The Chemistry of Platinum Complexes and Hydrosilation

By

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ABSTRACT

This thesis describes the study of a series of platinum complexes, with particular emphasis towards hydrosilation.

Platinum bis(phosphine) azodicarbonyl complexes Pt(PR$_3$)$_2$(R$_2$OCNNCOR$^2$) (R$^1$ = Ph, Me; R$^2$ = Ph, Me, OEt, Pr$^t$) were synthesised and studied. Multinuclear NMR spectroscopy on Pt(PR$_3$)$_2$(R$_2$OCNNCOR$^2$) revealed that the dicarbonyl substituted azo ligand is co-ordinated asymmetrically, consistent with a five membered, Pt–N–N–C–O ring. The crystal structure of Pt(PPh$_3$)$_2$(PrO$_2$CNNCO$_2$Pr$^t$) shows that the co-ordination sphere of platinum is essentially square planar and co-planar with the five-membered, Pt(1)–O(1)–C(5)–N(2)–N(1) ring. The Pt(PR$_3$)$_2$(R$_2$OCNNCOR$^2$) complexes show sensitivity towards chlorinated solvents (CH$_2$Cl$_2$, CHCl$_3$) under photolysis conditions forming the corresponding platinum bis(phosphine) dichloride complexes; the same products are formed in a slower thermal reaction but only for complexes with azodicarboxylate ligands. Complexes with azodicarboxylate ligands also react photochemically with ethylene in d$_8$-THF yielding Pt(PPh$_3$)$_2$(C$_2$H$_4$) but the azodiacyl analogues are inert in this respect.

Azodicarboxylate compounds R$_2$CNNCO$_2$R (R = Et, Pr$^t$, Bu$^t$) are inhibitors of the catalytic activity of [(Pt{$^4$}(CH$_2$=CHSiMe$_2$)$_2$O)]$_2$($^4$-(CH$_2$=CHSiMe$_2$)$_2$O) for the hydrosilation reaction. The inhibited species can be decomposed thermally or photochemically to give active hydrosilation catalysts. It was found that the bulky azo compound Bu$^t$O$_2$CNNCO$_2$Bu$^t$ was the least effective inhibitor of [(Pt{$^4$}(CH$_2$=CHSiMe$_2$)$_2$O)]$_2$($^4$-(CH$_2$=CHSiMe$_2$)$_2$O)].

The photochemistry of platinum bis(phosphine) malonates and phthalates was found to be limited, and their reactivities were much lower compared to the analogous oxalate complexes.

Silyl hydride complexes, cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$), were synthesised from the reaction of Pt(PCy$_3$)$_2$ and the corresponding silane. These complexes were undergo dynamic exchange in solution. Two exchange processes were identified; the first involves mutual phosphine exchange, i.e. positional interchange between the hydride and the silyl ligands. The second process occurs at higher temperatures (above 290 K) and involves the elimination and re-addition of the silane ligand HSiR$_3$. Thermodynamic and activation parameters are obtained for cis-Pt(PCy$_3$)$_2$(SiR$_3$) (R = Ph, SiR$_3$ = SiMe$_2$CH$_2$CH=CH$_2$, SiMe$_2$Et). The reaction of Pt(PCy$_3$)$_2$ with the disilane HSiMe$_2$(1,2-C$_6$H$_4$)SiMe$_2$H is thought to form a Pt(IV) bis(silyl) dihydride trigonal bipyramidal species of the form, Pt(PCy$_3$)(H)$_2$[SiMe$_2$(1,2-C$_6$H$_4$)SiMe$_2$], where the hydride ligands are in the axial positions. All of the platinum silyl hydride complexes studied degrade thermally to form trans-Pt(PCy$_3$)$_2$(H)$_2$ at, or above, room temperature.
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**LIST OF ABBREVIATIONS**

**Spectroscopy**

<table>
<thead>
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<tbody>
<tr>
<td>IR</td>
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<tr>
<td>UV/VIS</td>
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<td>$\varepsilon$</td>
<td>extinction co-efficient</td>
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**NMR**

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**Nuclear Magnetic Resonance**

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**MS**

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**FAB**

fast atom bombardment

**GC**

gas chromatography

**Units**

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**Chemical**

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<td>Bu$^t$</td>
<td>$-\text{C(\text{CH}_3)}_3$</td>
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**Others**

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<td>MO</td>
<td>molecular orbital</td>
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<tr>
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<td>lowest unoccupied molecular orbital</td>
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CHAPTER 1

INTRODUCTION
1.1 GENERAL BACKGROUND

The hydrosilation, or hydrosilylation, reaction involves the addition of the Si–H bond across an unsaturated bond and plays an immensely important role in industry. Commercially, the hydrosilation reaction most commonly involves an unsaturated hydrocarbon, and leads to the formation of a new Si–C bond (Equation 1.1). This reaction can be used to generate a diverse range of novel organosilanes, cross-linked silicone polymers and cross-linked silicone co-polymers with organic monomers, some of its many applications being in silicone gels, rubbers and paper coatings.

\[
\begin{align*}
R & + \text{SiR}_3\text{–H} \rightarrow \text{R'}_3\text{Si} \text{–CHR} & (1.1)
\end{align*}
\]

In this thesis, we explore the thermal and photochemical reactivity of a variety of platinum complexes, the roles they play in the hydrosilation reaction and the type of interaction formed between the platinum metal centre and the Si–H bond of various silanes.

1.2 THE HYDROSILATION REACTION

The hydrosilation reaction can take place by two distinct routes. The first route to be developed involved a free radical chain mechanism, and was initiated either thermally (ca. 300 °C), with UV or γ radiation, or with the use of a radical initiator, e.g. the decomposition of acyl peroxides or azonitriles. However, the main drawback of this pathway is that complex functional groups attached to the unsaturated hydrocarbon are rarely tolerant of the harsh conditions employed. Not surprisingly, these methods find little use in the industries of today.

The second pathway utilises transition metals to catalyse the hydrosilation reaction, and it is the method of choice today. The use of transition metal catalysts allows the hydrosilation reaction to proceed more smoothly, at lower temperatures and in higher yields. Speier pioneered the first commercially successful transition metal hydrosilation catalyst in the 1950s and prompted tremendous interest in the subject. In 1957, Speier showed chloroplatinic acid, H₂PtCl₆, also known as Speier’s Catalyst, to be an extremely effective hydrosilation catalyst precursor, with as little as 10⁻⁵–10⁻⁸ moles of H₂PtCl₆ required per mole of Si–H function.

The catalytic hydrosilation reaction cycle was generally assumed to proceed initially via a platinum(0) species derived from a HSiR₃ induced reduction of H₂PtCl₆. However, Lewis and co-workers have suggested that Speier’s catalyst and other highly active platinum catalysts require the formation of colloidal platinum for hydrosilation.
Lewis also offers an explanation for the induction period and oxygen sensitivity often observed for the catalysed hydrosilation reaction. This is discussed in Section 1.2.6.

In more recent years, Karstedt's catalyst, or solution, has been used most widely to catalyse the hydrosilation reaction. This catalyst is formed by the reaction of $\text{H}_2\text{PtCl}_6$ with vinylsiloxane. Lappert and co-workers found that reacting $\text{Pt(COD)}_2$ with sym-tetramethyldivinylidisiloxane, $(\text{H}_2\text{C}=\text{CHSiMe}_2)_2\text{O}$, yielded a catalytically active solution which has the same $^1\text{H}$, $^{29}\text{Si}$ ($^1\text{H}$) and $^{195}\text{Pt}$ ($^1\text{H}$) NMR features as obtained for the reaction between $\text{H}_2\text{PtCl}_6$ and $(\text{H}_2\text{C}=\text{CHSiMe}_2)_2\text{O}$. They have also determined the crystal structure of the precursor to the active catalyst which corresponds to the species $[(\text{Pt}(\eta^4-(\text{H}_2\text{C}=\text{CHSiMe}_2)_2\text{O}))_2\mu-(\text{H}_2\text{C}=\text{CHSiMe}_2)_2\text{O}]]$ 1, with one bridging and two chelating $(\text{H}_2\text{C}=\text{CHSiMe}_2)_2\text{O}$ ligands.

![Chemical structure](image)

Besides platinum, complexes of other transition metals have also been found to be active as hydrosilation catalysts. These include Rh, Co, Ru, Pd and Ni, and the studies on these and other metals have led to the identification of key intermediates. This has helped to construct a more detailed and accurate understanding of the individual steps involved in the hydrosilation mechanism for a homogeneous system catalysed by transition metals.

1.2.1 The Chalk-Harrod Mechanism for Hydrosilation

The first and most widely accepted mechanism for the transition metal catalysed hydrosilation reaction was proposed by Chalk and Harrod in 1965. In their studies of the reaction between 1-hexene and various silanes initiated by platinum(II) and rhodium(I) olefin complexes, they proposed a mechanism which initially involves the oxidative addition of the Si–H bond to a catalytically active transition metal centre, yielding a metal silyl hydride intermediate. This is then followed by alkene addition and hydride transfer to form a metal alkyl silyl intermediate. The final step of the catalytic cycle sees
the reductive elimination of the alkyl and silyl groups to produce the organosilane product, regenerating the active transition metal catalyst in the process (Scheme 1.1).

\[
\text{R'} \text{SiR}_3 \xrightarrow{[M]} \text{H-SiR}_3
\]

**Scheme 1.1** The Chalk-Harrod mechanism for olefin hydrosilation.\(^{17}\)

Studies by Speier *et al.* on the addition of DSiCl\(_3\) to a series of terminal olefins have shown that extensive exchange occurs between the Si–D group of the deuterated silane and the C–H group of the alkene, along with alkene isomerisation (Equation 1.2).\(^{18}\)

\[
2.5 \text{DSiCl}_3 + \text{CH}_2=\text{C(CH}_3)_2 \xrightarrow{\text{H}_2\text{PtCl}_6} \text{SiCl}_3\text{C}_4\text{H}_{6.5}\text{D}_{2.5} + 1.5 \text{HSiCl}_3
\] (1.2)

Speier also reacted isobutene with DSiCl\(_3\) in the presence of H\(_2\)PtCl\(_6\) and found the product, isobutytrichlorosilane, was 70 % deuterated at the tertiary position and deuterium was found in every other possible position so that an average of 2.5 deuterium atoms were present in each molecule of the product.\(^{18}\) This observation supports the reversibility of the steps shown in Schemes 1.1 and 1.3.

Interestingly, isomerisation of alkenes often occurs during hydrosilation with long chain terminal alkenes converting to internal alkenes which are thermodynamically more favourable and often unreactive to hydrosilation.\(^{19,20}\) Haszeldine *et al.* studied the hydrosilation of 1-hexene with various silanes using Wilkinson’s complex, Rh(PPh\(_3\))\(_3\)Cl, to catalyse the reaction. They found that when using HSiPh\(_3\), 100 % conversion to the n-hexylsilane was obtained but only 70 % and 8 % n-hexylsilane was formed when HSiEt\(_3\) and HSiCl\(_3\) were used, respectively. The rest of the 1-hexene had
undergone complete isomerisation to internal hexenes. From this observation it would appear that alkene isomerisation is in direct competition with hydrosilation.

Internal alkenes have been reported to undergo hydrosilation, but only after isomerisation of the alkene. Speier reacted a series of methylcyclohexenes with HSiCl₃ to form SiCl₃(C₇H₁₃) (Scheme 1.2).¹⁸,²¹ This study demonstrated that the preferred location of the silyl group is at the terminal alkene positions over any internal positions.

Scheme 1.2 Hydrosilation of methylcyclohexenes with trichlorosilane.

The proposed mechanisms for the isomerisation of alkenes generally involves either a metal alkyl hydride or an η³-allyl metal intermediate.²² Chalk and Harrod proposed that the isomerisation of alkenes during the hydrosilation reaction can occur after the formation of the metal silyl hydride alkene intermediate (Scheme 1.3).¹⁶ This can go on to form either the primary (1°) or secondary (2°) alkyl silyl intermediate. If alkene isomerisation occurs, then the 2° alkyl silyl intermediate either reductively eliminates to form a 3° organosilane product or undergoes β-hydride elimination to yield an internal alkene (Scheme 1.3).

Scheme 1.3 Chalk-Harrod mechanism for alkene hydrosilation, involving alkene isomerisation.¹⁷
It should be noted, however, that alkyl silyl reductive elimination is not a common process and only a few examples have been documented. The first stoichiometric example was reported by Gladysz and co-workers. They found that Fe(CO)₄(SiMe₃)R (R = alkyl) decomposed slowly at room temperature to yield RSiMe₃. Later Milstein and co-workers demonstrated that competitive C–H and Si–C reductive elimination occurs in the Ir(III) complex, Ir(PMe₃)₃(H)(SiEt₃)(CH₃)₂, to form CH₄ or SiMeEt₃ (Scheme 1.4).

More recently, Milstein and co-workers were able to demonstrate exclusive Si–C bond formation from the reaction of a platinum(II) alkyl complex 3, with various silanes (Scheme 1.5), but they were uncertain of the explanation for this observation. However, they did propose that phosphine can dissociate from 3 to form 5 (Scheme 1.6). This was said to be due to the strong trans-influence of the σ-benzyl ligand and the steric hindrance of the cyclometallated ligand. Si–H oxidative addition to the co-ordinatively unsaturated metal centre in 5 would then afford 6, a Pt(IV) species. Three possible pathways are available from 6, the first is Si–H reductive elimination, the second is C–H reductive elimination and the third is Si–C reductive elimination. They argued that because of the strong trans-influence of silyl ligands, which is comparable with or even higher than that of hydride ligands, ArCH₂–H formation, a reverse cyclometallation process to 7, might be preferred over CH₄ or CH₃SiR₃ formation. This would then allow Si–C reductive elimination to yield the Pt(0) species 8, which can undergo cyclometallation to form the final product 4.

Ozawa et al. have also demonstrated that facile Si–C reductive elimination occurs in cis-PtMe(SiPh₃)(PMePh₂)₂ 9 to give MeSiPh₂ and a platinum(0) species. This was an unexpected result since cis-PtMe₂(PMePh₂)₂ 10 is thermally inactive towards reductive elimination.
Scheme 1.5 Reaction of 3 with HSiR₃ resulting in exclusive Si–C bond formation.²⁵

Scheme 1.6 Possible pathway for Si–C formation in the reaction between 3 and HSiR₃.²⁵
1.2.2 The modified Chalk-Harrod Mechanism for Hydrosilation

Wrighton et al. were the first to propose a modified version of the Chalk-Harrod mechanism\textsuperscript{16} which identified a pathway for Si–C bond formation\textsuperscript{30} other than Si–C reductive elimination.\textsuperscript{23,24,25,28} Their modified Chalk-Harrod mechanism also provides a plausible pathway for the silation reaction, \textit{i.e.} formation of vinyl silanes (Equation 1.3),\textsuperscript{31} which sometimes occurs during hydrosilation.

$$2 \text{CH}_2=\text{CH}_2 + \text{HSiR}_3 \rightarrow \text{CH}_2=\text{CHSiR}_3 + \text{C}_2\text{H}_6$$ \hspace{1cm} (1.3)

Wrighton studied the catalytic activities of Fe(CO)\textsubscript{5} \textsuperscript{11} under irradiation in the presence of an alkene and various silanes and found good conversion to a mixture of alkane, alkylsilane and vinylsilane products.\textsuperscript{30} They proposed that a silyl group migration, instead of a hydride migration, was the step responsible for the formation of the Si–C bond (Scheme 1.7). Subsequent C–H reductive elimination leads to the hydrosilation product, whilst β-hydride elimination forms a vinylsilane and an alkane (Scheme 1.7). It is important to note that the classification between migration and insertion reactions is subjective and generally has no mechanistic implications. According to Braunstein and Knorr, silyl group migration onto a co-ordinated alkene can also be viewed as alkene insertion into a M–Si bond.\textsuperscript{32}

![Scheme 1.7 The modified Chalk-Harrod Mechanism.\textsuperscript{17}](image-url)
1.2.3 The Seitz-Wrighton Mechanism for Hydrosilation

Seitz and Wrighton later produced more evidence that silyl migration could occur during hydrosilation by establishing that Co(CO)$_4$(SiEt$_3$) 12, an effective hydrosilation catalyst, undergoes alkene insertion into the Co–Si bond upon photolysis in the presence of silane, and under an atmosphere of ethene (Scheme 1.8). In Seitz and Wrighton’s mechanism (Scheme 1.8), 12 loses CO upon photolysis to generate the co-ordinatively unsaturated 16-electron species, Co(CO)$_3$(SiEt$_3$) 13, which can be observed by FTIR in a methylcyclohexane or ethene matrix at 77 K. The next step sees the co-ordination of ethene to the unsaturated complex to form Co(CO)$_3$(CH$_2$=CH$_2$)(SiR$_3$) 14, observable by $^1$H NMR spectroscopy, and it is then followed by insertion of ethene into the Co–Si bond in the presence of silane. The silane then oxidatively adds to the cobalt centre and a C–H reductive elimination completes the cycle. Unlike the modified Chalk-Harrod mechanism in Scheme 1.7, the catalytic cycle proposed by Seitz and Wrighton (Scheme 1.8) does not involve the formation of a metal ethene silyl hydride and silyl migration occurs before oxidative addition of the silane to the metal. Studies by Wrighton on the iron complex, ($\eta^5$-C$_5$Me$_5$)(CO)$_2$Fe(SiR$_3$)$_2$ 15, have also provided similar evidence supporting the mechanism in Scheme 1.8.

Scheme 1.8 The Seitz-Wrighton Mechanism for Hydrosilation.
1.2.4 The Two Silicon Cycle for Hydrosilation

Perutz and co-workers have shown that on photolysing the rhodium(I) complex, \( \text{CpRh}(C_2H_4)_2 \) \( 16 \), in the presence of various silanes, the rhodium(III) complex \( \text{CpRh}(C_2H_4)(\text{SiR}_3)\text{H} \) is formed, as are various hydrosilation and silation products.\(^{36} \) \( \text{CpRh}(C_2H_4)(\text{SiR}_3)\text{H} \) was found to catalyse the hydrosilation reaction and contains all the ligands for the key intermediate found in the Chalk-Harrod mechanism (Scheme 1.1 and 1.3).\(^{16} \) Duckett and Perutz later demonstrated, through deuterium labelling, cross-alkene and cross-silane experiments, that silyl migrations were operative in their system and concluded that \( \text{CpRh}(C_2H_4)(\text{SiR}_3)\text{H} \) is actually a catalyst precursor and lies outside the catalytic cycle.\(^{37} \) They proposed that the active catalytic species in their system is in fact \( \text{CpRh}(C_2H_5)\text{SiR}_3 \), where the ethyl group is only a spectator in the hydrosilation reaction. Like Seitz and Wrighton’s mechanism,\(^{33} \) the “Two Silicon Cycle”, proposed by Duckett and Perutz, has the key feature of alkene inserting into the metal silicon bond and an intermediate \( A \) containing two \( \text{SiR}_3 \) groups (Scheme 1.9). In fact, this cycle is equivalent to that of Seitz and Wrighton’s\(^{33} \) with \( \text{Co(CO)}_3 \) replaced by \( \text{CpRhEt} \). Although silation products were present in the hydrosilation system studied by Duckett and Perutz, no mechanistic pathway was proposed for their formation.

![Scheme 1.9 The “Two Silicon Cycle” for Hydrosilation.](image-url)
Duckett and Perutz found that the hydrosilation of C2D4 in the presence of CpRh-(C2H4)(SiEt3)H 17 failed to produce significant quantities of CpRh(C2D4)(SiEt3)H 18 and concluded that the ethene ligand in the rhodium(III) complex is not directly involved in the hydrosilation reaction. The silyl group in CpRh(C2H4)(SiR3)H, however, does play a part in the hydrosilation reaction since hydrosilation of ethene with HSiR3 resulted in the formation of CpRh(C2H4)(SiR3)H. However, reductive elimination of SiR3H and oxidative addition of SiR3H to rhodium is another possible pathway for silane exchange (Equation 1.4).38 Duckett and Perutz demonstrated that hydrosilation of ethene and HSi[CH2CH(CH3)H with CpRh(C2H4)(SiMe3)H 19 produced 30% CpRh-(C2H4){Si[CH2CH(CH3)H}H 20 after 7 days whereas a mixture of HSi[CH2CH(CH3)H3 and 19 produced only 10% 20 after 9 days.

\[ \text{CpRh(C2H4)(SiR3)H} + \text{HSiR3} \xleftrightarrow{\text{CpRh(C2H4)(SiR3)H} + \text{HSiR3}} \quad (1.4) \]

The formation of the CpRh(C2H4) 21 fragment in the catalytic cycle was ruled out by Duckett and Perutz because of the high Rh(I)/Rh(III) product ratio (1.0:0.6), generated during the hydrosilation of ethene and HSiPr3 with CpRh(C2H4)(SiEt3)H 17. Laser flash photolysis studies have demonstrated that HSiEt3 reacts much faster with 21 than ethene which is contrary to the observations made by Duckett and Perutz if 21 is involved in the hydrosilation reaction.39

According to Duckett and Perutz, the formation of the rhodium(V) intermediate, CpRh(SiR3)2(H)2, in their mechanism (Scheme 1.9) was plausible because this oxidation state is accessible and has been known to catalyse the hydrosilation reaction, e.g. Cp∗Rh(SiEt3)2(H)2 22.40

1.2.5 Direct Evidence for Silyl Migration in the hydrosilation reaction

Brookhart et al.'s studies on alkene polymerisation and oligomerisation41 catalysed by the electrophilic Co(III) complex, \([\text{Cp}^*\{\text{P(OMe)}_3\}\text{CoCH}_2\text{CH}_2-\mu-\text{H}\}^+ [\text{BAr}_4]^{-} 23\), led them to investigate the hydrosilation of alkenes.42
Brookhart found the hydrosilation of 1-hexene with HSiEt₃ catalysed by 23 yielded exclusively Et₃Si(CH₂)₅CH₃ in 75% yield. Low temperature ¹H NMR spectroscopy of the working catalyst solution revealed the formation of ethane in the early stages of the hydrosilation reaction between 1-hexene and HSiEt₃. Also, an intermediate formed in situ, at low temperature, during hydrosilation was identified by Brookhart as [Cp⁺{P(OMe)₃}Co{CH[(CH₂)₃CH₃]CH₂-µ-H(SiEt₃)}]⁺ 24.

![Scheme 1.10 Inversion at Co in 24.](image)

The identity of the intermediate 24 has provided direct evidence for silyl migration during the cobalt-catalysed hydrosilation reaction. Brookhart has also shown by dynamic ¹H NMR spectroscopy that 24 undergoes inversion at the cobalt centre (Scheme 1.10). ⁴²

From further low temperature ¹H NMR studies, Brookhart found that the intermediate 24 undergoes a number of β-elimination/migratory insertion steps to form a series of alkyl substituted agostic species. One of these species, 25, was determined to be part of the catalytic cycle from deuterium labelling experiments (Scheme 1.11). The overall pathway proposed by Brookhart can be seen in Scheme 1.12.

The mechanisms proposed by Brookhart et al., ⁴² Duckett and Perutz, ³⁸ and Seitz and Wrighton ⁴³ are all very similar in that all three mechanisms have silyl migration, or alkene insertion, as the key step in the formation of the Si–C bond. Also, these
mechanisms do not have a metal alkene silyl hydride intermediate as part of the catalytic cycle which is found in Chalk and Harrod's mechanism and its variant.\textsuperscript{16,30}

Scheme 1.11 Conversion of 24 to 25 during the hydrosilation of 1-hexene with HSiEt\textsubscript{3}.\textsuperscript{42}

Scheme 1.12 Overall pathway for the hydrosilation of 1-hexene using 23.\textsuperscript{42}
1.2.6 Ruthenium catalysed hydrosilation, formation of Si–C bond via both reductive elimination and silyl migration.

Ozawa and co-workers \(^\text{43}\) have recently proposed that Si–C bond formation during hydrosilation can occur via both reductive elimination and silyl migration in the same system. This incorporates all the key steps found in the Chalk-Harrod and variants of the Chalk-Harrod mechanism, ie. Si–C reductive elimination and alkene insertion, or silyl migration.\(^{16,30,33,35,37,42}\) Ozawa and co-workers found that the ruthenium hydride complex, RuHCl(CO)(PPh\(_3\))\(_3\) 26, was able to catalyse the hydrosilation of 1-(trimethylsilyl)-1-butene-3-yne 27 with various silanes.

Complex 26 itself was inactive towards silanes but readily reacts with 1-(trimethylsilyl)-1-butene-3-yne 27 to form the ruthenium dienyl complex, Ru(CH=CH-CH=CHSiMe\(_3\))Cl(CO)(PPh\(_3\))\(_2\) 28 via pathway A1 (Scheme 1.13).\(^\text{43}\) Reaction of 28 with excess silanes, HSiR\(_3\) (SiR\(_3\) = SiMePh\(_2\), SiMe\(_2\)Ph and SiEt\(_3\)), yielded hydrosilation products SiR\(_3\)CH=CH=CHSiMe\(_3\) 29 and SiR\(_3\)CH\(_2\)CH=CH=CH\(_2\)SiMe\(_3\) 30, as well as forming the ruthenium silyl complex 31 and regenerating the hydride 26 (Scheme 1.13).

\[ \text{Scheme 1.13 Reaction of 26 with 29 (pathway A1). Reaction of 28 with HSiR}_3 \text{ (pathway A2 and B).} \]
From the product ratios observed for the reaction shown in Scheme 1.13, Ozawa concluded that two reaction pathways are present, A2 and B. According to Ozawa, pathway A2 yields 26 and 29 via C-Si and Ru-H bond formation, i.e., the Chalk-Harrod Mechanism.16 In the second pathway, B, C-H and Ru-Si bond formation occurs, leading to the ruthenium silyl complex 31 and 1-(trimethylsilyl)-1,3-butadiene, which is then apparently hydrosilated to form 30 (Scheme 1.13). More details of this pathway are described below.

Ozawa showed that the reaction of the ruthenium silyl complex 31 with 27 formed the insertion product 32 via pathway C1 (Scheme 1.14). Complex 32 can react with various silanes via pathway C2 to give two types of hydrosilation product, 33 and 34, but the presence of PPh3 inhibits this reaction and leads to the formation of the ruthenium hydride 26 and the silation product SiR₃C=CH=CHSiMe₃ 35 via pathway D (Scheme 1.14). According to Ozawa, hydrosilation product 34 derives from the allenylmethylruthenium species 36 which is formed from a 1,3-hydride shift of the dienyl ligand in 32 (Scheme 1.14, pathway C2).

Scheme 1.14 Reaction of the ruthenium silyl complex 31 with 27 in the presence of PPh3 (pathways C1 and D) and in the absence of PPh3 (pathways C1 and C2).43

In summary, Ozawa’s mechanism for hydrosilation of 1-(trimethylsilyl)-1-butene-3-yne 27 with HSiR3 by the ruthenium hydride 26 contains two major pathways, A (A1 and A2 in Scheme 1.13) and C (C1 and C2 in Scheme 1.14). Pathway A can be seen as the traditional Chalk-Harrod mechanism,16 whereas pathway C represents the silyl
migration mechanism.\textsuperscript{30,33,35,37,42} Pathways A and C are connected by processes B and D. The overall mechanism for the hydrosilation reaction proposed by Ozawa using the ruthenium hydride 26 is summarised in Scheme 1.15.

\textbf{Scheme 1.15} Mechanism for hydrosilation by ruthenium-based catalyst RuHCl(CO)-(PPh$_3$)$_3$ 26.\textsuperscript{43}

1.2.7 Hydrosilation reactions involving colloidal platinum

Lewis and co-workers were the first to demonstrate, with light scattering, TEM and ESCA, that platinum colloid formation occurs in Speier’s catalyst, H$_2$PtCl$_6$, and other highly active platinum hydrosilation catalysts, e.g. Pt(COD)Cl$_2$ 37, Pt(COD)$_2$ 38 and Karstedt’s catalyst 1.\textsuperscript{13}

Crabtree\textsuperscript{44} and Whitesides\textsuperscript{45} have shown that elemental mercury can selectively poison heterogeneous based catalysts, whilst homogeneous based catalysts are unaffected. Crabtree has also used dibenzo[a,e]cyclooctetraene (DBCOT) as a selective poison for homogeneous transition metal catalysts.\textsuperscript{44} Lewis and co-workers showed that Speier’s catalyst, 37 and 38, were poisoned upon addition of elemental mercury.\textsuperscript{13} This demonstrates that H$_2$PtCl$_6$, 37 and 38, require the formation of colloidal platinum as a key step in the hydrosilation reaction.

The mechanism which Lewis proposed for the formation of colloidal platinum requires the compound to form a platinum(0) species which is free of ligands (Scheme 1.13). According to Lewis, Speier’s catalyst and 37 were reduced to platinum(0) by the silanes present in the hydrosilation reaction. This was offered as an explanation of the
initial induction period often observed for these catalysts during the hydrosilation reaction.\(^3\)

\[
\begin{align*}
\text{Induction Period} & \quad \{ \\
\text{Pt}(2a)X_{2a}L_b & \quad \text{slow} \\
\text{H}_2L + 2aXSiR_3 + [\text{Pt}(0)]_n & \quad \text{slow} \\
R' + R_3SiH & \quad \text{slow}
\end{align*}
\]

\(a = 0, 1; \quad b = 0 - 4\)

\(X = \text{halogen, pseudohalogen}\)

\(L = \text{"reducible" ligand (alkene)}\)

Scheme 1.16 Proposed mechanism for platinum colloid formation during hydrosilation.\(^{13}\)

It has been observed that both Speier’s and Karstedt’s catalysts require the presence of oxygen to drive the hydrosilation reaction to completion.\(^{46,47}\) Lewis suggested that oxygen acts as a weakly co-ordinating ligand to the platinum colloids formed during hydrosilation, preventing irreversible aggregation to larger colloids, since larger particle colloids would have reduced activity.\(^{48}\) Lewis has observed that if the oxygen is depleted in a typical hydrosilation reaction, the reaction stops and large platinum colloids are formed.\(^{49}\)

Broadman showed that photolysis of the platinum(IV) complex, \(\text{CpPtMe}_3\) \(39\), formed an active species which catalysed the hydrosilation of 1-octene with \(\text{HMe}_2\text{SiOSiMe}_3\) (Equation 1.5).\(^{50}\)

\[
\text{Me}_3\text{SiOSiMe}_2\text{H} + \text{H}_2\text{C}=\text{CHC}_8\text{H}_{13} \xrightarrow{\text{hv, CpPtMe}_3} \text{Me}_3\text{SiOSiMe}_2(\text{C}_8\text{H}_{17}) \quad (1.5)
\]

Broadman demonstrated that the active species formed in the reaction were colloidal in nature and elemental mercury deactivated the catalysts, whilst dibenzo[a,e]cyclooctetraene (DBCOT) had no effect.\(^{50}\) Analysis by TEM provided evidence that platinum colloids are formed upon photolysis of \(39\). Irradiation of \(39\) with only the silane, \(\text{HMe}_2\text{SiOSiMe}_3\), yielded a bis(silyl) hydride species, \(\text{CpPt(SiMe}_2\text{OSiMe}_3)_2\text{H} 40\) (Scheme 1.17). Broadman compared the activities of \(39\) and
and found that 39 was the more active catalyst under photolysis conditions. However, in the absence of light 40 initiated the hydrosilation reaction of 1-octene and \( \text{HMe}_2\text{SiOSiMe}_3 \) whereas for 39 no reaction was observed. Broadman concluded that the platinum silyl hydride species, 40, was not an intermediate in the conversion of 39 to the active species under photolysis conditions. Scheme 1.15 outlines the mechanism proposed by Broadman for colloidal platinum formation upon irradiation of 39 in the hydrosilation reaction.

Scheme 1.17 Photolysis of \( \text{CpPtMe}_3 \) 39 with \( \text{HSiMe}_2\text{OSiMe}_3 \).\textsuperscript{50}

Scheme 1.18 Proposed mechanism for colloidal platinum formation of photolysis of 39 in the presence of \( \text{HSiR}_3 \).\textsuperscript{50}
1.2.8 Theoretical investigation of the hydrosilation reaction

Harrod and co-workers\textsuperscript{51,52} have shown in the past that organotitanium compounds can act as catalysts for the hydrosilation reaction and the polymerisation of primary organosilanes \textit{via} dehydrogenative coupling of organosilanes. Recent \textit{ab initio} calculations of the hydrosilation reaction by Bode \textit{et al.} have shown that titanium(II) is an effective catalyst for this process.\textsuperscript{53} Using TiH\textsubscript{2} as the simplest model catalyst for the hydrosilation of C\textsubscript{2}H\textsubscript{4} and SiH\textsubscript{4}, Bode \textit{et al.} calculated that the catalysed reaction proceeds \textit{via} a reaction pathway that is barrierless, whilst the uncatalysed reaction has an activation barrier of 326 kJ mol\textsuperscript{-1}.\textsuperscript{53}

In their calculations, Bode \textit{et al.} showed that ethene adds to TiH\textsubscript{2} to form a three-membered metallacycle (Scheme 1.19). This process was shown to be exothermic by 259 kJ mol\textsuperscript{-1}, and is followed by silane addition to form 41 which is also exothermic by 27 kJ mol\textsuperscript{-1}. Overall the formation of species 41 is exothermic by 286 kJ mol\textsuperscript{-1} (Scheme 1.19). Alternatively, silane addition to TiH\textsubscript{2} followed by ethene addition can occur which also results in the formation of 41. The very large drop in energy due to the initial formation of 41 was said to be the driving force of the whole reaction (Scheme 1.19).\textsuperscript{53}

Scheme 1.19 Formation of 41 from TiH\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} and SiH\textsubscript{4} as the driving force for the hydrosilation reaction (bond lengths in Å).\textsuperscript{53}

Scheme 1.20 shows Bode \textit{et al.}'s calculated minimum energy pathway for ethylsilane formation from 41.\textsuperscript{53} Silyl ligand migration to the α carbon (41 to 46), is followed by hydrogen transfer from Ti to the β carbon (46 to 47), and removal of the TiH\textsubscript{2} catalyst. They calculated the overall process (Schemes 1.19 and 1.20) to be exothermic by 117 kJ mol\textsuperscript{-1}.

Bode \textit{et al.} noted, however, that although the calculations for the simple TiH\textsubscript{2} model catalyst system might be very accurate, they do not take into account electronic or steric factors if the substituents on the Ti catalyst were anything but hydrogen, \textit{e.g.} TiCl\textsubscript{2} or TiCp\textsubscript{2}.\textsuperscript{53}
2.715

**INTRODUCTION**

- **kJ mol⁻¹**
- Silyl migration
- Silyl rotation
- **kJ mol⁻¹**
- Ti-Si bond
- **kJ mol⁻¹**
- Hydride transfer
- **kJ mol⁻¹**
- C-H elimination

**Scheme 1.20** Formation of ethylsilane from C₂H₄ and SiH₄ using TiH₂ as catalyst. Structures shown are calculated for the minimum energy pathway (TS = transition state).

**1.3 Silane Activation**

The activation of silanes by transition metal centres to form metal silyl species has been widely studied since they have been shown to be key intermediates in hydrosilation. One of the most convenient routes to transition metal silyl complexes is via the oxidative addition of a Si–H bond to a co-ordinatively unsaturated metal centre. Examples of the oxidative addition of a Si–H bond are known for nearly all of the transition metals.

Addition of Si–X (X = Cl, C, Si) bonds to transition metals occurs less readily and is less common. Oxidative addition of Si–X bonds is normally found with the later transition metals, e.g. Rh, Pd and Pt.
1.3.1 Comparison between C–H and Si–H activation

The interaction of silanes with transition metal centres is often a facile process when compared to C–H activation. *Ab initio* calculations by Sakaki\(^57\) have shown that Si–H oxidative addition of SiH\(_4\) to Pt(PH\(_3\))\(_2\) proceeds more easily when compared to C–H oxidative addition of CH\(_4\) to Pt(PH\(_3\))\(_2\). Sakaki showed that the calculated activation barrier for SiH\(_4\) addition to Pt(PH\(_3\))\(_2\) is much smaller and the process is exothermic (\(\Delta H^\ddagger = 2.9 \text{ kJ mol}^{-1}\); \(\Delta H^\circ = -110.5 \text{ kJ mol}^{-1}\)) whilst for CH\(_4\) the barrier is large and the process is endothermic (\(\Delta H^\ddagger = 120 \text{ kJ mol}^{-1}\); \(\Delta H^\circ = 27.2 \text{ kJ mol}^{-1}\)). Sakaki concluded that the driving force for Si–H activation arises from the formation of a Pt–SiH\(_3\) bond which is stronger [\(D(\text{Pt–SiH}_3)_{\text{calc.}} = 257.3 \text{ kJ mol}^{-1}\)], compared with a Pt–CH\(_3\) bond [\(D(\text{Pt–CH}_3)_{\text{calc.}} = 166.1 \text{ kJ mol}^{-1}\)].\(^57\)

Puddephatt provided the first experimental estimation of a Pt–Si bond energy using differential scanning calorimetry (DSC).\(^58\) The estimated Pt–Si bond energy, \(D(\text{Pt–SiMe}_3)\), of PtIMe\(_2\)(SiMe\(_3\))(bpy) (bpy = 2,2'-bipyridine) 48 was found to be 233 ± 14 kJ mol\(^{-1}\). Values of 137 and 129 kJ mol\(^{-1}\) have been found for Pt–Me bonds in cis-PtMe\(_4\)(MeCN)\(_2\) 49 and cis-PtMe\(_4\)(2,6-Me\(_2\)C\(_6\)H\(_3\)N)\(_2\) 50, also by Puddephatt using DSC.\(^59\)

Experimental evidence from Puddephatt\(^58,59\) and *ab initio* calculations by Sakaki\(^57\) both showed that a Pt–Si bond is approximately 100 kJ mol\(^{-1}\) stronger than a Pt–C bond. Furthermore, the Si–H bond of SiH\(_4\) \([D(\text{Si–H}) = 378 \text{ kJ mol}^{-1}]\)\(^60\) is weaker than the C–H bond of CH\(_4\) \([D(\text{C–H}) = 438 \text{ kJ mol}^{-1}]\).\(^61\) However, it must be noted that Si–H bond strengths of HSiR\(_3\) will vary depending on the substituent R.\(^62\)

1.3.2 Bonding in metal silyl hydride and \(\eta^2\)-silane complexes

In general, oxidative addition of an Si–H bond to a transition metal centre can result in either full cleavage of the Si–H bond to give a product with a classical 2-centre 2-electron interaction, or an \(\eta^2\)-Si–H σ complex with a non-classical 3-centre 2-electron interaction. In the non-classical 3-centre 2-electron situation, two types of bonding interaction can take place. Firstly, the Si–H σ bonding orbital can interact with the metal \(d\)-orbital and secondly the metal \(d\) σ orbital can interact with the Si–H \(\sigma^*\)-antibonding orbital (Scheme 1.21). Sufficient π backbonding from the metal centre would result in the full oxidative addition of the Si–H bond. Therefore the extent of σ-donor and σ*-acceptor ability of the Si–H bond can be tuned by varying the substituents on the silicon atom.
Scheme 1.21 Non classical 3-centre 2-electron bonding interaction between Si–H and the metal, M. (a) σ-bonding interaction. (b) metal π-backbonding interaction.

