitated a yellow solid, which was

filtered off and recrystallised again from toluene - light petroleum as above to give a pale yellow microcrystalline solid (0.029g). The product was studied spectroscopically but could not be identified. The spectroscopic data is given here for completeness. I.r. (as KBr disc, spectral region between 400-200 cm^{-1} taken additionally as a Nujol mull between polythene sheets), $\nu_{\text{asym}}(\text{SO}_2)$ at 1320w cm^{-1} ; $\nu_{\text{sym}}(\text{SO}_2)$ at 1140 m cm^{-1} ; $\nu(\text{Pt-Cl})$ at 310w cm^{-1} . N.m.r. spectra: ^1H (300 MHz), δ 7.79-6.70 (m, Ph), 6.23 {d, CH, $-\text{CH}_2\text{Ph}$, $^2\text{J}(\text{HH})$ 16}, 3.73 {d, CH, $-\text{CH}_2\text{Ph}$, $^2\text{J}(\text{HH})$ 16}, 3.33 {d, CH, $-\text{CH}_2\text{Ph}$, $^2\text{J}(\text{HH})$ 14}, 3.27 {d, $-\text{CH}$, $-\text{CH}_2\text{Ph}$, $^2\text{J}(\text{HH})$ 14}, and 2.27 p.p.m. (s, Me); reliable integration values could not be obtained from this spectrum; $^{13}\text{C}\{-^1\text{H}\}$ (75.5 MHz), δ 142.86-125.46 (m, Ph), 42.86 (s, CH_2), 38.09 (s, CH_2), and 21.40 p.p.m. (s, Me); $^{31}\text{P}\{-^1\text{H}\}$ (24 MHz, toluene), second-order AB spin-system, δ 14.82 {d, P_A , $^1\text{J}[\text{PtP}_\text{A}]$ 4009, $^2\text{J}[\text{P}_\text{B}\text{P}_\text{A}]$ 22.0}, and 7.87 p.p.m. {d, P_B , $^1\text{J}[\text{PtP}_\text{B}]$ 3193, $^2\text{J}[\text{P}_\text{A}\text{P}_\text{B}]$ 22.0}. Attempts to obtain crystals suitable for X-ray diffraction studies, by slow evaporation of a toluene solution of the product over several days, led to deposition of a gummy brown solid. Recrystallisation of a portion of the reaction product from dichloromethane - diethyl ether over several days gave mainly cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$, with a small amount of triphenylphosphine oxide and other unidentified phosphorus-containing compounds, as shown by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy.

(ii) with deoxybenzoin p-tosylhydrazone (156)

Triphenylphosphine (0.15g, 0.57 mmol), deoxybenzoin p-tosylhydrazone (156), (0.099g, 0.27 mmol) and silver(I) oxide (0.40g, 1.72 mmol) were added in succession to a stirred solution of $[\text{PtCl}_2(\text{COD})]$ (0.10g, 0.27 mmol) in dichloromethane (35 cm^3), and the mixture refluxed for 4h. Work-up as in (i) above gave a pale yellow solid (0.052g), which was studied spectroscopically but could not be identified. The spectroscopic data is given here for completeness. I.r. (as KBr disc, spectral region between 400-200 cm^{-1} taken additionally as a Nujol mull between polythene sheets), $\nu_{\text{asym}}(\text{SO}_2)$ at 1306w cm^{-1} ; $\nu_{\text{sym}}(\text{SO}_2)$ at 1152s cm^{-1} ; $\nu(\text{Pt-Cl})$ at 316w cm^{-1} . N.m.r. spectra: ^1H (300 MHz), δ 7.96-6.97 (m, Ph), 6.70 {d, $-\text{CH}$, $-\text{CH}_2\text{Ph}$, $^2\text{J}(\text{HH})$ 16}, 4.51 {d, $-\text{CH}$, $-\text{CH}_2\text{Ph}$, $^2\text{J}(\text{HH})$ 16}, and 2.28 p.p.m. (s, Me); reliable integration values could not be obtained from this spectrum; $^{13}\text{C}\{-^1\text{H}\}$ (75.5 MHz,

DEPT), δ 140.08-125.32 (m, Ph), 36.06 (s, CH₂), and 21.12 p.p.m. (s, Me); ³¹P-¹H (24 MHz, toluene), second-order AB spin-system, δ 14.22 {d, P_A, ¹J[PtP_A] 3970, ²J[P_BP_A] 24.4}, and 7.56 p.p.m. {d, P_B, ¹J[PtP_B] 3237, ²J[P_AP_B] 24.4}.