An $\eta^2$-Si–H σ bonded complex can be considered as an arrested state in the course of the oxidative addition pathway and is, in some ways, analogous to the bonding found in π-complexes. Since the substituents at either the silicon or the metal centre will have a dramatic impact on the oxidative addition pathway of the Si–H bond to the metal, the stage at which the oxidative addition process is stopped can be tuned by altering the substituents on the silicon or the metal. Structural evidence of the first σ-bonded Si–H complex was first obtained by Graham for Cp(OC)$_2$Mn(HSiPh$_3$)$_5$ by X-ray diffraction.\textsuperscript{61} A more accurate analysis by Schubert was later performed using neutron diffraction techniques on (115-C$_5$H$_4$Me)(OC)$_2$Mn(HSiFPh$_2$)$_5$ in which a Si–H bond distance of 1.8 Å was observed.\textsuperscript{64,65} This is about 0.3 Å longer than the covalent Si–H bond lengths found in normal tetrahedral silanes (1.5 Å).\textsuperscript{66}

NMR spectroscopy is by far the most convenient tool in determining if a 3-centre 2-electron interaction is present in a M–H–Si system. The magnitude of the coupling constant $J$(SiMH) is a reliable indicator of the strength of any Si–H interaction. In the upper limit, where the silicon is directly bonded to the hydride, $J$(SiH) is of the magnitude of about 200 Hz.\textsuperscript{66} In the lower limit, where there is no bonding interaction between the silicon atom and the hydride, $^2J$(SiH) can be found in the range of 3.5-20 Hz.\textsuperscript{67,68,69}

In Schubert’s review of $\eta^2$-Si–H σ complexes,\textsuperscript{66} the M–H–Si 3-centre 2-electron bonding interactions in the complexes of the type ($\eta^5$-C$_5$H$_4$Me)(CO)$_2$Mn(H)(SiR$_3$)$_5$ were discussed in detail.\textsuperscript{65} Firstly, Schubert examined the effect of changing the substituent on the silicon atom. This had the effect of reducing the $J$(SiMnH) value as more electronegative groups are present next to the silicon atom. For example, ($\eta^5$-C$_5$H$_4$Me)(CO)$_2$Mn(H)HPh$_2$)$_5$ has a $J$(SiMnH) value of 65.4 Hz, whereas ($\eta^5$-C$_5$H$_4$Me)(CO)$_2$Mn(H)Cl$_3$)$_5$ has a $J$(SiMnH) value of 54.8 Hz. This could be explained by the fact that the more electronegative chlorine atoms are promoting π-metal backbonding to the Si–H σ*-antibonding orbital and thereby decreasing the Si–H bond character. Schubert also demonstrated that altering the substituents on the metal itself can have a dramatic effect on the Si–H bond interaction. On substituting one of...
the CO ligands for the more electron donating PMe₃ ligand, the complex (η⁵-C₅H₄Me)\((\text{CO})\text{(PMe₃)}\text{Mn(H)(SiCl₃)}\) 55 has an even lower value of J(SiMnH) (20.0 Hz). Here the Si–H bond character is said to be negligible because the σ-donating PMe₃ ligand is enriching the metal centre with electron density, thus enhancing the metal π-backbonding to the Si–H σ*-antibonding orbital. Data from molecular orbital calculations and from PE (Photo-Electron) spectra support this idea.⁶⁶

Kubas and co-workers have shown that η²-Si–H σ-interactions can also be found in the molybdenum complexes of Mo(CO)(PP)₂(η²-HSiR₃) (PP = depe, dppe), e.g. Mo(CO)(depe)₂(η²-HSiHPh₂) 56, which are analogous to the η²-H₂ molybdenum complexes, e.g. Mo(CO)(dppe)₂(H₂) 57 (Figure 1.1). Interestingly, the molybdenum silane complex 56 has the Si–H moiety cis to the carbonyl, whereas the dihydrogen complex has the H₂ ligand trans to the carbonyl (Figure 1.1).

![Diagrams of complexes 56 and 57](image)

Figure 1.1 cis vs. trans co-ordination of H–X (X = SiR₃, H) in the silane complex 56 and the dihydrogen complex 57.⁷⁰

Ab initio calculations by Lin and co-workers on the model complex Mo(CO)(PH₃)₃(η²-HSiH₃) 58 have shown that the cis isomer of 58 is 41.4 kJ mol⁻¹ lower in energy than the trans isomer of 58. Lin and co-workers pointed out that in dihydrogen, the H–H σ*-antibonding orbital lies quite high in energy, whereas in silanes the H–Si σ*-antibonding orbital lies lower in energy. This would mean that in the dihydrogen complexes, the dihydrogen ligand is less susceptible to metal to H–H σ*-backbonding, whereas for η²-silane complexes metal to σ*-backbonding is more pronounced. Lin then argued that if η²-silane molybdenum complexes, e.g. 56, have the silane ligand trans to the carbonyl ligand, both the silane and the carbonyl ligand would be sharing the same d-orbital, and there will be competition between the two ligands for the metal d-electrons. Hence, the presence of the H–Si moiety would destabilise the trans configuration due to the better σ*-accepting ability of Si–H function. The dihydrogen complex 57 on the other hand has a H–H distance of approximately 0.8 Å which is only slightly larger than that of molecular dihydrogen.⁷¹ This further reinforces Lin’s argument that there is little π backbonding from the metal to the H–H σ*-antibonding orbital, and the reason why dihydrogen is found trans to the carbonyl
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Interestingly, for classical molybdenum dihydride complexes, e.g. Mo(H)₂(depe)₂(CO) 59 a 7-co-ordinate pentagonal bipyramidal complex, the hydride ligands are cis to the carbonyl ligand. ⁷²

Kubas and co-workers have recently demonstrated the versatility of dihydrogen as a ligand. ⁷³ In their work, the highly electrophilic cationic manganese complex, [Mn(CO)₃(PCy₃)₂][B{C₆H₃(3,5-CF₃)₂}₄] 60, was found only to bind with H₂ and very weakly with SO₂ (Scheme 1.22). Ligands like N₂, ethene and silanes which are normally reliant on a large amount of metal π-backbonding, e.g. M→σ* and M→π*, did not bind to 60 in solution. This demonstrates again that dihydrogen complexes favour H–H-to-metal σ-bonding interaction over metal-to-H–H σ*-antibonding interaction.

![Scheme 1.22](image)

Scheme 1.22 Reversible binding of dihydrogen to 60. ⁷³

Sabo-Etienne and co-workers isolated the first mono-nuclear transition metal complex containing two co-ordinated η²-Si–H σ-bonds. ⁷⁴ They showed that the reaction of the ruthenium bis(dihydrogen) complex, RuH₂(H₂)₂(PCy₃)₂ 62, with the disilanes (HSiMe₂)₂X [X = C₆H₄, O] yielded the complex RuH₂[(η²-HSiMe₂)₂X](PCy₃)₂ [X = C₆H₄ (63), O (64)] as determined from their crystal structures (Scheme 1.23). ⁷⁴

![Scheme 1.23](image)

Scheme 1.23 Synthesis of RuH₂[(η²-HSiMe₂)₂X](PCy₃)₂ [X = C₆H₄ (61), O (62)]. ⁷⁴

Sabo-Etienne and co-workers said that the chelating effect of the disilane (HSiMe₂)₂X was responsible for the stabilisation of 63 and 64. It was also observed that the flexible disiloxane ligand in 64 is more susceptible to substitution reactions than 63 which contains the more rigid disilane ligand (HSiMe₂)₂C₆H₄. For example, bubbling...
H₂ and CO through a solution of 64 yielded 62 and RuH₂(CO)₂(PC₃)₂ 65 respectively, whereas for 63 no such ligand substitution reaction was observed.

The ruthenium bis(dihydrogen) complex 62 has been found to be an effective silation catalyst of ethene. Sabo-Etienne and co-workers reported that 62 can selectively catalyse the reaction between HSiEt₃ and ethene to give the vinylsilane CH₂=CHSiEt₃ in 97% yield. The catalytic resting state for this reaction is said to be RuH[(η³-C₆H₈)P(C₆H₁₁)₂](C₂H₄)(PC₃) 66 formed on reacting 62 with ethene. Complex 62 then reacts with HSiEt₃ to form the formally Ru(IV) complex Ru(H)₂(SiEt₃)[((η³-C₆H₈)P(C₆H₁₁)₂](C₂H₄)(PC₃)] 67 (Scheme 1.24). Sabo-Etienne and co-workers observed 66 during all of their catalytic studies and this species was the only detected complex after total conversion of HSiEt₃. Complex 67 was also reported to be an effective catalyst precursor.

Scheme 1.24 Formation of the catalytic resting state 65 during the silation of ethene.

Sabo-Etienne and co-workers have recently studied the interaction of the ruthenium bis(dihydrogen) complex 62 with the allylsilane CH₂=CHCH₂SiMe₂H, in an attempt to evaluate the competition between the co-ordination of the alkene function and the Si−H function. In their work, reaction of 62 with CH₂=CHCH₂SiMe₂H yielded the ruthenium(II) dihydride complex, Ru(H)₂[η⁴-HSiMe₂(CH=CHMe)](PC₃)₂ 68 (Scheme 1.25), where the vinylsilane ligand co-ordinates to ruthenium via an η²-Si−H σ-bond and an η²-C=C π-bond as characterised from its crystal structure. The η⁴-co-ordinated vinylsilane ligand in 67 is only weakly bound and can be easily displaced with H₂, CO or C₂H₄ to form 62, 65 and 66, respectively. This is also reflected in the large J(SiRuH) coupling constant of 105 Hz, indicating that the Si−H bond is only weakly activated and suggests a reduced metal to Si−H σ*-backbonding interaction.

Scheme 1.25 Synthesis of Ru(H)₂[η⁴-HSiMe₂(CH=CHMe)](PC₃)₂ 68.
Sabo-Etienne and co-workers have shown that 62 catalyses the reaction between ethene and the allylsilane HSiMe₂CH₂CH=CH₂ to give initially a variety of hydrosilation and silation products (Table 1.1). They have also observed that redistribution around the silicon atom occurs once all the allylsilane has been consumed in the reaction, resulting mainly in the conversion of (CH₂=CHCH₂)Me₂Si(CH=CH₂)₂ to Me₂Si(CH=CH₂). Complex 68 was found to possess similar catalytic activities to 62, whereas the ethene silation catalyst, RuH[(η⁵-C₅H₅)P(C₆H₁₁)](C₂H₄)(PCY₃) 66,³¹ had reduced catalytic activities in this reaction and redistribution at the silicon atom was not as significant.

![Product / %](image)

**Table 1.1** Reaction of ethene with HSiMe₂CH₂CH=CH₂ catalysed by 62, 66 or 68. a Time after which HSiMe₂CH₂CH=CH₂ is totally consumed. b No more reaction after 70 min.⁷⁵

The Si–H bond can sometimes interact with the metal centre intramolecularly even though the silicon atom is not directly attached to the metal centre. Baumannn and Rosenthal have recently shown that the reduction of the titanocene dichloride, [Cp₂TiCl₂], with magnesium in the presence of the alkynylsilane, MeC≡CSiMe₂H, yielded the titanocene complex Cp₂Ti(MeC≡CSiMe₂H) 69, which contains a β agostic Si–H interaction (Scheme 1.26).⁷⁶ However, it was found that if the cyclopentadienyl ligands on the titanium were replaced by pentamethylcyclopentadienyl ligands to form Cp*₂Ti(MeC≡CSiMe₂H) 70 then no β agostic Si–H interaction was observed (Scheme 1.27).
1.3.3 Fluxional behaviour of silyl hydride complexes

Transition metal silyl hydride complexes are often found to exhibit fluxional behaviour at room temperature. For example, Kubas and co-workers demonstrated that the reaction of SiH₄ with the formally 16-electron molybdenum complex, Mo(CO)(dppe)₂, yielded the six-co-ordinate cis-Mo(η²-HSiH₃)(CO)(dppe) octahedral complex. However, on changing the phosphine ligand from dppe to depe, Kubas found that reacting cis-Mo(CO)(depe) with SiH₄ yielded the tautomers cis-Mo(η²-H-SiH₃)(CO)(depe) and MoH(SiH₃)(CO)(depe) which are in equilibrium with one another at room temperature (Scheme 1.28). This is presumably because the more σ-donating phosphine in populates the σ*-antibonding orbital of the silane to favour the oxidative addition product, whereas in only π-acceptor ligands are bound to molybdenum, favouring only the η²-Si-H σ-complex.

Scheme 1.26 Synthesis of 69.

Scheme 1.27 Synthesis of 70.

Scheme 1.28 Reaction of Mo(CO)(depe) with SiH₄ to form the tautomers 74a and 74b.
Kubas found that the ratio between $74a$ and $74b$ is temperature dependent and the thermodynamic parameters for conversion of $74a$ to $74b$ were $\Delta H^\circ = -2.55 \pm 0.8$ kJ mol$^{-1}$ and $\Delta S^\circ = -8.8 \pm 3.0$ J mol$^{-1}$ K$^{-1}$.

Pidcock and co-workers have shown the platinum complex, cis-Pt(PPh$_3$)$_2$(H)-(SiPh$_3$) $75$, exhibits mutual phosphine exchange. It can also alternatively be viewed as the interchange of position between the silyl and hydride ligand (Scheme 1.29).

Pidcock and co-workers deduced from the variable temperature hydride NMR spectra of $75$ that the exchange of phosphines occurs without dissociation of silane. Clark and Hampden-Smith later showed that the more sterically demanding analogue, cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) $76$, displays the same type of mutual phosphine exchange, plus, reductive elimination and re-addition of the silane (Scheme 1.30). The dynamic processes present in $76$ and other silyl hydride derivatives will be discussed in more detail in Chapter 5.

![Scheme 1.29 Mutual phosphine exchange in cis-Pt(PPh$_3$)$_2$(H)(SiPh$_3$) $75$.](image)

![Scheme 1.30 Reversible oxidative addition/reductive elimination of silane in cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) $76$.](image)

### 1.4 PHOTOACTIVATED HYDROSILATION CATALYSTS

Hydrosilation catalysts are often inhibited commercially in order to exert control on catalyst activities. It has been shown that maleates and fumarates displace the labile bridging vinylsiloxane ligand in Karstedt’s catalyst 1 to form species which are inactive toward the hydrosilation reaction (Scheme 1.31). Reactivation of the latent catalyst is then achieved *in situ* by heating the hydrosilation reaction mixture. An alternative method for activation of latent hydrosilation catalysts would be by photochemical
means. This latter method has the advantage of being less energy intensive compared to the more conventional thermal activation methods. Several examples of photoactivated hydrosilation systems have already been encountered in this chapter. For instance, Wrighton and co-workers have shown both Fe(CO)$_5$ and Co(CO)$_4$(SiEt$_3$) eject CO upon photolysis to form a 16-electron species which is highly active towards the hydrosilation reaction.$^{30,33}$ However, no photoactivated hydrosilation catalysts have yet been found which are suitable for commercial application.

Heaton identified the azo series as potential photo-sensitive inhibitor ligands, where azo-inhibited hydrosilation catalysts can be reactivated photochemically.$^{84}$ In Heaton's work, Karstedt's catalyst was reacted with various azo ligands to test for catalyst inhibition. Heaton found that only the azo ligands with adjacent carbonyl groups, i.e. RCON=NCOR, were effective as inhibitors and adequate inhibition of catalytic activities was achieved only when the concentration of the azo inhibitors was in excess of the catalyst. Reactivation of the azo inhibited catalyst was reported to be attainable either thermally or photochemically. However, the co-ordination mode of the azo ligand to the platinum metal centre in Heaton's system was unclear.$^{84}$

Three possible co-ordination modes to the metal centre are open to the azo ligand, RCON=NCOR. The first possibility would involve the co-ordination of one of the lone pairs on the azo nitrogen to the metal centre to form a $\sigma$-complex [Figure 1.2 (a)], the second possibility would involve the formation of an $\eta^2$-azo complex [Figure 1.2 (b)],

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**Scheme 1.31** Inhibition and reactivation of a platinum hydrosilation catalyst.

1.4.1 Azo complexes

Azo, or diazene, ligands are known to degrade on photolysis or thermolysis, usually resulting in the elimination of a dinitrogen molecule and a radical pair (Equation 1.6).$^{83}$

$$R-N=NR \xrightarrow{\text{hv}} N_2 + 2 R'$$  \hspace{1cm} (1.6)
and the final possibility has the carbonyl group directly involved in the binding of the azo dicarbonyl ligand to the metal centre [Figure 1.2 (c)]. Numerous examples of compounds exhibiting the binding mode shown in Figure 1.2 (a) are discussed in detail in a review by Kisch and Holzmeier. There are relatively few well documented $\pi^2$-azo complexes of the type shown in Figure 1.2 (b); some examples include the azobenzene and diazofluorene complexes of nickel(0), e.g. Ni(PhNC)$_2$(PhN=NP) $\text{77}$. However, in the complexes found with co-ordination modes displayed in Figures 1.2 (a) and (b), the ligated azo ligand does not contain an adjacent carbonyl group. Indeed the co-ordination mode shown in Figure 1.2 (c) is generally observed for the azo ligand of the type ROCNNCOR, as first demonstrated by Ibers and Ittel in the complex Pt(PPh$_3$)$_2$(PhOCNNCOR) $\text{78}$.88

![Figure 1.2 Possible metal-azo co-ordination modes. (a) $\sigma$ azo complex, (b) $\pi^2$-azo complex, (c) metallacyclic azo complex if an adjacent CO is present.]

The co-ordination mode and photochemistry of several azo diacyl, ROCNNCOR, and azo dicarboxylate, RO$_2$CNNCOR, model platinum phosphine complexes, Pt(PR$_3$)$_2$(R'OCNNCOR') and Pt(PR$_3$)$_2$(R'O$_2$CNNCOR'R'), are investigated in detail in Chapter 2.

1.4.2 Oxalate complexes

It has been shown that irradiation of transition metal oxalate complexes leads to the fragmentation of the oxalate dianion to form two molecules of carbon dioxide. The process is thought to occur via a two-electron transfer to two metal centres. A well known example is Co(C$_2$O$_4$)$_3$$^-$ $\text{79}$, where photolysis leads to reduction of two metal centres and the formation of Co(II) (Equation 1.7 and 1.8).$^89$

\[ \text{Co(C}_2\text{O}_4)_3$$^-$ \xrightleftharpoons[\text{hv}]{\text{H}_2\text{O}} \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{C}_2\text{O}_4^{2-} + \text{"C}_2\text{O}_4"\text{.} \] (1.7)

\[ \text{"C}_2\text{O}_4"\text{.} + \text{Co(C}_2\text{O}_4)_3$$^-$ \rightarrow \text{Co}^{2+}(\text{aq}) + 3\text{C}_2\text{O}_4^{2-} + 2\text{CO}_2 \] (1.8)
Trogler and co-workers observed that photolysis of the platinum oxalate complex, \( \text{Pt(PEt}_{3}\text{h(C}_2\text{O}_4) \) 80, leads to the formation of a highly reactive 14-electron bis(phosphine)platinum fragment and two molecules of carbon dioxide (Equation 1.9).  

\[
\text{Pt(PEt}_{3}\text{h(C}_2\text{O}_4) \xrightarrow{\text{hv}} \text{[Pt(PEt}_{3}\text{2] + 2CO}_2 \) (1.9)
\]

Although the 14-electron species was not observed directly, its presence was inferred from reaction with ethene and diphenylacetylene to form \( \text{Pt(PEt}_{3}\text{h(C}_2\text{H}_4) \) 81 and \( \text{Pt(PEt}_{3}\text{h(PhC=CPh)} \) 82, respectively.

According to Trogler, on photolysis of 80, rapid transfer of two electrons from the oxalate ligand to one metal occurs. Trogler argued that a successive, or simultaneous, transfer of two electrons would yield the more stable Pt(0) oxidation state, whereas transfer of one electron to the metal centre would produce the relatively unstable PtCD oxidation state.

Later, Trogler demonstrated that the reactive 14-electron bis(phosphine)platinum fragment formed on photolysis of 80 and the silica supported analogue (Figure 1.3) proved to be effective as a hydrosilation catalyst.

![Figure 1.3 Silica supported Pt(PEt}_{3}\text{h(C}_2\text{O}_4) \) 80.](image)

As expected Trogler found marked differences between the unsupported and supported bis(phosphine)platinum oxalates as hydrosilation catalysts. Irradiation of unsupported 80 resulted in a long and variable induction period for the hydrosilation reaction of 1-heptene and HSiMeCl2, whereas for silica supported 80, the rate of reaction was more consistent. Furthermore, the presence of elemental mercury does not appear to poison the catalytic activity of the photoactivated supported 80 but the presence of oxygen or co-ordinating solvent does. Unfortunately, the effect of elemental mercury on unsupported 80 was not discussed. Trogler's explanation was that unsupported 80 can form cluster compounds upon irradiation in the presence of silane, and these clusters may be catalytically inactive towards the hydrosilation reaction. This is not dissimilar to the observation made by Lewis on platinum colloid formation during
the hydrosilation process for Speier’s and Karstedt’s catalyst (Section 1.2.6). Since the photo-generated active metal sites in supported 80 cannot interact with each other, Trogler argued that metal cluster formation was not possible and hydrosilation proceeds via monomeric active sites on the silica support.

Anderson and co-workers later studied the photochemical reactions of some platinum chelate phosphine oxalate complexes. MO model calculations have shown that a bent 14-electron ML₂ metal fragment is more reactive than a linear ML₂ fragment and is isolobal with CH₂. Indeed, Whitesides demonstrated that the bent Pt(dcpe) fragment [dcpe = 1,2-bis(dicyclohexylphosphino)ethane], formed by thermolysis of Pt(dcpe)(H)(CH₂CMe₃) 83, is reactive towards the oxidative addition of C–H bonds. In Anderson’s work photolysis of Pt(dppe)(C₂O₄) 84 with PhC≡CPh yielded a mixture of Pt(dppe)(PhC≡CPh) 85 and Pt(dppe)(Ph)(C≡CPh) 86, which is consistent with the formation of a 14-electron Pt(dppe) fragment and two equivalents of CO₂. However, photolysis of 84 in the absence of substrate in CH₃CN/C₆H₆ yielded two species, one of which was identified as Pt(dppe)(CO) 87; the other species remained unidentified. It was suggested by Anderson that two possible pathways were responsible for this observation, (i) photolysis of 84 initially generates the Pt(dppe) fragment and CO₂, the photogenerated CO₂ then reacts with the Pt(dppe) fragment to form 87 and CO, or (ii) photolysis of 84 gives 87 and CO.

1.5 OUTLINE OF THESIS

The first part of this thesis investigates various ways in which platinum-based hydrosilation catalysts can be activated on photolysis. The latter part of this thesis investigates the interaction of the platinum metal centre with various silanes in a sterically crowded environment.

In Chapter 2, the structure and reactivities of several platinum azodicarbonyl complexes, Pt(PR₃)₂(R'OCNNCOR') (R = Ph, Me; R' = Ph, Me, OEt and O'Pr) are investigated. Here, we examine the role that the carbonyl group has on the co-ordination mode of the azodicarbonyl ligand to the platinum centre. The photochemistry of these compounds is also discussed in this chapter.

In Chapter 3, photoactivation of azo-inhibited Karstedt’s catalyst 1 is examined. In this chapter, azo dicarboxylates of the form RO₂CNNCO₂R (R = Et, 'Pr and 'Bu) are used to inhibit the catalytic activities of 1. The effect of the R group on the azo-inhibited catalyst is investigated.

In Chapter 4, the synthesis and photochemistry of platinum complexes of malonate (O₂CCH₂CO₂) and phthalate (O₂CC₆H₄CO₂) are examined.
In Chapter 5, dynamic processes of \( \text{cis-Pt(PCY}_3\text{)}\text{2(H(SiR}_3\text{))} \) are studied. In this chapter, we examine the interaction between the Si–H bond of various silanes with the platinum centre by variable temperature NMR spectroscopy.

**1.6 REFERENCES**


CHAPTER 2

PLATINUM AZODICARBONYL COMPLEXES
2.1 INTRODUCTION

Heaton has shown that azo, or diazene, compounds with carbonyl groups adjacent to the azo function can inhibit the activities of Karstedt’s catalyst. As discussed in Chapter 1 (Section 1.4.1), Heaton demonstrated that after inhibition by azodicarbonyl ligands, Karstedt’s catalyst can be reactivated thermally or photochemically. However, the co-ordination mode of the azodicarbonyl compound to the platinum centre in Karstedt’s catalyst has not been clearly identified.

There are, in general, two ways in which an azo ligand can co-ordinate to transition metals. The usual mode requires the azo group to utilise its lone pair(s) on the nitrogen atom(s), often the HOMO, to form σ bond(s) with the metal. This method of co-ordination can generate both mononuclear and binuclear complexes (Figure 2.1).

![Figure 2.1](image.png)

Figure 2.1 (a) Mononuclear azo transition metal σ complex. (b) Binuclear azo transition metal σ complex.

The second mode of co-ordination involves the symmetrical binding of the azo moiety to the metal by the transfer of electron density from the N=N π-bonding molecular orbital to the metal and from the metal to the N=N π*-antibonding molecular orbital (Figure 2.2). Both of these bonding methods will be discussed in more detail in Section 2.3.2.

![Figure 2.2](image.png)

Figure 2.2 η²-azo transition metal complex.

Introduction of substituents other than simple alkyl or aryl groups into the azo compound can provide additional co-ordination sites for the metal. A carbonyl-substituted azo compound, for instance, can bind through oxygen as well as nitrogen. Ittel and Ibers have shown by X-ray crystallography that the azo ligand in the complex
Pt(PPh₃)₂(PhOCNNCOPh) 1 co-ordinates to the metal as a metallacycle, binding to the metal through one oxygen and one nitrogen atom to form a five-membered ring.⁷

Bond lengths from the crystal structure of 1 revealed that the N=N double bond had lengthened to that of a single bond and one of the C–N single bonds had shortened to that of a C=N double bond when compared to the free ligand. Thus, this form can be described as a Pt(II) complex with a substituted hydrazido ligand.⁷

![Diagram](image)

(1)

Stone and co-workers in the late 1960s postulated that Pt(PPh₃)₂-(EtO₂CNNCO₂Et) 2 adopts a symmetrical structure, where the azodicarboxylate ligand is co-ordinated to the metal in an η²-fashion (Figure 2.2).⁸ Cenini and co-workers later revealed that 2 in fact contains two inequivalent phosphorus nuclei,⁹ indicating that the azodicarboxylate ligand in 2 co-ordinates to platinum in the same way as the azodibenzoyl ligand found in 1.

It is also important to note that transition metal complexes of diazo RNNR(O), diazenido NNR(O) and hydrazido NRNR₂(1−) or NNR₂(2−), represent important stages of dinitrogen activation by transition metals.¹⁰,¹¹ This is of special relevance to nitrogen fixation in biological systems where molecular dinitrogen is converted to ammonia by the enzyme nitrogenase. The active site of nitrogenase, believed to be responsible for the co-ordination and activation of dinitrogen, was found to contain Fe and Mo atoms.¹² Extensive research in this area has produced a wide variety of dinitrogen complexes many of which can be protonated to form hydrazines and/or ammonia. For example, the complexes M(N₂)₂P₄ [M = Mo or W; P = mono(phosphine) or P₂ = bis(phosphine)] have been shown to react with halogen acid or HBF₄ to yield the diazenido or hydrazido metal complex with chelating phosphate attached to the metal, or ammonia with monophosphate attached to the metal.¹³,¹⁴ The ultimate aim of this area of research is to produce an efficient catalytic system which mimics the biological system.

In this chapter, the full characterisation of Pt(PMe₃)₂(PhOCNNCOPh) 3 and Pt(PMe₃)₂(MeOCNNCOMe) 4, the trimethylphosphine analogues of 1, is reported. New routes to the platinum azodicarboxylate complexes Pt(PPh₃)₂(EtO₂CNNCO₂Et) 2 and Pt(PPh₃)₂(Pt'O₂CNNCO₂Pr) 5 have also been developed. A crystal structure of 5 has been obtained, which provides unambiguous evidence on the binding mode of the
azodicarboxylate ligand to the platinum centre. These compounds were synthesised in order to test their photochemical properties.

2.2 RESULTS

2.2.1 Preparation of Pt(PR$_3^1$)$_2$(R$_2^1$OCNNCOR$_2^1$) complexes [R$_1^1$ = R$_2^2$ = Ph (1); R$_1^1$ = Me, R$_2^2$ = Ph (3); R$_1^1$ = R$_2^2$ = Me (4)]

The procedure reported by Dilworth and Kasenally$^{15}$ for the preparation of the complex Pt(PPh$_3^1$)$_2$(PhOCNNCOPh) 1 was used to synthesise the two analogues, Pt(PMe$_3^1$)$_2$(PhOCNNCOPh) 3 and Pt(PMe$_3^1$)$_2$(MeOCNNCOMe) 4. Reaction of the cis-platinum bisphosphine dichloride complex with the appropriate diacyl hydrazine in refluxing ethanol, in the presence of NaHCO$_3$, yielded air-stable crystals of the azo platinum complex after work up (60-70% yield, Equation 2.1).

Complex 1 was also synthesised by the same method as shown in Equation 2.1 in order to obtain comparative spectroscopic data. Complexes 1, 3 and 4 are all highly soluble in benzene, THF and chlorinated solvents.

\[
\text{cis-Pt(PR}_3^1\text{Cl}_2 + R_2^1\text{OCNHNHCOR}_2^1 \xrightarrow{\text{NaHCO}_3} \text{Pt(PR}_3^1\text{Cl}_2(R_2^1\text{OCNNCOR}_2^1)} + \text{NaCl + CO}_2 + \text{H}_2\text{O}
\]

R$_1^1$ = R$_2^2$ = Ph (1)
R$_1^1$ = Me; R$_2^2$ = Ph (3)
R$_1^1$ = R$_2^2$ = Me (4)  (2.1)

2.2.2 NMR characterisation of Pt(PR$_3^1$)$_2$(R$_2^1$OCNNCOR$_2^1$) complexes [R$_1^1$ = R$_2^2$ = Ph (1); R$_1^1$ = Me, R$_2^2$ = Ph (3); R$_1^1$ = R$_2^2$ = Me (4)]

Multinuclear NMR spectroscopy of complexes 1, 3 and 4 (Tables 2.1-2.4) indicates that the co-ordination of the azo ligand R$_2^1$OCNNCOR$_2^1$ (R$_2^2$ = Me, Ph) to the platinum centre is via the oxygen and nitrogen atoms (Scheme 2.1) as in the crystal structure of 1.$^7$

\[\text{Scheme 2.1 The complexes Pt(PR}_3^1\text{Cl}_2(R_2^1\text{OCNNCOR}_2^1), showing the binding mode of the azodicarbonyl ligand.}\]
The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of 4 in CDCl$_3$ shows two inequivalent phosphorus nuclei that are mutually coupled and possess $^{195}\text{Pt}$ satellites (Figure 2.3). The two $^1J(\text{PtP})$ coupling constants of 4 differ by about 400 Hz. Generally, a phosphorus nucleus trans to an oxygen donor has a larger $^1J(\text{PtP})$ value compared to a phosphorus trans to a nitrogen donor; this is discussed in more detail in Section 2.3.1. Following this trend we can assign the resonance at $\delta_P -37.0$ [$^1J(\text{PtP}) = 3448 \text{ Hz}$] to the phosphorus nucleus trans to the oxygen donor and the resonance at $\delta_P -28.0$ [$^1J(\text{PtP}) = 3010 \text{ Hz}$] to the phosphorus nucleus trans to the nitrogen donor. The phosphorus resonances for complexes 1-7 have been assigned in the same fashion (Table 2.2).

The $^1\text{H}$ NMR spectrum of 4 (Figure 2.4) in CD$_2$Cl$_2$ shows two methyl resonances on the azodiacyl ligand as a singlet at $\delta_H 2.08$ and a doublet at $\delta_H 1.91$ [$^3J(\text{PH}) = 0.9 \text{ Hz}$]. The two PMe$_3$ groups appear as separate doublets at $\delta_H 1.62$ and $\delta_H 1.72$, each possessing overlapping $^{195}\text{Pt}$ satellites. On selective phosphorus decoupling at $\delta_P -37$, phosphorus trans to oxygen, the doublet resonances at $\delta_H 1.91$ (COMe) and $\delta_H 1.72$ (PMe$_3$) in the $^1\text{H}$ NMR spectrum collapse into singlets. On selective phosphorus decoupling at $\delta_P -28$, phosphorus trans to nitrogen, only the doublet resonance at $\delta_H 1.62$ (PMe$_3$) in the $^1\text{H}$ NMR spectrum collapses into a singlet. Hence the resonance at $\delta_H 1.62$ is due to the PMe$_3$ trans to nitrogen and the resonance at $\delta_H 1.72$ is due to the PMe$_3$ trans to oxygen. On changing the solvent to C$_6$D$_6$ we observe a substantial downfield shift of the azodiacyl methyl resonances and an upfield shift of the PMe$_3$ doublets, with increased separation between them (Figure 2.5).

The $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of 4 (Figure 2.6) shows two CO resonances at $\delta_C 175.4$ and $\delta_C 165.4$, the former resonance being a doublet [$J(\text{PC}) = 3 \text{ Hz}$] with $^{195}\text{Pt}$ satellites [$J(\text{PtC}) = 67 \text{ Hz}$] and the latter a doublet of doublets [$J(\text{PC}) = 9$ and 4 Hz] without detectable $^{195}\text{Pt}$ satellites (Figure 2.7). The azodiacyl methyl carbon atoms can be detected as two doublet resonances at $\delta_C 22.1$ [$J(\text{PC}) = 4 \text{ Hz}$] and $\delta_C 16.5$ [$J(\text{PC}) = 5 \text{ Hz}$] (Figure 2.8).

The $^{195}\text{Pt} \{^1\text{H}\}$ NMR spectrum of 4 (Figure 2.9, Table 2.4) confirms the presence of two inequivalent phosphine ligands attached to the platinum centre. In Figure 2.9, we see a set of doublet of doublets whose $J(\text{PtP})$ values roughly correspond to the $J(\text{PtP})$ values obtained from the $^{31}\text{P} \{^1\text{H}\}$ spectrum of 4 (Figure 2.3, Table 2.2).
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PPh$_3$)$_2$(PhOCNNCOPh) 1$^a$</td>
<td>7.00-8.00 (m, Ph)</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_2$(EtO$_2$CNNCO$_2$Et) 2$^b$</td>
<td>1.14 (3 H, br. t, CH$_2$CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>1.35 [3 H, t, CH$_2$CH$_3$, J(HH) = 7.0]</td>
</tr>
<tr>
<td></td>
<td>4.12 (2 H, br., CH$_2$CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>4.57 [2 H, quart, CH$_2$CH$_3$, J(HH) = 7.0]</td>
</tr>
<tr>
<td></td>
<td>7.00-8.00 (30 H, m, Ph)</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_2$(PhOCNNCOPh) 3$^a$</td>
<td>1.80 [9 H, d, PCH$_3$, $^2$J(PH) = 11.0]$^c$</td>
</tr>
<tr>
<td></td>
<td>1.90 [9 H, d, PCH$_3$, $^2$J(PH) = 11.3]$^c$</td>
</tr>
<tr>
<td></td>
<td>7.00-8.00 (10 H, m, Ph)</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_2$(MeOCNNCOMe) 4$^d$</td>
<td>1.62 [9 H, d, PCH$_3$, $^2$J(PH) = 10.7]$^c$</td>
</tr>
<tr>
<td></td>
<td>1.72 [9 H, d, PCH$_3$, $^2$J(PH) = 11.2]$^c$</td>
</tr>
<tr>
<td></td>
<td>1.91 [3 H, d, COCH$_3$, $^5$J(HH) = 0.9]</td>
</tr>
<tr>
<td></td>
<td>2.08 (3 H, s, COCH$_3$)</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_2$(Pr$_i$O$_2$CNNCO$_2$Pr$_i$) 5$^e$</td>
<td>0.75 [6 H, d, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
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<tr>
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<td>1.06 [6 H, d, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>4.08 [1 H, sept, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>4.12 [1 H, sept, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>7.00-8.00 (30 H, m, Ph)</td>
</tr>
<tr>
<td>Pt(dppe)(EtO$_2$CNNCO$_2$Et) 6$^b$</td>
<td>0.97 [3 H, t, CH$_2$CH$_3$, J(HH) = 7.2]</td>
</tr>
<tr>
<td></td>
<td>1.23 [3 H, t, CH$_2$CH$_3$, J(HH) = 7.2]</td>
</tr>
<tr>
<td></td>
<td>4.00 [2 H, d, CH$_2$CH$_3$, J(HH) = 7.2]</td>
</tr>
<tr>
<td></td>
<td>4.62 [2 H, d, CH$_2$CH$_3$, J(HH) = 7.2]</td>
</tr>
<tr>
<td>Pt(dppe)(Pr$_i$O$_2$CNNCO$_2$Pr$_i$) 7$^b$</td>
<td>1.10 [6 H, d, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>1.36 [6 H, d, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>4.79 [1 H, sept, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>5.40 [1 H, sept, CH(CH$_3$)$_2$, J(HH) = 6.2]</td>
</tr>
<tr>
<td></td>
<td>7.00-8.00 (30 H, m, Ph)</td>
</tr>
</tbody>
</table>

Table 2.1 $^1$H (300.13 MHz, 295 K) NMR spectroscopic data for complexes 1-7. $^0$ indicates phosphorus trans to oxygen and $^N$ indicates phosphorus trans to nitrogen. $^a$ In CDCl$_3$. $^b$ In C$_6$D$_6$. $^c$ Contain overlapping $^{195}$Pt satellites. $^d$ In CD$_2$Cl$_2$. $^e$ In [6H$_8$]THF.
<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (J / Hz)</th>
</tr>
</thead>
</table>
| Pt(PPh₃)₂(PhOCCNCOPh) 1<sup>a</sup> | 17.5 [d, P<sup>N</sup>, 2J(PP) = 22, J(PtP) = 3261]  
|  | 3.1 [d, P<sup>O</sup>, 2J(PP) = 22, J(PtP) = 3685] |
| Pt(PPh₃)₂(EtO₂CCNCO₂Et) 2<sup>b</sup> | 6.2 [br. d, P<sup>O</sup>, J(PtP) ≈ 3790]  
|  | 16.6 [d, P<sup>N</sup>, 2J(PP) = 23, J(PtP) = 3166] |
| Pt(PMe₃)₂(PhOCCNCOPh) 3<sup>a</sup> | -10.9 [d, P<sup>N</sup>, 2J(PP) = 26, J(PtP) = 3028]  
|  | -20.1 [d, P<sup>O</sup>, 2J(PP) = 26, J(PtP) = 3435] |
| Pt(PMe₃)₂(MeOCCNCOMe) 4<sup>c</sup> | -28.0 [d, P<sup>N</sup>, 2J(PP) = 27, J(PtP) = 3010]  
|  | -37.0 [d, P<sup>O</sup>, 2J(PP) = 27, J(PtP) = 3448] |
| Pt(PPh₃)₂(PrO₂CCNCO₂Pr)<sup>i</sup> 5<sup>d</sup> | 5.8 [d, P<sup>O</sup>, 2J(PP) = 23, J(PtP) = 3859]  
|  | 16.5 [d, P<sup>N</sup>, 2J(PP) = 23, J(PtP) = 3158] |
| Pt(dppe)(EtO₂CCNCO₂Et) 6<sup>b</sup> | 31.1 [d, P<sup>O</sup>, 2J(PP) = 11, J(PtP) = 3839]  
|  | 38.1 [d, P<sup>N</sup>, 2J(PP) = 11, J(PtP) = 3041] |
| Pt(dppe)(PrO₂CCNCO₂Pr)<sup>i</sup> 7<sup>b</sup> | 31.0 [d, P<sup>O</sup>, 2J(PP) = 12, J(PtP) = 3843]  
|  | 38.1 [d, P<sup>N</sup>, 2J(PP) = 12, J(PtP) = 3023] |

Table 2.2: Table 2.2: ³¹P {¹H} (121.49 MHz, 295 K) NMR spectroscopic data for complexes 1-7. Couplings to Pt refer to the satellites from ¹⁹⁵Pt. P<sup>O</sup> indicates phosphorus trans to oxygen and P<sup>N</sup> indicates phosphorus trans to nitrogen. <sup>a</sup> In CDCl₃. <sup>b</sup> In C₆D₆. <sup>c</sup> In CD₂Cl₂. <sup>d</sup> In [²H₈]THF.
<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PPh₃)₂(PhOCNNCOPh) 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>127.1-135.2 (Ph)</td>
</tr>
<tr>
<td></td>
<td>163.2 [dd, CO, J(PC) = 10, 3]</td>
</tr>
<tr>
<td></td>
<td>171.7 [d, CO, J(PC) = 4]</td>
</tr>
<tr>
<td>Pt(PMe₃)₂(PhOCNNCOPh) 3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16.6 [d, PCH₃, J(PC) = 38, 2J(PtC) = 33]</td>
</tr>
<tr>
<td></td>
<td>19.7 [dd, PCH₃, J(PC) = 44, 2; 2J(PtC) = 43]</td>
</tr>
<tr>
<td></td>
<td>124.2-131.8 (Ph)</td>
</tr>
<tr>
<td></td>
<td>163.4 [dd, CO, J(PC) = 9, 3]</td>
</tr>
<tr>
<td>Pt(PMe₃)₂(MeOCNNCOMe) 4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16.3 [d, PCH₃, J(PC) = 38, 2J(PtC) = 33]</td>
</tr>
<tr>
<td></td>
<td>16.5 [d, CH₃, J(PC) = 5]</td>
</tr>
<tr>
<td></td>
<td>19.6 [dd, PCH₃, J(PC) = 45, 2; J(PtC) = 45]</td>
</tr>
<tr>
<td></td>
<td>22.1 [d, CH₃, J(PC) = 4]</td>
</tr>
<tr>
<td></td>
<td>165.4 [dd, CO, J(PC) = 9, 4]</td>
</tr>
<tr>
<td>Pt(PPh₃)₂(PrO₂CNCO₂Pr) 5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>23.8 (s, CH₃)</td>
</tr>
<tr>
<td></td>
<td>24.1 (s, CH₃)</td>
</tr>
<tr>
<td></td>
<td>67.6 (s, CH)</td>
</tr>
<tr>
<td></td>
<td>71.2 (s, CH)</td>
</tr>
<tr>
<td></td>
<td>128.8-136.6 (Ph)</td>
</tr>
</tbody>
</table>

Table 2.3<sup>1</sup><sup>3</sup>C<sup>1</sup>H (75.47 MHz, 295 K) NMR spectroscopic data of complexes 1 and 3-5. Couplings to Pt refer to satellites from <sup>195</sup>Pt. <sup>a</sup>In CDCl₃. <sup>b</sup>In [²H₈]THF, no CO resonances were detected.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PPh₃)₂(PhOCNNCOPh) 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-4291 [dd, J(PtP&lt;sup&gt;O&lt;/sup&gt;) = 3680, J(PtP&lt;sup&gt;N&lt;/sup&gt;) = 3302]</td>
</tr>
<tr>
<td>Pt(PMe₃)₂(PhOCNNCOPh) 3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-4257 [dd, J(PtP&lt;sup&gt;O&lt;/sup&gt;) = 3458, J(PtP&lt;sup&gt;N&lt;/sup&gt;) = 3028]</td>
</tr>
<tr>
<td>Pt(PMe₃)₂(MeOCNNCOMe) 4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-4260 [dd, J(PtP&lt;sup&gt;O&lt;/sup&gt;) = 3446, J(PtP&lt;sup&gt;N&lt;/sup&gt;) = 3010]</td>
</tr>
<tr>
<td>Pt(PPh₃)₂(PrO₂CNCO₂Pr) 5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-4168 [dd, J(PtP&lt;sup&gt;O&lt;/sup&gt;) = 3871, J(PtP&lt;sup&gt;N&lt;/sup&gt;) = 3118]</td>
</tr>
</tbody>
</table>

Table 2.4<sup>1</sup><sup>9</sup>Pt<sup>1</sup>H (107.52 MHz, 300 K) NMR spectroscopic data of complexes 1 and 3-5. P<sup>O</sup> indicates phosphorus trans to oxygen and P<sup>N</sup> indicates phosphorus trans to nitrogen. <sup>a</sup>In CD₂Cl₂. <sup>b</sup>In [²H₈]THF.
Figure 2.3 $^{31}\text{P} \ {^1\text{H}} (121.49 \text{ MHz})$ NMR spectrum of Pt(PMe$_3$h(MeOCNNCOMe)$_2$ in CDCl$_3$ (295 K) consisting of two mutually coupled doublets, each with $^{195}\text{Pt}$ satellites.

Figure 2.4 $^1\text{H} (300.13 \text{ MHz})$ NMR of Pt(PMe$_3$h(MeOCNNCOMe)$_2$ in CD$_2$Cl$_2$ (295 K). a COCH$_3$, b PCH$_3$ (trans to nitrogen). c PCH$_3$ (trans to oxygen).
Figure 2.5 $^1$H (300.13 MHz, 295 K) NMR spectrum of Pt(PMe$_3$)$_2$(MeOCNCOMe)$_4$. (a) in CD$_2$Cl$_2$, (b) in C$_6$D$_6$.

Figure 2.6 $^{13}$C ($^1$H) (75.47 MHz, 295 K) NMR spectrum of 4 in CDCl$_3$. a CH$_3$ resonances from PMe$_3$ and azodiacyl ligands. b impurities. c CDCl$_3$. d CO resonances from azodiacyl ligand.
Figure 2.7 \(^{13}\text{C}\{^1\text{H}\} (75.47\text{ MHz}, 295\text{ K})\) NMR spectrum of 4 in CDCl\(_3\), showing the azodiacyl CO resonances.

Figure 2.8 \(^{13}\text{C}\{^1\text{H}\} (75.47\text{ MHz}, 295\text{ K})\) NMR spectrum of 4 in CDCl\(_3\), showing the methyl resonances of the PMe\(_3\) and azodiacyl ligands. \(a\) PCH\(_3\) with \(^{195}\text{Pt}\) satellites. \(b\) CO\(_3\)CH\(_3\).
2.2.3 UV/VIS and IR spectroscopic data of 1, 3 and 4

The UV/VIS spectra of complexes 1, 3 and 4 show a prominent low-energy band at around 300 nm (Figure 2.8 and Table 2.5). Both complexes 1 and 3 show a band maximum at ca. 320 nm, whereas the band for 4 is shifted 15 nm to higher energy. This effect is observed on changing the azo from the aryl PhOCNNCOPh ligand to the alkyl MeOCNNCOMe ligand. No such effects are observed on changing the phosphine ligand from PPh$_3$ to PMe$_3$. Since the crystal structure of 1 shows a conjugated metallacycle, this band is assigned as a transition of the metallacycle, rather than attempting to distinguish intra-ligand transitions from charge-transfer transitions.
Figure 2.8 UV/VIS spectra of 1, 3 and 4 in THF, showing the band assigned as the transition of the metallacycle. Complexes 1, 3 and 4 are of different concentration.

The IR spectra of 1, 3 and 4 show two broad bands in the region of 1560-1600 cm$^{-1}$ (Figure 2.9 and Table 2.5), which were assigned as $\nu$(C=O) and $\nu$(C=N) and agree with Kasenally and Dilworth's observations.$^{15}$ However, from the appearance of the spectra in Figure 2.9, other smaller peaks are evidently present, which could be due to a number of different CO/CN stretching bands present in the solid state.
<table>
<thead>
<tr>
<th>Compound</th>
<th>UV/VIS in THF λ / nm (ε / dm³ mol⁻¹ cm⁻¹)</th>
<th>IR, v(CO), v(CN) v / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PPh₃)₂(PhOCNNCOPh) 1</td>
<td>318 (12000)</td>
<td>1565ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1595ᵃ</td>
</tr>
<tr>
<td>Pt(PPh₃)₂(Et₂OCNCO₂Et) 2</td>
<td>333 (3100)</td>
<td>1618ᵇ</td>
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<tr>
<td></td>
<td></td>
<td>1642ᵇ</td>
</tr>
<tr>
<td></td>
<td>463 (400)</td>
<td>1610ᶜ</td>
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<tr>
<td></td>
<td></td>
<td>1621ᶜ</td>
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<tr>
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<tr>
<td></td>
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<td>1668ᶜ</td>
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<td>Pt(PMe₃)₂(PhOCNNCOPh) 3</td>
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<td>1576ᵃ</td>
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<td></td>
<td>1612ᵃ</td>
</tr>
<tr>
<td>Pt(PH)(Pri₂OCNCO₂Pri) 5</td>
<td>337 (3100)</td>
<td>1613ᶜ</td>
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<tr>
<td></td>
<td>465 (400)</td>
<td>1635ᶜ</td>
</tr>
</tbody>
</table>

Table 2.5 UV/VIS and IR data for complexes 1-5. ᵃ in KBr pellet. ᵇ in CH₂Cl₂. ᶜ in Nujol.
Figure 2.9 IR spectra of 1, 3-4 in KBr pellets.

2.2.4 Preparation of Pt(PPh$_3$)$_2$(R$_2$OCNNCOR$^2$) complexes \([R^2 = \text{OEt} \ (2), \text{OPr}^i \ (5)]\)

Reaction of Pt(PPh$_3$)$_2$(C$_2$H$_4$) with an equivalent amount or excess (up to threefold) of R$_2$OCNNCOR$^2$ \((R^2 = \text{OEt}, \text{OPr}^i)\) in benzene at room temperature in the absence of light yields Pt(PPh$_3$)$_2$(R$_2$OCNNCOR$^2$) \([R^2 = \text{OEt} \ (2), \text{OPr}^i \ (5)]\) and ethene gas (Equation 2.2).

\[
\text{Pt(PPh}_3\text{)}_2(\text{C}_2\text{H}_4) + R^2\text{OCNNCOR}^2 \xrightarrow{\text{C}_2\text{H}_4} \text{Pt(PPh}_3\text{)}_2(R^2\text{OCNNCOR}^2) \\
\text{[R}^2 = \text{OEt} \ (2), \text{OPr}^i \ (5)]
\]  

(2.2)

These compounds are yellow/orange in colour and relatively stable as solids. Both 2 and 5 are slightly soluble in benzene, with 5 being more soluble in THF. Based on the evidence of Cenini et al.\textsuperscript{9} and our own work, the binding mode of the azo ligand in 2 corresponds to that found in complexes 1, 3 and 4, co-ordinating via the nitrogen and oxygen atoms to form a metallacycle.
2.2.5 NMR characterisation of Pt(PPh$_3$)$_2$(R$^2$OCNNCOR$^2$) complexes \([R^2 = \text{OEt (2), OPr}$]$ \( \text{OPr}^\dagger (5) \)]

Multinuclear NMR spectra of Pt(PPh$_3$)$_2$(EtO$_2$CNNCO$_2$Et) 2 and Pt(PPh$_3$)$_2$(Pr$^\dagger$O-OCNNCO$_2$Pr$^\dagger$) 5 confirm that both complexes have inequivalent phosphorus atoms as well as inequivalent alkyl groups on the azo ligand (Tables 2.1-2.4). Due to solubility problems suitable $^{13}$C \( \{^1\text{H}\} \) and $^{195}$Pt \( \{^1\text{H}\} \) NMR spectra of complex 2 could not be obtained. Furthermore no CO resonances were observed in the $^{13}$C \( \{^1\text{H}\} \) NMR spectrum of 5 even after long periods of acquisition.

2.2.6 UV/VIS and IR spectroscopic data of 2 and 5

The IR spectra of 2 and 5 show CO/CN stretching bands in the 1610-1670 cm$^{-1}$ region, which are higher in wavenumbers and more intense compared to the CO/CN bands assigned to 1, 3-4 (Table 2.5). In the IR spectrum of 2, two broad peaks are observed at around 1600 cm$^{-1}$ in dichloromethane, but in Nujol we can observe up to five peaks in the same region. The UV/VIS spectra of 2 and 5 contain low-energy shoulders at ca. 330 and 460 nm (Table 2.5).

2.2.7 Crystal Structure of Pt(PPh$_3$)$_2$(Pr$^\dagger$O$_2$CNNCO$_2$Pr$^\dagger$)-(C$_6$H$_6$)$_2$ 5

Crystals of 5 suitable for X-ray data collection were grown by slow evaporation of a 2:1 THF-benzene solution of 5 at room temperature. The crystal data were collected and refined by Leroy Cronin at the University of York. The structure of 5 consists of monomolecular units of the complex with two molecules of benzene per unit cell (Figure 2.10). Crystallographic details are summarised in Table 2.6. The structure of 5 in Figure 2.11 and 2.12 clearly shows that the azo ligand co-ordinates to the platinum centre through the oxygen atom of one carbonyl group and the nitrogen atom of the azo function remote from the co-ordinated carbonyl.

The principal bond lengths and angles (Figure 2.13) follow a very similar pattern to that reported for 1 and related azodiacyl metal complexes. The platinacycle contains O–C and N–N bonds which are extended relative to those of the free ligand, while the C–N bond is shortened. The platinacycle containing Pt, O1, C5, N2 and N1 is planar within 0.012 Å (Plane 1) and essentially co-planar with the co-ordinated atoms P1, P2, O1 and N1 which are planar within 0.028 Å (Plane 2). The exocyclic carbon atom C4 is co-planar with the metallacycle, atoms Pt1, N1, N2 and C4 are planar within 0.001 Å (Plane 3). Calculations of least-squares planes 1, 2 and 3 are summarised in Tables 2.7 and 2.8. The phosphorus-metal bond lengths differ only slightly \( [\bar{r}(\text{Pt–P}) = \ldots \)
0.012 Å, but there is a substantial difference in the angles to adjacent ligands: P1–Pt–N1 = 97.5(1)°, P2–Pt–O1 = 87.1(1)°.

Figure 2.10 Packing arrangement in a unit cell of Pt(PPh₃)₂(Pr'O₂CNNCO₂Pr') (5), showing two molecules of benzene of crystallisation.
Figure 2.11 ORTEP\textsuperscript{17} drawing of \(\text{Pt}(\text{PPh}_3)_2(\text{PrO}_2\text{C}N\text{C}O_2\text{Pr})\) (5) showing non-hydrogen atoms with thermal ellipsoids at the 30\% probability level. The two molecules of benzene of crystallisation are not shown.

Figure 2.12 ORTEP\textsuperscript{17} drawing of 5 from an alternative perspective.
Figure 2.13 Inner co-ordination sphere of 5, showing (a) bond distances in Å and (b) bond angles in degrees.
Table 2.6 Crystallographic data for complex 5.

<table>
<thead>
<tr>
<th>Crystal Data</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C(<em>{56}H</em>{60}N_2O_2P_2Pt)</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>1078.06</td>
</tr>
<tr>
<td><strong>Temperature / K</strong></td>
<td>293(2)</td>
</tr>
<tr>
<td><strong>Crystal dimensions / mm</strong></td>
<td>0.4 x 0.4 x 0.4</td>
</tr>
<tr>
<td><strong>Crystal description</strong></td>
<td>Brown block</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>(P\overline{1}) (No. 2)</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td>(a = 15.395(10) , \text{Å} ), (\alpha = 104.86(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 15.8857) (7) (, \text{Å} ), (\beta = 95.38(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 11.481(2) , \text{Å} ), (\gamma = 66.95(3)^\circ)</td>
</tr>
<tr>
<td><strong>Volume / (\text{Å}^3)</strong></td>
<td>2497(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1092</td>
</tr>
<tr>
<td><strong>Density (calcd) / g cm(^{-3})</strong></td>
<td>1.434</td>
</tr>
<tr>
<td><strong>(\mu / \text{cm}^{-1})</strong></td>
<td>29.21</td>
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<table>
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<tr>
<th>Data Collection</th>
<th>Value</th>
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<tbody>
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<td><strong>Diffractometer</strong></td>
<td>Rigaku AFC6S</td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoK(\alpha), graphite monochromated</td>
</tr>
<tr>
<td><strong>Wavelength / Å</strong></td>
<td>0.7107</td>
</tr>
<tr>
<td><strong>Scan type</strong></td>
<td>(\omega-2\theta)</td>
</tr>
<tr>
<td><strong>Scan rate / min(^{-1})</strong></td>
<td>16.0(^{\circ})</td>
</tr>
<tr>
<td><strong>Scan width / (^{\circ})</strong></td>
<td>((1.21 + 0.30 \tan \theta))</td>
</tr>
<tr>
<td><strong>2(\theta) range for data collection / (^{\circ})</strong></td>
<td>5.18–50.02</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>9336 (including 195 standard reflections)</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>8783 ([R %\text{(int)} = 3.12])</td>
</tr>
<tr>
<td><strong>Transmission co-efficients</strong></td>
<td>0.90 (min), 1.00 (max), 0.96 (average)</td>
</tr>
<tr>
<td><strong>Data corrections</strong></td>
<td>Lorentz-polarisation</td>
</tr>
<tr>
<td><strong>Average intensity change</strong></td>
<td>(-0.9%) (3 reflx checked every 150 data)</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>(0 \leq h \leq 18, \ -16 \leq k \leq 18, \ -13 \leq l \leq 13)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure Solution</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Patterson methods with SAPI91</strong></td>
<td>expanded with DIRDIF(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Expansion of data collection and structure solution procedures is required.\(^b\) Exploits the equivalence of atoms (59).\(^c\) Earlier study. \(^d\) Earlier study.
Table 2.6 (cont.)

<table>
<thead>
<tr>
<th>Refinement method</th>
<th>Full-matrix least squares on $F^2$ with SHELXL93(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-hydrogen atoms</td>
<td>Anisotropic</td>
</tr>
<tr>
<td>Hydrogen atoms</td>
<td>Riding model, isotropic</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>$w = [\sigma^2(F^2_o) + (0.0457P)^2]^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P = \max(I_{obs}, 0) + 2F_c^2 / 3$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8783 / 0 / 586</td>
</tr>
<tr>
<td>Data-to-parameter ratio</td>
<td>14.98</td>
</tr>
<tr>
<td>Goodness-of-fit(^g) on $F^2$</td>
<td>1.00</td>
</tr>
<tr>
<td>$R(%)$(^h) indices</td>
<td></td>
</tr>
<tr>
<td>$[I_o &gt; 2\sigma(I_o)]$</td>
<td>$R1 = 0.0391, , wR2 = 0.0854$</td>
</tr>
<tr>
<td>All data</td>
<td>$R1 = 0.0650, , wR2 = 0.0932$</td>
</tr>
<tr>
<td>Final difference map</td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak(^i) and hole / e Å(^{-3})</td>
<td>0.77 and -0.64</td>
</tr>
<tr>
<td>Largest shift / esd in final cycle</td>
<td>0.00</td>
</tr>
</tbody>
</table>

\(a\) Unit cell parameters and their esds were determined from a least-squares fitting of the setting angles of 20 reflections in the range $13.96^\circ \leq 2\theta \leq 15.82^\circ$.  
\(b\) $R(\text{int}) = \Sigma|F^2_o - F^2_o(\text{mean})|/\Sigma[F^2_o]$; 358 reflections measured twice.  
\(c\) Ref. 18(a).  
\(d\) Ref. 18(b).  
\(e\) Ref. 18(c).  
\(f\) Zero reflections suppressed in the refinement.  
\(g\) GOF = $\{\Sigma[w(F^2_o - F^2_c)^2]/(n - p)\}^{1/2}$ where $p$ = number of parameters, $n$ = number of data.  
\(h\) $R1 = \Sigma|F^2_o| - |F^2_c|/\Sigma|F^2_o|$.  
\(i\) Located 1.10 Å away from Pt1.
PLATINUM AZODICARBONYL COMPLEXES

Table 2.7 Least-squares planes of: Pt1, P1, P2, N1 (Plane 1), Pt1, O1, C5, N2, N1 (Plane 2) and Pt1, N1, N2, C4 (Plane 3). Plane equation is defined as $Ax + By + Cz = D$, where $x$, $y$, $z$ are the crystal co-ordinates.

<table>
<thead>
<tr>
<th>Plane</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.35(1)</td>
<td>-1.41(1)</td>
<td>-1.62(2)</td>
<td>8.14(1)</td>
</tr>
<tr>
<td>2</td>
<td>13.64(2)</td>
<td>-0.80(4)</td>
<td>-1.65(2)</td>
<td>8.80(4)</td>
</tr>
<tr>
<td>3</td>
<td>13.90(2)</td>
<td>-0.26(4)</td>
<td>-1.59(2)</td>
<td>9.41(5)</td>
</tr>
</tbody>
</table>

Table 2.8 Deviations from the calculated least-squares planes (Plane 1, 2 and 3). (Plane 1)$^\gamma$(Plane 2) = 2.3(2)$^\circ$, (Plane 2)$^\gamma$(Plane 3) = 2.1(2)$^\circ$. $a$ Atoms used to define the plane.

<table>
<thead>
<tr>
<th></th>
<th>Plane 1</th>
<th>Plane 2</th>
<th>Plane 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1</td>
<td>0.047(2)$^a$</td>
<td>0.008(2)$^a$</td>
<td>-0.001(1)$^a$</td>
</tr>
<tr>
<td>P1</td>
<td>0.005(1)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>-0.020(1)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.093(6)</td>
<td>-0.002(3)$^a$</td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.022(1)$^a$</td>
<td>-0.016(3)$^a$</td>
<td>0.003(4)$^a$</td>
</tr>
<tr>
<td>N2</td>
<td></td>
<td>0.018(4)$^a$</td>
<td>-0.001(1)$^a$</td>
</tr>
<tr>
<td>C4</td>
<td></td>
<td></td>
<td>-0.001(2)$^a$</td>
</tr>
<tr>
<td>C5</td>
<td></td>
<td>-0.009(4)$^a$</td>
<td></td>
</tr>
</tbody>
</table>

2.2.8 Preparation of Pt(dppe)(R\textsuperscript{1}OCNNCOR\textsuperscript{1}) [R\textsuperscript{1} = OEt (6); R\textsuperscript{1} = OPri (7)]

On addition of excess 1,2-bis(diphenylphosphino)ethane (dppe) to complex 2 or 4, a new singlet resonance was observed in the $^{31}$P \{\textsuperscript{1}H\} NMR spectrum at $\delta$ -4.7 (free PPh\textsubscript{3}) and two new doublet resonances at ca. $\delta$ 38.1 and $\delta$ 31.1, both with $^{195}$Pt satellites, which have been assigned to the complex Pt(dppe)(EtO\textsubscript{2}CNNCO\textsubscript{2}Et) 6 (Tables 2.1 and 2.2). The complex Pt(dppe)(Pr\textsubscript{i}O\textsubscript{2}CNNCO\textsubscript{2}Pr\textsuperscript{i}) 7 is formed by the same method (Equation 2.3).

\[
\text{Pt(PPh}_{3}\text{)}\text{2(R}^1\text{OCNNCOR}^1\text{)} + \text{dppe} \rightarrow \text{Pt(dppe)(R}^1\text{OCNNCOR}^1\text{)} + 2\text{PPh}_{3}
\]

\begin{align*}
\text{R}^1 &= \text{OEt (6)} \\
\text{R}^1 &= \text{OPri (7)}
\end{align*}

(2.3)

The displacement of triphenylphosphine with dppe is not uncommon in platinum complexes; for example, addition of dppe to cis-Pt(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} in chloroform produces Pt(dppe)Cl\textsubscript{2} in quantitative yield.\textsuperscript{19}
2.2.9 Reactions of Pt(PR₃)₂(R²OCNNCOR²) complexes (R¹ = Me, Ph; R² = Me, Ph, OEt, OPr)

Complexes 1, 3 and 4 show no reactivity towards ethene or diphenyl acetylene when photolysed in [²H₈]THF. Photolysis of complexes 1, 3-4 in CDCl₃ resulted in the formation of the corresponding cis-platinum bis(phosphine) dichloride complexes Pt(PR₃)₂Cl₂. Both complexes 2 and 5 react thermally with chlorinated solvents at room temperature to give cis-Pt(PPh₃)₂Cl₂ as the major product, with 5 being more readily converted to cis-Pt(PPh₃)₂Cl₂. UV irradiation in CHCl₃ generated the same products more rapidly. Irradiation of 5 with ethene or diphenylacetylene in [²H₈]THF resulted in the formation of Pt(PPh₃)₂(η²-C₂H₄) (δ_H 2.2, J(PtH) = 62 Hz) or Pt(PPh₃)₂(PhC=CPH) [δ_p 35, J(PtP) = 3000 Hz]. However, the same outcome can be achieved if the mixture is heated at 70 °C in the absence of light.

In addition to the organometallic species some organic photoproducts are observed on irradiation of 5 in [²H₈]THF. Their ¹H NMR spectra exhibit similar features to the ¹H NMR data of the photoproducts from the free diazene ligand Pr₂O₂CNNCO₂Pr. In general, azo compounds initially undergo photochemically induced trans-cis isomerisation prior to degradation, involving liberation of molecular N₂ and formation of a radical pair. Azodicarbonyl compounds are reported to form the corresponding diketone upon extrusion of N₂ on photolysis.

2.3 Discussions

2.3.1 Preparation of Pt(PR₃)₂(R²OCNNCOR²) (R¹ = Ph, Me; R² = Ph, Me, OEt, OPr) complexes containing a Pt–N–N–C–O metallacycle

The complex Pt(PR₃)₂(R²O₂CNNCO₂R²) was prepared by two methods. The first method involved the reaction between cis-Pt(PR₃)₂Cl₂ (R = Ph or Me) with the diacyl hydrazine ROCNHNHCOR (Ph or Me) which is deprotonated in the presence of NaHCO₃ under reflux conditions. The second method involved the displacement of the ethene ligand in Pt(PPh₃)₂(η²-C₂H₄) with the azodicarboxylate ligand RO₂CNNCO₂R. Both methods resulted in a structure where the azodicarbonyl ligand is N,O-bonded to platinum, forming a Pt–N–N–C–O metallacycle.
2.3.2 Structure and bonding in azo complexes

As discussed previously in Section 2.1, azo transition metal complexes can co-ordinate to the metal in two ways when the substituents on the azo function are simple alkyl or aryl groups, the first involves the HOMO of the nitrogen atom to form a \( \sigma \)-bond and in the second method, the azo function co-ordinates to the metal in an \( \eta^2 \)-fashion, utilising its \( \pi \)- and \( \pi^* \)-molecular orbitals to interact with the \( d_\sigma \)- and \( d_\pi \)-orbitals on the metal (Figures 2.1-2.2). The molecular orbital description of the azo compound reveals that there are \( n_1 \)- and \( n_2 \)-molecular orbitals present from the combination of the two \( sp^2 \) nonbonding \( n \)-orbitals on the two nitrogen atoms.\(^2\) \( n_1 \) is the antibonding combination (HOMO) and \( n_2 \) is the bonding combination of the \( n \)-orbitals where the energy difference between \( n_1 \) and \( n_2 \) is said to be sensitive to the NNX (\( X = \) substituent) bond angle.\(^23\) Figure 2.14 shows the \( n \)- and \( \pi \)-orbitals of the cis- and trans-azo function. In most circumstances, the order of orbitals going from the highest occupied down is \( n_1 \), \( \pi \) then \( n_2 \).\(^23\)

![Molecular orbitals description of the trans- and cis-azo function.](image-url)
The ability of an azo compound to co-ordinate to a metal centre relies mainly on the interaction of the HOMO \((n_1)\) of the azo function to form a mononuclear \(\sigma\)-complex. Additional involvement from the \(n_2\)-orbital generates a binuclear system. The formation of \(\pi\)-complexes involving the N=N function is rare. Examples of N=N \(\pi\)-complexes are found when the metal centre is electron rich (a poor \(\sigma\)-acceptor) and the azo ligand is a good \(\pi\)-acceptor and a poor \(\sigma\)-donor, e.g. Ni(Bu'NC)\(_2\)(PhN=NPh) and Ni(Bu'NC)\(_2\)-(diazofluorene).\(^{24,25}\)

2.3.2a Structure and bonding in azo carbonyl complexes

In cases where the azo ligand has a carbonyl adjacent to the azo function, the carbonyl groups should, according to Bent's rule,\(^{26}\) draw \(\pi\)-electrons away from the N=N function, increasing the s-character of the \(n_1\)- and \(n_2\)-orbitals, making them less available for \(\sigma\)-donation to the metal centre. The electron withdrawing nature of the carbonyl group should enable the azo function to act as a better \(\pi\)-acceptor, promoting \(\eta^2\)-co-ordination of the azo function to the metal centre. In fact the carbonyl group plays a more direct role in the co-ordination of the carbonyl substituted azo ligand and is found to act as an additional binding site for the carbonyl-substituted azo ligand.

Ibers and Ittel reported the first crystal structure of an azodicarbonyl platinum complex, Pt(PPh\(_3\))\(_2\)(PhOCNNCOPh) 1.\(^7\) As mentioned previously in Section 2.1, the structure of 1 was reported to have the azodibenzoyl ligand co-ordinated to the platinum centre via the oxygen and nitrogen atom of the azo ligand to form a metallacycle.

Closer examination of the bond lengths in the metallacycle revealed that the N=N bond has lengthened to that of a single bond and one of the C=N has shortened to that of a double bond. This prompted Ittel and Ibers to identify that the azodibenzoyl ligand has been reduced to a hydrazido ligand on co-ordination to the platinum centre, and now formally carries a \(-2\) charge in complex 1, with the platinum centre in the +2 oxidation state. Our current work shows that complex 5 adopts the same type of structure

Marabella et al. later suggested that there is a correlation between M–N and M–O bond distances in these types of metallacyclic azo carbonyl complexes.\(^5\) In their investigation, they compared several related metal complexes, all of which contained the M–O–C–N–N metallacycle (Figure 2.15). They found that C–O, C–N and N–N distances varied very little but large and significant variations do occur in the M–N and M–O distances (Table 2.9). They have demonstrated that a plot of \(r(M–N) – r(M–O)\) vs. \(r(M–N)\) (Figure 2.16) shows some correlation between the parameters for the complexes found in Table 2.9, which involve three different metals, a range of ancillary ligands and a variety of co-ordination geometries (4, 6 and 7).
Figure 2.15 Metallacycles investigated by Marabella et al.\(^5\) \([R = H, C_6H_4CH_3, C(CH_3)_2, COPh; R' = Ph]\).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>COPh</td>
<td>2.047 (6)</td>
<td>2.016 (5)</td>
<td>1.401 (9)</td>
<td>1.286 (10)</td>
<td>1.318 (10)</td>
</tr>
<tr>
<td>5</td>
<td>CO(_2)Pr(^i)</td>
<td>2.050 (5)</td>
<td>2.027 (4)</td>
<td>1.421 (6)</td>
<td>1.273 (7)</td>
<td>1.314 (7)</td>
</tr>
<tr>
<td>A</td>
<td>COPh</td>
<td>2.119 (18)</td>
<td>2.054 (14)</td>
<td>1.418 (14)</td>
<td>1.295 (10)</td>
<td>1.314 (11)</td>
</tr>
<tr>
<td>B</td>
<td>C(_6)H(_4)CH(_3)</td>
<td>1.984 (8)</td>
<td>2.110 (7)</td>
<td>1.38 (1)</td>
<td>1.30 (1)</td>
<td>1.30 (1)</td>
</tr>
<tr>
<td>C</td>
<td>H</td>
<td>1.945 (8)</td>
<td>2.131 (7)</td>
<td>1.41 (1)</td>
<td>1.33 (1)</td>
<td>1.27 (1)</td>
</tr>
<tr>
<td>D</td>
<td>Ph</td>
<td>2.030 (17)</td>
<td>2.159 (12)</td>
<td>1.38 (2)</td>
<td>1.35 (3)</td>
<td>1.24 (3)</td>
</tr>
<tr>
<td>E</td>
<td>C(CH(_3)_2)</td>
<td>2.127 (10)</td>
<td>2.013 (7)</td>
<td>1.41 (1)</td>
<td>1.31 (2)</td>
<td>1.32 (1)</td>
</tr>
</tbody>
</table>

Table 2.9 Examples of transition metal complexes containing the M–O–C–N–N metallacycle, adapted from ref. 5. 
1-Pt(PPh\(_3\))\(_2\)(PhOCNNCOPh), 5-Pt(PPh\(_3\))\(_2\)(Pt\(^i\)O\(_2\)C–NNCO\(_2\)Pr\(^i\)), A-MoO(S\(_2\)CNMe\(_2\))\(_2\)(PhOCNNCOPh), B-Mo(NC\(_6\)H\(_4\)CH\(_3\))Cl\(_2\)(PMe\(_2\)Ph)–(PhOCNNC\(_6\)H\(_4\)CH\(_3\)), C-Mo(NNCOPh)Cl(PMe\(_2\)Ph)\(_2\)(PhCONNH), D-[MoOCl\(_3\)(Cl-PhOCNNPh)]\(^+\), E-ReOCl\(_2\)(PPh\(_3\))[PhOCNN=C(CH\(_3\)_2)].
According to Marabella et al. the substituent R attached to the co-ordinated nitrogen atom in Figure 2.15 directly affects the degree of M–N bonding, which in turn leads to a correlated variation in the M–O bonding. It was said that the azo ligand can be represented by one of three valence bond structures F, G and H (Figure 2.17). Structure F is the usual representation of the azo ligand, whereas G is the resonance form of F. Structure H represents the reduced hydrazido(2−) ligand. The charges on the nitrogen co-ordinated atom in structures G and H can be stabilised by the attached R group via multiple N–R bonding. Their theory said that strong multiple N–R bonding occurs at the expense of multiple M–N bonding.

---

**Figure 2.16** Plot of (M–N) − (M–O) vs. (M–N) distances for compounds that contain N,O-co-ordinated azocarbonyl ligands, adapted from ref. 5. See also Table 2.9.

---

**Figure 2.17** Valence bond representation of the azocarbonyl ligand.\(^5\)
The substituent on the azodicarbonyl ligand also affects the electronic transitions of the metal azo complexes. As noted in Section 2.2.3 a change in the phosphine ligand affects the band maxima at ca. 300 nm in the UV/VIS spectra of Pt(PPh$_3$)$_2$(PhOCNNCOPh) I and Pt(PMe$_3$)$_2$(PhOCNNCOPh) 3 very little. However, on changing the azo ligand from azodibenzoyl (1 and 3) to azodiacetyl (4), we notice a shift of 15 nm to higher energy. This has also been noted by Campbell et al. in the related organic oxadiazine compound I.$^{31}$

Campbell et al. reported the C=O and C=N stretching frequencies as 1652 cm$^{-1}$ and 1635 cm$^{-1}$ respectively for Ia, and 1673 cm$^{-1}$ and 1660 cm$^{-1}$ respectively for Ib. A band maximum at ca. 290 nm ($\varepsilon = 19800$ dm$^3$ mol$^{-1}$ cm$^{-1}$) is reported for Ia and was assigned as the electronic transition in the Ph–(O)C=N chromophore.$^{31}$ They have noted that if R is an alkyl group in the R–(O)C=N chromophore then the band maximum shifts to around 240 nm. It would be tempting to make a direct comparison between the C=N electronic transition in the oxadiazines and the electronic transitions observed for the azodicarbonyl metallacycles investigated in this chapter. However, it should be realised that the metallacycles found in I and 5 are planar according to their crystal data, and the metal centre will also have a strong influence on any electronic transitions found in the azo ligand.

It is clear, however, that for the azodiacetyl complexes 1, 3 and 4 the N=N double bond character is very weak, and this has been shown from the crystal structure of 1.$^7$ The UV/VIS spectra of 1, 3-4 also provide evidence that the N=N double bond character is weak due to the absence of an electronic transition from the N=N bond. For instance the free azodibenzoyl ligand is reported to have a N=N transition at $\lambda_{\text{max}} = 474$ nm,$^{32}$ and azodicarboxylates were found in this study to contain band maxima at around 403 nm. In $\sigma$-bonded azo transition metal complexes, where the N=N double bond is thought to be retained, band maxima are reported to occur at around 400-500 nm. For instance, Fe(CO)$_4$L (L = cyclic azo) complexes have band maxima in the range of 430-480 nm and for W(CO)$_5$(azo) complexes their band maxima are reported to occur at around 391 nm.$^{4,33}$ This tends to suggest that the azodiacyl ligands are functioning less as azo groups due to the apparent lack of N=N double bond character, and the term
hydrazido, as originally used by Ittel and Ibers, would be a more accurate description of the ligand (Figure 2.18).

The azodicarboxylate complexes 2 and 5 appear to have a stronger N=N double bond compared to 1, 3 and 4, due to the presence of a band at around 460 nm which is associated with the N=N transition. Interestingly, the band at 330 nm, assigned for C=N transitions for oxadiazines, is much weaker for 2 and 5 compared to the azodiacyl complexes. Again it is tempting to draw parallels from this and suggest that the azodicarboxylate complexes retain more N=N double bond character than the azodiacyl complexes and that the C=N double bond character in 2 and 5 is weaker. Unfortunately, comparison between the C–N and N–N distances obtained from the crystal structures of Pt(PPh$_3$)$_2$(PhOCNNCOPh)$_7$ and Pt(PPh$_3$)$_2$(Pri$_2$CNNCO$_2$Pri)$^5$ proved inconclusive since the C–N and N–N distances are not statistically significant (Table 2.9).

![Figure 2.18](image)

**Figure 2.18** Representation of platinum(0) azodicarbonyl and platinum(II) hydrazido resonance forms.

Even though the azodicarboxylate complexes 2 and 5 might appear to have more N=N double character than the azodiacyl complexes 1, 3-4, both types of complex still lie to the right hand side of the resonance pair presented in Figure 2.18, with the azodiacyl complexes more so than the azodicarboxylate complexes.