(iii) with benzophenone p-tosylhydrazone (157)

Triphenylphosphine (0.15g, 0.57 mmol), benzophenone p-tosylhydrazone (157), (0.095g, 0.28 mmol) and silver(I) oxide (0.40g, 1.72 mmol) were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (35 cm³), and the mixture refluxed for 20h. The mixture was filtered to afford a reddy-orange solution, which was evaporated to dryness under reduced pressure. A ³¹P-¹H n.m.r. spectrum of the residue showed only the presence of cis-[PtCl₂(PPh₃)₂].

(iv) with acetone p-tosylhydrazone (158)

Triphenylphosphine (0.15g, 0.57 mmol), acetone p-tosylhydrazone (158), (0.062g, 0.27 mmol) and silver(I) oxide (0.40g, 1.72 mmol) were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (35 cm³), and the mixture refluxed overnight. The mixture was filtered and the resulting solution evaporated to dryness under reduced pressure. A ³¹P-¹H n.m.r. spectrum of the residue showed the presence of a mixture of phosphorus-containing compounds. Attempts to obtain pure samples of the components in the mixture were unsuccessful.

(b) in liquid ammonia

(i) with 1,3-diphenylacetone p-tosylhydrazone (155)

1,3-Diphenylacetone p-tosylhydrazone (155) (0.053g, 0.14 mmol) was added to liquid ammonia (ca. 10 cm³) at -78°C, all of the solid dissolving to give a colourless solution. The mixture was stirred for 15 min and then cis-[PtCl₂(PPh₃)₂] (0.10g, 0.13 mmol) was added. The resulting pale yellow suspension was stirred at -78°C for 0.5h, and then the reaction mixture was allowed to warm slowly to room temperature, during which time the ammonia boiled off. A pale yellow solid remained, which was extracted with dichloromethane (ca. 10 cm³), the resulting mixture being filtered. The filtrate was evacuated to ca. 1 cm³ under

reduced pressure, the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the concentrated solution showing only the presence of cis-[PtCl₂(PPh₃)₂].

(ii) with acetone p-tosylhydrazone (158)

Acetone p-tosylhydrazone (158) (0.044g, 0.19 mmol) was added to liquid ammonia (ca. 30 cm³) at -78°C, all of the solid being dissolved to give a colourless solution. The solution was stirred for 0.5h at -78°C and then cis-[PtCl₂(PPh₃)₂] (0.15g, 0.19 mmol) was added at this temperature to form a white suspension. The mixture was stirred at -78°C for 0.5h, and then allowed to warm slowly to room temperature, during which time a pale creamy-yellow solid was formed. Work-up as in (i) above gave a pale yellow solution which showed in its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum only the presence of cis-[PtCl₂(PPh₃)₂].

4.8.2 Reaction of cis-[PtCl₂(PPh₃)₂] with the 1,4-dianion of 1,3-diphenylacetone p-tosylhydrazone

The dianion was prepared by an adaptation of the literature procedure.¹⁷⁵ 1,3-Diphenylacetone p-tosylhydrazone (155) (0.380g, 1.00 mmol) was dissolved in THF (13 cm³) and n-butyllithium (0.8 cm³, 2.5 mol dm⁻³, 2.00 mmol) was added carefully to the solution at -78°C, to give a pale orange colouration. The mixture was stirred at -78°C for 15 min, and was then allowed to warm slowly to 0°C, whereupon it was stirred for 1h. The colour of the solution remained the same throughout the stirring periods. The solution containing the dianion was stored at 0°C.

One mole equivalent of the dianion was added to a stirred suspension of cis-[PtCl₂(PPh₃)₂] (0.15g, 0.19 mmol) in THF (50 cm³) at -78°C, resulting in the immediate formation of a white precipitate. The mixture was stirred at -78°C for 15 min, and was then allowed to warm slowly to 0°C, whereupon it was stirred overnight. The white precipitate remained during the stirring period. The mixture was filtered to yield a deep orange solution, which was evaporated to dryness under reduced pressure. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the resulting residue showed only the presence of cis-[PtCl₂(PPh₃)₂].

4.8.3 Reaction of platinum(II) dichloride complexes with sulphonamides in the presence of silver(I) oxide

(i) Preparation of *cis*-[Pt{NHS(O)₂C₆H₄-p-Me}₂(PPh₃)₂] (167)

Triphenylphosphine (0.15g, 0.57 mmol), p-toluenesulphonamide (0.096g, 0.56 mmol) and an excess of silver(I) oxide were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (30 cm³), and the mixture refluxed for 3.5h. The insoluble silver salts were removed by filtration to give a very pale yellow filtrate, which was reduced in volume to ca. 1 cm³ under reduced pressure. Addition of light petroleum gave a white powdery solid, which was filtered off and dried in vacuo to yield *cis*-[Pt{NHS(O)₂C₆H₄-p-Me}₂(PPh₃)₂] (167) (0.186g, 65%), identified by comparison of its ¹H n.m.r. and i.r. spectra with those of an authentic sample.¹⁷⁶ The spectroscopic data is given here for completeness. I.r. $\nu_{(\text{NH})}$ at 3356w cm⁻¹; $\nu_{\text{asym}}(\text{SO}_2)$ at 1316s and 1288s cm⁻¹; $\nu_{\text{sym}}(\text{SO}_2)$ at 1143s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.63-6.82 (m, 38H, Ph), 3.15 (s, 2H, NH), and 2.23 p.p.m. (s, 6H, Me); ¹³C-¹H (75.5 MHz, DEPT), δ 143.62-125.85 (m, Ph), and 21.19 p.p.m. (s, Me); ³¹P-¹H (24 MHz), δ 8.87 p.p.m. [s, ¹J(PtP) 3437].

(ii) Preparation of *cis*-[Pt{NHS(O)₂Ph}₂(PMePh₂)₂] (168)

Methyldiphenylphosphine (0.11g, 0.55 mmol), benzenesulphonamide (0.086g, 0.55 mmol) and silver(I) oxide (0.20g, 0.86 mmol) were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (35 cm³), and the mixture refluxed for 3h. The mixture was filtered and the resulting solution was reduced in volume to ca. 1 cm³ under reduced pressure. Addition of diethyl ether gave a white solid which was filtered off, washed with light petroleum and diethyl ether and dried in vacuo to give *cis*-[Pt{NHS(O)₂Ph}₂(PMePh₂)₂] (168) (0.146g, 60%), identified by comparison of its ³¹P-¹H n.m.r. spectrum with that of an authentic sample.¹³⁸

4.8.4 Reaction of *cis*-[PtCl₂(PPh₃)₂] with urea

(i) in the presence of silver(I) oxide

Triphenylphosphine (0.15g, 0.57 mmol), urea (0.016g, 0.27 mmol) and silver(I) oxide

(0.40g, 1.72 mmol) were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (30 cm³), and the mixture refluxed for 3h. Work-up in 4.8.3 (i) above gave a white powdery solid (0.117g), which showed the following spectroscopic properties; I.r. ν_{\max} at 2230 vs cm⁻¹ and 1637 s cm⁻¹. N.m.r. spectra: ¹H (300 MHz): this spectrum only showed the presence of phenyl protons; shaking the sample with [²H₂]-water resulted in no change; ³¹P-¹H (24 MHz), δ 12.50 p.p.m. [s, ¹J(PtP) 3286].

Repeating the reaction in the absence of silver(I) oxide under the same conditions did not result in any reaction, only cis-[PtCl₂(PPh₃)₂] being recovered.

For the purposes of spectroscopic comparison, an authentic sample of cis-[Pt(NCO)₂(PPh₃)₂] was synthesised in dichloromethane using the literature procedure.¹⁷⁸ Selected spectroscopic data for this compound are given here for completeness. I.r. $\nu_{\text{asym}}(\text{NCO})$ at 2246 vs cm⁻¹ and 2230 vs cm⁻¹. N.m.r. spectrum: ³¹P-¹H (24 MHz), δ 7.68 p.p.m. [s, ¹J(PtP) 3564]. Repeating the literature procedure, under refluxing conditions for 3h, without protection from light, also led to formation of cis-[Pt(NCO)₂(PPh₃)₂].

(ii) in liquid ammonia

Urea (0.012g, 0.20 mmol) was added to liquid ammonia (ca. 10 cm³) at -78°C, all of the solid dissolving to give a colourless solution. The mixture was stirred for 15 min at -78°C, and then cis-[PtCl₂(PPh₃)₂] (0.15g, 0.19 mmol) was added to give a white suspension. The mixture was stirred at -78°C for 0.5h, and then allowed to warm slowly to room temperature, leaving a white solid. Extraction of the solid into dichloromethane, filtration of the resulting mixture and addition of light petroleum to the filtrate gave a white powdery solid which was identified as cis-[PtCl₂(PPh₃)₂] by ³¹P-¹H n.m.r. spectroscopy.