### 2.3.3 The trans-influence of the metallacycle in 1-7

$^{31}$P {$_1^1$H} NMR data of the azodiacyl complexes 1-7 have shown that the $^1$J(PtP) coupling constant is strongly dependent on the atom trans to the phosphorus ligand in the metallacycle. This phenomenon is generally known as the "trans-influence" of the ligand and is sometimes in parallel to the "trans-effect". In summary, the trans-effect of a ligand describes a kinetic effect and is a partial description of the transition state in a substitution reaction, whereas the trans-influence of a ligand is defined as the extent to which that ligand weakens the bond trans to it in the equilibrium state, i.e. the ground state of the complex. It should also be noted that the trans-effect of a ligand may or may not be related to its trans-influence in the equilibrium state.
In a review by Appleton et al., the trans-influence was described as being affected by two major factors. The first is the effect of a ligand \( L \) on the hybrid orbitals used by the metal in its bond to the trans-ligand \( A \), and the second is the electronegativity of the ligand \( L \). In an early model by Syrkin, it was described that the metal ion in a square planar complex uses \( 5d_{x^2-y^2}, 6s, 6p_x \) and \( 6p_y \) hybrid orbitals (Figure 2.14). The \( s + d \) hybrid orbital was said to be more available since the orbital energies are \( 5d = 6s < 6p \). Therefore, if a ligand \( L \) forms a strong covalent \( L-M \) bond with the metal, the trans-ligand \( A \) will form a weaker \( A-M \) bond since both ligands \( L \) and \( A \) must share the same \( s + d \) hybrid orbital if they are trans to each other.

![Figure 2.14 Sykin's \( s \pm d \) hybrid orbitals.](image)

Early molecular orbital analysis performed by Zumdahl and Drago on \( \text{cis-[Pt(NH}_3)_2L_2]^{2+} \) \((L = \text{H}_2\text{O, NH}_3, \text{Cl}^-, \text{H}_2\text{S, PH}_3, \text{H}^-, \text{and CH}_3^-)\) showed that the trans-influence of \( L \) on the Pt–N bond increases in the following order; \( \text{H}_2\text{O} < \text{NH}_3 < \text{Cl}^- < \text{H}_2\text{S} < \text{PH}_3 < \text{H}^- < \text{CH}_3^- \). The weakening of the Pt–N bond trans to \( L \) was said to be mainly due to Pt(\( 6s \))-N and Pt(\( d_{x^2-y^2} \))-N interactions and not due to the decreased availability of Pt(\( 6p_x, 6p_y \)), in accordance with Syrkin’s model. More recent perturbation calculations by Shustorovich have also shown that \( d^8 \) square planar complexes use hybrid orbitals which have large contribution from the \( s \) and \( d_\sigma \) orbitals and relatively little from the \( p_\sigma \) orbitals.

Various experimental techniques have been employed to measure the trans-influence of a ligand, e.g., X-ray crystallography, infrared spectroscopy and NMR spectroscopy. The spin-spin coupling constant obtained from NMR experiments often gives a good indication of the \( s \)-component of the bond involved. The coupling constant \( ^1J(\text{XY}) \), where atoms \( X \) and \( Y \) are covalently bonded and both have spin quantum
numbers \( I = 1/2 \), is thought to be dominated by the Fermi contact term.\(^{43}\) This assumes that contributions to the coupling from interaction of the nuclear spin of the atom \( X \), or \( Y \), with the electronic orbital motion are negligible, and that the Fermi contact interaction at the nuclear spin and the \( s \)-electrons makes the dominant contribution. Equation 2.4 shows the approximate expression for the coupling constant \( ^1J(PtP) \).\(^{44}\)

\[
^1J(PtP) \propto \gamma_X \gamma_P \alpha_X^2 \alpha_P^2 |\psi_{P(6s)}(0)|^2 |\psi_{P(3s)}(0)|^2 (\Delta E)^{-1}
\]

\( \gamma_X \) = gyromagnetic ratio of the nucleus \( X \).
\( \alpha_X^2 \) = \( s \)-character of the hybrid bonding orbital used by \( X \) in the \( X-Y \) bond.
\( |\psi_{P(3s)}(0)|^2 \) = electron density of the \( ns \) valence orbital.
\( (\Delta E)^{-1} \) = average excitation energy.

Pidcock \textit{et al.} said that \((\Delta E)^{-1}, \alpha_P^2\) and \(|\psi_{P(3s)}(0)|^2\) would not vary very much in a related series of compounds. This would then leave \( \alpha_X^2 \) and \(|\psi_{P(6s)}(0)|^2\) as the factors which will vary the most.\(^{44}\) In the complex \textit{cis}-\textit{Pt(PEt}_{3}\textit{hMeCl}, \( ^1J(PtP) \text{ trans} \) to \( CH_3 \) is 1719 Hz, whereas \( ^1J(PtP) \text{ trans} \) to Cl is 4179 Hz.\(^{45}\) Since the term \(|\psi_{P(6s)}(0)|^2\) is common to both coupling constants, the remaining dominant variant is \( \alpha_P^2 \) which is related to the Pt–P bond, and implies that the \( CH_3 \) ligand has a higher \textit{trans}-influence than the chloride ligand.

Pidcock also suggested that \( \pi \)-backbonding does not play an important part in the \textit{trans}-influence of phosphines. It is well known that \textit{cis}-bis(phosphine) Pt(II) complexes have higher \( ^1J(PtP) \) values compared to their \textit{trans} counterpart.\(^{46}\) One explanation for this effect assumes that in \textit{trans}-bis(phosphine) Pt(II) complexes, the two phosphine ligands are competing for electrons in the same \( d_\sigma \)-orbital when \( \pi \)-backbonding, whereas in the \textit{cis}-complex the two phosphine ligands are not competing for the same \( d_\pi \)-orbital.\(^{47}\) Since \( \pi \)-backbonding is synergically linked with \( \sigma \)-bonding, any changes in \( \pi \)-backbonding will affect the \( \sigma \)-bond. Hence \textit{trans}-complexes will have a weaker phosphorus-platinum bond compared to the \textit{cis}-complexes, which is reflected in the \( ^1J(PtP) \) coupling constants. Pidcock \textit{et al.} threw doubts on this theory when they showed that \( ^1J(PtP)_{\text{cis}}/^1J(PtP)_{\text{trans}} \) for Pt(PBu\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} [Pt(II)] and Pt(PBu\textsubscript{3})\textsubscript{2}Cl\textsubscript{4} [Pt(IV)] are 1.47 and 1.41 respectively. Pidcock \textit{et al.} argued that \( \pi \)-backbonding should not be as dominant in Pt(IV), but the \( ^1J(PtP)_{\text{cis}}/^1J(PtP)_{\text{trans}} \) ratio for Pt(IV) is almost the same as Pt(II). This led to Pidcock \textit{et al.} to conclude that \( \sigma \)-inductive effects are responsible for the \textit{trans}-influence observed and not \( \pi \)-backbonding. In conclusion they said that phosphine has a higher \textit{trans}-influence than chloride due to the phosphine ligand being a stronger \( \sigma \)-donor. However, Hartley responded that the similarity of the \( ^1J(PtP)_{\text{cis}}/^1J(PtP)_{\text{trans}} \) ratio could arise from not only a decrease in \( \pi \)-backbonding in the Pt(II) case on going from the \textit{cis}- to \textit{trans}-isomer but also a decrease in \( \sigma \)-bonding as
well.\textsuperscript{46} Hence, the ratio of coupling constants of the \textit{cis}- and \textit{trans}-isomers would be very similar for both Pt(II) and Pt(IV) oxidation states. The decrease in \( \sigma \)-bonding in the Pt(IV) state on going from \textit{cis} to \textit{trans} should be similar to the decrease in \( \pi \)-backbonding and \( \sigma \)-bonding in the Pt(II) state. Hartley concluded that the oxidation state of the Pt atom does not necessarily indicate whether or not \( \pi \)-backbonding is present in the lower oxidation state of platinum phosphine complexes.

A more recent survey by Orpen and co-workers on numerous crystal structures of phosphine complexes has shown that metal \( \pi \)-backbonding remains an integral part of bonding interaction in metal phosphine complexes.\textsuperscript{48,49} They have shown that an increase in oxidation state of the metal results in the increase of the M–P metal phosphorus bond length, which is accompanied by the shortening of the P–A bond and an increase in the A–P–A bond angle in the PA\textsubscript{3} phosphine ligand. The shortening of the P–A bond resulting from the metal going to a higher oxidation state is consistent with a decrease of metal \( \pi \)-backbonding into the \( \sigma^* \)-orbital of the P–A bond and not the 3\textit{d} orbitals on phosphorus.\textsuperscript{50,51} The A–P–A bond angle was said to be influenced by the population of the phosphine’s LUMOs from metal \( \pi \)-backbonding.\textsuperscript{52} Population of the phosphine’s LUMOs was said to drive the phosphine to a pyramidal structure, therefore the LUMOs of the phosphine will not be populated for complexes in high oxidation state due to the lack of metal \( \pi \)-backbonding, hence the A–P–A bond angle will increase.

Allen and Sze obtained a \textit{trans}-influence series, combining results from a wide range of Pt(II) bis(phosphine) and bis(phosphite) complexes,\textsuperscript{53} and showed that \( ^1J(PtP) \) decreases in the following series: ONO\textsubscript{2}\textsuperscript{−} < I\textsuperscript{−}, Br\textsuperscript{−}, Cl\textsuperscript{−} < NCS\textsuperscript{−}, NCO\textsuperscript{−}, N\textsubscript{3}\textsuperscript{−}, pyridine < NHEt\textsubscript{2} < NH\textsubscript{2}Et < p-toluidine < NO\textsubscript{2}\textsuperscript{−} < AsEt\textsubscript{3} < CN\textsuperscript{−} < P(OPh\textsubscript{3}) < PP\textsubscript{3} < PMe\textsubscript{2}Ph < PBU\textsubscript{n} \textsubscript{3} < PET\textsubscript{3} < Me\textsuperscript{−} < Ph\textsuperscript{−} < SiMe\textsubscript{3}Ph. According to Allen and Sze, this order represents an increase in tendency for the ligands to concentrate Pt(6\textit{s}) character into their bonds with Pt(II).

From the \textit{trans}-influence series of Allen and Sze,\textsuperscript{53} we can see that oxygen donors have a weaker \textit{trans}-influence than nitrogen donors, \textit{i.e.} a phosphine \textit{trans} to oxygen will have a larger \( ^1J(PtP) \) value than a phosphine \textit{trans} to nitrogen. A similar trend is observed if we examine the \( ^1J(PtP) \) value for the Pt(II) square planar complex \textit{cis}-Pt(PET\textsubscript{3})\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsuperscript{54} and \textit{cis}-Pt(PET\textsubscript{3})\textsubscript{2}(PhN–N=N–NPh).\textsuperscript{55}
In cis-Pt(PEt₃)₂(C₂O₄) both phosphines are trans to the oxygen of the oxalate ligand and have a \( ^1J(\text{PtP}) \) value of 3522 Hz and in cis-Pt(PEt₃)₂(PhN-N=N-NPh) both phosphines are trans to nitrogen and have a \( ^1J(\text{PtP}) \) value of 3355 Hz, again demonstrating that nitrogen ligands have a higher trans-influence compared to oxygen ligands. We have assigned the phosphine ligands in complexes 1-7 on this basis.

The X-ray crystal structure of 5 also gives us an indication, but to a lesser extent, that the co-ordinated nitrogen atom in the metallacycle has a higher trans-influence than the co-ordinated oxygen atom. In Figure 2.13, the Pt-P₁ [2.266(2) Å] bond trans to O₁ in the metallacycle is slightly shortened compared to Pt-P₂ [2.278(2) Å] bond trans to N₁ but the difference is only 0.012 Å.

### 2.3.4 Photochemical reactions of azodicarbonyl metallacycles

Photolysis of complexes 1-5 in chlorinated solvents formed the corresponding cis-bis(phosphine) platinum dichloride. The photochemical process presumably occurs via a free radical mechanism, where the source of free radicals derives from the chlorinated solvent and/or the co-ordinated azodicarbonyl ligand. Evidence suggests that for complexes 1, 3 and 4, the source of free radicals is most likely from the chlorinated solvents since photolysis of complexes 1, 3 and 4 with trapping agents (ethene, diphenylacetylene) in benzene or THF did not yield any photoproducts. One possible mechanism could involve excitation of a complex-to-solvent charge transfer band to induce a photochemical reaction.⁵⁶ This is reported for several metallocene complexes where the appearance of a new complex-to-solvent charge transfer band was observed on dissolving the metallocene in halogenated solvent.⁵⁷,⁵⁸ For example, Traverso and Scandola have shown that Cp₂Fe undergoes photooxidation in chlorinated solvents RCl to yield \([\text{Cp}_2\text{Fe}]^+\), Cl⁻ and the radical \(R^*\) (Equation 2.5).⁵⁷

\[
\text{Cp}_2\text{Fe} + \text{RCl} \xrightarrow{\text{hv}} [\text{Cp}_2\text{Fe}]^+ + \text{Cl}^- + \text{R}^* \quad (2.5)
\]

However, this mechanism seems unlikely to be responsible for the photochemical reactions observed since no significant difference can be observed in the UV/VIS
spectra of 1-5 whether the solvent employed was THF or CHCl₃. An alternative mechanism which can create free radicals from the chlorinated solvents would involve homolytic bond cleavage of the azo ligand. In solvents such as THF, homolytic bond cleavage by photolysis of the azo ligand should lead to rapid reversible recombination due to the solvent cage effect (Scheme 2.2). However, in chlorinated solvents the newly cleaved bond in the azo ligand can react with a chlorine atom on the solvent molecule, thus forming the radical R·, which can initiate other free radical reactions (Scheme 2.3).

Scheme 2.2 Possible mechanism involving photoinduced homolytic bond cleavage of the azo ligand in PtL₂(ROCNCOR) in THF.
Complexes 2 and 5, however, proved to be much more active compared to their azodiacyl counterpart. This would suggest that the azodiacyl ligand is more photoresistant than the azodicarboxylate ligand. The most likely reason is that the azodicarboxylate ligand binds to platinum much more weakly than azodiacyl, as discussed in Section 2.3.1. The thermal reactivity of 2 and 5 with ethene and diphenylacetylene again demonstrates the lability of the azodicarboxylate ligand, since 1, 3 and 4 show no similar thermal activities. However, possible mechanisms for the thermal/photochemical reactions of 2 and 5 remain unclear.
2.4 Conclusion

This chapter reports simple synthetic routes to complexes Pt(PR$_3$)$_2$-(R$_2$OCNNCOR$_2$), containing the Pt–N–N–C–O metallacyclic unit. The structural evidence indicates that the metallacycle is a fully conjugated planar system. The role that the carbonyl group plays is an important factor in the co-ordination of this type of azo ligand, and it seems likely that if a carbonyl group is present next to the azo function, the metallacycle structure will always be preferred over other co-ordination modes. This should always apply unless the structure of the azo ligand is restricted to a cis only configuration, i.e. a cyclic azo compound. Here the carbonyl group would now find it harder to co-ordinate to the metal centre along with the nitrogen of the azo function due to steric constraints. The formation of a metallacycle complex with a cyclic azodicarbonyl complex would now appear to be improbable, and the co-ordination options now left would be either σ-bonding through the nitrogen atom(s) to form a σ-complex or π-bonding through the azo function to form an η$^2$-azo complex.

The azodicarbonyl ligand is readily displaced photochemically in chlorinated solvents. The azodicarboxylate ligand of 2 and 5 has also been replaced photochemically and thermally in THF and benzene, but the azodiacyl complexes 1, 3 and 4 proved photostable in these solvents.

2.5 References

3.1 INTRODUCTION

The hydrosilation reaction represents an important branch of chemistry in the silicone industry. Of the choice of transition metal catalysts, platinum catalysts are used the most often because they generally offer higher activity and larger catalytic turnovers compared to other transition metal catalysts.\textsuperscript{1,2,3} Due to the high activity of platinum catalysts, they are often inhibited to control hydrosilation. This is especially important when a pre-mixed composition of reactants and catalyst is required and initiation of hydrosilation is not desired until all the reactants are uniformly dispersed. For example, in the paper coating industry, a mixture of hydrosiloxane, vinylsiloxane and inhibited catalyst mixture is applied as a thin liquid film onto paper. The siloxane film solidifies, or cures, on \textit{in situ} activation of the latent catalyst.\textsuperscript{4} The latent catalyst can then be re-activated thermally, and/or photochemically (Scheme 3.1). Industrially, inhibited catalysts are generally thermally activated. Photoactivated catalysts, however, would offer a less energy intensive pathway for initialising hydrosilation. No photoactivated hydrosilation catalysts have yet been found suitable for commercial applications.

![Scheme 3.1 Inhibition of platinum hydrosilation catalysts.](image)

Heaton has previously reported that certain azo compounds can successfully inhibit the activity of Karstedt's catalyst, \([\text{[(Pt}^\eta-(\text{CH}_2=\text{CHSiMe}_2\text{O})_2\mu-(\text{CH}_2=\text{CHSiMe}_2\text{O})_2\text{]}]}\).\textsuperscript{8,5,6,7}
Azo inhibitors were identified by Heaton as a potential method of photoactivating the hydrosilation reaction. It was found that only azo compounds with a carbonyl group adjacent to the azo function were effective as inhibitors of 8. Unfortunately, characterisation of inhibited 8 with azodicarbonyl compounds revealed little structural features. $^1$H NMR spectroscopy data of the inhibition product showed that the co-ordinated azodicarboxylate inhibitor, RO$_2$CNNCO$_2$R, contains equivalent R groups, which would initially suggest that the inhibitor is co-ordinating to platinum in an $\eta^2$ fashion via the azo's N=N group. However, reported co-ordination behaviour of several complexes containing an azo ligand with a carbonyl group adjacent to the azo function suggested otherwise. In these azodicarbonyl complexes it was found that the azo ligand co-ordinates to the metal centre via the nitrogen of the azo function and the oxygen of the carbonyl group, thus forming a Pt–N–N–C–O metallacycle, e.g. Pt(PPh$_3$)$_2$(PhOCNNCOPh) 1. Based on these findings, Heaton proposed a polymeric structure for the inhibition product, whereby the azo ligand forms a Pt–N–N–C–O metallacycle and acts as a bridging ligand, rendering all the R groups on the azo ligand equivalent (Figure 3.1).
Figure 3.1 The top figure shows the proposed structure for azodicarbonyl inhibited 8. The bottom figure shows possible delocalisation of electron density in the azo ligand (adapted from ref. 7).

It was found that excess azodicarbonyl inhibitor is needed to prevent 8 from initiating hydrosilation. Activation of azo-inhibited 8 was reported to occur by heating or photolysis. In Heaton’s previous investigation only the azo inhibitor PrO₂CNNCO₂Pr was examined in detail and no comparison between different azo inhibitors was made. Also work done on model platinum phosphine complexes Pt(PPh₃)₂(EtO₂CNNCO₂Et) 2 and Pt(PPh₃)₂(PrO₂CNNCO₂Pr) 5 has now shown them to be thermally and photochemically sensitive towards chlorinated solvents. This could have possible implications on the reported characterisation of azo-inhibited 8 which was carried out by Heaton in chlorinated solvent systems. In this chapter, further studies on azo-inhibited 8 are presented in non-chlorinated solvent systems, with the azo inhibitor
under investigation being ROCNNCOR (R = OEt, OPr and OBut). The effect of changing the substituent R on the azo inhibitor will also be discussed.

3.2 RESULTS

3.2.1 Preparation of [(Pt\{η^4-(CH_2=CHSiMe_2)_2O}\)\_2(μ-(CH_2=CHSiMe_2)_2O)] 8

The platinum divinylsiloxane compound 8 was prepared by the method reported by Lappert and co-workers, with minor modifications.\(^{10}\) Hexachloroplatinic acid, H_2PtCl_6, and excess tetramethyldivinyldisiloxane, (H_2C=CHSiMe_2)O, were refluxed, with added water, under a nitrogen atmosphere. Alternatively, the complex PtCl_2(η^2-CH_2=CHPh)_2 suspended in toluene can be used in place of H_2PtCl_6. A slightly yellow oil was obtained after the refluxed mixture was neutralised with NaHCO_3 (Equation 3.1). The crude product obtained displays NMR features corresponding to those reported for [(Pt\{η^4-(CH_2=CH-SiMe_2)_2O\)\_2(μ-(CH_2=CHSiMe_2)_2O)] 8 (Table 3.1).\(^{6}\)

\[
\begin{align*}
H_2PtCl_6 + (CH_2=CHSiMe_2)_2O & \rightarrow [Pt(\eta^4-(CH_2=CHSiMe_2)_2O)_2(\mu-(CH_2=CHSiMe_2)_2O)] \\
\text{or } PtCl_2(\eta^2-CH_2=CHPh)_2 & + Me_2RSiO(SiMe_2O)_xSiRMe_2
\end{align*}
\]

Resonances were found to be present at ca. δ_{Si} -21 in the ^{29}Si {^1H} NMR spectrum of 8 which is indicative of oligomeric siloxane materials, Me_2RSiO(SiMe_2O)_xSiRMe_2 [R = (CH=CH_2), CH_2CH_3, CH_2CH_2Cl; x = 0-14].\(^{5}\) The presence of oligomeric materials has also been reported by Lappert and co-workers from GC/MS analysis.\(^{10}\) The ^{29}Si NMR signals due to unreacted (CH_2=CHSiMe_2)_2O were also detected at δ_{Si} -3.2. The majority of the impurities found in 8 can be removed by flash chromatography. An unidentified impurity can be detected sometimes at δ_{Si} -4.2.

A yield of 74 % for the synthesis of 8 was determined by its quantitative ^{29}Si {^1H} NMR spectrum using an inverse gated pulse sequence.

Complex 8 was found to be thermally, photochemically and aerobically unstable as an oil or in solution, tending to turn from yellow to dark brown in colour when left at room temperature. The change to a darker colour is normally indicative of colloidal platinum formation.\(^{11,12}\)

In the ^{29}Si {^1H} NMR spectrum of 8, three resonances are present at δ 3.24, 2.41 and -0.55. The signals at δ 3.24 and δ 2.41 are from the chelating (CH_2=CHSiMe_2)_2O ligands and a broad signal at δ -0.55 are from the bridging (CH_2=CHSiMe_2)_2O ligand (Figure 3.2). The ^{195}Pt {^1H} NMR spectrum of 8 showed two singlets with a separation of 50 Hz between them. The signals observed in the ^{29}Si {^1H} NMR spectrum of 8 correspond to those reported by Lappert and co-workers, except that we did not observe the second signal for the bridging (CH_2=CHSiMe_2)_2O ligand (Tables 3.1 and 3.2).
Table 3.1 NMR data of 8 in C₆D₆ at 295 K. $^{29}$Si observed at 59.63 MHz and $^{195}$Pt observed at 85.28 MHz. a Signal contains two singlets with a separation of ca. 50 Hz.

<table>
<thead>
<tr>
<th>$^{29}$Si $^1$H, δ (J / Hz)</th>
<th>$^{195}$Pt $^1$H, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.24 [2Si, s, $\eta^4$-(CH₂=CHSiMe₂)O, J(PtSi) = 42.9]</td>
<td>$-6143^a$</td>
</tr>
<tr>
<td>2.41 [2Si, s, $\eta^4$-(CH₂=CHSiMe₂)O, J(PtSi) = 42.9]</td>
<td>-</td>
</tr>
<tr>
<td>-0.55 [2Si, br., $\mu$-(CH₂=CHSiMe₂)O]</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.2 NMR data of 8 in $[^2]$H₈ toluene reported by Lappert and co-workers. a Signal contains two singlets with ca. 20 Hz separation.

<table>
<thead>
<tr>
<th>$^{29}$Si $^1$H, δ (J / Hz)</th>
<th>$^{195}$Pt $^1$H, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.45 [2Si, s, $\eta^4$-(CH₂=CHSiMe₂)O, J(PtSi) = 42.9]</td>
<td>$-6151^a$</td>
</tr>
<tr>
<td>2.63 [2Si, s, $\eta^4$-(CH₂=CHSiMe₂)O, J(PtSi) = 42.9]</td>
<td>-</td>
</tr>
<tr>
<td>0.18 [2Si, br., $\mu$-(CH₂=CHSiMe₂)O]</td>
<td>-</td>
</tr>
<tr>
<td>0.17 [2Si, br., $\mu$-(CH₂=CHSiMe₂)O]</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.2 $^{29}$Si (59.63 MHz) $^1$H NMR spectrum of complex 8 in C₆D₆ at 295 K. a Chelating (CH₂=CHSiMe₂)O ligand. b Bridging (CH₂=CHSiMe₂)O ligand. c Oligomeric impurities.

The appearance of two $^{29}$Si signals for the bridging ligand and two $^{29}$Si signals for the two chelating ligands was, according to Lappert and co-workers, due to the conformation of the bridging ligand in 8. In the crystal structure of 8, it was found that
both the chelating ligands adopt the “chair” conformation, whereas the bridging ligand adopts a “V” conformation (Figure 3.3).

![Figure 3.3 A drawing of 8 representing the crystal structure reported by Lappert and co-workers. Both chelating (CH₂=CHSiMe₂)₂O ligands adopt the “chair” conformation.](image)

Lappert and co-workers assumed that in solution both chelating ligands would adopt the “chair” conformation, as was the case in the crystal structure of 8. The silicon atoms in the chelating (CH₂=CHSiMe₂)₂O ligand are inequivalent if 8 is stereochemically rigid. However, it was suggested that rapid rotation occurs about the vinyl bond in the bridging (CH₂=CHSiMe₂)₂O ligand at room temperature, hence the silicon atoms in the chelate ligand would now become equivalent. It was also suggested that the bridging (CH₂=CHSiMe₂)₂O ligand can adopt either the “V” or the “chair” conformation. In the “V” conformation, the α-carbons on the two vinyl groups (α-carbon is next to silicon) are either (R,R) or (S,S) giving one isomer, (rac) (Figure 3.4). In the “chair” conformation, the α-carbons on the bridging ligand are either (R,S) or (S,R) giving another isomer, (meso). This then would leave us with two possible isomers (R,R)/(S,S) (rac) or (R,S) (meso), which was suggested to be responsible for the four signals observed in the ²⁹Si {¹H} NMR spectrum and two signals in the ¹⁹⁵Pt {¹H} NMR spectra of 8.
AZO-INHIBITED HYDROSILATION CATALYSTS

Figure 3.4 Possible conformation of the bridging (CH₂=CHSiMe₂)₂O ligand in 8. The (S,S) and (R,R) isomers adopts the “V” conformation, whereas the (R,S) isomer adopts the “chair” conformation. The two chelating (CH₂=CHSiMe₂)₂O ligands are omitted for clarity.

3.2.2 Inhibition of [(Pt{η⁴-(CH₂=CH-SiMe₂)₂O})₂(μ-(CH₂=CHSiMe₂)₂O)] 8

Heaton has previously shown that azodicarbonyl compounds can act successfully as inhibitors of 8.⁷ His results from model hydrosilation systems have shown that azodicarbonyl-inhibited 8 does not initiate hydrosilation until it is thermally or photochemically activated. In this study, azodicarboxylates, RO₂CNNCO₂R (R = Et, Pr⁴Bu¹), are studied further as inhibitors of 8.

3.2.2a Characterisation of azodicarboxylate inhibited 8

A two fold excess of azodicarboxylate compound was added to 8 in toluene, then purified by flash chromatography to remove excess vinylsiloxane and azo inhibitors, to yield a light brown solid (Equation 3.2).

\[
\text{8} + (\text{RO}_2\text{CNNCO}_2\text{R}) \rightarrow \text{Pt}_y(\text{RO}_2\text{CNNCO}_2\text{R})_y
\]

R = Et (9); Pr⁴ (10); Bu¹ (11)  \hspace{1cm} (3.2)

¹H NMR spectra of 9 and 10 indicate the presence of only one set of resonances associated with the R group of the azodicarboxylate inhibitor (Figures 3.5-3.6 and Table 3.3). Compound 11 showed several unidentified features in the ¹H NMR spectrum.
which were not found in either 9 and 10 (Figure 3.7). Table 3.4 summarises the \(^1\)H NMR data for the free azo inhibitors, RO\(_2\)CNNCO\(_2\)R (R = Et, Pri, Bu). 

The \(^1\)H ethyl resonances in 9 were broad at room temperature, but sharpen at elevated temperature (Figure 3.5). This is also observed for the \(^1\)H isopropyl resonances in 10 (Figure 3.6). This is indicative of a fluxional exchange process. The \(^{29}\)Si \(^1\)H NMR spectra of 9-11 did not show any signals due to chelating or bridging (CH\(_2\)=CHSiMe\(_2\)-O ligands, demonstrating that RO\(_2\)CNNCO\(_2\)R displaces both the bridging and chelating divinylsiloxane ligand (CH\(_2\)=CHSiMe\(_2\)-O. Attempts to obtain \(^{195}\)Pt \(^1\)H spectra were unsuccessful.

\(^{29}\)Si \(^1\)H NMR spectra of 8 in Figure 3.8 show that by increasing the concentration of EtO\(_2\)CNNCO\(_2\)Et in an NMR sample of 8, the intensity of the signals corresponding to the two chelating (CH\(_2\)=SiMe\(_2\)-O ligands and the one bridging (CH\(_2\)=CHSiMe\(_2\)-O ligand decreases and the intensity of the signal due to free (CH\(_2\)=CHSiMe\(_2\)-O increases.

<table>
<thead>
<tr>
<th>Ra</th>
<th>(^1)H, (\delta) (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Et 0.87 [3H, br. t, CH(_3)CH(_2), J(HH) = 7.4]</td>
</tr>
<tr>
<td></td>
<td>3.89 [2H, br. quart, CH(_3)CH(_2), J(HH) = 7.4]</td>
</tr>
<tr>
<td>10(b)</td>
<td>Pri(^i) 0.97 [6H, br. d, (CH(_3))(_2)CH, J(HH) = 6.1]</td>
</tr>
<tr>
<td></td>
<td>4.87 [1H, br. sept, (CH(_3))(_2)CH, J(HH) = 6.1]</td>
</tr>
<tr>
<td>11</td>
<td>Bu(^i) 0.87 (br. t)</td>
</tr>
<tr>
<td></td>
<td>1.22 (br.)</td>
</tr>
<tr>
<td></td>
<td>1.33 (br.)</td>
</tr>
</tbody>
</table>

Table 3.3 \(^1\)H (399.65 MHz) NMR data for 9-11 in C\(_6\)D\(_6\) at 295 K. a R is the alkyl group on the azodicarboxylate ligand, RO\(_2\)CNNCO\(_2\)R. b Values reported by Heaton occur at \(\delta\) 1.30 [d, (CH\(_3\))\(_2\)CH, J(HH) = 6.0 Hz], \(\delta\) 4.90 [sept, (CH\(_3\))\(_2\)CH, J(HH) = 6.0 Hz] recorded in CDCl\(_3\) at 293 K.\(^7\)

<table>
<thead>
<tr>
<th>(^1)H, (\delta) (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO(_2)CNNCO(_2)Et 0.85 [3H, t, CH(_3)CH(_2), J(HH) = 7.0]</td>
</tr>
<tr>
<td>3.92 [2H, quart, CH(_3)CH(_2), J(HH) = 7.0]</td>
</tr>
<tr>
<td>Pr(^i)O(_2)CNNCO(_2)Pr(^i) 1.01 [6H, d, (CH(_3))(_2)CH, J(HH) = 7.0]</td>
</tr>
<tr>
<td>4.91 [1H, sept, (CH(_3))(_2)CH, J(HH) = 7.0]</td>
</tr>
<tr>
<td>Bu(^i)O(_2)CNNCO(_2)Bu(^i) 1.23 (s)</td>
</tr>
</tbody>
</table>

Table 3.4 \(^1\)H (399.65 MHz) NMR data for RO\(_2\)CNNCO\(_2\)R (R = Et, Pri, Bu) in C\(_6\)D\(_6\) at 295 K.
At room temperature

Figure 3.5 $^1$H (399.65 MHz) NMR spectra of 9 in C$_6$D$_6$. 

at 55 °C
At room temperature

at 55 °C

Figure 3.6 $^1$H (399.65 MHz) NMR spectra of 10 in C$_6$D$_6$. 
Figure 3.7 $^1$H (399.65 MHz) NMR spectra of 11 in C$_6$D$_6$. 

free ligand
Figure 3.8 $^{29}\text{Si}$ (79.30 MHz) $^{1}\text{H}$ NMR spectra of 8 in C$_6$D$_6$ at 295 K with increasing concentration of EtO$_2$CNNCO$_2$Et. (i) 0 %. (ii) 30 %. (iii) 60 %. (iv) 90 %.
The UV/VIS spectra of 9 and 10 in THF show a shoulder band at ca. 312 nm (Figure 3.9). However, for 11 the shoulder in this region was very weak compared to 9 and 10, a slight band probably exists at ca. 307 nm. The values of 312 nm for the shoulder band of 9 and 10 are slightly lower in energy than for the values reported by Heaton, ca. 305 nm, which was recorded in CH$_2$Cl$_2$. No such band exists for the uninhibited complex 8. The UV/VIS spectra of the free azo inhibitor, RO$_2$CNNCO$_2$R (R = Et, Pri and Bu) all show band maxima at ca. 403 nm.

![Figure 3.9 UV/VIS spectrum of 9 in THF.](image)

IR spectra of compounds 9-11 were measured in THF, broad bands were detected for all three compounds at ca. 1750 cm$^{-1}$ and were assigned as a mixture of CO/CN stretches (Table 3.5 and Figures 3.10-3.12). Compound 11 contains an additional band at 1778 cm$^{-1}$, which roughly corresponds to that of the free azodicarboxylate inhibitor. Bu'O$_2$CNNCO$_2$Bu$^l$.

<table>
<thead>
<tr>
<th></th>
<th>$\nu$(CO/CN) / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1737</td>
</tr>
<tr>
<td>10</td>
<td>1734</td>
</tr>
<tr>
<td>11</td>
<td>1730, 1778</td>
</tr>
<tr>
<td>EtO$_2$CNNCO$_2$Et</td>
<td>1782$^a$</td>
</tr>
<tr>
<td>PriO$_2$CNNCO$_2$Pri$^l$</td>
<td>1778$^a$</td>
</tr>
<tr>
<td>Bu'O$_2$CNNCO$_2$Bu$^l$</td>
<td>1775$^a$</td>
</tr>
</tbody>
</table>

Table 3.5 IR data of $\nu$(CO/CN) stretches for 9-10. $^a$ stretching frequencies reported for free azo inhibitor RO$_2$CNNCO$_2$R (R = Et, Pri, Bu$^l$) are for $\nu$(CO) stretches only.
Figure 3.10 IR spectrum of 9 in THF. The spectrum of the free azo inhibitor EtO₂CNNCO₂Et is superimposed on top.

Figure 3.11 IR spectrum of 10 in THF. The spectrum of the free azo inhibitor PrO₂CNNCO₂Pr¹ is superimposed on top.
Figure 3.12 IR spectrum of 11 in THF. The spectrum of the free azo inhibitor Bu'O₂CNNCO₂Bu is superimposed on top.

3.2.2b Photolysis of compounds 9-11 in THF

Compounds 9-10 were dissolved in THF and photolysed with UV radiation and monitored by UV/VIS spectroscopy. The absorbance at 312 nm, the region of the shoulder in the spectra of 9-10, was observed to decrease with increasing photolysis time (Table 3.6 and Figures 3.13-3.14).

<table>
<thead>
<tr>
<th>Photolysis time</th>
<th>9 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>10 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>11 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>88.2</td>
<td>84.0</td>
<td>94.3</td>
</tr>
<tr>
<td>2</td>
<td>80.6</td>
<td>68.4</td>
<td>88.4</td>
</tr>
<tr>
<td>3</td>
<td>72.0</td>
<td>60.9</td>
<td>80.3</td>
</tr>
<tr>
<td>4</td>
<td>67.0</td>
<td>58.1</td>
<td>75.7</td>
</tr>
<tr>
<td>5</td>
<td>61.9</td>
<td></td>
<td>72.5</td>
</tr>
<tr>
<td>6</td>
<td>58.9</td>
<td></td>
<td>70.2</td>
</tr>
</tbody>
</table>

Table 3.6 Data showing the percentage (%) of absorbance at 312 nm for 9-10 with increasing photolysis time. <sup>a</sup> Percentage of absorbance is related to absorbance before photolysis.
Figure 3.13 UV/VIS spectra of 9 after various photolysis times.

Figure 3.14 Plot showing the decrease in percentage of absorbance at 312 nm for compound 9-10 with increasing photolysis time. $a$ Percentage of absorbance is related to the original absorbance value before photolysis.
The plots for the decrease in absorbance at 312 nm show that 10 requires the least irradiation time to reach 60% of its original value, this is then followed by 9 (Figure 3.14). However, 11 did not follow the same trend as 9 and 10, as its absorbance value at 312 nm tended towards a higher percentage of its original value from the others. This could be due to the difficulty in observing a prominent band for 11 near the 312 nm region, so a fair comparison of 11 with 9 and 10 might not be valid.

3.2.3 Hydrosilation using azo-inhibited 8

3.2.3a Model hydrosilation system

The model hydrosilation system employed consisted of an equal molar amount of 1-octene and 1,1,1,3,5,5,5-heptamethyltrisiloxane. Addition of 8 to the model hydrosilation system causes instantaneous reaction between the silane and the alkene. A ratio of 1:1x10^{-5} of Si-H to Pt was used in the model hydrosilation system. GC analysis showed that the major product formed was due to hydrosilation (ca. 90%) and the minor products were from hydrogenation and silation (Scheme 3.2).

Heaton reported that addition of mercury to a mixture of siloxane and alkene containing the azodicarbonyl inhibited 8 did not inhibit hydrosilation upon thermal activation. This result indicated that the species formed on thermal activation gave a homogeneous hydrosilation catalyst. However, Lewis and co-workers have reported that 8 itself forms platinum colloids during hydrosilation and that it is affected by the presence of mercury.
Scheme 3.2 Reaction of 1-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane catalysed by complex 8.

3.2.3b Photoactivation of azo-inhibited 8 in a model hydrosilation system

Complex 8 was inhibited with a 40 fold excess of the azo compound RO₂CNNCO₂R (R = Et, Pr, Bu) in 1-octene to form the azo-inhibited species 9a (R = Et), 10a (R = Pr) and 11a (R = Bu). Addition of 1,1,1,3,5,5,5-heptamethyltrisiloxane did not initiate the hydrosilation reaction, as shown by the GC analysis of the reaction mixture. However, compounds 9-10, purified by flash chromatography to remove excess azo, did initiate hydrosilation between 1-octene and 1,1,1,3,5,5,5-heptamethyltrilsiloxane. This observation is in agreement with Heaton's previous investigation of
azo-inhibited 8. Heaton found that up to 40 fold excess of azo to Pt was required to prevent hydrosilation.\(^7\)

Figure 3.15 shows the experimental set-up for the model hydrosilation studied using inhibited catalysts 9a, 10a and 11a. Two identical samples containing the reaction mixture of alkene, silane and the inhibited catalyst 9a, 10a or 11a were photolysed; one of the samples was shielded from light to observe thermal effects. Photolysis time of the samples varied from one to five minutes. At the end of photolysis the samples were analysed by GC to monitor for signs of hydrosilation over time.

![Photolysis set-up](image)

**Figure 3.15** Photolysis set-up for the photoactivation of inhibited catalysts 9a-11a in a model hydrosilation system.

It was found that the model hydrosilation system using the inhibited catalyst 9a and 10a required the longest photolysis time before hydrosilation was initiated, whereas for 11a hydrosilation began only after 1 min of photolysis (Tables 3.7-3.13 and Figures 3.16 and 3.17).
### Table 3.7

Percentage of hydrosilation product formed after 2 min photolysis on the model hydrosilation system with azo-inhibited catalyst 9a. Amount of hydrosilation product generated from the control sample is 4 %. *a* Time starts at the end of photolysis.

<table>
<thead>
<tr>
<th>Time / min&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Hydrosilation Product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2</td>
</tr>
<tr>
<td>11.0</td>
<td>3</td>
</tr>
<tr>
<td>29.8</td>
<td>3</td>
</tr>
<tr>
<td>42.5</td>
<td>3</td>
</tr>
<tr>
<td>65.3</td>
<td>4</td>
</tr>
</tbody>
</table>

### Table 3.8

Percentage of hydrosilation product formed after 5 min photolysis on the model hydrosilation system with azo-inhibited catalyst 9a. Amount of hydrosilation product generated from control sample is 4 %. *a* Time starts at the end of photolysis.

<table>
<thead>
<tr>
<th>Time / min&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Hydrosilation product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>13</td>
</tr>
<tr>
<td>12.7</td>
<td>16</td>
</tr>
<tr>
<td>23.0</td>
<td>26</td>
</tr>
<tr>
<td>36.0</td>
<td>45</td>
</tr>
<tr>
<td>50.0</td>
<td>69</td>
</tr>
<tr>
<td>78.3</td>
<td>76</td>
</tr>
<tr>
<td>89.0</td>
<td>78</td>
</tr>
<tr>
<td>98.5</td>
<td>81</td>
</tr>
</tbody>
</table>

### Table 3.9

Percentage of hydrosilation product formed after 2 min photolysis on the model hydrosilation system with azo-inhibited catalyst 10a. Amount of hydrosilation product generated from control sample is 2 %. *a* Time starts at the end of photolysis.

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Hydrosilation product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2</td>
</tr>
<tr>
<td>8.9</td>
<td>5</td>
</tr>
<tr>
<td>18.7</td>
<td>5</td>
</tr>
<tr>
<td>27.5</td>
<td>5</td>
</tr>
<tr>
<td>36.5</td>
<td>8</td>
</tr>
<tr>
<td>45.6</td>
<td>3</td>
</tr>
<tr>
<td>55.0</td>
<td>4</td>
</tr>
<tr>
<td>Time / min</td>
<td>Hydrosilation product / %</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>0.0</td>
<td>8</td>
</tr>
<tr>
<td>10.3</td>
<td>58</td>
</tr>
<tr>
<td>32.2</td>
<td>80</td>
</tr>
<tr>
<td>52.0</td>
<td>90</td>
</tr>
</tbody>
</table>

**Table 3.10** Percentage of hydrosilation product formed after 5 min photolysis on the model hydrosilation system with azo-inhibited catalyst 10a. Amount of hydrosilation product generated from controlled sample is 2 %.

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Hydrosilation product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5</td>
</tr>
<tr>
<td>8.6</td>
<td>12</td>
</tr>
<tr>
<td>17.8</td>
<td>16</td>
</tr>
<tr>
<td>37.8</td>
<td>34</td>
</tr>
<tr>
<td>50.7</td>
<td>51</td>
</tr>
<tr>
<td>68.2</td>
<td>67</td>
</tr>
<tr>
<td>90.0</td>
<td>71</td>
</tr>
</tbody>
</table>

**Table 3.11** Percentage of hydrosilation product formed after 1 min photolysis on the model hydrosilation system with azo-inhibited catalyst 11a. Amount of hydrosilation product generated from control sample is 4 %.

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Hydrosilation product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>12</td>
</tr>
<tr>
<td>9.5</td>
<td>60</td>
</tr>
<tr>
<td>19.0</td>
<td>82</td>
</tr>
<tr>
<td>20.3</td>
<td>86</td>
</tr>
<tr>
<td>44.3</td>
<td>90</td>
</tr>
</tbody>
</table>

**Table 3.12** Percentage of hydrosilation product formed after 2 min photolysis on the model hydrosilation system with azo-inhibited catalyst 11a. Amount of hydrosilation product generated from control sample is 10 %.
Table 3.13 Percentage of hydrosilation product formed after 5 min photolysis on the model hydrosilation system with azo-inhibited catalyst 11a. Amount of hydrosilation product from control sample is 15 %.

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Hydrosilation product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>20.0</td>
</tr>
<tr>
<td>9.0</td>
<td>84.4</td>
</tr>
<tr>
<td>18.4</td>
<td>90.8</td>
</tr>
<tr>
<td>36.5</td>
<td>91.1</td>
</tr>
</tbody>
</table>

Figure 3.16 Plots of amount of hydrosilation product formed with respect to time after 2 min photolysis on the model hydrosilation system using the inhibited catalysts 9a, 10a or 11a. Amount of hydrosilation product generated from the control sample; 9a (4 %), 10a (2 %), 11a (10 %).
Figure 3.17 Plots of amount of hydrosilation product formed with respect to time after 5 min photolysis on the model hydrosilation system using the inhibited catalysts 9a, 10a or 11a. Amount of hydrosilation product generated from the control sample: 9a (4 %), 10a (2 %), 11a (10 %).

Figure 3.18 shows that as the photolysis time for activating azo-inhibited 8 increases, so does the rate of hydrosilation between 1-octene and 1,1,1,3,5,5,5-heptamethyl-trisiloxane. For systems using 9a and 10a as catalyst there is relatively little variation in the amount of hydrosilation product formed from the control sample (2-4 %), whereas for systems using 11a as catalysts the amount of hydrosilation product formed is comparatively higher and was found to increase with increasing photolysis time.

This indicates that 11a is thermally and photochemically more labile compared to 9a and 10a, which suggests that azo inhibitor Bu'\text{O}_2\text{CNNCO}_2\text{Bu}' in 11a is a weaker inhibitor compared to EtO_2\text{CNNCO}_2\text{Et} (9a) and Pr'\text{O}_2\text{CNNCO}_2\text{Pr}' (10a). From Figure 3.15, it appears that EtO_2\text{CNNCO}_2\text{Et} is the most effective, and Bu'\text{O}_2\text{CNNCO}_2\text{Bu}' is the least effective azo inhibitor.
Figure 3.18 Plots of amount of hydrosilation product formed with respect to time after various photolysis time on the model hydrosilation system with inhibited catalyst 11a. Amount of hydrosilation product generated from controlled samples; after 1 min photolysis (4 %), after 2 min photolysis (10 %) and after 5 min photolysis (15 %).

3.3 DISCUSSIONS

3.3.1 Preparation of \([(\text{Pt}\{\eta^4-(\text{CH}_2=\text{CHSiMe}_2\text{O})\}_2)(\mu-(\text{CH}_2=\text{CHSiMe}_2\text{O}))]\) 8

The reaction between \(\text{H}_2\text{PtCl}_6\) or \(\text{PtCl}_2(\eta^2-\text{CH}_2=\text{CHPh})_2\) with (CH\(_2\)=CHSiMe\(_2\)O) produces the highly active Karstedt's catalyst.\(^5\) The active component of Karstedt’s catalyst has been shown to be the tris-tetramethyldivinyldisiloxane platinum(0) complex \([(\text{Pt}\{\eta^4-(\text{CH}_2=\text{CHSiMe}_2\text{O})\}_2)(\mu-(\text{CH}_2=\text{CHSiMe}_2\text{O}))]\) 8.\(^6\) The reduction of \(\text{H}_2\text{PtCl}_6\), a Pt(IV) species, to complex 8, a Pt(0) species, by (CH\(_2\)=CHSiMe\(_2\)O) was examined by Lappert using a Pt(II) model.\(^16\) It was reported that \(\text{PtCl}_2(\eta^2-\text{CH}_2=\text{CHPh})_2\) was reduced by (CH\(_2\)=CHSiMe\(_2\)) \(2\) to form \(\text{Pt}[\eta^4-(\text{CH}_2=\text{CHSiMe}_2\text{O})](\eta^2\text{-styrene})\). The vinyl group in (CH\(_2\)=CHSiMe\(_2\)O) was thought to undergo substitution with a chloride ligand on PtCl\(_2(\eta^2-\text{CH}_2=\text{CHPh})_2\) to form chlorosilane, leading to the reduction of Pt(II) to Pt(0) (Scheme 3.3). A similar process is believed to occur between \(\text{H}_2\text{PtCl}_6\) and (CH\(_2\)=CHSiMe\(_2\)O).\(^16\)
The oligomeric siloxane impurities $\text{Me}_2\text{RSiO(SiMe}_2\text{O)}_x\text{SiRMe}_2$ [$R = (\text{CH}=\text{CH}_2)$, $\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{CH}_2\text{Cl}$; $x = 0-14$] are believed to be formed from the chlorosilanes produced on reduction of $\text{H}_2\text{PtCl}_6$ by $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$.\textsuperscript{17} The chlorosilanes formed are believed to react with water present in the system to form silanols. The silanols in turn couple with any chlorosilane to form the siloxane oligomer (Scheme 3.4).
As discussed in Section 3.2.1, the \((\text{CH}_2=\text{CHSiMe}_2)\text{O}\) ligands in the crystal structure of complex 8 were found by Lappert and co-workers to adopt the "chair" conformation for both the chelating ligands, whilst the bridging ligand adopts a "V" shape conformation.\(^6\) It was briefly mentioned by Lappert that NMR spectra of complex 8 exhibited fluxional behaviour in solution, but unfortunately no further details were given.\(^6\) The chelated ligands of 8 in solution were assumed to adopt the same type of conformation as in the solid state, \textit{i.e.} the "chair" conformation. One possible fluxional process would involve a "flipping" motion of the chelating \((\text{CH}_2=\text{CHSiMe}_2)\text{O}\) chair conformer, which was observed with NMR spectroscopy by Bassindale \textit{et al.} for the related complex \(\text{Pt}[(\eta^2-\text{CH}_2=\text{CHSiMe}_2)\text{O}]\text{(PBu}_3^\text{t})\) (Scheme 3.5).\(^18\)

\[\text{Scheme 3.4} \text{ Formation of oligomeric siloxane impurity from the preparation of 8 (adapted from ref. 5).}\]

\[\text{Scheme 3.5} \text{ Fluxional process of } \text{Pt}[(\eta^2-\text{CH}_2=\text{CHSiMe}_2)\text{O}]\text{(PBu}_3^\text{t})].\(^18\)
dissociation-reassociation mechanism (Scheme 3.6). Both mechanisms would maintain Pt–C and P–C coupling despite the fact that the second mechanism is dissociative. This is because bonding is always maintained on at least one end of the chelate ligand.19

Scheme 3.6 Proposed mechanism for the “flipping” motion of the chelate ligand in Pt[η2-(CH2=CHSiMe2)2O](PBut3). (a) nondissociative mechanism. (b) dissociative mechanism.

3.3.2 Inhibition of [(Pt{η4-(CH2=CHSiMe2)2O})2(μ-(CH2=CHSiMe2)2O)] 8

Present work on the catalytic inhibition of 8 with azodicarbonyl compounds supports the finding reported previously by Heaton that the azodicarbonyl inhibitor appears to displace completely both the bridging and chelating (CH2=CHSiMe2)2O ligands in 8.5 This is unlike other inhibitors of 8, whereby only the bridging (CH2=CHSiMe2)2O ligand was found to be displaced. For example, investigations on fumarates and maleates, known inhibitors of 8, have shown that the bridging
divinylsiloxane ligand in 8 is replaced by the inhibitor ligands whilst the chelating divinylsiloxane ligand is retained.\textsuperscript{5,20,21}

Further examples of the lability of the bridging (CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O ligand in 8 are reported by Lappert and co-workers.\textsuperscript{22} They have shown that the bridging (CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O ligand can be displaced by a variety of alkene ligands. For instance, treatment of 8 with maleic anhydride, styrene and excess (CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O ligands yields Pt[\eta\textsuperscript{4}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O][\eta\textsuperscript{2}-CHC(O)OC(O)CH],\textsuperscript{5} Pt[\eta\textsuperscript{4}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O]- (\eta\textsuperscript{2}-styrene),\textsuperscript{16} and Pt[\eta\textsuperscript{4}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O][\eta\textsuperscript{2}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})-OSiMe\textsubscript{2}CH=CH\textsubscript{2}],\textsuperscript{16} respectively (Figure 3.19).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.19.png}
\caption{A-Pt[\eta\textsuperscript{4}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O][\eta\textsuperscript{2}-CHC(O)OC(O)CH], B-Pt[\eta\textsuperscript{4}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O]- (\eta\textsuperscript{2}-styrene) and C-Pt[\eta\textsuperscript{4}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O][\eta\textsuperscript{2}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})-OSiMe\textsubscript{2}CH=CH\textsubscript{2}].}
\end{figure}

Stoichiometric amounts of phosphines have also been found to displace the bridging (CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O ligand in 8 successfully. For example, monodentate phosphine PR\textsubscript{3} (R = C\textsubscript{6}H\textsubscript{4}Me, Cy) reacts with 8 to form Pt[\eta\textsuperscript{2}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O](PR\textsubscript{3}).\textsuperscript{22} Surprisingly, reaction of the bis(phosphine) ligand dppe with 8 resulted in the formation of the binuclear species [Pt[\eta\textsuperscript{2}-(CH\textsubscript{2}=CHSiMe\textsubscript{2})\textsubscript{2}O)]\textsubscript{2}(\mu-dppe) (Figure 3.20) where the dppe ligand now acts as a bridging ligand instead of chelating as usual.

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The fact that azodicarbonyl inhibitors displace both the bridging and chelating ligands suggests that azodicarbonyl inhibitors bind more strongly to the platinum centre than the ligands/inhibitors mentioned previously. Supporting evidence from model studies on Pt(PR₃)₂(R'OCCNCONCOR') (R = Ph, Me; R' = Ph, Me, OEt, OPr) complexes have shown that the azodicarbonyl ligand forms a Pt-N-N-C-O metallacycle. The formation of the more rigid Pt-N-N-C-O metallacycle structure would be favoured over the bridging and chelating structure adopted by the flexible (CH₂=CHSiMe₂)O ligand in 8. The absence of a band maximum at λₘ₅ = 400 nm in the UV/VIS spectra for 9-11 also indicates a lack of N=N double bond character in the azo inhibitor of 9-11, which is again a feature of the Pt-N-N-C-O metallacycle. Transition metal azo complexes with an intact N=N double bond normally have a band maximum at ca. 400 nm, e.g. for Fe(CO)₄L (L = cyclic azo) the band maximum is observed at around 430-480 nm. However, there is still no definitive proof as to whether or not the azodicarbonyl inhibitors in 9-11 adopt the same binding mode as the azo ligands in Pt(PR₃)₂(ROCCNCONCOR). It is clear, nevertheless, that the carbonyl group on the azo inhibitor plays an important role in binding to the platinum centre in 9-11, since azo compounds without carbonyl groups adjacent to the azo function were found to be ineffective as inhibitors of 8.

3.3.3 Effectiveness of EtO₂CNNCO₂Et, Pr'O₂CNNCO₂Pr' and Bu'O₂CNNCO₂Bu' as inhibitors of 8

Heaton found that an excess of azo inhibitor relative to platinum in 8 was required to prevent hydrosilation and that increasing the amount of azo-inhibitors also increases the photolysis time required to initiate hydrosilation. Hydrosilation was therefore believed to occur only when all the azo inhibitors in the system are destroyed, forming CO₂, N₂ and a radical pair.

In our present studies, the photoactivation of azo-inhibited 8, i.e. 9a, 10a and 11a, in a model hydrosilation system revealed that after 5 min photolysis, the rate of hydrosilation was found to increase with the inhibited catalyst 9a < 10a < 11a (Figure 3.17). Photolysis times of 1-2 minutes on model hydrosilation systems containing...
inhibited catalysts 9a and 10a did not successfully initiate hydrosilation (Figure 3.15). This indicates that the azo inhibitor RO2CNNCO2R binds to platinum with decreasing strength as the substituent R increases in size. The IR spectrum of complex 11 shows the presence of the free azo inhibitor, Bu'O2CNNCO2Bu', whereas for complexes 9 and 10, no free azo inhibitor was detected. This again indicates that the bulky Bu'O2CNNCO2Bu' azo inhibitor binds to platinum most weakly. Similar properties are also present in the model complexes of Pt(PPh3)2(R'02CNNC02R) [R = Et (2), Pr1 (5)].9

It was found that photolysis of Pt(PPh3)2(Pt'O2CNNCO2Pr) 5 in a chlorinated solvent yielded cis-Pt(PPh3)2Cl2 at a faster rate than photolysis of Pt(PPh3)2(EtO2CNNCO2Et) 2, suggesting that azodicarbonyl ligands with smaller R groups bind to platinum stronger. We must also stress that after photoactivation of azo-inhibited catalysts 9a-11a, which resulted in hydrosilation in our model system, the reaction mixture still appears to contain some free azo inhibitors since their distinctive yellow colour persists after up to 5 minutes of photolysis. This is contrary to the findings of Heaton who reported that thermolysis or photolysis of complex 8 in chloroform with azo inhibitors 1,1'- (azodicarbonyl)dipiperidine, diethylazodicarboxylate or diisopropylazodicarboxylate initiated hydrosilation only after a loss of yellow colouration, which indicates that all the azo inhibitors are destroyed prior to hydrosilation.7 It was suggested that photolysis of 8 with azo inhibitors results in the destruction of both co-ordinated and free azo inhibitors, and as the co-ordinated azo inhibitor is destroyed it is immediately replaced by free azo. The fact that the yellow colouration of free azo persists in our hydrosilation system suggests a different process is operative. One explanation is that platinum colloids are formed during photolysis and are responsible for catalysing hydrosilation and are unaffected by the azo's inhibiting effect. However, Heaton reported that addition of mercury to the reaction did not impede hydrosilation, indicating the active catalyst is homogeneous, and not colloidal in nature.7,13,14 At present, it is not clear whether or not the absence of chlorinated solvents in our system plays a major role in the observed differences with Heaton’s results.

3.4 CONCLUSIONS

In our present studies on azodicarboxylate-inhibited 8, ie. 9a, 10a and 11a, we have shown that the size of substituent R on the azodicarboxylate inhibitor RO2CNNCO2R can influence the effectiveness of inhibition to 8, and thus effectiveness of binding to platinum. The effect observed was steric in origin only, though electronic alteration to the azo inhibitor is also expected to have a marked influence. For instance, the azodiacyl ligand proved to be both thermally and photochemically more robust in the platinum phosphine complex Pt(PPh3)2(ROCNNCOR) when compared to the azodicarboxylate ligand in Pt(PPh3)2(RO2CNNCO2R).9 However, the binding mode of
the azodicarbonyl inhibitors in 9, 10 and 11 has not been proved unambiguously but it is likely that they adopt the same Pt–N–N–C–O metallacyclic structure found in Pt(PPh$_3$)$_2$(ROCNNCOR) (R = Me, Ph, OEt, OPri)$_3$.8,23,9

3.5 REFERENCES


CHAPTER 4

PLATINUM CARBOXYLATE COMPLEXES
4.1 INTRODUCTION

It has been reported by Trogler and co-workers\(^1\) that photolysis of the oxalate complex, Pt(PEt\(_3\))(C\(_2\)O\(_4\)), results in the irreversible formation of two molecules of carbon dioxide and the reactive 14-electron fragment, Pt(PEt\(_3\)). Although the Pt(PEt\(_3\)) metal fragment was not observed directly, it was trapped with either ethene or diphenylacetylene to form Pt(PEt\(_3\))(\(\Pi\)-CH\(_2\)=CH\(_2\)) or Pt(PEt\(_3\))(\(\Pi\)-PhC=CPh) respectively.\(^1\) Also, the metal fragment formed on photolysis of Pt(PEt\(_3\))(C\(_2\)O\(_4\)) proved to be an effective hydrosilation catalyst and reacts with HSiEt\(_3\) to yield cis-Pt(PEt\(_3\))(H)(SiEt\(_3\)).\(^1,2\) Anderson and co-workers reported that photolysis of the Pt(dppe)(C\(_2\)O\(_4\)) analogue also yields a similar 14-electron fragment.\(^3\)

Malonates and phthalates are dicarboxylate compounds with a carbon bridge between the two carboxylate groups, and in some ways resemble oxalates. Like the oxalate ligand, malonate and phthalate ligands can act as chelates in transition metal complexes to form six- and seven-membered rings, co-ordinating to the metal via the oxygen atom on the carboxylate group, e.g. Pt(dppe)(O\(_2\)CCH\(_2\)CO\(_2\)) and Pt(PPh\(_3\))(O\(_2\)C(C\(_6\)H\(_4\))CO\(_2\)).\(^4\) If the malonate and phthalate ligands are proved to be as photosensitive as the oxalate ligand, there is the potential to alter the carbon backbone which connects the carboxylate groups which would allow us to change the properties of the ligand. For example, attaching a long carbon chain would allow the ligand to be more soluble in hydrocarbon solvents. Also, addition of chromophores to the backbone should make the photosensitivity of the ligand tunable.

In this chapter, platinum(II) malonate and phthalate complexes, Pt(dppe)(O\(_2\)CCH\(_2\)CO\(_2\)) \(^12\), Pt(PMe\(_3\))(O\(_2\)C(1,2-C\(_6\)H\(_4\))CO\(_2\)) \(^13\) and Pt(COD)-(O\(_2\)CCH\(_2\)CO\(_2\)) \(^14\) are prepared and characterised. The ability of malonate and phthalate to act as photosensitive ligands in complexes \(^12-14\) will be discussed.

4.2 RESULTS

4.2.1 Preparation of platinum(II) carboxylate complexes

The platinum(II) malonate and phthalate complexes, PtL\(_2\)[O\(_2\)C(X)CO\(_2\)] \([L_2 = \text{dppe}, \ X = \text{CH}_2 \ (12); L = \text{PMe}_3, \ X = 1,2-\text{C}_6\text{H}_4 \ (13); L_2 = \text{COD}, \ X = \text{CH}_2 \ (14)\)] were prepared using the procedure described by Anderson and co-workers for the synthesis of \(^12\).\(^4\) This involved the reaction of cis-platinum(II) dichloride, cis-PtL\(_2\)Cl\(_2\) \((L_2 = \text{dppe}, \ \text{COD}; \ L = \text{PMe}_3)\), with an excess of the silver carboxylate salt, Ag\(_2\)[O\(_2\)C(X)CO\(_2\)], suspended in CH\(_2\)Cl\(_2\) (Equation 4.1). The silver carboxylate salt was easily prepared from precipitation by dissolving K\(_2\)[O\(_2\)C(X)CO\(_2\)] and AgNO\(_3\) in water (Equation 4.2).\(^5\)
Chapter 4

\[ \text{PtL}_2\text{Cl}_2 + \text{Ag}_2[\text{O}_2\text{C}(\text{X})\text{CO}_2] \rightarrow \text{PtL}_2[\text{O}_2\text{C}(\text{X})\text{CO}_2] + 2\text{AgCl} \]

\( L_2 = \text{dppe}, \text{X} = \text{CH}_2 \) (12)

\( L = \text{PMe}_3, \text{X} = 1,2-\text{C}_6\text{H}_4 \) (13)

\( L_2 = \text{COD}, \text{X} = \text{CH}_2 \) (14)

(4.1)

\[ \text{AgNO}_3 (\text{aq}) + \text{K}_2[\text{O}_2\text{C}(\text{X})\text{CO}_2] (\text{aq}) \rightarrow \text{Ag}_2[\text{O}_2\text{C}(\text{X})\text{CO}_2] (\text{s}) + 2\text{KCl} (\text{aq}) \] (4.2)

All synthetic procedures were carried out in the absence of light to prevent possible photo-degradation of the product. The resultant platinum(II) carboxylate complexes \( \text{Pt(dppe)}(\text{O}_2\text{CCH}_2\text{CO}_2) \) 12, \( \text{Pt(PMe}_3)_2[\text{O}_2\text{C}(1,2-\text{C}_6\text{H}_4)\text{CO}_2] \) 13 and \( \text{Pt(COD)}(\text{O}_2\text{CCH}_2\text{CO}_2) \) 14 were obtained as white powders, in moderate to high yields (60-80\%). All of the platinum(II) carboxylate complexes were found to be sparingly soluble in acetonitrile and chlorinated solvents and were insoluble in THF or benzene. Attempts to prepare \( \text{Pt(dppe)}[\text{O}_2\text{C}(1,2-\text{C}_6\text{H}_4)\text{CO}_2] \) using the above procedure yielded a black/brown solution which is indicative of metallic platinum formation.

4.2.2 NMR Characterisation of platinum(II) carboxylate complexes

The \( ^{31}\text{P} \{^1\text{H}\} \) NMR spectrum of 12 in CD\(_3\)CN displays a singlet resonance at \( \delta 32.7 \), with \(^{195}\text{Pt}\) satellites \( ^1J(\text{PtP}) = 3665 \text{ Hz} \), indicating that both the phosphorus nuclei are equivalent. This is in fairly good agreement with the values reported by Anderson and co-workers for the same compound \( \delta_P 29.1, ^1J(\text{PtP}) = 3665 \text{ in CDCl}_3 \).\(^4\) In the \( ^1\text{H} \) NMR spectrum of 12 we can observe a singlet resonance at \( \delta 3.34 \) which is assigned to the methylene group on the malonate ligand. The doublet at \( \delta 2.58 \) and the multiplets at \( \delta 7.60-8.00 \) are assigned to the \(-\text{CH}_2\text{CH}_2-\) and Ph groups respectively, which are found on the dppe ligand (Figure 4.1). In the \( ^{13}\text{C} \{^1\text{H}\} \) NMR spectrum of 12 the signal for the carboxylate carbon atoms can be found at \( \delta 174.0 \) (Figure 4.2).

Complex 13 contains a singlet phosphorus resonance at \( \delta -27.4 \) in its \( ^{31}\text{P} \{^1\text{H}\} \) NMR spectrum which is accompanied by \(^{195}\text{Pt}\) satellites \( ^1J(\text{PtP}) = 3564 \text{ Hz} \) (Table 4.1). The \( ^1\text{H} \) NMR spectrum of 13 shows a symmetrical set of multiplets in the aromatic region, \( \delta 7.35-7.50 \), which is indicative of a AA'BB' spin system\(^7\) and is assigned to the
protons on the phenylene backbone of the phthalate ligand (Figures 4.3 and 4.4). A doublet resonance with $^{195}\text{Pt}$ satellites at δ 1.51 is assigned to the methyl protons on the PMe$_3$ ligand. On closer inspection of the resonance at δ 1.51 we find that it is a filled in doublet, belonging to an [A$_2$X$_2$] pattern. This is typically found for mutually cis-phosphine complexes where $^2J(PP')$ is large and the two phosphines are chemically equivalent. According to theoretical calculations, a 1:2:1 triplet will be observed when $|J(AX) - J(AX')|^2 < 2J(XX')\Delta(v/2)$, where $\Delta(v/2)$ is the resolving power of the spectrometer. A 1:1 doublet will be observed when $|J(AX) - J(AX')|^2 > 4J(XX')\Delta(v/2)$. Intermediate coupling is said to give filled in doublets, when neither of the two previous conditions are met. In the previous case of complex 12, the $^1$H NMR spectrum only showed a doublet resonance for CH$_2$ in dppe, which indicates that $^2J(PP')$ is small (0-15 Hz).  

The $^{13}$C ($^1$H) NMR spectrum of 13 also shows the methyl carbons on the PMe$_3$ giving rise to the multiplets observed at δ 14.6, which is described as an AX$_2$ spin system (Table 4.3 and Figure 4.5). For the $^{13}$C ($^1$H) spectrum of 12, only a doublet resonance for CH$_2$ in dppe was observed (Table 4.3). This indicates that $^2J(PP')$ is very small and that $^3J(PC)$ is less than the resolving power of the spectrometer.

A summary of NMR data for complexes 12-14 can be found in Tables 4.1-4.3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (J / Hz)</th>
</tr>
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<tbody>
<tr>
<td>Pt(dppe)(O$_2$CCH$_2$CO$_2$) 12$^a$</td>
<td>2.58 [4H, d, CH$_2$, J(PH) = 17.3]</td>
</tr>
<tr>
<td></td>
<td>3.34 (2H, s, CH$_2$)</td>
</tr>
<tr>
<td></td>
<td>7.00-8.00 (10H, m, Ph)</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_2$(O$_2$C(1,2-C$_6$H$_4$)CO$_2$) 13$^a$</td>
<td>1.51 [18H, $^b$ db, CH$_3$, J(PH) = 11.7, J(PtH) = 36.2]</td>
</tr>
<tr>
<td></td>
<td>7.35-7.50 (4H, m, Ph)</td>
</tr>
<tr>
<td>Pt(COD)(O$_2$CCH$_2$CO$_2$) 14$^c$</td>
<td>2.30, 2.73 [8H, br. m, CH$_2$CH$_2$ (COD)]</td>
</tr>
<tr>
<td></td>
<td>3.37 (2H, s, CH$_2$)</td>
</tr>
<tr>
<td></td>
<td>5.39 [4H, br. s, CH=CH (COD), J(PtH) = 66.5]</td>
</tr>
</tbody>
</table>

Table 4.1 $^1$H (300.13 MHz, 295 K) NMR spectroscopic data of complexes 12-14. Couplings to Pt refer to satellites from $^{195}$Pt. $^a$ In CD$_3$CN. $^b$ filled in doublet. $^c$ In CD$_2$Cl$_2$. 

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Table 4.2 $^{31}P$ {^1H} (121.49 MHz, 295 K) NMR spectroscopic data of complexes 12 and 13 in CD$_3$CN. Couplings to Pt refer to satellites from $^{195}$Pt.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(dppe)(O$_2$CCH$_2$CO$_2$) 12</td>
<td>32.7 [s, J(PtP) = 3665]</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_2$[O$_2$C(1,2-C$_6$H$_4$)CO$_2$] 13</td>
<td>-27.4 [s, J(PtP) = 3564]</td>
</tr>
</tbody>
</table>

Table 4.3 $^{13}$C {^1H} (75.47 MHz, 295 K) NMR spectroscopic data for complexes 12 and 13 in CD$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (J / Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(dppe)(O$_2$CCH$_2$CO$_2$) 12</td>
<td>27.5 [d, PCH$_2$, J(PC) = 51]</td>
</tr>
<tr>
<td></td>
<td>51.1 (s, CH$_2$)</td>
</tr>
<tr>
<td></td>
<td>126.4-133.7 (Ph)</td>
</tr>
<tr>
<td></td>
<td>174.0 (s, CO)</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_2$[O$_2$C(1,2-C$_6$H$_4$)CO$_2$] 13</td>
<td>14.6 (m, PCH$_3$)</td>
</tr>
<tr>
<td></td>
<td>127.4-139.2 (Ph)</td>
</tr>
<tr>
<td></td>
<td>175.3 (s, CO)</td>
</tr>
</tbody>
</table>

Figure 4.1 $^1$H (300.13 MHz, 295 K) NMR spectrum of 12 in CD$_3$CN. $a$ CH$_2$ (dppe). $b$ CH$_2$ (malonate). $c$ CHCl$_3$. $d$ Ph (dppe).
Figure 4.2 $^{13}$C ($^1$H) (75.47 MHz, 295 K) NMR spectrum of 12 in CD$_2$Cl$_2$. $a$ ether. $b$ PCH$_2$. $c$ CD$_2$Cl$_2$. $d$ O$_2$CCCH$_2$CO$_2$. $e$ Ph, $f$ O$_2$CCCH$_2$CO$_2$. 
Figure 4.3 $^1$H (300.13 MHz, 295 K) NMR spectrum of 13 in CD$_3$CN. a. PCH$_3$ with $^{195}$Pt satellites. b acetonitrile. c O$_2$C(1,2-C$_6$H$_4$)CO$_2$.

Figure 4.4 $^1$H (300.13 MHz, 295 K) NMR spectrum of 13 in CD$_3$CN, showing the expanded regions of (a) O$_2$C(1,2-C$_6$H$_4$)CO$_2$ and (b) PCH$_3$ with $^{195}$Pt satellites.
4.2.3 IR characterisation of platinum(II) carboxylate complexes

The IR spectra of 12 and 14 show C=O stretching bands at ca. 1650 cm\(^{-1}\), they are broad in appearance and their shapes suggest that they are composites of several overlapping bands (Table 4.4 and Figure 4.6). The weaker C–O stretching bands are located at ca. 1350 cm\(^{-1}\). The C=O and C–O stretching bands of complexes 12 and 14 are slightly lower in energy than those of platinum(II) bis(phosphine) oxalate complexes, e.g. for Pt(PMe\(_3\))\(_2\)(C\(_2\)O\(_4\)), \(\nu\)(C=O) is 1703 cm\(^{-1}\) and \(\nu\)(C–O) is 1363 cm\(^{-1}\).
<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$(C=O) / cm$^{-1}$</th>
<th>$v$(C-O) / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(dppe)(O$_2$CCH$_2$CO$_2$) $^{12a}$</td>
<td>1649</td>
<td>1354</td>
</tr>
<tr>
<td></td>
<td>1650$^b$</td>
<td>1357$^b$</td>
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**Table 4.4** IR spectroscopic data for platinum(II) carboxylate complexes. $a$ In KBr pellet. $b$ From ref. 4, in KBr pellet. $c$ In CH$_2$Cl$_2$. $d$ From ref. 1, in CH$_2$Cl$_2$. $e$ From ref. 13, in nujol. $f$ From ref. 3, in KBr pellet. $g$ From ref. 14, in KBr pellet.

**Figure 4.6** IR spectrum for complex 14 in CH$_2$Cl$_2$ showing the $v$(C=O) and $v$(C-O) stretching bands of the malonate ligand.
4.2.4 Photolysis of platinum(II) dicarboxylate complexes

Photolysis of complex 12 in CD$_3$CN in the presence of either diphenylacetylene or ethene (1 atm) resulted in the appearance of an unidentified singlet phosphorus resonance, assigned as product A4, at $\delta_P$ 47.6 ($J(PtP) = 3625$ Hz). Despite prolonged photolysis, up to 4 days, conversion of 12 to the unidentified product A4 remained very low. The singlet phosphorus resonance of product A4 does not correspond to the formation of either Pt(dppe)(PhC=Ph) [bp 53.5, $J(PtP) = 3278$ Hz] or Pt(dppe)(PhC=Ph) [bp 48.7, $J(PtP) = 3125$ Hz]. This suggests that the 14-electron fragment Pt(dppe) was not formed on photolysis of 12.

Complex 13 was similarly photolysed in CD$_3$CN in the presence of either diphenylacetylene or ethene with the expectation of detecting the formation of the Pt(PMe$_3$)$_2$ metal fragment. Like with complex 12, formation of Pt(PMe$_3$)$_2$(PhC=Ph) was not detected. However, prolonged photolysis did yield a small amount of product B4, which displays two doublet resonances in the $^{31}$P {IH} NMR spectrum, both with $^{195}$Pt satellites, at $\delta_P$ -11.2 ($J(PtP) = 1849$ Hz) and $\delta_P$ -29.7 ($J(PtP) = 3712$ Hz), with $J(PP) = 19$ Hz. A second product C4 was also detected and has a singlet resonance at $\delta_P$ -28.2 with $^{195}$Pt satellites [$J(PtP) = 3960$ Hz]. Hence, the $^{31}$P NMR data indicate that B4 contains two mutually cis phosphine ligands which are inequivalent and C4 contains a single phosphorus environment. The presence of products B4 and C4 is also confirmed by $^1$H NMR spectroscopy. The methyl groups on the two inequivalent phosphines of B4 can be seen as two doublet resonances at $\delta_H$ 1.78 [$^2J(PH) = 11.2$ Hz] and $\delta_H$ 1.86 [$^2J(PH) = 11.0$ Hz], with overlapping $^{195}$Pt satellites which were not clearly defined. The methyl groups on the phosphines of C4 can be located at $\delta_H$ 1.62 as a doublet [$^2J(PH) = 9.8$ Hz] with $^{195}$Pt satellites which are obscured by the methyl signals of unreacted 13.

Product B4 is likely to have a similar structure to the compound formed on photolysis of Pt(PPh$_3$)$_2$[O$_2$C(1,2-C$_6$H$_4$)CO$_2$]. It has been reported that thermolysis or photolysis of Pt(PPh$_3$)$_2$[O$_2$C(1,2-C$_6$H$_4$)CO$_2$] resulted in the loss of one molecule of carbon dioxide from the phthalate ligand, yielding the five-membered Pt-O-C-C-C metallacycle Pt(PPh$_3$)$_2$[O$_2$C(1,2-C$_6$H$_4$)] [$\delta_P$ 15.5, $J(PtP^O) = 4128$ Hz; $\delta_P$ 27.8, $J(PtP^C) = 1977$ Hz; $J(PP) = 15$ Hz].

![Diagram](from reference 14)
From the data in the $^{31}\text{P} \{^{1}\text{H}\}$ NMR spectrum of B4, we envisage that B4 contains the same Pt–O–C–C–C metallacycle. The doublet resonance at $\delta_P -11.2$ has a $J(\text{PtP})$ value of 1849 Hz which is consistent with a phosphorus atom trans to an aryl ligand and the doublet resonance at $\delta_P -29.7$ has a $J(\text{PtP})$ value of 3712 Hz which is consistent with a phosphorus trans to an oxygen ligand.$^{14}$ The identity of C4 remains unclear.

Photolysis of 12-14 in chlorinated solvents resulted in the formation of the corresponding platinum(II) dichloride complexes, ie. Pt(dppe)Cl$_2$, cis-Pt(PMe$_3$)$_2$Cl$_2$ and Pt(COD)Cl$_2$.

4.3 DISCUSSIONS

4.3.1 Preparation of platinum(II) carboxylate complexes

Platinum(II) carboxylate complexes were easily prepared from the reaction between platinum(II) chloride and a silver carboxylate salt, the driving force of this reaction being the formation of the highly insoluble silver chloride compound. An alternative method for preparing these type of complexes uses the platinum(0) bis(phosphine) dioxygen complex, PtP$_2$(η$_2$-O$_2$) ($P = $ phosphine), and the dicarboxylic acid, X(CO$_2$H)$_2$ ($X = $ carbon backbone), which yields the corresponding platinum(II) bis(phosphine) dicarboxylate complex and hydrogen peroxide.$^{14}$

4.3.2 Reactivity of platinum(II) carboxylate complexes

Platinum(II) malonate and phthalate complexes of the type PtL$_2$(O$_2$CXCO$_2$) ($L = $ PMe$_3$, $L_2 = $ dppe, $X = $ carbon backbone) were found to display different photochemical properties to their platinum(I) oxalate analogues, e.g. Pt(PEt$_3$)$_2$(C$_2$O$_4$).$^{1}$ Our observations indicate that platinum(II) malonate and phthalate complexes do not yield the PtL$_2$ 14-electron metal fragment upon photolysis. This is almost certainly due to the presence of the carbon backbone which connects the two carboxylate groups attached to the metal.