4.8.5 Reaction of cis-[PtCl₂(PPh₃)₂] with diphenylacetic acid in the presence of silver(I) oxide

Triphenylphosphine (0.15g, 0.57 mmol), diphenylacetic acid (0.115g, 0.54 mmol) and silver(I) oxide (0.40g, 1.72 mmol) were added in succession to a stirred solution of [PtCl₂(COD)] (0.10g, 0.27 mmol) in dichloromethane (35 cm³), and the mixture refluxed for

4h. The mixture was filtered to give a cherry-red filtrate, which was reduced in volume to ca. 1 cm³ under reduced pressure. Addition of light petroleum gave a microcrystalline white solid which was recrystallised from dichloromethane - light petroleum, filtered off, washed with light petroleum and diethyl ether and dried in vacuo to give white feathery needles of cis-[Pt{OC(O)CHPh₂}₂(PPh₃)₂] (170) (0.030g, 10%) (Found: C, 66.7; H, 4.5; N, <0.3. C₆₄H₅₂O₄P₂Pt requires C, 67.3; H, 4.6; N, 0.0%), m.p. 214-217°C (decomp., with gas evolution); $\nu_{(C=O)}$ at 1650s cm⁻¹ and 1639s cm⁻¹. N.m.r. spectra: ¹H (300 MHz), δ 7.55-6.91 (m, 50H, Ph), and 4.23 p.p.m. [s, 2H, CH, OC(O)CHPh₂]; ³¹P-(¹H) (24 MHz), δ 6.05 p.p.m. [s, ¹J(PtP) 3848].

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APPENDIX

Crystal Data for X-Ray Crystal Structures in this Thesis.

- (i) $[\text{Pt}\{\overline{\text{NPhC(=NPh)S}}\}(\text{PPh}_3)_2](107)$. $\text{C}_{49}\text{H}_{40}\text{N}_2\text{P}_2\text{PtS}$, $M = 945.97$,
 monoclinic, space group $P2_1/a$, $a = 24.267(20)$, $b = 9.547(13)$, $c = 17.746(15)$ Å, $\gamma = 94.56(10)^\circ$ (unique axis = c), $U = 4098.2$ Å³, $Z = 4$, $D_c = 1.53$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 34.3$ cm⁻¹.
- (ii) $[\text{Pt}\{\overline{\text{NPhC(=NPh)S}}\}(\text{PMePh}_2)_2](108)$. CH_2Cl_2 . $\text{C}_{39}\text{H}_{36}\text{N}_2\text{P}_2\text{PtS}\cdot\text{CH}_2\text{Cl}_2$, $M = 906.77$, monoclinic, space group $P2_1/n$, $a = 15.420(3)$, $b = 22.507(21)$, $c = 11.571(10)$ Å, $\beta = 105.09(4)^\circ$, $U = 3877.3$ Å³, $Z = 4$, $D_c = 1.42$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 36.42$ cm⁻¹.
- (iii) $[\text{Pt}\{\overline{\text{NHS(O)}_2\text{NH}}\}(\text{PMePh}_2)_2](129)$. 2CHCl_3 . $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_2\text{P}_2\text{PtS}\cdot 2\text{CHCl}_3$, $M = 927.34$, monoclinic, space group $C2/c$, $a = 21.360(7)$, $b = 13.588(4)$, $c = 12.291(2)$ Å, $\beta = 101.92(3)^\circ$, $U = 3485.5$ Å³, $Z = 4$, $D_c = 1.77$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 44.57$ cm⁻¹.
- (iv) $[\text{Pt}\{\overline{\text{NPhS(O)}_2\text{NPh}}\}(\text{COD})](141)$. $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{PtS}$, $M = 549.56$, monoclinic, space group $I2/c$ (non-standard setting of $C2/c$), $a = 12.862(4)$, $b = 13.901(4)$, $c = 11.220(1)$ Å, $\beta = 110.21(1)^\circ$, $U = 1882.57(1.26)$ Å³, $Z = 4$, $D_c = 2.04$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 72.71$ cm⁻¹.
- (v) $[\text{Pt}\{\overline{\text{C(CO}_2\text{Me)=C(CO}_2\text{Me)NHS(O)}_2\text{NH}}\}(\text{PMePh}_2)_2](148)$. $\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_6\text{P}_2\text{PtS}$, $M = 831.73$, monoclinic, space group $P2_1/c$, $a = 16.330(27)$, $b = 11.114(19)$, $c = 18.728(9)$ Å, $\beta = 100.03(2)^\circ$, $U = 3347.1$ Å³, $Z = 4$, $D_c = 1.66$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 42.0$ cm⁻¹.