The photochemical formation of Pt(PET$_3$)$_2$ from Pt(PET$_3$)$_2$(C$_2$O$_4$) is believed to occur via transfer of two electrons from the platinum centre to the oxalate ligand, either simultaneously or in rapid succession.$^{1}$ The oxalate dianion thus formed irreversibly fragments to two molecules of carbon dioxide, leaving behind the Pt(PET$_3$)$_2$ metal moiety (Equation 4.3)

$$\text{Pt(PET}_3\text{)}_2(\text{C}_2\text{O}_4) \xrightarrow{hv} \text{Pt(PET}_3\text{)}_2 + 2\text{CO}_2$$  \hspace{1cm} (4.3)
This mechanism is unlikely to occur for platinum(II) malonate and phthalate complexes because of the presence of the carbon backbone connecting the two carboxylate groups, so that formation of two molecules of carbon dioxide is now unfavourable.

Based on our NMR data, and those reported by Scherer et al.,\textsuperscript{14} we believe that B4, formed on photolysis of 13, contains a five-membered Pt–C–C–C–O metallacyclic structure (Equation 4.4).

Possible mechanisms for this photoprocess could be better understood by examining the reactivity of complexes with chelating dicarboxylate ligands. It has been reported that one end of the dicarboxylate ligand in platinum(II) oxalate and malonate complexes can be displaced in the presence of phosphine to yield non-chelating platinum(II) oxalate and malonate complexes (Equations 4.5 and 4.6).\textsuperscript{1,4}

Anderson and co-workers reported that the co-ordinated malonate ligand is more labile than the oxalate ligand, and suggested that this could be due to the greater ionic character present in the Pt–O bond in the malonate complexes and that five-membered chelate rings, or metallacycles, e.g. oxalate complexes, are thermodynamically more stable than six-membered chelate rings, e.g. malonate complexes.\textsuperscript{4} It therefore seems
likely that the phthalate ligand in 13 also possess these properties. Hence, one possible mechanism for the formation of B4 from photolysis 13 would initially involve the displacement of one carboxylate group by a solvent molecule (CD3CN). Further photolysis would yield a molecule of carbon dioxide from the dangling end of the phthalate ligand and the formation of a stable five-membered metallacycle (Scheme 4.1).

It would be plausible that 12 should also eject one molecule of carbon dioxide to form a metallacycle which is similar to the process suggested for the formation of B4 from 13, but this was not observed. One reason could be that ejection of a molecule of carbon dioxide on photolysis of 12 would yield a strained four-membered metallacycle, D4, which is expected to be unfavourable.
The photo-products $A_4$, formed from photolysis of $12$, and $C_4$, the second product formed from photolysis of $13$, both contain equivalent phosphorus atoms as shown by their $^{31}P$ \{$^1H$\} NMR spectra. The possibility of $A_4$ and $C_4$ being platinum(II) carbonate complexes, $\text{PtL}_2(\text{CO}_3)$ ($L$ = phosphine) was ruled out since the $^{31}P$ chemical shifts and $J(\text{PtP})$ values did not correspond to the values quoted in literature\textsuperscript{3,16}. The identities of photo-products $A_4$ and $C_4$ remain unclear.

4.4 CONCLUSIONS

In this chapter, the photochemistry of platinum(II) malonate and phthalate complexes were found to be different from those of platinum(II) oxalate complexes\textsuperscript{1,2,3}. Formation of the 14-electron platinum bis(phosphine) fragment was not observed on photolysis of the platinum(II) malonate and phthalate complexes prepared. This was thought to be due to the presence of the carbon backbone which connects the two carboxylate groups. A mechanism for the photochemical formation of a five-membered metallacycle $B_4$ formed from the photolysis of the seven-membered metallacycle $13$ is proposed which involves the unhinging of the chelating phthalate ligand initially to form a monodentate phthalate complex. This was largely based on reports by Anderson and co-workers who suggested that the chelating malonate ligand is more labile than the oxalate ligand, and is easily converted to a monodentate ligand by displacement with an incoming phosphine ligand\textsuperscript{4}.

The low solubilities and photo-sensitivities of the platinum(II) malonate and phthalate complexes described in this chapter indicate that malonate and phthalate ligands are ultimately poor ligands to use for initiating photochemical processes.

4.5 REFERENCES

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CHAPTER 5

PLATINUM SILYL HYDRIDE COMPLEXES
5.1 INTRODUCTION

5.1.1 Transition Metal Silyl Hydride complexes

There is tremendous interest in the chemistry of silyl and silyl hydride transition metal complexes. This is because they play an important role in industry, representing key species in catalytic processes, namely hydrosilation and, of more recent interest, competitive dehydrogenative silation.

Originally proposed by Chalk and Harrod, the initial stage of the transition metal catalysed hydrosilation reaction involves the formation of a metal silyl hydride. Harrod’s work on transition metal catalysed polysilane formation also involves the formation of a metal silyl hydride. Platinum silyl hydride complexes are therefore of special interest since platinum is the metal of choice for hydrosilation catalysts.

5.1.2 Dynamic Processes in Platinum Metal Silyl Hydride Complexes

Complexes of the type cis-Pt(PR₃)₂(H)(SiR₃) exhibit two forms of dynamic exchange in solution: (a) mutual phosphine exchange, where the PR₃ positions interchange intramolecularly whilst retaining phosphorus-proton spin correlation (this can also be viewed as the interchange of position between the silyl and hydride ligand). (b) reversible reductive elimination, oxidative addition of the silane. An example of the mutual phosphine exchange process in a platinum silyl hydride complex was noted by Pidcock et al. for cis-Pt(CPh)₃HCH(SiPh₃) from the variable temperature ¹H NMR spectra. The corresponding ³¹P ¹H NMR spectra revealed behaviour indicative of phosphine dissociation rather than reversible addition-elimination of the silane ligand.

Clark and Hampden-Smith later found that the analogous compound cis-Pt(PCY₃)₂(H)(SiPh₃) undergoes both intramolecular phosphine interchange and reversible addition-elimination of silane. Clark and Hampden-Smith argued that the absence of the reversible addition-elimination equilibrium of the silane ligand in the PPh₃ analogue was due to the lack of inter-ligand repulsion found in the PCY₃ analogue. They have also proposed that a platinum species with η²-silane is the intermediate responsible for the intramolecular phosphine exchange. The η²-bound silane ligand in this intermediate facilitates scrambling of the phosphines by rotation about the Si-H bond.

Silane exchange has also been observed for [CpPt(SiMe₂OSiMe₃)₂H] and [(dppe)Pt(SiMe₃)₂] with the disilane HSiMe₂OSiMe₂H to form the corresponding chelating disilyl complex.

Similar mutual phosphine exchange processes have been seen for other transition metal silyl hydride complexes. For example, Sun et al. found that the manganese
complex \(\text{CpMn}(P_2)(H)(\text{SiPh}_n\text{H}_{3-n})\) \([P_2 = \text{dmpe}, \text{dmpp}, \text{dmpm}]\) undergoes positional exchange of the silyl and hydride ligand, which also corresponds to mutual phosphine exchange.\(^{13}\) This complex was described as having a four-legged piano stool geometry\(^8\) with the silyl and hydride ligand lying \(c\text{is}\) to each other. Two possible mechanisms were suggested to account for this exchange process. The first mechanism involves an \(\eta^2\)-silane intermediate, which is similar to the intermediate proposed by Clark and Hampden-Smith for the mutual phosphine exchange process in \(c\text{is-}\text{Pt}(\text{PCy}_3)_2(H)-(\text{SiPCy}_3)\).\(^{10}\) The second, and according to Sun \textit{et al.} the more likely mechanism, involves the pseudorotation of the four ligands. This involves forming a trigonal bipyramidal intermediate with the cyclopentadienyl ring in the axial position and the chelating phosphine ligand in the equatorial plane. The silyl and the hydride ligand can be located in either of the remaining axial or equatorial positions (Scheme 5.1).

![Diagram](image)

\textbf{Scheme 5.1} Proposed mechanisms for phosphine exchange in \(\text{CpMn}(P_2)(H)(\text{SiR}_3)\) \((\text{R} = \text{Ph or H}; \, P_2 = \text{dmpe}, \text{dmpp}, \text{dmpm})\). (a) Involves the formation of a trigonal bipyramidal complex. (b) Involves the formation of an \(\eta^2\)-silane complex.
In this chapter the platinum silyl hydride system, cis-Pt(PC\textsubscript{3})(H)(SiR\textsubscript{3}), studied originally by Clark and Hampden-Smith, is examined in more detail. Thermodynamic and activation parameters are obtained for silyl and phosphine exchange in cis-Pt(PC\textsubscript{3})(H)(SiMe\textsubscript{2}CH=CH\textsubscript{2}) 16 and cis-Pt(PC\textsubscript{3})(H)(SiMe\textsubscript{2}Et) 17. In addition, \textsuperscript{1}H and \textsuperscript{31}P \{\textsuperscript{1}H\} NMR data are obtained for cis-Pt(PC\textsubscript{3})(H)(SiMe\textsubscript{2}OCH\textsubscript{2}C(Me)=CH\textsubscript{2}) 18, cis-Pt(PC\textsubscript{3})(H)(Si(OMe)CH\textsubscript{2}CH=CH\textsubscript{2}) 19 and cis-Pt(PC\textsubscript{3})(H)(SiPh\textsubscript{2}OSiPh\textsubscript{2}H) 20. The thermal and photochemical reactions of these complexes are also investigated.

5.2 RESULTS

5.2.1 Preparation of cis-Pt(PC\textsubscript{3})(H)(SiR\textsubscript{3}) complexes

The 14-electron Pt(PC\textsubscript{3}) complex was reacted with various silanes to form the Si-H oxidative addition product cis-Pt(PC\textsubscript{3})(H)(SiR\textsubscript{1}R\textsubscript{2}) \{R\textsubscript{1} = R\textsubscript{2} = Ph (15); R\textsubscript{1} = Me, R\textsubscript{2} = (CH\textsubscript{2}CH=CH\textsubscript{2}) (16); R\textsubscript{1} = Me, R\textsubscript{2} = Et (17); R\textsubscript{1} = Me, R\textsubscript{2} = [OCH\textsubscript{2}C(Me)=CH\textsubscript{2}] (18); R\textsubscript{1} = OMe, R\textsubscript{2} = (CH\textsubscript{2}CH=CH\textsubscript{2}) (19)\}. The complexes cis-Pt(PC\textsubscript{3})(H)(SiPh\textsubscript{3}) 15 and cis-Pt(PC\textsubscript{3})(H)(SiMe\textsubscript{2}CH=CH\textsubscript{2}) 16 were synthesised by reaction of Pt(PC\textsubscript{3}) with the corresponding silane in pentane or hexane at 0 °C. These reactions yielded the products as white solids in moderate yields (40-50 %) (Scheme 5.2). Complexes 17-19 were characterised in solution by \textsuperscript{1}H and \textsuperscript{31}P \{\textsuperscript{1}H\} NMR spectroscopy; attempts to isolate them yielded only oily residues [Table 5.1 (a) and (b)].

Pt(PC\textsubscript{3}) was also reacted with the disilanes, HSiPh\textsubscript{2}OSiPh\textsubscript{2}H and HSiMe\textsubscript{2}C\textsubscript{6}H\textsubscript{4}SiMe\textsubscript{2}H. The reaction of Pt(PC\textsubscript{3}) with HSiPh\textsubscript{2}OSiPh\textsubscript{2}H formed the complex cis-Pt(PC\textsubscript{3})(H)(SiPh\textsubscript{2}OSiPh\textsubscript{2}H) 20. The reaction of Pt(PC\textsubscript{3}) with HSiMe\textsubscript{2}C\textsubscript{6}HSiMe\textsubscript{2}H at -77 °C formed an as yet unidentified species A\textsubscript{5}. When the reaction was carried out at room temperature a further, as yet unknown, compound B\textsubscript{5} was formed alongside A\textsubscript{5}.

\[
\text{Scheme 5.2 Preparation of cis-Pt(PC}_{3}\text{(H)}(\text{SiR}_{1}\text{R}_{2}^2).}
\]
5.2.2 $^1\text{H}$ and $^{31}\text{P} \{^1\text{H}\}$ NMR characterisation of cis-Pt(PCY$_3$)$_2$(H)(SiR$_3$)

Complexes 15-20 all yield a hydride resonance at around $\delta -3.5$ in their $^1\text{H}$ NMR spectra. All the complexes studied undergo temperature dependent dynamic behaviour as first described by Clark and Hampden-Smith. The limiting low temperature $^1\text{H}$ NMR spectra of complexes 15-20 contain hydride resonances with doublet of doublets multiplicity and $^{195}\text{Pt}$ satellites (Figure 5.1). The limiting low temperature $^{31}\text{P} \{^1\text{H}\}$ NMR spectra for complexes 15-20 contain two doublet resonances with $^{195}\text{Pt}$ satellites at ca. $\delta 40$ (Figure 5.2). Both $^1\text{H}$ and $^{31}\text{P} \{^1\text{H}\}$ NMR data of 15-20 confirm that they are monohydride species with two mutually cis phosphine ligands of the form cis-Pt(PCY$_3$)$_2$(H)(SiR$_3$). Note that the coupling constants $J(\text{PtP})$ differ quite substantially, the lower platinum-phosphorus coupling constant is indicative of the phosphorus atom trans to silicon due to the higher trans-influence compared to the hydride ligand (see Section 2.3.1 for a brief discussion of the trans-influence of a ligand). NMR data for complexes 15-20 are summarised in Tables 5.1 (a) and (b).

On addition to the platinum centre, all the proton resonances of the silyl group are shifted to lower field relative to the proton resonances of the corresponding free silane. This is demonstrated in Figure 5.1 where the allyl proton resonances of the silyl ligand in cis-Pt(PCY$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 are shifted to lower field when compared to the free silane ligand HSiMe$_2$CH$_2$CH=CH$_2$. Also of interest are the two methyl groups and the methylene group adjacent to the silicon atom in complex 16. Both groups are sufficiently close to the platinum centre to show coupling. The methyl resonance is a doublet at $\delta 0.83$ due to weak coupling to the trans phosphorus atom; it also possesses $^{195}\text{Pt}$ satellites [$^4J(\text{PH})_{\text{trans}} = 1.6$ Hz, $^3J(\text{PtH}) = 26.7$ Hz]. The methylene resonance is a doublet at $\delta 2.41$, which arises from coupling to the vinyl CH group and possesses $^{195}\text{Pt}$ satellites [$^3J(\text{HH}) = 8.3$, $^3J(\text{PtH}) = 30.8$]. The complexes cis-Pt(PCY$_3$)$_2$(H)(SiMe$_2$Et) 17, cis-Pt(PCY$_3$)$_2$(H)(SiMe$_2$OCH$_2$CH=CH$_2$) 18 and cis-Pt(PCY$_3$)$_2$(H)[Si(OMe)$_2$CH$_2$-CH=CH$_2$] 19 also contain methyl groups on the silicon atom whose proton resonances show couplings to $^{195}\text{Pt}$. The species formed in the reaction of Pt(PCY$_3$)$_2$ with the disilanes HSiPh$_2$OSiPh$_2$H and HMe$_2$Si(C$_6$H$_4$)SiMe$_2$H are discussed in Section 5.2.8.
Table 5.1a ¹H NMR spectroscopic data of complexes 15-20. a In [²H₅]toluene at 250 K, ¹H (500.13 MHz). b In [²H₅]toluene at 240 K, ¹H (500.13 MHz). c In C₆D₆ at 295 K, ¹H (200.13 MHz).
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| **15**\(^a\) | 37.3 [d, \(\text{P}^\text{H}\), \(J(\text{PP}) = 13, J(\text{PtP}) = 2642\)]  
| | 41.1 [d, \(\text{P}^\text{Si}\), \(J(\text{PP}) = 13, J(\text{PtP}) = 1560\)] |
| **16**\(^a\) | 41.6 [d, \(\text{P}^\text{H}\), \(J(\text{PP}) = 12, J(\text{PtP}) = 2677\)]  
| | 42.8 [d, \(\text{P}^\text{Si}\), \(J(\text{PP}) = 12, J(\text{PtP}) = 1420\)] |
| **17**\(^a\) | 42.2 [d, \(\text{P}^\text{H}\), \(J(\text{PP}) = 12, J(\text{PtP}) = 2704\)]  
| | 43.1 [d, \(\text{P}^\text{Si}\), \(J(\text{PP}) = 12, J(\text{PtP}) = 1387\)] |
| **18**\(^b\) | 41.9 [d, \(\text{P}^\text{H}\), \(J(\text{PP}) = 13, J(\text{PtP}) = 2658\)]  
| | 42.0 [br., \(\text{P}^\text{Si}\), \(J(\text{PtP}) = 1369\)] |
| **19**\(^c\) | 41.9 [d, \(\text{P}^\text{H}\), \(J(\text{PP}) = 14, J(\text{PtP}) = 2638\)]  
| | 42.4 [br. d, \(\text{P}^\text{Si}\), \(J(\text{PtP}) = 1408\)] |
| **20**\(^c\) | 43.1 [d, \(\text{P}^\text{Si}\), \(J(\text{PP}) = 15, J(\text{PtP}) = 1428\)]  
| | 43.4 [d, \(\text{P}^\text{H}\), \(J(\text{PP}) = 15, J(\text{PtP}) = 2612\)] |

**Table 5.1b** \(^{31}\text{P} \{^1\text{H}\} \) NMR spectroscopic data of complexes 15-20. \(\text{P}^\text{H}\) indicates phosphorus is *trans* to hydride and \(\text{P}^\text{Si}\) indicates phosphorus is *trans* to silicon. \(^a\) In \(\text{[}^2\text{H}_8\text{]}\)toluene at 250 K, \(^{31}\text{P}\) (202.46 MHz). \(^b\) In \(\text{[}^2\text{H}_8\text{]}\)toluene at 240 K, \(^{31}\text{P}\) (202.46 MHz). \(^c\) In \(\text{C}_6\text{D}_6\) at 295K, \(^{31}\text{P}\) (81.02 MHz).
Figure 5.1 $^1$H (500.13 MHz, 250 K) NMR spectrum of cis-Pt(PCy$_3$h(H)-(SiMe$_2$CH$_2$CH=CH$_2$)$_6$ in [D$_8$]toluene with excess free silane. (i) Complete spectrum. (ii) Expansion of $^{185}$Pt coupled resonances. a Pt-H. b SiMe$_2$. c CH$_2$CH=CH$_2$. d CH$_2$CH=CH$_2$. e CH$_2$CH=CH$_2$. f Free silane. g Toluene.
5.2.3 Fluxional behaviour of cis-Pt(PCy₃)₂(H)(SiR₃)

Complexes 15-20 all show signs of fluxional behaviour; for 16-18 these dynamic processes are slowed down to give low-temperature limiting spectra at ca. 250 K. In complexes 19 and 20, where there are oxygen based substituents attached to the silicon, the low temperature limit is reached at around room temperature. This indicates that electron withdrawing groups are able to reduce the rate of exchange. These features are illustrated by comparing the spectra in Figures 5.3 and 5.4. The hydride spectra shown in Figure 5.4 were recorded at 300 K on a 500 MHz spectrometer and show that the hydride resonances of complexes 16 and 17 are substantially distorted whereas the hydride resonances of 15 and 18 are affected to a much smaller extent.
Figure 5.3 $^1$H (200.13 MHz) NMR spectrum of cis-Pt(PCy$_3$)$_2$(H)[Si(OMe)$_2$-CH$_2$CH=CH$_2$] 19 in C$_6$D$_6$ (295 K) showing the hydride region only.

Figure 5.4 $^1$H (500.13 MHz) NMR spectra of cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) in [H$_8$]toluene (300 K) showing the hydride region only. (i) cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17. (ii) cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH=CH$_2$) 16. (iii) cis-Pt(PCy$_3$)$_2$(H)[SiMe$_2$OCH$_2$C(Me)=CH$_2$] 18. (iv) cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15. a trans-Pt(PCy$_3$)$_2$(H)$_2$. 
From Figure 5.4, complex 17 appears to have the highest rate of exchange at room temperature when compared to complexes 15, 16 and 18. In complex 17 the hydride resonance is almost indistinguishable from the baseline at 300 K [Figure 5.4 (i)]. It appears that \( \pi \)-acceptors and electronegative groups stabilise the complexes, since only 16 and 17 appear to be undergoing fast exchange processes at 300 K and both complexes only contain alkyl groups adjacent to the silicon atom. Complexes 15 and 18 appear to have a comparatively slow rate of exchange at 300 K and both complexes have \( \pi \)-acceptors or electronegative groups adjacent to the silicon atom.

NMR samples of 15, 16, 17 and 18 prepared \textit{in situ}, all contain hydride resonances as normal, undistorted doublet of doublets at 250 K. On warming these samples the hydride resonances begin to show signs of dynamic behaviour. The hydride resonance of complex 16 at 250 K has the expected doublet of doublets fine structure. On warming, the outer lines of this pattern gradually decrease in intensity whilst the inner lines remain sharp with constant separation \( |^2J(\text{PH})_{\text{trans}}| - |^2J(\text{PH})_{\text{cis}}| \). This situation holds until 285 K at which point the outer lines of the doublet of doublets are no longer visible. Further warming of the complex results in the broadening of the inner lines until eventual thermal decomposition of complex 16 to \textit{trans}-Pt(PCY3)\(_2\)(H)\(_2\) occurs (Figure 5.5a). Figure 5.5b shows the corresponding \(^{31}\text{P} \{^1\text{H}\} \) NMR spectra of 16 over the temperature range 250-300 K. On warming the sample from 250 K to 300 K the two doublet resonances initially collapse into two broad singlets, and then coalesce. Despite some decomposition to \textit{trans}-Pt(PCY3)\(_2\)(H)\(_2\) at around 290 K, identical spectra were reproduced upon subsequent cooling.

The \textit{cis}-platinum silyl hydride complexes, 15-20, all eventually decompose in solution to \textit{trans}-Pt(PCY3)\(_2\)(H)\(_2\) as indicated by the appearance of a new hydride resonance \( \delta_{\text{H}} \) (500.15 MHz, 300 K) -3.08, t, \(^2J(\text{PH})_{\text{cis}}\) = 17.2 Hz, \( J(\text{PtH}) = 793.1 \) Hz; \( \delta_\text{p} \) (202.46 MHz, 300 K) 52.4, s, \( J(\text{PtP}) = 2887 \) Hz. The rate of conversion of the \textit{cis}-platinum silyl hydride complex to the \textit{trans}-platinum dihydride complex depends critically on the R groups adjacent to silicon, and on the concentration of free silane. As can be seen from Figure 5.4 both 16 and 17 show signs of decomposition to \textit{trans}-Pt(PCY3)\(_2\)(H)\(_2\) while 15 and 18 are essentially intact.
Figure 5.5 (a) Variable temperature $^1$H (500.13 MHz) NMR spectra of cis-Pt(PC$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 in [D$_8$]toluene showing the hydride region.

a trans-Pt(PC$_3$)$_2$(H)$_2$. 
Figure 5.5 (b) Low temperature $^{31}$P {$^1$H} (202.46 MHz) NMR spectra of cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 in [2$^3$H$_8$]toluene. $a$ Phosphine oxide. $b$ trans-Pt(PCy$_3$)$_2$(H)$_2$. 
5.2.3a Mutual Exchange of Phosphine Ligands in cis-Pt(PCY₃)₂(H)(SiR₃)

The invariant lines observed for the monohydride resonance in the temperature dependent ¹H NMR spectra [Figure 5.5 (a)] are characteristic of an intramolecular process where the phosphine ligands undergo mutual exchange whilst retaining P–H spin correlation (Scheme 5.2). Figure 5.6 shows the phosphorus spin states associated with the transitions of the hydride resonance depends on the signs of the cis and trans proton-phosphorus coupling constants.

Scheme 5.2 Mutual exchange of phosphine in cis-Pt(PCY₃)₂(H)(SiR₃).

a) Phosphorus nucleus 1 \(\alpha\) \(\beta\) \(\alpha\) \(\beta\)
   Phosphorus nucleus 2 \(\beta\) \(\beta\) \(\alpha\) \(\alpha\)

b) Phosphorus nucleus 1 \(\beta\) \(\alpha\) \(\beta\) \(\alpha\)
   Phosphorus nucleus 2 \(\beta\) \(\beta\) \(\alpha\) \(\alpha\)

Figure 5.6 Calculated ¹H NMR spectrum of cis-Pt(PCY₃)₂(H)(SiR₃) showing possible labelling of phosphorus spin states for the doublet of doublets hydride transitions using DNMR-SIM, simulated at 500.13 MHz. \(^{195}\)Pt satellites are not displayed. a) \(^2\)J(PH)\(_{tr}\) and \(^2\)J(PH)\(_{ci}\) are of opposite sign, b) \(^2\)J(PH)\(_{tr}\) and \(^2\)J(PH)\(_{ci}\) are of the same sign.

The mutual phosphine exchange process of cis-Pt(PCY₃)₂(H)(SiR₃) in solution was simulated using the dynamic NMR spectra simulation programme DNMR-SIM, see Section 5.2.6. In Figure 5.7 the result of simulating the mutual phosphine exchange is illustrated. Figure 5.7 (a) shows the effect of increasing the rate of mutual phosphine exchange when both \(^2\)J(PH)\(_{tr}\) and \(^2\)J(PH)\(_{ci}\) are of the opposite signs while Figure 5.7 (b) corresponds to the situation where \(^2\)J(PH)\(_{tr}\) and \(^2\)J(PH)\(_{ci}\) are of the same sign. Initially, the outer lines of the doublet of doublets of the simulated hydride resonance
decreased in intensity as was observed in the real temperature dependent NMR spectra. As the rate of mutual phosphine exchange was increased the outer lines not only decreased in intensity but broaden until they are no longer observed. Further increase in the rate of mutual phosphine exchange resulted in the appearance of a new resonance in the centre of the hydride signal. The inner lines remained sharp and invariant at all times with a separation of $|\frac{1}{2}J(\text{PH})_{\text{trans}} - \frac{1}{2}J(\text{PH})_{\text{cis}}|$. When $2J(\text{PH})_{\text{trans}}$ and $2J(\text{PH})_{\text{cis}}$ are of the same sign, the inner lines of the simulated doublet of doublets hydride resonance collapsed and reformed in the centre as the rate of mutual phosphine exchange was increased. The outer lines remained invariant throughout. Note the separation between the two invariant lines in this case is $\frac{1}{2}J(\text{PH})_{\text{trans}} + \frac{1}{2}J(\text{PH})_{\text{cis}}$. This situation does not therefore match the experimental data.

Notice that the invariant lines of the hydride transitions are associated with the phosphorus spin states $\alpha\alpha$ and $\beta\beta$ and that the collapsing lines are the proton transitions associated with the $\alpha\beta$ and $\beta\alpha$ phosphorus spin states which are permuted by interchange of the phosphorus atoms (Figure 5.6). At the higher mutual phosphine exchange rate limit both phosphorus atoms will appear to be equivalent and a triplet hydride resonance will be observed. If $2J(\text{PH})_{\text{trans}}$ and $2J(\text{PH})_{\text{cis}}$ are of the same sign, the observed $2J(\text{PH})$ will have a value of $\frac{1}{2}J(\text{PH})_{\text{trans}} + \frac{1}{2}J(\text{PH})_{\text{cis}}$. If $2J(\text{PH})_{\text{trans}}$ and $2J(\text{PH})_{\text{cis}}$ are of opposite sign, the observed $2J(\text{PH})$ will have a value of $\frac{1}{2}J(\text{PH})_{\text{trans}} - \frac{1}{2}J(\text{PH})_{\text{cis}}$.

As Figure 5.7 clearly demonstrates, the collapse of the outer lines rather than the inner lines indicates that $2J(\text{PH})_{\text{trans}}$ and $2J(\text{PH})_{\text{cis}}$ are of opposite sign as was the case for $cis$-Pt($PCY_3$)$_2$(H)(SiPh$_3$)$. Since we only observe the collapse of the outer lines of the hydride resonance in the variable temperature $^1H$ NMR spectra for 15-18, $2J(\text{PH})_{\text{trans}}$ and $2J(\text{PH})_{\text{cis}}$ must be of opposite sign.

Comparing the real and simulated hydride NMR spectra, Figures 5.5 (a) and 5.7 (a) respectively, we find that the simulated spectra of the phosphine interchange process at a slow rate agree well with the experimental hydride spectra of $cis$-Pt($PCY_3$)$_2$(H)-(SiMe$_2$CH$_2$CH=CH$_2$) 16 at low temperatures. However, as the temperature is increased, the inner lines of the doublet of doublets resonance of 16 do not remain sharp and invariant, but instead, they begin to broaden. This is also true in the cases of complexes 15, 17 and 18. The appearance of a new central line is not observed at higher temperatures as is predicted in the simulated spectra for high rates of mutual phosphine exchange. This is because of a second dynamic exchange, involving the addition-elimination of the free silane. This clearly demonstrates that mutual phosphine exchange is not the sole dynamic process occurring in $cis$-Pt($PCY_3$)$_2$(H)(SiR$_3$) in solution at higher temperatures. However, it is clear that mutual phosphine exchange is the dominant process at lower temperatures.
Figure 5.7 Calculated $^1$H hydride NMR spectra of cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$)$_2$ showing the effects of altering the rate of the phosphine interchange process using DNMR-SIM, simulated at 500.13 MHz. $^{195}$Pt satellites are not simulated. (a) $^2$J(PH)$_{trans}$ and $^2$J(PH)$_{cis}$ are of opposite sign. (b) $^2$J(PH)$_{trans}$ and $^2$J(PH)$_{cis}$ are of the same sign.
5.2.3b Reversible dissociation of silane from \( \text{cis-Pt(PCy}_3\text{)}_2(\text{H})(\text{SiR}_3) \)

As well as the mutual phosphine interchange process (Scheme 5.2), complexes 15-18 exhibit another type of dynamic exchange process in solution in our studies. This is evident from the broadening of the hydride resonances upon warming the solutions of \( \text{cis-Pt(PCy}_3\text{)}_2(\text{H})(\text{SiR}_3) \) from low temperature. As mentioned previously the hydride resonances coalesced into a very broad band on warming, accompanied by decomposition to \( \text{trans-Pt(PCy}_3\text{)}_2(\text{H})_2 \) [Figure 5.5 (a)]. Two possible dynamic processes could account for the broadening of the hydride resonance: (a) reversible dissociation of phosphine from \( \text{cis-Pt(PCy}_3\text{)}_2(\text{H})(\text{SiR}_3) \) and (b) reversible dissociation of silane from \( \text{cis-Pt(PCy}_3\text{)}_2(\text{H})(\text{SiR}_3) \) (Scheme 5.3).

![Scheme 5.3 Possible processes responsible for the broadening of the hydride resonance at elevated temperature in \( \text{cis-Pt(PCy}_3\text{)}_2(\text{H})(\text{SiR}_3) \). (a) reversible phosphine dissociation. (b) reversible silane dissociation.](image)

Both processes (a) and (b) in Scheme 5.3 involve the disruption of the spin-spin coupling between the phosphorus atoms and the hydride through bond scission. Both these processes are said to be non-mutual exchange processes. As originally noted by Clark and Hampden-Smith, the non-mutual exchange process observed was that of the reversible silane dissociation mechanism.\(^\text{10}\) We observed several pieces of evidence to support this. For example, upon dissolving the complex \( \text{cis-Pt(PCy}_3\text{)}_2(\text{H})(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2) \) 16 in \( \text{C}_6\text{D}_6 \) at room temperature, detectable traces of free silane and \( \text{Pt(PCy}_3\text{)}_2 \) were observed by \(^1\text{H} \) and \(^{31}\text{P} \) \(^{1}\text{H} \) NMR spectroscopy, although no free phosphine was detected. Similarly, GC analysis of a benzene solution of 16 at room temperature produced a peak at the same retention time as that of \( \text{HSiMe}_2\text{CH}_2\text{CH}=\text{CH}_2 \). When an NMR sample of 16 was prepared at low temperature in \( [\text{\textsuperscript{2}H}_8]\text{toluene} \) and \(^{31}\text{P} \) \(^{1}\text{H} \) NMR spectra were subsequently measured at 250 K only signals due to 16 were observed. However, on warming the sample to 290 K a signal
corresponding to Pt(PCy3)2 was detected (Figure 5.8). Similarly, the 1H NMR spectrum of complex 15 at 315 K shows free silane but not at 280 K (Figure 5.9).

These observations support silane exchange over phosphine exchange, since trace amounts of the free phosphine PCy3 should be detectable if free phosphine exchange was significant at elevated temperatures.

Further support for the silane dissociation process was found in a spin saturation transfer NMR experiment.17 The intensity of the Si–H resonance from the free silane in the 1H NMR spectrum decreased markedly upon irradiation (or saturation) of the hydride resonance in the complex. By irradiating the hydride resonance the spin population of the α and β states of the hydride ligand are equalised. If the silyl and the hydride ligands are in rapid exchange with the free silane, the spin saturated hydride will be converted to a free silane ligand. Since α and β spin states in the newly formed free silane have equal population, they will not contribute to the Si–H resonance of the free silane. Hence, we observe an overall decrease in intensity of the Si–H resonance upon irradiation of the hydride resonance (Figure 5.10).

**Figure 5.8** Quantitative 31P [1H] (202.46 MHz) NMR spectra of cis-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 16 showing dissociation to Pt(PCy3)2 (top figure) at elevated temperatures. a Pt(PCy3)2. b Phosphine oxide. c Complex 16. d 195Pt satellites from complex 16 at low temperature (bottom figure).
Figure 5.9 $^1$H NMR (500.13 MHz) spectra of cis-Pt(PCy$_3$)$_2$(H(SiPh$_3$)) 15 in C$_6$D$_6$, showing dissociation of HSiPh$_3$ at elevated temperatures. $a$ Si–H from HSiPh$_3$, $b$ Pt–H from complex 15 with $^{195}$Pt satellites.

Figure 5.10 $^1$H (500.13 MHz) NMR spectra of cis-Pt(PCy$_3$)$_2$(H(SiMe$_2$CH$_2$CH=CH$_2$)) 16 with excess free silane. The top spectrum shows the normal free silane resonances. The bottom spectrum shows that there is a decrease in intensity in the Si–H resonance when the Pt–H hydride resonance of 16 is irradiated. $a$ CH=CH$_2$, $b$ Si–H.
It is clear, therefore, that at least two dynamic exchange processes are occurring in solution at high temperatures for cis-Pt(PCy₃)₂(H)(SiR₃). These involve both mutual phosphine exchange and reversible silane dissociation (Scheme 5.4).

Scheme 5.4 Dynamic exchange processes of cis-Pt(PCy₃)₂(H)(SiR₃) in solution at high temperatures: (a) mutual phosphine exchange and (b) free silane exchange.

When both exchange processes (a) and (b) in Scheme 5.4 were calculated in a NMR simulation programme, the dynamic ¹H NMR spectra obtained matched those observed experimentally. From these calculations, the rate constants k₁, k₂ and k₃ in Scheme 5.4 were obtained for a range of temperatures. Using these rate constants, activation parameters ΔH°, ΔS°, and ΔG° can be calculated for the processes (a) and (b) in Scheme 5.4. These processes are discussed in section 5.2.5.

5.2.4 Thermodynamic parameters for the free silane exchange process in cis-Pt(PCy₃)₂(H)(SiR₃)

As mentioned previously in section 5.2.3b, the silane ligand dissociates reversibly from the complex cis-Pt(PCy₃)₂(H)(SiR₃) in solution at high temperatures [Scheme 5.4 (b)]. Since the relative concentrations of cis-Pt(PCy₃)₂(H)(SiR₃), HSiR₃ and Pt(PCy₃) can be measured using quantitative ¹H and ³¹P [¹H] NMR spectroscopy, the equilibrium constant Kₛ for these steps can be obtained (Equation 5.1).

\[
cis\text{-Pt(PCy}_3\text{)}_2(H)(SiR_3) \rightleftharpoons K_s \rightleftharpoons Pt(PCy_3)_2 + HSiR_3
\]

\[
K_s = \frac{[Pt(PCy_3)][HSiR_3]}{[cis\text{-Pt(PCy}_3\text{)}_2(H)(SiR_3)]}
\]

(5.1)
$^{31}$P ($^1$H) NMR spectra were recorded using an inverse gated pulse sequence, with a delay period of at least ten times the acquisition time.\(^{18}\) The inverse gated pulse sequence suppresses the build up of the Nuclear Overhauser effect,\(^{19}\) whilst still decoupling $^1$H, and thus provides a quantitative measurement of $^{31}$P intensities. The $^1$H NMR resonance of the Si–H group on the free silane was found to have a long relaxation time of up to 8 seconds at room temperature. A 60 seconds delay between acquisition was therefore used to allow for reliable integration analysis of the proton spectrum.

Once $K_s$ is established for a range of temperatures, $\Delta H^o$ and $\Delta S^o$ for the dissociation of cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) can be obtained by applying the van't Hoff isochore (Equation 5.2, $R$ = gas constant). Since $\Delta H^o$ is only weakly temperature dependent, we should observe an almost linear relationship when plotting $\ln (K_s)$ against $T^{-1}$.

$$\ln (K_s) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (5.2)$$

5.2.4a Standard enthalpy and entropy of reaction for the dissociation of cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$)$_{15}$ to Pt(PCy$_3$)$_2$ and HSiPh$_3$

A sample of 15 was prepared in [§H$_3$]toluene and kept in ice prior to recording the corresponding NMR spectra. Quantitative $^1$H and $^{31}$P ($^1$H)NMR spectra were recorded initially at 290 K and subsequently at +5 degree intervals to 310 K. Table 5.2 shows the calculated equilibrium constants of dissociation (or free silane exchange) of cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 from 290 K to 310 K. The relative concentrations of 15, [HSiPh$_3$] and [Pt(PCy$_3$)$_2$] were obtained from the integrals of the hydride resonance of 15, the Si–H resonance of HSiPh$_3$ in the $^1$H NMR spectra and the integrals of the phosphorus resonance of 15 and Pt(PCy$_3$)$_2$. Figure 5.11 shows the van't Hoff plot of $\ln (K_s)$ against $T^{-1}$ as a straight line. The thermodynamic parameters for the dissociation of 15 were determined as $\Delta H^o = 74 \pm 10$ kJ mol$^{-1}$ and $\Delta S^o = 243 \pm 35$ J K$^{-1}$ mol$^{-1}$.
Table 5.2 The effect of temperature on the equilibrium constant $K_S$ for $cis$-$Pt(PCY_3)_2(H)(SiPh_3)$ 15 in $[^2H_8]$toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$K_S$</th>
<th>$\ln (K_S)$</th>
<th>$T^{-1} \times 10^3$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>0.189</td>
<td>-1.66</td>
<td>3.45</td>
</tr>
<tr>
<td>295</td>
<td>0.276</td>
<td>-1.28</td>
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<tr>
<td>300</td>
<td>0.531</td>
<td>-0.63</td>
<td>3.33</td>
</tr>
<tr>
<td>305</td>
<td>0.821</td>
<td>-0.20</td>
<td>3.28</td>
</tr>
<tr>
<td>310</td>
<td>1.330</td>
<td>0.28</td>
<td>3.23</td>
</tr>
</tbody>
</table>

Figure 5.11 Plot of $\ln (K_S)$ against $T^{-1}$ for the dissociation of $cis$-$Pt(PCY_3)_2(H)(SiPh_3)$ 15 in $[^2H_8]$toluene. The squares are the experimental points, the line shows the calculated line of best fit.

5.2.4b Standard enthalpy and entropy of reaction for the dissociation of $cis$-$Pt(PCY_3)_2(H)(SiMe_2CH_2CH=CH_2)$ 16 to $Pt(PCY_3)_2$ and $HSiMe_2CH_2CH=CH_2$

An NMR sample of $cis$-$Pt(PCY_3)_2(H)(SiMe_2CH_2CH=CH_2)$ 16 was prepared in $[^2H_8]$toluene and stored in liquid nitrogen prior to running the appropriate NMR spectra. This precaution was required to prevent excessive decomposition to $trans$-$Pt(PCY_3)_2(H)_2$ which occurs at room temperature during sample preparation. Equilibrium constants of
dissociation were obtained as for 15 (Table 5.3, Figure 5.12) yielding $\Delta H^\circ = 45 \pm 8$ kJ mol$^{-1}$ and $\Delta S^\circ = 155 \pm 30$ J K$^{-1}$ mol$^{-1}$.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$K_S$</th>
<th>$\ln (K_S)$</th>
<th>$T^{-1} / 10^3$ K$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>265</td>
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<td>3.77</td>
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<tr>
<td>270</td>
<td>0.267</td>
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<td>3.70</td>
</tr>
<tr>
<td>275</td>
<td>0.354</td>
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<td>3.64</td>
</tr>
<tr>
<td>280</td>
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<td>-0.53</td>
<td>3.57</td>
</tr>
<tr>
<td>285</td>
<td>0.725</td>
<td>-0.32</td>
<td>3.51</td>
</tr>
</tbody>
</table>

Table 5.3 The effect of temperature on the dissociation equilibrium constant $K_S$ for cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 in $[\text{^{2}H}_8]$toluene.

5.2.4c Standard enthalpy and entropy of reaction for the dissociation of cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17 to Pt(PCy$_3$)$_2$ and HSiMe$_2$Et.

An NMR sample of cis-Pt(PCy$_3$)$_2$(H)SiMe$_2$Et) 17 was prepared by adding a slight excess of the silane HSiMe$_2$Et to a $[\text{^{2}H}_8]$toluene solution of Pt(PCy$_3$)$_2$ where the SiH:Pt ratio was 1.06:1.00. Again to prevent thermal decomposition to the trans platinum dihydride the NMR sample was prepared at low temperature and kept frozen in liquid nitrogen prior to data collection. Equilibrium constants for dissociation were obtained, as for 15 and 16 (Table 5.4, Figure 5.12), yielding $\Delta H^\circ = 27 \pm 2$ kJ mol$^{-1}$ and $\Delta S^\circ = 94 \pm 7$ J K$^{-1}$ mol$^{-1}$.

The standard enthalpies ($\Delta H^\circ$) and standard entropies ($\Delta S^\circ$) of the dissociation of complexes 15-17 are summarised in Table 5.5. The combined van’t Hoff plots of complexes 15-17 are in Figure 5.12.
Table 5.4 The effect of temperature on the equilibrium constant of dissociation $K_S$ for cis-$\text{Pt(PCY}_3\text{)}_2(\text{H})(\text{SiMe}_2\text{Et})$ 17 in $[^2\text{H}_8]\text{toluene}$.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$K_S$</th>
<th>$\ln (K_S)$</th>
<th>$T^{-1} / 10^{-3} \text{K}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
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<td>-1.52</td>
<td>4.00</td>
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<tr>
<td>255</td>
<td>0.284</td>
<td>-1.26</td>
<td>3.92</td>
</tr>
<tr>
<td>260</td>
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<td>-1.00</td>
<td>3.85</td>
</tr>
<tr>
<td>265</td>
<td>0.455</td>
<td>-0.79</td>
<td>3.77</td>
</tr>
<tr>
<td>270</td>
<td>0.562</td>
<td>-0.58</td>
<td>3.70</td>
</tr>
</tbody>
</table>

Table 5.5 Summary of thermodynamic parameters of the dissociation of cis-$\text{Pt(PCY}_3\text{)}_2(\text{H})(\text{SiR}_3)$ in $[^2\text{H}_8]\text{toluene}$ (error bars as 95% probability on least squares fit).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ / \text{kJ mol}^{-1}$</th>
<th>$\Delta S^\circ / \text{J K}^{-1} \text{mol}^{-1}$</th>
<th>$\Delta G^\circ_{300} / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{cis-Pt(PCY}_3\text{)}_2(\text{H})(\text{SiPh}_3)$ 15</td>
<td>74 ± 10</td>
<td>243 ± 35</td>
<td>2</td>
</tr>
<tr>
<td>$\text{cis-Pt(PCY}_3\text{)}_2(\text{H})(\text{SiMe}_2\text{CH}_2\text{CH}=$\text{CH}_2)$ 16</td>
<td>45 ± 8</td>
<td>155 ± 30</td>
<td>-2</td>
</tr>
<tr>
<td>$\text{cis-Pt(PCY}_3\text{)}_2(\text{H})(\text{SiMe}_2\text{Et})$ 17</td>
<td>27 ± 2</td>
<td>94 ± 7</td>
<td>-2</td>
</tr>
</tbody>
</table>

Figure 5.12 Linear plots of $\ln (K_S)$ against $T^{-1}$ for the dissociation of cis-$\text{Pt(PCY}_3\text{)}_2(\text{H})(\text{SiR}_3)$ in $[^2\text{H}_8]\text{toluene}$. 

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5.2.5 Activation parameters for the dynamic processes of \textit{cis-Pt(PCy}_3\textit{)}_2\textit{(H)(SiR}_3\textit{)} in solution

Using the programme DNMR-SIM, dynamic NMR spectra were calculated for the complex \textit{cis-Pt(PCy}_3\textit{)}_2\textit{(H)(SiR}_3\textit{)}. The two dynamic exchange processes simulated were the reversible silane dissociation process (\(k_1\) and \(k_2\)) and the mutual phosphine exchange process (\(k_3\)) (Scheme 5.4). The DNMR-SIM programme allows for the input of the forward rate constant between each different chemical configurations. Hence the rate of exchange for the two dynamic processes observed in \textit{cis-Pt(PCy}_3\textit{)}_2\textit{(H)(SiR}_3\textit{)} in solution can be extracted from the calculated spectra using DNMR-SIM. Since \(k_1\), \(k_2\) and \(k_3\) values are a function of temperature, the activation parameters of these dynamic processes, \(\Delta H^\ddagger\), \(\Delta S^\ddagger\) and \(\Delta G^\ddagger\) at 300 can be calculated using the Eyring equation (Equation 5.3, \(\hbar\) = Planck constant, \(k\) = Boltzmann constant and \(R\) = gas constant).

\[
\ln \left( \frac{k}{T} \right) = \ln \left( \frac{k}{\hbar} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}
\]  

(5.3)

5.2.6 DNMR-SIM

The programme DNMR-SIM allows for the simulation of dynamic NMR spectra for a system with a maximum total of five different magnetically equivalent groups. The programme consists of four main areas: (a) Main Parameters, (b) Configurations, (c) Rate Constants, (d) Populations for systems which contain non mutual exchange processes or Exchange Vectors for systems which contain purely mutual exchange processes.

5.2.6a Main Parameters

In this section, the first parameter which the programme requires is the maximum number of magnetically equivalent nuclei in the system. For the platinum silyl hydride system, \textit{cis-Pt(PCy}_3\textit{)}_2\textit{(H)(SiR}_3\textit{)}, we are only concerned with the hydride ligand which is coupled to the two magnetically inequivalent phosphorus atoms. Couplings to \(^{195}\text{Pt}\) and \(^{29}\text{Si}\) are ignored to simplify the situation, so we only examine the dynamic behaviour of the doublet of doublets hydride resonance, and not the \(^{195}\text{Pt}\) satellites. The maximum number of magnetically equivalent nuclei in this case was three.

The next parameter is the number of different chemical configurations in the system. In our proposed mechanism in Scheme 5.4, we have three different chemical configurations. That is two configurations for the silyl and hydride ligand exchange, or phosphine mutual exchange and one configuration for silane dissociation.
The number of data points and the output range of the simulated spectrum are required next. In all our simulations, the number of data points used was 4720 and the range of the simulated spectrum corresponds to 1500 Hz at 500.13 MHz. The programme then asks if the system is undergoing pure mutual exchange. Although we have mutual phosphine exchange present in our system, silane dissociation, which is not a mutual exchange process, is also present. The width at half height is set corresponding to the line width obtained for the hydride spectrum at low temperature at which point there are no fluxional processes apparent.

5.2.6b Configuration

In this section we need to enter the necessary NMR data for each of the three chemical configurations. This is illustrated in Scheme 5.5 and Table 5.6 for cis-Pt(PCy₃)₂(H)(SiPh₃) 15. In configuration 1, (w1), (w2) and (w3) represent the hydride, trans and cis phosphine ligands in Pt(PCy₃)₂(H)(SiPh₃) 15, respectively. In configuration 2, (w1) represents the SiH in the free silane, (w2) and (w3) represent the two phosphine ligands in Pt(PCy₃)₂. In configuration 3, (w1), (w2) and (w3) represent the hydride, cis and trans phosphine ligands in Pt(PCy₃)₂(H)(SiPh₃) (15), respectively.

![Scheme 5.5 Proposed dynamic exchange processes of cis-Pt(PCy₃)₂(H)(SiPh₃). (1), (2) and (3) are the three chemical configurations used in DNMR-SIM. The labels (w1), (w2) and (w3) refer to the labelling system used in DNMR-SIM, see also Table 5.6.](image-url)
<table>
<thead>
<tr>
<th>Configuration 1</th>
<th>(w1)</th>
<th>(w2)</th>
<th>(w3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Shift (Hz)</td>
<td>-1975.5</td>
<td>-12000.0</td>
<td>-12769.3</td>
</tr>
<tr>
<td>$J(w1, \text{Hz})$</td>
<td>141.8</td>
<td>-23.3</td>
<td></td>
</tr>
<tr>
<td>$J(w2, \text{Hz})$</td>
<td></td>
<td></td>
<td>13.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Configuration 2</th>
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<th>(w2)</th>
<th>(w3)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-15000.0</td>
<td>-15000.0</td>
</tr>
<tr>
<td>$J(w1, \text{Hz})$</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$J(w2, \text{Hz})$</td>
<td></td>
<td></td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Configuration 3</th>
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<th>(w2)</th>
<th>(w3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Shift (Hz)</td>
<td>-1975.5</td>
<td>-12769.3</td>
<td>-12000.0</td>
</tr>
<tr>
<td>$J(w1, \text{Hz})$</td>
<td>-23.3</td>
<td>141.8</td>
<td></td>
</tr>
<tr>
<td>$J(w2, \text{Hz})$</td>
<td></td>
<td></td>
<td>13.0</td>
</tr>
</tbody>
</table>

**Table 5.6** Data entries for the chemical configurations in DNMR-SIM. Data shown are for cis-Pt(PCY$_3$)$_2$(H)(SiPh$_3$)$_15$. See Scheme 5.5 for the labelling of (w1), (w2) and (w3).

### 5.2.6c Rate Constants

In this section, the estimated forward rate constants between all the specified chemical configurations are entered into the programme. Configuration 1 to configuration 2 is the dissociation of silane ($k_1$), configuration 1 to configuration 3 is the mutual phosphine exchange ($k_3$) and configuration 2 to configuration 3 is the addition of silane to Pt(PCY$_3$)$_2$ ($k_2$) (Table 5.7 and Scheme 5.5). Note, $k_1$ and $k_2$ are related to the equilibrium constant for silane dissociation, $K_S$, calculated in Section 5.2.4.

<table>
<thead>
<tr>
<th>Configuration 2</th>
<th>Configuration 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration 1</td>
<td>$k_1$</td>
</tr>
<tr>
<td>Configuration 2</td>
<td>$k_2$</td>
</tr>
</tbody>
</table>

**Table 5.7** Data entries for the forward rate constant between each chemical configurations in DNMR-SIM. $k_1$ = silane dissociation. $k_2$ = silane addition. $k_3$ = mutual phosphine exchange.
5.2.6d Population Levels

The population levels of all three different chemical configurations are specified in this section. Since configurations 1 and 3 are the same, they will have the same population. The population of 2, at a specific temperature, was calculated from the thermodynamic data obtained in Section 5.2.4.

5.2.6e Comparison between simulated and observed spectra.

The output of the simulated spectra from DNMR-SIM were compared against the observed spectra graphically using the spreadsheet package Origin. Rate constants $k_1$, $k_2$ and $k_3$ are adjusted in order to obtain the best fit between the simulated spectrum and the observed spectrum. This procedure was repeated for all the observed dynamic $^1H$ NMR spectra of complexes 15-17.

5.2.7 Simulation of dynamic NMR spectra

5.2.7a Simulations of the dynamic NMR spectra of cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$)$_15$

$^1H$ NMR spectra of complex 15 were obtained from 285 K to 315 K in [D$_8$]toluene. The hydride spectra for complex 15 were then calculated using DNMR-SIM with the aim to match the observed spectra by varying the rate constants $k_1$, $k_2$ and $k_3$ as described in Section 5.2.6. Figure 5.13 shows the results obtained from the dynamic NMR spectra simulation programme DNMR-SIM. Rate constants were calculated as for a first-order process since different concentrations of silane did not affect the line shape of the hydride resonance in the dynamic $^1H$ NMR spectra.

The rate constants $k_1$ were calculated between the temperature range of 280 K to 315 K (Table 5.8). The Eyring plot of ln $(k_1 / T)$ against $T^{-1}$ yielded a straight line (Figure 5.14) with activation parameters $\Delta H^\ddagger_{k_1} = 106 \pm 5 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger_{k_1} = 123 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger_{300(k_1)} = 70 \text{ kJ mol}^{-1}$.

The rate constants $k_2$ were calculated for the temperature range of 300 K to 315 K (Table 5.9). The Eyring plot of ln $(k_2 / T)$ against $T^{-1}$ yielded a straight line (Figure 5.15) with activation parameters $\Delta H^\ddagger_{k_2} = 32 \pm 4 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger_{k_2} = -121 \pm 14 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger_{300(k_2)} = 68 \text{ kJ mol}^{-1}$.

The rate constants $k_3$ were calculated for the temperature range 300 K to 315 K (Table 5.10). The Eyring plot of ln $(k_3 / T)$ against $T^{-1}$ yielded a straight line (Figure 5.16) with activation parameters $\Delta H^\ddagger_{k_3} = 73 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger_{k_3} = 29 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger_{300(k_3)} = 64 \text{ kJ mol}^{-1}$. All error bars represent 95% probability for a least squares fit.
Figure 5.13 Observed and calculated 500.13 MHz $^1$H hydride NMR spectra of *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 as a function of temperature. $k_1$ = silane dissociation, $k_2$ = silane addition and $k_3$ = mutual phosphine exchange.
<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$k_1$ / s$^{-1}$</th>
<th>ln (k$_1$ / T)</th>
<th>$T^{-1} / 10^3$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>5</td>
<td>-4.09</td>
<td>3.33</td>
</tr>
<tr>
<td>305</td>
<td>10</td>
<td>-3.42</td>
<td>3.28</td>
</tr>
<tr>
<td>310</td>
<td>20</td>
<td>-2.74</td>
<td>3.23</td>
</tr>
<tr>
<td>315</td>
<td>40</td>
<td>-2.06</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Table 5.8 The effect of temperature on the rate of silane dissociation, $k_1$, for cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 in [H$_8$]toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$k_2$ / s$^{-1}$</th>
<th>ln (k$_2$ / T)</th>
<th>$T^{-1} / 10^3$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>10</td>
<td>-3.40</td>
<td>3.33</td>
</tr>
<tr>
<td>305</td>
<td>12</td>
<td>-3.24</td>
<td>3.28</td>
</tr>
<tr>
<td>310</td>
<td>15</td>
<td>-3.03</td>
<td>3.23</td>
</tr>
<tr>
<td>315</td>
<td>19</td>
<td>-2.81</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Table 5.9 The effect of temperature on the rate of silane addition, $k_2$, for cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 in [H$_8$]toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$k_3$ / s$^{-1}$</th>
<th>ln (k$_3$ / T)</th>
<th>$T^{-1} / 10^3$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>5</td>
<td>-4.13</td>
<td>3.57</td>
</tr>
<tr>
<td>285</td>
<td>9</td>
<td>-3.46</td>
<td>3.51</td>
</tr>
<tr>
<td>290</td>
<td>14</td>
<td>-3.03</td>
<td>3.45</td>
</tr>
<tr>
<td>295</td>
<td>25</td>
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<td>3.39</td>
</tr>
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<td>3.28</td>
</tr>
<tr>
<td>310</td>
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<tr>
<td>315</td>
<td>180</td>
<td>-0.56</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Table 5.10 The effect of temperature on the rate of mutual phosphine exchange, $k_3$, for cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 in [H$_8$]toluene.
Figure 5.14 Eyring plot showing the temperature dependence of the rate of silane dissociation, $k_1$, for cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 in [$^2$H$_8$]toluene.

Figure 5.15 Eyring plot showing the temperature dependence of the rate silane addition, $k_2$, for cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 in [$^2$H$_8$]toluene.
3.1 3.2 3.3 3.4 3.5 3.6

Figure 5.16 Eyring plot showing the temperature dependence of the rate of silane addition, $k_3$, for cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) $15$ in $[^2H_8]$toluene.

5.2.7b Simulations of the dynamic NMR spectra of cis-Pt(PCy$_3$)$_2$(H)-(SiMe$_2$CH$_2$CH=CH$_2$) $16$

$^1$H NMR spectra of $16$ were recorded for temperatures from 255 K to 300 K in $[^2H_8]$toluene. The rate constants $k_1$, $k_2$ and $k_3$ were calculated as for $15$ using DNMR-SIM.

The activation parameters for silane dissociation, $k_1$ (Table 5.11), were calculated as $\Delta H^\ddagger_{k_1} = 99 \pm 9$ kJ mol$^{-1}$, $\Delta S^\ddagger_{k_1} = 124 \pm 32$ J mol$^{-1}$ K$^{-1}$ and $\Delta G^\ddagger_{300(k_1)} = 61$ kJ mol$^{-1}$.

The activation parameters for silane addition, $k_2$ (Table 5.12), were calculated as $\Delta H^\ddagger_{k_2} = 50 \pm 5$ kJ mol$^{-1}$, $\Delta S^\ddagger_{k_2} = -42 \pm 16$ J mol$^{-1}$ K$^{-1}$ and $\Delta G^\ddagger_{300(k_2)} = 63$ kJ mol$^{-1}$.

The activation parameters for mutual phosphine exchange, $k_3$ (Table 5.13), were calculated as $\Delta H^\ddagger_{k_3} = 69 \pm 2$ kJ mol$^{-1}$, $\Delta S^\ddagger_{k_1} = 40 \pm 7$ J mol$^{-1}$ K$^{-1}$ and $\Delta G^\ddagger_{300(k_3)} = 58$ kJ mol$^{-1}$. 
### Table 5.11 The effect of temperature on the rate of silane dissociation, $k_1$, for cis-$\text{Pt(PCy}_3)_2\text{(H)(SiMe}_2\text{CH}_2\text{CH}=$CH$_2)$16 in $[^2\text{H}_8]$toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$k_1$ / s$^{-1}$</th>
<th>ln ($k_1$ / T)</th>
<th>$T^{-1} / 10^{-3}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
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<td>3.57</td>
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<td>285</td>
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</tr>
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<td>70</td>
<td>-1.44</td>
<td>3.39</td>
</tr>
<tr>
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<td>-0.92</td>
<td>3.33</td>
</tr>
</tbody>
</table>

### Table 5.12 The effect of temperature on the rate of silane addition, $k_2$, for cis-$\text{Pt(PCy}_3)_2\text{(H)(SiMe}_2\text{CH}_2\text{CH}=$CH$_2)$16 in $[^2\text{H}_8]$toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$k_2$ / s$^{-1}$</th>
<th>ln ($k_2$ / T)</th>
<th>$T^{-1} / 10^{-3}$ K$^{-1}$</th>
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</thead>
<tbody>
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<tr>
<td>290</td>
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<td>-2.30</td>
<td>3.45</td>
</tr>
<tr>
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<td>40</td>
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<tr>
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</tr>
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</table>

### Table 5.13 The effect of temperature on the rate of mutual phosphine exchange, $k_3$, for cis-$\text{Pt(PCy}_3)_2\text{(H)(SiMe}_2\text{CH}_2\text{CH}=$CH$_2)$16 in $[^2\text{H}_8]$toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>$k_3$ / s$^{-1}$</th>
<th>ln ($k_3$ / T)</th>
<th>$T^{-1} / 10^{-3}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
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<td>-4.44</td>
<td>3.92</td>
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<td>260</td>
<td>6</td>
<td>-3.77</td>
<td>3.85</td>
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<tr>
<td>265</td>
<td>10</td>
<td>-3.27</td>
<td>3.77</td>
</tr>
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<td>270</td>
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<td>3.70</td>
</tr>
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<td>0.49</td>
<td>3.33</td>
</tr>
</tbody>
</table>
5.2.7c Simulations of the dynamic NMR spectra of cis-Pt(PCy3)2(H)(SiMe2Et) 17

\(^1\)H NMR spectra of 17 were recorded for temperatures ranging from 240 K to 300 K in \([\text{^2}H_8]\)toluene. The rate constants \(k_1\), \(k_2\) and \(k_3\) were calculated as for 15 and 16 using DNMR-SIM. Figure 5.17 shows the observed and the calculated variable temperature \(^{31}\)P \(^1\)H NMR spectra of 17. The calculated spectra in Figure 5.19 were simulated using DNMR-SIM. The rate constants \(k_1\), \(k_2\) and \(k_3\), obtained from the \(^1\)H NMR spectra of 17, were used without change for the simulation of the \(^{31}\)P \(^1\)H NMR spectra.

The activation parameters for silane dissociation, \(k_1\) (Table 5.14), were calculated as

\[
\Delta H^*_k_1 = 100 \pm 11 \text{ kJ mol}^{-1}, \quad \Delta S^*_k_1 = 142 \pm 38 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{and} \quad \Delta G^*_{300(k_1)} = 57 \text{ kJ mol}^{-1}.
\]

The activation parameters for silane addition, \(k_2\) (Table 5.15), were calculated as

\[
\Delta H^*_k_2 = 74 \pm 11 \text{ kJ mol}^{-1}, \quad \Delta S^*_k_2 = 49 \pm 39 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{and} \quad \Delta G^*_{300(k_2)} = 59 \text{ kJ mol}^{-1}.
\]

The activation parameters for mutual phosphine exchange, \(k_3\) (Table 5.16), were calculated as

\[
\Delta H^*_k_3 = 66 \pm 2 \text{ kJ mol}^{-1}, \quad \Delta S^*_k_3 = 33 \pm 7 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{and} \quad \Delta G^*_{300(k_3)} = 56 \text{ kJ mol}^{-1}.
\]

Summaries of the activation parameters of 15-17 can be found in Tables 5.17-5.19 and Figures 5.18-5.20.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>(k_1) / s(^{-1})</th>
<th>(\ln \left( k_1 / T \right) )</th>
<th>(T^{-1} / 10^3 \text{ K}^{-1} )</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>3.60</td>
</tr>
<tr>
<td>280</td>
<td>38</td>
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<td>283</td>
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</tr>
<tr>
<td>288</td>
<td>110</td>
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</table>

Table 5.14 The effect of temperature on the rate of free silane exchange, \(k_1\), for cis-Pt(PCy3)2(H)(SiMe2Et) 17 in \([\text{^2}H_8]\)toluene.
Figure 5.17 Selected calculated and observed 202.46 MHz $^{31}$P $^1$H NMR spectra of $cis$-$Pt(PCy)_2(H)(SiMe_2CH_2CH=CH_2)$ 17 as a function of temperature.
<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>k₂ / s⁻¹</th>
<th>ln (k₂ / T)</th>
<th>T⁻¹ / 10³ K⁻¹</th>
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</thead>
<tbody>
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<td>11</td>
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<td>278</td>
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<td>3.60</td>
</tr>
<tr>
<td>280</td>
<td>44</td>
<td>-1.85</td>
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<td>288</td>
<td>92</td>
<td>-1.14</td>
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<tr>
<td>290</td>
<td>108</td>
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<td>3.45</td>
</tr>
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</table>

**Table 5.15** The effect of temperature on the rate of silane addition, k₂, for cis-Pt(PCy₃)₂(H)(SiMe₂Et) 17 in [²H₈]toluene.

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>k₃ / s⁻¹</th>
<th>ln (k₃ / T)</th>
<th>T⁻¹ / 10³ K⁻¹</th>
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<tbody>
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<td>4.17</td>
</tr>
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<td>-4.24</td>
<td>4.00</td>
</tr>
<tr>
<td>260</td>
<td>14</td>
<td>-2.92</td>
<td>3.85</td>
</tr>
<tr>
<td>270</td>
<td>43</td>
<td>-1.84</td>
<td>3.70</td>
</tr>
<tr>
<td>273</td>
<td>53</td>
<td>-1.64</td>
<td>3.66</td>
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<tr>
<td>278</td>
<td>105</td>
<td>-0.97</td>
<td>3.60</td>
</tr>
<tr>
<td>280</td>
<td>140</td>
<td>-0.69</td>
<td>3.57</td>
</tr>
<tr>
<td>283</td>
<td>190</td>
<td>-0.40</td>
<td>3.53</td>
</tr>
<tr>
<td>288</td>
<td>300</td>
<td>0.04</td>
<td>3.47</td>
</tr>
<tr>
<td>290</td>
<td>380</td>
<td>0.27</td>
<td>3.45</td>
</tr>
</tbody>
</table>

**Table 5.16** The effect of temperature on the rate of mutual phosphine exchange, k₃, for cis-Pt(PCy₃)₂(H)(SiMe₂Et) 17 in [²H₈]toluene.
<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\ddagger_{k_1}$ / kJ mol$^{-1}$</th>
<th>$\Delta S^\ddagger_{k_1}$ / J K$^{-1}$ mol$^{-1}$</th>
<th>$\Delta G^\ddagger_{300(k_1)}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15</td>
<td>106 ± 5</td>
<td>123 ± 15</td>
<td>70</td>
</tr>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16</td>
<td>99 ± 9</td>
<td>124 ± 32</td>
<td>61</td>
</tr>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17</td>
<td>100 ± 11</td>
<td>142 ± 38</td>
<td>57</td>
</tr>
</tbody>
</table>

Table 5.17 Activation parameters for silane dissociation, $k_1$, in cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15, cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 and cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17 in [^2H$_8$]toluene. (Error bars quoted as 95 % probability on least squares fit).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\ddagger_{k_2}$ / kJ mol$^{-1}$</th>
<th>$\Delta S^\ddagger_{k_2}$ / J K$^{-1}$ mol$^{-1}$</th>
<th>$\Delta G^\ddagger_{300(k_2)}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15</td>
<td>32 ± 12</td>
<td>-121 ± 14</td>
<td>68</td>
</tr>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16</td>
<td>50 ± 5</td>
<td>-42 ± 16</td>
<td>63</td>
</tr>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17</td>
<td>74 ± 11</td>
<td>49 ± 39</td>
<td>59</td>
</tr>
</tbody>
</table>

Table 5.18 Activation parameters for silane addition, $k_2$, in cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15, cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 and cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17 in [^2H$_8$]toluene (Error bars quoted as 95 % probability on least squares fit).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\ddagger_{k_3}$ / kJ mol$^{-1}$</th>
<th>$\Delta S^\ddagger_{k_3}$ / J K$^{-1}$ mol$^{-1}$</th>
<th>$\Delta G^\ddagger_{300(k_3)}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15</td>
<td>73 ± 3</td>
<td>29 ± 9</td>
<td>64</td>
</tr>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16</td>
<td>69 ± 2</td>
<td>40 ± 7</td>
<td>58</td>
</tr>
<tr>
<td>cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17</td>
<td>66 ± 2</td>
<td>33 ± 7</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 5.19 Activation parameters for mutual phosphine exchange, $k_3$, in cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15, cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 and cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17 in [^2H$_8$]toluene (Error bars quoted as 95 % probability on least squares fit).
Figure 5.18 Eyring plots showing the temperature dependence of the rate of silane dissociation, $k_1$, of cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) in [H$_8$]toluene.

Figure 5.19 Eyring plots showing the temperature dependence of the rate of silane addition, $k_2$, of cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) in [H$_8$]toluene.
5.2.8 Thermal reactions of cis-Pt(PCy3)2(H)(SiR3)

As mentioned previously, the complex cis-Pt(PCy3)2(H)(SiR3) degrades thermally in solution to form trans-Pt(PCy3)2(H)2. The trans-platinum dihydride complex itself does not react with the tertiary silanes used in this investigation at room temperature. Interestingly, Ebsworth has reported that trans-Pt(PCy3)2(H)2 reacts with SiH4 or SiClH3 to give the corresponding trans-platinum silyl hydride complex.21 The identification of the organosilane thermal decomposition product would allow us to determine the most plausible mechanism for this thermal degradation process.

The complex cis-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 16 was used to identify the organosilane products formed on thermal decomposition to trans-Pt(PCy3)2(H)2. Complex 16 was dissolved in C6D6 under an argon atmosphere and then immediately analysed by GC. A peak is observed from the chromatograph corresponding to the presence of the silane HSiMe2CH2CH=CH2. The free silane peak gradually disappeared over 30 minutes and three new peaks were eventually formed with retention times of 7.2 minutes, 19.0 minutes and 33.9 minutes (for GC conditions see experimental section 6.5). The long retention time observed for the final peak at 33.9 minutes would suggest that oligomeric silanes are being produced. GC-MS analysis of the three peaks did not, however, reveal clearly the type of organosilane products formed on thermal
decomposition of 16. Nevertheless, the GC-MS of the organosilane with a retention time of 19.0 minutes did show a mass peak at \( m/z = 198 \) which could correspond to the dehydrogenative silation\(^3\) or dehydrosilyl coupling\(^5\) of two allyldimethylsilane molecules (Equation 5.4 and 5.5). In either case, molecular hydrogen is formed and can react with Pt(PCy\(_3\))\(_2\) to form trans-Pt(PCy\(_3\))\(_2\)(H)\(_2\), the thermal decomposition product of 16 (Scheme 5.6). We have also found that addition of hydrogen (1 atm) to an NMR sample 16 in C\(_6\)D\(_6\) at room temperature yielded trans-Pt(PCy\(_3\))\(_2\)(H)\(_2\) and signals due to dissolved H\(_2\) were not detected in the \(^1\)H NMR spectrum. This indicates that H\(_2\) reacts readily with 16 to form trans-Pt(PCy\(_3\))\(_2\)(H)\(_2\).

\[
2\text{HSiMe}_2\text{CH}_2\text{CH}==\text{CH}_2 \longrightarrow \text{HSiMe}_2\text{CH}_2\text{CH}==\text{CHSiMe}_2\text{CH}==\text{CH}_2 + \text{H}_2 \quad (5.4)
\]

\[
2\text{HSiMe}_2\text{CH}_2\text{CH}==\text{CH}_2 \longrightarrow \text{CH}_2==\text{CHCH}_2\text{(Me}_2\text{)Si}==\text{Si(Me}_2\text{)CH}_2\text{CH}==\text{CH}_2 + \text{H}_2 \quad (5.5)
\]

![Diagram](attachment:diagram.png)

**Scheme 5.6** Possible processes responsible for the thermal decomposition of cis-Pt(PCy\(_3\))\(_2\)(H)(SiMe\(_2\)CH\(_2\)CH==CH\(_2\)) 16 to trans-Pt(PCy\(_3\))\(_2\)(H)\(_2\).
5.2.9 Photochemical reactions of cis-Pt(PCy3)2(H)(SiR3)

Clark et al. found that the complex cis-Pt(PCy3)2(H)(SiPh3) 15 undergoes quantitative cis-trans isomerisation when irradiated by a weak UV source to yield trans-Pt(PCy3)2(H)(SiPh3) 21. However, no characterisation was reported for this complex. In our studies we have found that the complexes cis-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 16 and cis-Pt(PCy3)2(H)(SiMe2Et) 17 can also undergo cis-trans isomerisation when photolysed with UV light at 250 K to form trans-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 22 and trans-Pt(PCy3)2(H)(SiMe2Et) 23 respectively. For comparison, the cis-trans photoisomerisation of 15 was also studied. This isomerisation process proceeded at room temperature but thermal decomposition to trans-Pt(PCy3)2(H)2 was also observed.

Figure 5.21 (i) shows the 1H NMR spectrum of 16 after 4 hours photolysis at -78 °C. Here the new triplet resonance of the trans isomer 22 was observed at δ -2.64 [\(J(\text{PH}) = 18.1 \text{ Hz}, J(\text{PtH}) = 561.3 \text{ Hz}\)]. On warming the sample to 300 K [Figure 5.24 (ii)] complex 16 thermally decomposes to trans-Pt(PCy3)2(H)2. In contrast the trans isomer 22 was thermally stable at this temperature. Table 5.20 summarises some selected NMR data for trans-Pt(PCy3)2(H)(SiPh3) 21, trans-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 22 and trans-Pt(PCy3)2(H)(SiMe2Et) 23 as formed by photolysis of the corresponding cis-isomer.

![Figure 5.21](image_url)

Figure 5.21 1H NMR spectrum (500.13 Mhz) of cis-(PCy3)2(H)(SiMe2CH2CH=CH2) 16 in [\(^2\text{H}_8\)]toluene after 4 hours photolysis at -78 °C. Only the hydride regions are shown. (i) at 250 K. (ii) at 300 K. a Complex 16. b trans-Pt(PCy3)2(H)-(SiMe2CH2CH=CH2) 22. c trans-Pt(PCy3)2(H)2.
Table 5.20 Selected $^1$H (500.13 MHz) and $^{31}$P $[^1$H] (202.46 MHz) NMR data of complexes 21-23. $^a$ in $[^2$H$_8$]toluene at 250 K. $^b$ in $C_6D_6$ at 300 K.

5.2.9a Photolysis of trans-Pt(PCy$_3)_2$(H)$_2$ with HSiR$_3$

As mentioned previously, the complex trans-Pt(PCy$_3)_2$(H)$_2$ does not appear to react thermally with the tertiary silanes studied. However, low temperature photolysis of trans-Pt(PCy$_3)_2$(H)$_2$ with HSiPh$_3$ yielded trans-Pt(PCy$_3)_2$(H)(SiPh$_3$) 21. Complete conversion was not achieved possibly due to insufficient photolysis time (Figure 5.22).

![Figure 5.22](image)

Figure 5.22 $^1$H (500.13 MHz) NMR spectrum of trans-Pt(PCy$_3)_2$(H)$_2$ with HSiPh$_3$ in $[^2$H$_8$]toluene after 3 hours photolysis at $-77 \, ^\circ$C. Only the hydride region is shown.

Photolysis of an NMR sample of trans-Pt(PCy$_3)_2$(H)$_2$ with HSiMe$_2$Et in $C_6D_6$ at room temperature formed trans-Pt(PCy$_3)_2$(H)(SiMe$_2$Et) 23 in very low yield (Figure 5.23). The cis-platinum silyl hydride 17 was detected when an NMR sample of trans-Pt(PCy$_3)_2$(H)$_2$ and HSiMe$_2$Et in $[^2$H$_8$]toluene are photolysed in situ in the NMR spectrometer at 250 K (Figure 5.24).
Figure 5.23 $^1\text{H}$ (500.13 MHz, 300 K) NMR spectrum of trans-Pt(PCy$_3$)$_2$(H)$_2$ with excess HSiMe$_2$Et in C$_6$D$_6$ after 1 day photolysis at room temperature (only the hydride region is shown). $a$ trans-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 23. $b$ trans-Pt(PCy$_3$)$_2$(H)$_2$.

Figure 5.24 $^1\text{H}$ (300.13 MHz, 250 K) NMR spectrum of trans-Pt(PCy$_3$)$_2$(H)$_2$ with excess HSiMe$_2$Et in $[^2\text{H}_8]$toluene after 1 hour in-situ photolysis (only the hydride region is shown). $a$ cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17. $b$ trans-Pt(PCy$_3$)$_2$(H)$_2$.

The initial appearance of cis-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) 17 from the photolysis of trans-Pt(PCy$_3$)$_2$(H)$_2$ indicates that 17 is the complex formed in the first instance when trans-Pt(PCy$_3$)$_2$(H)$_2$ is photolysed with HSiMe$_2$Et. The cis-platinum silyl hydride 17 then proceeds to isomerise to the trans-isomer 23 on further UV irradiation.
5.2.10 Reaction of Pt(PCy$_3$)$_2$ with disilanes

Eaborn et al. have previously reported that reaction of Pt(PPh$_3$)$_2$(C$_2$H$_4$) with (HPh$_2$Si)$_2$O or HMe$_2$Si(C$_6$H$_4$)SiMe$_2$H at 45 °C yields the metallacyclic complexes Pt(PPh$_3$)$_2$(SiPh$_2$OSiPh$_2$) or Pt(PPh$_3$)$_2$(SiMe$_2$(C$_6$H$_4$)SiMe$_2$)$_2$. Their evidence for this product was based upon elemental analysis (C, H) and the absence of ν(Pt–H) at ca. 2100 cm$^{-1}$ in the IR spectrum.

In our studies, similar reactions between Pt(PCy$_3$)$_2$ and the disilanes (HPh$_2$Si)$_2$O and HMe$_2$Si(C$_6$H$_4$)SiMe$_2$H was carried out. NMR data of the product formed between Pt(PCy$_3$)$_2$ and (HPh$_2$Si)$_2$O show a doublet of doublets hydride resonance with $^{195}$Pt satellites in the $^1$H NMR spectrum and two inequivalent doublet resonances, again with $^{195}$Pt satellites, in the $^{31}$P {$^1$H} NMR spectrum. The $^1$H NMR spectrum also shows a singlet resonance at δ 6.06 which is close to the Si–H resonance of the free disilane. These features indicate that only one of the two Si–H bonds on the disilane has been oxidatively added to the platinum metal centre to form cis-Pt(PCy$_3$)$_2$(H)(SiPh$_2$OSiPh$_2$H)$_2$. The four-membered cyclic disilyl complex Pt(PCy$_3$)$_2$(SiPh$_2$OSiPh$_2$) was not observed even when excess Pt(PCy$_3$)$_2$ was reacted with (HPh$_2$Si)$_2$O at ambient temperatures.

The reaction of Pt(PCy$_3$)$_2$ with 1,2-bis(dimethylsilyl)benzene, HMe$_2$Si(C$_6$H$_4$)SiMe$_2$H, did not result in the formation of the cis oxidative addition product as was observed with (HPh$_5$Si)$_2$O. Instead, two platinum phosphine complexes were formed when the reaction was carried out at room temperature, as evident from the corresponding $^{31}$P {$^1$H} NMR spectrum. Here we observed two singlet resonances both with $^{195}$Pt satellites. One broad resonance was located at δ$^p$ 56.1 [$J$(PtP) = 1531 Hz] A5 and the other was a singlet resonance at δ$^p$ 33.5 [$J$(PtP) = 1437 Hz] B5. In the $^1$H NMR spectrum a broad hydride resonance was observed at δ$^h$ -1.89 [$J$(PtH) = 675.2 Hz] and the methyl resonance of a co-ordinated disilane was observed at δ$^h$ 0.94 possessing $^{195}$Pt satellites [$J$(PtH) = 28.3 Hz]. Reaction of Pt(PCy$_3$)$_2$ with HMe$_2$Si(C$_6$H$_4$)SiMe$_2$H at -78 °C only yielded the product with a broad phosphorus resonance at δ$^p$ 56.1 and the $^1$H resonances at δ$^h$ -1.89 and δ$^h$ 0.94. The ratio of the methyl and hydride resonances was 6:1. From these data, we can infer that the complex formed at low temperature is A5 and that it is a hydride species with the disilyl ligand attached to the platinum centre. Also, the $^1$H NMR spectrum of A5 with $^{195}$Pt selectively decoupled at δ ~5700 (see below) removes $^{195}$Pt coupling to both the hydride and methyl resonances.

Complex A5 decomposes thermally to trans-Pt(PCy$_3$)$_2$(H)$_2$ at room temperature, in a similar fashion to the cis-platinum silyl hydride complexes 15-20. However, A5 does not appear to form B5 at room temperature. On cooling an NMR sample of A5 to 200 K, the broad hydride resonance at δ$^h$ -1.89 sharpens to a doublet resonance with a coupling constant of 8.3 Hz (Figure 5.25) and the broad phosphorus resonance sharpens.
to a singlet resonance. Low temperature $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectroscopy of A5 shows one doublet resonance at $\delta_{\text{Pt}} -5700$ with a coupling to phosphorus of about 1540 Hz. The $^{195}\text{Pt}$ NMR spectrum of A5 with $^1\text{H}$ coupled shows a broad doublet of triplets where the doublet coupling corresponds to $J(\text{PtP})$ and the triplet coupling corresponds to $J(\text{PtH})$ (Figure 5.26). The triplet multiplicity of the $^1\text{H}$-coupled $^{195}\text{Pt}$ NMR spectrum indicates that there are two equivalent hydride ligands attached directly to platinum (The value of $J(\text{PtH})$ agrees with that derived from the $^1\text{H}$ spectrum). It is also clear from the low temperature $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of A5 that only one phosphorus atom is attached to the platinum centre. The doublet coupling observed for the hydride at low temperature is also consistent with coupling to one single phosphorus atom.

\[\text{Figure 5.25} \text{ } ^1\text{H} \text{ (500.13 MHz) NMR spectra of complex A5 in } ^2\text{H}_8\text{toluene (only the hydride region is shown. a unknown complex A5. b trans-Pt(PCy}_3\text{H}_2)(H)_2.}\]
5.3 DISCUSSIONS

5.3.1 Preparation of Platinum Silyl Hydride Complexes

The reaction of Pt(PCy3)2 with the silane HSiR3 has provided a convenient method of preparing the complex cis-Pt(PCy3)2(H)(SiR3) in this investigation. Other methods of preparation of silyl complexes using platinum(0) compounds such as Pt(PPh3)4 or Pt(PPh3)2(C2H4) with HSiR3 have been employed in the past.21 Early attempts at forming Pt-Si bonds by reaction of a platinum halide with LiSiR325 or Hg(SiMe3)2 have also been made.26 Ebsworth et al. have successfully reacted trans-Pt(PCy3)2(H)2 with a series of primary or secondary silanes, SiH2R2 (R = H, Cl or SiH3) to form the corresponding trans-Pt(PCy3)2(H)(SiH2R) or trans-Pt(PCy3)2(H)(SiHR2) complexes.21 They observed a six-co-ordinate trihydride platinum species of the type trans-Pt(PCy3)2(H)3(SiH2R) by 31P {1H} NMR spectroscopy at −80 °C when trans-Pt(PCy3)2(H)2 was reacted with SiH3R. On warming to room temperate the trihydride platinum species decomposed to trans-Pt(PCy3)2(H)(SiH2R). They reported that trans-Pt(PCy3)2(H)(SiH2R) has a relatively high field chemical shift for the hydride resonance, with 1J(PtH) and ν(Pt−H) values that were quite low. This suggested that the strong trans-influence of the silyl ligand is comparable to that of the hydride ligand.

In our studies, the IR bands of ν(Pt−H) for cis-Pt(PCy3)2(H)(SiPh3) 15 and cis-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 16 are at 2078 cm−1 and 2085 cm−1 respectively. It
has been reported that the IR band for v(Pt–H) is at 1872 cm$^{-1}$ for trans-Pt(PC$_3$)$_2$(H)(SiH$_2$Cl)$_2$. It is clear therefore that the v(Pt–H) IR bands for the cis-silyl hydride platinum complexes are much higher than those seen for the trans-silyl hydride complexes. The much higher value for the v(Pt–H) bands is clearly due to the absence of the high trans-influence of a silyl ligand. The high trans-influence of the silyl ligand is also demonstrated in the corresponding J(PtP) values, since Pt–P coupling constants give a good indication of how much s-character is present in the bond. As we can see from Table 5.1 (b), Pt–P bonds trans to silyl ligands have a much smaller J(PtP) value than Pt–P bonds trans to hydride. The J(PtP) value of the phosphorus atom trans to the silyl ligand is over 1000 Hz smaller in magnitude compared to the phosphorus atom trans to the hydride ligand.

It is possible, because of steric factors, that the tertiary silanes we used in this study have restricted access to the metal centre of trans-Pt(PC$_3$)$_2$(H)$_2$, due to the bulky PC$_3$ ligands (cone angle$^{28}$ 179$^\circ$). As a result, interaction of the Si–H bond with the metal centre may be less favoured, while for sterically undemanding silanes, e.g. SiH$_4$, oxidative addition to the trans-platinum dihydride should be possible and a six-co-ordinate platinum(IV) species Pt(PC$_3$)$_2$(H)$_3$(SiH$_3$) is accessible. The six-co-ordinate trihydride species can undergo facile reductive elimination of molecular dihydrogen to yield trans-Pt(PC$_3$)$_2$(H)(SiH)$_3$. Six-co-ordinate platinum dihydride complexes containing smaller phosphine ligands have been isolated when hydrogen halides add to trans-Pt(PEt$_3$)$_2$(H)(X) (X = Cl, Br, I). Here, the products generally assume a trans, cis, cis-PtL$_2$H$_2$X$_2$ structure (Equation 5.6).

$$\text{trans-Pt(PEt}_3)_2(H)(X) + HX \rightarrow \begin{array}{c}
\text{Pt} \\
X \\
\text{PEt}_3 \\
H
\end{array} \\
\text{trans-Pt(PEt}_3)_2(H)(X) + HX \rightarrow \begin{array}{c}
\text{Pt} \\
X \\
\text{PEt}_3 \\
H
\end{array}$$

(Troger and co-workers have also isolated several six-co-ordinate platinum(IV) dihydride species by reacting Pt(PMe$_3$)$_2$(H)$_2$ with HMPh$_3$ (M = Sn or Ge) to give cis, cis, trans-Pt(PMe$_3$)$_2$(H)$_2$(MPH)$_3$ (Equation 5.7) which have been identified from their NMR spectra. Reaction of HSiPh$_3$ with Pt(PMe$_3$)$_2$H$_2$ only yielded cis-Pt(PMe$_3$)$_2$(H)(SiPh$_3$).}^{30}
Trogler reported that the six-co-ordinate platinum(IV) cis, cis, trans-Pt(PMe$_3$)$_2$(H)$_2$(MPh$_3$)$_2$ complexes are stable as solids but decompose in solution to the four-co-ordinate platinum(II) compounds, Pt(PMe$_3$)$_2$(MPh$_3$)$_2$ (M = Sn or Ge). Unfortunately, the geometry of the four-co-ordinate platinum(II) complex was not reported. The small size and good donor properties of the PMe$_3$ ligand accounted for the stabilisation of the six-co-ordinated platinum(IV) dihydride species, which was not possible for the PCy$_3$ analogue.

Recently, Gusev and co-workers reported the first d$^8$ Pt(II) dihydrogen complex, [Pt(PBu$_3$)$_2$(H)(H$_2$)]$^+$ in their study of the bulky dihydride complex trans-Pt(PBu$_3$)$_2$(H)$_2$ (Equation 5.8).32

\[
\text{Pt(PBu}_3\text{)}_2(\text{H})_2 + \text{ZH} \rightarrow \text{Pt(PBu}_3\text{)}_2(\text{H})_2^+ + \text{Z-} \quad \text{Pt(PBu}_3\text{)}_2\text{H}^+ + \text{ZH} + \text{H}_2
\]  

$Z = \text{F}_2\text{CSO},$

The dihydrogen complex [Pt(PBu$_3$)$_2$(H)(H$_2$)]$^+$ was reported to undergo facile intermolecular H$_2$ exchange. The activation parameters for H$_2$ dissociation from [Pt(PBu$_3$)$_2$(H)(H$_2$)]$^+$ was found to be, $\Delta H^\ddagger = 46 \pm 2$ kJ mol$^{-1}$ and $\Delta S^\ddagger = 8 \pm 6$ J K$^{-1}$ mol$^{-1}$.

5.3.2 Dynamic Exchange in cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$)

The thermodynamic parameters obtained for the dissociation of silane (Table 5.5), $K_S$, show that out of complexes 15-17, complex 15 is the most thermodynamically stable on the basis of enthalpy with $\Delta H^o = 74 \pm 10$ kJ mol$^{-1}$. This is followed by 16 ($\Delta H^o = 45 \pm 8$ kJ mol$^{-1}$) and 17 ($\Delta H^o = 27 \pm 2$ kJ mol$^{-1}$). This result was as expected, since good $\pi$-acceptor groups, such as SiPh$_3$ in complex 15, normally stabilise the Si–H oxidative addition product.33 This is mainly due to strong metal to ligand $\pi$-backbonding into the Si–H $\sigma^*$-orbital which leads to the cleavage of the Si–H bond and the formation of a strong M–Si bond (see Section 1.3.2). Metal to ligand backbonding is not expected to be as strong in complexes 16 and 17, hence the Pt–Si bond is expected to be comparatively weaker. Complex 15 was also found to be entropically more favoured to dissociate HSiPh$_3$, possibly due to the release of steric strain upon dissociation of HSiPh$_3$, the largest silane released on elimination in these studies. As a
result of the enthalpic and entropic factors working in opposite directions, the values of \( \Delta G^{\circ}_{300} \) for complexes 15, 16 and 17 turn out to be the same.

The second exchange process in cis-Pt(PhC\(_3\)\(_2\)H)(SiR\(_3\)) is mutual phosphine exchange, which involves the positional change of the silyl and the hydride ligand. From the dynamic NMR data of complexes 15, 16, and 17, we found that mutual phosphine exchange \( (k_3) \) is dominant at low temperatures in the range of 250 K to 270 K. Silane elimination and addition, \( k_1 \) and \( k_2 \) respectively, were only observed at higher temperatures. Scheme 5.7 summarises the activation parameters obtained for 15-17.

From the relative energy diagram in Scheme 5.7 the activation barrier for mutual phosphine exchange is very similar for 15-17, all three complexes possessing a \( \Delta H^{\ddagger}_{k_3} \) value of approximately 70 kJ mol\(^{-1}\). However, small but significant differences can be found; 17 appears to have the smallest barrier of activation for mutual phosphine exchange, and this is followed by 16 and 15 (Table 5.19). The most obvious explanation would be due to the size of the substituents on the silicon atom, since large substituents such as phenyl rings would offer the most resistance to any form of rearrangement, compared to smaller methyl or ethyl groups.

In the elimination of silane from Pt(PhC\(_3\)\(_2\)H)(SiR\(_3\)), 15-17, it was found that all three complexes possess a \( \Delta H^{\ddagger}_{k_1} \) value of approximately 100 kJ mol\(^{-1}\). \( \Delta S^{\ddagger} \) values for silane elimination indicate that 17 has the most dissociative transition state, whilst 15 and 16 are virtually the same. As a result, the free energy barrier to silane dissociation follows the order 17 < 16 < 15.
Scheme 5.7 Energy diagram showing the activation enthalpies of mutual phosphine exchange and silane dissociation/addition. All energy levels are relative to cis-Pt(PCy₃)₂(H)(SiR₁₂R²).
Significant variation can be seen in the activation barrier of re-addition of silane to Pt(PCy₃)₂. We found that ΔH°₂₃ is smallest for HSiPh₃ and largest for HSiMe₂Et (Table 5.18). Parallels can be drawn from the reported ΔH° values of dissociation of HSiR₃ from CpMn(CO)₂(H)(SiR₃) (Scheme 5.8). The ΔH° of dissociation of silane was found to be lower for HSiEt₃ (ΔH° = 115 ± 3 kJ mol⁻¹) than HSiPh₃ (ΔH° = 122 ± 1 kJ mol⁻¹).

![Scheme 5.8](image)

**Scheme 5.8** Silane elimination from CpMn(CO)₂(H)(SiR₃), adapted from ref. 34.

The intermediate involved in the mutual phosphine exchange process is most likely to be an η²-silane complex, as suggested originally by Clark and Hampden-Smith. Thus, rotation about the Si–H bond in the η²-silane intermediate would explain the phosphine exchange observed in the variable temperature NMR spectra (Scheme 5.9).

![Scheme 5.9](image)

**Scheme 5.9** Mutual phosphine exchange with an η²-silane intermediate as the suggested activated complex.

It is important to note that rate constants measured by dynamic NMR methods are rarely the same as those for the actual chemical exchange processes considered. For the phosphine exchange process shown in Scheme 5.9, the transition state C is equally likely to proceed to either structure D or go back to structure B, since B and D have the same energy. If the process goes from A to E, only half the exchange process will be visible to NMR. Therefore the actual exchange rate is twice the observed rate, _i.e._ k_{act} = 2k₃. Taking this into account, the actual activation parameters for phosphine exchange are summarised in Table 5.21. Compared to the activation parameters obtained for the
observed rate in Table 5.19, there are no substantial differences between $\Delta H^\ddagger$ and $\Delta G^\ddagger$, but $\Delta S^\ddagger$ is slightly higher.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\ddagger_{\text{kact}} / $</th>
<th>$\Delta S^\ddagger_{\text{kact}} / $</th>
<th>$\Delta G^\ddagger_{300(\text{kact})} / $</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>J K$^{-1}$ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>cis-Pt(PC$_2$H)$_2$(H)(SiPh$_3$) 15</td>
<td>73 ± 3</td>
<td>35 ± 9</td>
<td>62</td>
</tr>
<tr>
<td>cis-Pt(PC$_2$H)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16</td>
<td>70 ± 2</td>
<td>45 ± 7</td>
<td>56</td>
</tr>
<tr>
<td>cis-Pt(PC$_2$H)$_2$(H)(SiMe$_2$Et) 17</td>
<td>66 ± 2</td>
<td>39 ± 6</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 5.21 Activation parameters for actual mutual phosphine exchange in cis-Pt(PC$_2$H)$_2$(H)(SiPh$_3$) 15, cis-Pt(PC$_2$H)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) 16 and cis-Pt(PC$_2$H)$_2$(H)(SiMe$_2$Et) 17 in [H$_8$]toluene (Error bars quoted as 95% probability on least squares fit).

Tsuji has recently reported a similar type of mutual phosphine exchange process in cis-bis(silyl)bis(phosphine)platinum and cis-bis(stanny)bis(phosphine)palladium complexes.$^{37}$ They reported that the spin-spin couplings between P, Si and Pt are retained during the fluxional process observed in their system, similar to our own findings in this investigation where the spin-spin coupling between H, P and Pt are retained during the mutual phosphine exchange process. The mechanism of exchange was attributed to a unimolecular twist-rotation process, occurring via a pseudotetrahedral transition state (Scheme 5.10). Activation parameters for cis-Pt(PMe$_2$Ph)$_2$(SiPh$_2$Me)$_2$ and cis-Pt(PMe$_2$Ph)$_2$(SiMe$_2$F)$_2$ were reported to be $\Delta H^\ddagger = 57 \pm 2$ kJ mol$^{-1}$, $\Delta S^\ddagger = 17 \pm 9$ J K$^{-1}$ mol$^{-1}$ and $\Delta H^\ddagger = 34 \pm 1$ kJ mol$^{-1}$, $\Delta S^\ddagger = -60 \pm 6$ J K$^{-1}$ mol$^{-1}$, respectively. One unusual feature of these complexes is that they are already non-planar at platinum in the ground state with a dihedral angle of 38°.

Scheme 5.10 Proposed mechanism for mutual exchange of phosphine ligands in cis-bis(silyl)bis(phosphine) platinum complex, adapted from ref. 37.

Oxidative addition of silane is commonly believed to occur initially via interaction between the metal and the hydrogen of the approaching Si–H bond, and is
then followed by the silicon atom. Figure 5.27 illustrates a similar type of interaction for C–H oxidative addition.\textsuperscript{38}

![Figure 5.27 A kinetic pathway for the reaction M + C–H → C–M–H as deduced from a series of structures of agostic complexes (adapted from ref. 38).](image)

\textit{Ab initio} calculations by Sakaki on the oxidative addition of SiH\textsubscript{4} to Pt(PH\textsubscript{3})\textsubscript{2} have also shown that the transition state of the reaction involves SiH\textsubscript{4} approach platinum with the H atom in the lead (Figure 5.28).\textsuperscript{39,40} It was also suggested that the initial interaction between the silane and Pt(PH\textsubscript{3})\textsubscript{2} results in a precursor complex, which can be considered as a van der Waals complex (Figure 5.29). However, according to Sakaki the stabilisation energy gained from the formation of such a complex is very small, \textit{ca.} 6 kJ mol\textsuperscript{-1}.\textsuperscript{40}

![Figure 5.28 Optimised structure of transition state of Si–H oxidative addition to Pt(PH\textsubscript{3})\textsubscript{2}, bond lengths in Å.\textsuperscript{39,40}](image)
In the transition state calculated by Sakaki for Si–H oxidative addition to Pt(PH₃)₂ (Figure 5.28), the Si–H bond has only lengthened slightly compared to free SiH₄, and the Pt–H and Pt–Si distances are still relatively long compared to that of the final product.³⁹,⁴⁰ This indicates that the transition state is reached near the beginning of the oxidative addition pathway, and hence the barrier for silane addition should be small. Interestingly, it was also demonstrated that the transition state for C–H oxidative addition to Pt(PH₃)₂ is reached relatively late in the oxidative addition pathway. The reason for the difference in the activation barrier for C–H and Si–H oxidative addition can be explained by the bond strengths involved and has been discussed in Section 1.3.1.

In relation to the addition/elimination of silane to Pt(PCY₃)₂, it seems plausible to suggest that the activated intermediate involved is similar to the structure in Figure 5.28. In this investigation, the enthalpy of activation for silane addition, ΔH²kₛ, is significantly smaller than the enthalpy of activation for silane elimination, ΔH¹kₙ. These findings support the argument that Si–H addition is reached early on in the oxidative addition pathway. Addition of HSiPh₃ to the Pt(PCY₃)₂ moiety was found to be the most entropically disfavoured; the negative value for the entropy of activation indicates a associative transition state.

It is plausible that silane dissociation at higher temperatures goes via an η²-silane intermediate as proposed in Scheme 5.9 for mutual phosphine exchange, since the energy difference between the activated complex for silane addition/dissociation and mutual phosphine exchange is ca. 30 kJ mol⁻¹ for 15-17. Scheme 5.11 presents two possible reaction profiles for cis-Pt(PCY₃)₂(H)(SiR₃). At low temperature only mutual phosphine exchange is dominant, and occurs via an η²-silane intermediate. At higher temperatures it is presumed that the barrier from the η²-silane intermediate to the next intermediate, responsible for silane addition/dissociation, is overcome and both processes can occur.

Figure 5.29 Optimised structure of precursor complex Pt(PH₃)₂(SiH₄), bond lengths in Å.³⁹,⁴₀
It is important to note that we are only considering the dominant processes exhibited in the dynamic NMR data. One other possible process which was not observed was phosphine dissociation from \( \text{cis-Pt(PCY}_3\text{)}(\text{H})(\text{SiR}_3) \) (Scheme 5.3). This could be because phosphine dissociation occurs on a much slower timescale than that accessible to NMR spectroscopy. However, no PCY\(_3\) was detected in the temperature range studied.

### 5.3.3 Photochemistry of trans-Pt(PCY\(_3\))\(_2\)(H)\(_2\) and cis-Pt(PCY\(_3\))\(_2\)(H)(SiR\(_3\))

Photolysis of trans-Pt(PCY\(_3\))\(_2\)(H)\(_2\) in the presence of silane was found to yield a small amount of the oxidative addition product trans-Pt(PCY\(_3\))\(_2\)(H)(SiR\(_3\)). It was revealed by low temperature photolysis that the initial product formed was cis-Pt(PCY\(_3\))\(_2\)(H)(SiR\(_3\)). One probable mechanism for this process would involve the isomerisation of trans-Pt(PCY\(_3\))\(_2\)(H)\(_2\) to the unstable cis-dihydride complex which can lose molecular hydrogen leaving the 14-electron bis(phosphine) complex Pt(PCY\(_3\))\(_2\). Pt(PCY\(_3\))\(_2\) can then react with the excess silane present to form the cis-silyl hydride oxidative addition product; further photolysis would then isomerise the cis-silyl hydride complex to the trans-isomer (Scheme 5.12).
Scheme 5.12 Probable photochemical routes to *trans*-Pt(PCY₃)₂(H)(SiR₃)₂.

However, even after long photolysis time, the conversion of *trans*-Pt(PCY₃)₂(H)₂ to *trans*-Pt(PCY₃)₂(H)(SiR₃) is very low at room temperature. One possible explanation for this is that addition of H₂ occurs at a much faster rate than that of silane. This is supported by the fact that H₂ reacts rapidly with *cis*-Pt(PCY₃)₂(H)(SiR₃) to form *trans*-Pt(PCY₃)(H)₂.

5.3.4 Reactions of Pt(PCY₃)₂ with disilanes

The reaction of (SiPh₂H)₂O with Pt(PCY₃)₂ yielded the complex *cis*-Pt(PCY₃)₂(H)(SiPh₂OSiPh₂H) 20. It was found that reaction of the disilane (SiPh₂H)₂O with excess Pt(PCY₃)₂ did not yield a dimeric Pt complex, where the disilane is acting as a bridging ligand, or a platinum cyclic silyl complex (Scheme 5.13).
The absence of a cyclic silyl complex or a dimeric complex as illustrated in Scheme 5.13 is probably due to the flexibility of the Si–O–Si linkage and the repulsion between the PCy₃ ligand and the unattached HSiPh₂ group. For instance, Eaborn has reported the formation of Pt(PPh₃)₂(SiPh₂OSiPh₂), using the less sterically demanding PPh₃ ligand.²² It was envisaged that the use of a more rigid disilane, HSiMe₂(C₆H₄)SiMe₂H, would lead to the participation of both silyl groups in co-ordinating to the metal centre, forming a chelate structure. Reaction of excess HSiMe₂(C₆H₄)SiMe₂H with Pt(PCy₃)₂ was found to form two separate species A₅ and B₅ at room temperature and only A₅ at low temperature (ca. 250 K). As mentioned previously, Eaborn reported a similar reaction with Pt(PPh₃)₂(CH₂=CH₂) and HSiMe₂(C₆H₄)SiMe₂H to yield the chelating disilyl complex cis-Pt(PPh₃)₂[SiMe₂(C₆H₄)SiMe₂].²² The NMR data of A₅ revealed that this species contains one phosphine ligand, the disilyl ligand SiMe₂(C₆H₄)SiMe₂ and a hydride resonance (Section 5.2.8). At low temperatures, A₅ exhibits a chemical shift of δ ≈ –5700 in the ¹⁹⁵Pt ¹H NMR spectrum, which is coupled to one phosphorus nucleus. Tanaka and co-workers have previously reported that the ¹⁹⁵Pt NMR signals of Pt(II) bis(phosphine) disilyl complexes are usually found in the region of 8 –3800 to 8 –5240 and that of Pt(IV) silyl complexes are located at ca. 8 –6000.⁴¹ This suggests that A₅ could be a Pt(IV) species since it lies outside the reported upper limits for Pt(II) complexes. For comparison, cis-Pt(PCy₃)₂(H)(SiPh₃) has a chemical shift of 8ₚt ≈ –5205. Proton coupled ¹⁹⁵Pt NMR spectrum of A₅ shows that Pt is coupled to two equivalent hydride ligands, providing further evidence that A₅ is a Pt(IV) complex. Hence A₅ would probably be a Pt(IV) disilyl dihydride complex (Figure 5.30).
Compound B5, the species which was formed at room temperature when Pt(PCy3)2 was reacted with HSiMe2(C6H4)SiMe2H, was first suspected to be similar to the one reported by Eaborn for the analogous PPh3 complex. This would then suggest that A5 is an intermediate on the way to B5. However, compound A5 does not appear to convert to B5 at room temperature, but instead A5 decomposes slowly to \( \text{trans-Pt(PCy3)2(H)}_2 \), see Section 5.2.8. The identity of B5 remains unclear.

Figure 5.30 Possible structure for complex A5.

Analogues of the proposed structure for A5 could also be involved in the thermal degradation of \( \text{cis-Pt(PCy3)2(H)(SiR3)} \) to \( \text{trans-Pt(PCy3)2(H)}_2 \). Scheme 5.14 outlines a possible mechanism for conversion of \( \text{cis-Pt(PCy3)2(H)(SiR3)} \) to \( \text{trans-Pt(PCy3)2(H)}_2 \) involving a Pt(IV) disilyl dihydride species above room temperature. The proposed trigonal bipyramidal structure in Scheme 5.14 reductively eliminates disilane, forming a silicon-silicon bond.

Scheme 5.14 Proposed mechanism for the thermal degradation of Pt(PCy3)2(H)(SiR3) to \( \text{trans-Pt(PCy3)2(H)}_2 \).

The proposed trigonal bipyramidal Pt(IV) bis(silyl) dihydride in Scheme 5.14 has both hydrides in the axial positions, which is probably the least sterically demanding position with respect to the PCy3 and silyl ligands.
5.4 CONCLUSIONS

In this chapter we have demonstrated that cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) complexes undergo mutual phosphine exchange and silane dissociation near room temperature and only mutual phosphine exchange at lower temperatures. The substituent R on the silyl group plays an important part in determining the strength of the Pt–Si interaction. General observations indicated that strong electron withdrawing or π-accepting R groups help to stabilise the Si–H oxidation product to platinum. Thermodynamic data obtained for 15–17 further demonstrated this fact with cis-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) 15 having the highest ΔH° of silane dissociation and the alkyl substituted silylligands in 16 and 17 have significantly smaller values of ΔH°. Due to the bulk of the PCy$_3$ ligands, 15 was also found to be the most entropically favoured to eliminate silane with 17 being the least favoured. This in turn gave very similar ΔG°$_{300}$ values of 2, −2, and −2 kJ mol$^{-1}$ for 15, 16 and 17, respectively, an example of enthalpy-entropy compensation.

The activation barrier for dissociation of silane is greatest for 15 by a fairly substantial margin. However, the reverse situation was found for the activation barrier of addition of HSiPh$_3$ to Pt(PCy$_3$)$_2$ which is much smaller compared to those for HSiMe$_2$CH$_2$CH=CH$_2$ and HSiMe$_2$Et. It was also found that silane elimination from 15–17 resulted in an entropically similar transition state, whilst the transition state for silane addition is entropically unfavourable for HSiPh$_3$. ΔG$_{300}^+$ values for both silane addition and elimination were found to be marginally more favourable for HSiMe$_2$Et, possibly due to its small size. The activation parameter for mutual phosphine exchange was found to be similar for 15–17, but again 15 was revealed to possess the largest enthalpy of activation for this process. Again the complex containing the smallest silane HSiMe$_2$Et has the lowest ΔG$_{300}^+$ value.

An η$^2$-silane complex is proposed to be responsible for the mutual silane exchange observed in cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) and it is implicated in the reaction profile for silane elimination from cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$). The involvement of a pseudotetrahedral intermediate, proposed by Tsuji for the phosphine exchange process in cis-bis(silyl)bis(phosphine)platinum complex,$^{37}$ instead of an η$^2$-silane intermediate could also account for this exchange. However, this seems unlikely in our case since the existence of a pseudotetrahedral complex should allow relatively easy cis-trans isomerisation which was not observed without photolysis.

Slow thermal decomposition of cis-Pt(PCy$_3$)$_2$(H)(SiR$_3$) to trans-Pt(PCy$_3$)$_2$(H)$_2$ was observed. Involvement of a Pt(IV) complex containing two silyl and two hydride ligands is possible. Formation of a Pt(IV) species was also suggested to be observed for the reaction between Pt(PCy$_3$)$_2$ and the disilane, HSiMe$_2$(C$_6$H$_4$)SiMe$_2$H. Trans-Pt(PCy$_3$)$_2$(H)(SiR$_3$) was found to be thermally stable and can be easily obtained by photolysis of the corresponding cis compound. Trans-Pt(PCy$_3$)$_2$H$_2$ was found to be
thermally unreactive towards the tertiary silanes used in this investigation; photochemical reactions of the trans dihydride complex with silanes also proved to be difficult.

5.5 REFERENCES


CHAPTER 6

EXPERIMENTAL
6.1 General Methods

All syntheses and manipulations were carried out under argon using standard Schlenk and high vacuum techniques. All preparative solvents (Fison AR grade) were dried over sodium/benzophenone and distilled under argon (chlorinated solvents were dried over P₂O₅, ethanol was dried over magnesium metal turnings and iodine). NMR solvents were obtained from Aldrich, Apollo or Goss Scientific and were dried over potassium metal under argon and distilled on a high vacuum line prior to use (chlorinated solvents were dried over molecular sieves or P₂O₅).

Chemicals were obtained from the following sources and used without further purification:

Gases: Argon, carbon dioxide, ethene, nitrogen and oxygen (BOC).
Silanes: (CH₂=CHSiMe₂)₂O, (Aldrich or donated by Dow Corning, Barry). HSiMe₂Et, (HSiMe₂)₂C₆H₄, HSiClMe₂, HSiMe(OSiMe₃)₂, (Aldrich). HSiMe₂CH₂CH=CH₂, HSi(OMe)CH₂CH=CH₂ (Gelest), (HSiPh₂)₂O (donated by Fabien Delpech, Toulouse).
Azo compounds: EtO₂CNNC₀₂Et, PrO₂CNNCO₂Pr¹, Bu'O₂CNNCO₂Bu¹ and 1,1'-(azodicarbonyl)diipiperidine (Aldrich).
Phosphines: PPh₃, PCy₃, (Aldrich). dppe (Aldrich or Lancaster). PMe₃ (Strem).
Other reagents: PtCl₂ (donated by Dow Corning). K₂PtCl₄, K₂C₂O₄, Na₂(O₂C)₂CH₂, Na₂(O₂C)₂C₆H₄ AgNO₃, PhOCNHNHCOPh, MeOCNHNHCOME, CH₂=C(Me)-CH₂OH, 1,5-cyclooctadiene, diphenylacetylene, 1-hexene, 1-octene, celite, molecular sieves, sodium, potassium, triethylamine (Aldrich). Na₂CO₃, NaOH, KOH, Mg, MgSO₄, P₂O₅, Iodine (Fisons). Sodium dispersion (Strem).

UV/Visible spectra were recorded on a Perkin-Elmer Lambda 7 spectrophotometer. Infrared spectra were recorded on a Mattson RS FTIR instrument at York or on a Nicolet FTIR instrument at Dow Corning, Barry. Mass Spectra were recorded on a VG Auto-Spec mass spectrometer by the University of York analytical services. X-Ray data were collected on a Rigaku AFC6S diffractometer by Leroy Cronin at the University of York. Elemental analyses were performed by Elemental Microanalysis Ltd, Devon, UK.

The work on platinum catalysed hydrosilation reaction was carried out at Dow Corning in Barry, on a Hewlett Packard capillary GC with FID detection. The instrument was fitted with a BPI column and temperature ramping was employed.

GC-MS work on organosilane products from the decomposition of cis-Pt(PCy₃)₂(H)(SiMe₂CH₂CH=CH₂) 16 was carried out by the Laboratoire de Chimie de Co-ordination analytical services in Toulouse, on a Hewlett Packard HP 5890 capillary GC, using a 12 m column packed with methylsilicone, connected to a Hewlett Packard HP 5970 mass spectrometer. Elemental analysis on cis-Pt(PCy₃)₂(H)(SiPh₃)₂ 15 was
also carried out by the Laboratoire de Chimie de Co-ordination analytical services in Tolouse.

NMR spectra were recorded on a Bruker MSL 300 (1H, 300.13 MHz; 13C, 75.47 MHz; 31P 121.49 MHz; 195Pt, 64.41 MHz; 29Si, 59.62 MHz) and AMX 500 (1H, 500.13 MHz; 13C, 125.78 MHz; 31P 202.46 MHz; 195Pt, 167.57 MHz; 29Si, 99.36 MHz) spectrometers in York, and on a Jeol EX400 spectrometer in Dow Corning (1H, 399.65 MHz; 29Si, 79.38 MHz; 195Pt, 85.28 MHz), and on a Bruker AC200 (1H, 200.13 MHz; 31P 81.02 MHz) or AC250 (1H, 250.13 MHz; 31P 101.26 MHz) spectrometers in Toulouse. 1H NMR spectra were referenced relative to the peaks of the residual protio solvents: benzene (δ 7.15), chloroform (δ 7.30), dichloromethane (δ 5.30), tetrahydrofuran (δ 1.73), toluene (δ 2.10). 31P spectra were referenced to external H3PO4 (δ 85%). 13C spectra were referenced to the solvent peak: benzene (δ 28.0), dichloromethane (δ 54.5), chloroform (δ 77.7) and tetrahydrofuran (δ 25.2), toluene (δ 21.1). 195Pt spectra were referenced to external Pt(COD)Cl2 in CDCl3 (δ -3361).

Photolysis of samples was carried out in Pyrex NMR tubes (λ > 290 nm) using a Philips HPK 125 W medium pressure mercury lamp at room temperature. Typically, both a cut-off filter (295-410 nm) and a water filter were placed in front of the lamp output. For low temperature photolysis, samples were immersed in a partially silvered Dewar containing a dry-ice/acetone mixture (ca. -77 °C). 1H NMR spectroscopy with in situ photolysis was performed by John Lowe at York on a Bruker 300 MSL NMR spectrometer. Generally, samples were kept for 24 hours at room temperature and shielded from ambient light prior to photolysis. Their NMR spectra were then recorded in order to check for competing thermal reaction at room temperature.

6.2 SYNTHESIS AND REACTIONS OF PLATINUM BIS(PHOSPHINE) AZODICARBONYL COMPLEXES

The complexes cis-Pt(PPh3)2Cl2,2 cis-Pt(PMe3)2Cl23 and Pt(PPh3)2(C2H4)4 were prepared according to literature procedures. Mass spectral peaks are quoted only when they have a major contribution from 194Pt.

6.2.1 Preparation of Pt(PPh3)2(PhOCNNCOPh) 1

This synthesis follows the procedure of Dilworth and Kasenally.5 Pt(PPh3)2Cl2 (0.20 g, 0.2 mmol) and PhOCNHNHCOPh (0.06 g, 0.2 mol) were suspended in ethanol (20 mL) with sodium hydrogen carbonate (0.06 g). The mixture was refluxed under argon for 4 h. During this time the white suspension gradually dissolved yielding a yellow solution. The solvent was removed under vacuum. The crude product was re-
dissolved in benzene, and hexane was added until precipitation began. Yellow crystals were formed overnight (Yield 1.30 g, 70%). Mass spectrum (FAB): $m/z$ 956 ($M^+$, $^{194}$Pt, 63 %), $m/z$ 957 ($M^+$, $^{195}$Pt and [$M + H$]$^+$, $^{194}$Pt, 100 %). $^1$H NMR spectrum (300.13 MHz, CDCl$_3$, 295 K): $\delta$ 7.00-8.00 (m, Ph). $^{13}$C $^1$H NMR spectrum (75.47 MHz, CDCl$_3$, 295 K): $\delta$ 127.1-135.2 (Ph), $\delta$ 163.2 (dd, CO, J(PC) = 10.3 Hz), $\delta$ 171.7 (d, CO, J(PC) = 4). $^{31}$P $^1$H NMR spectrum (121.94 MHz, CDCl$_3$, 295 K): $\delta$ 3.1 (d, PO, $^2$J(PP) = 22 Hz, J(PtP) = 3685 Hz), $\delta$ 17.5 (d, P$^N$, $^2$J(PP) = 22 Hz, J(PtP) = 3261 Hz). $^{195}$Pt $^1$H NMR spectrum (107.52 MHz, Cd$_2$Cl$_2$, 300 K): $\delta$ -4291 (dd, $^2$J(PP) = 3302 Hz, $^3$J(PP) = 3680 Hz). IR (KBr): $v$(CO, CN) 1565, 1595 cm$^{-1}$.

6.2.2 Preparation of Pt(PPh$_3$)$_2$(Et$_2$OCCNCO$_2$Et) 2

Pt(PPh$_3$)$_2$(C$_2$H$_4$) (0.64 g, 0.9 mmol) and Et$_2$OCCNCO$_2$Et (0.60 g, 3.4 mmol) were dissolved in benzene (20 mL) under an atmosphere of argon at room temperature. On mixing the two compounds together a gas was evolved and the solution changed from yellow to red. Within 1 hour of addition, a yellow precipitate began to form. The mixture was shielded from ambient light and left stirring for 12 h. The product was collected and recrystallised from ethanol to form yellow crystals (0.63 g, 69 % yield) (Found: C, 56.1; H, 4.6; N, 3.1. Calc. for C$_{42}$H$_{40}$N$_2$O$_4$Pt$_2$: C, 56.4; H, 4.5; N, 3.1). Mass spectrum (FAB): $m/z$ 892 ($M^+$, $^{194}$Pt, 18 %), $m/z$ 893 ($M^+$, $^{195}$Pt and [$M + H$]$^+$, $^{194}$Pt, 79 %). $^1$H NMR spectrum (300.13 MHz, C$_6$D$_6$, 295 K): $\delta$ 1.14 (3H, br t, CH$_2$CH$_3$), $\delta$ 1.35 [3H, t, CH$_2$CH$_3$, J(HH) = 7.0 Hz], $\delta$ 4.12 (2H, br, CH$_2$CH$_3$), $\delta$ 4.57 [2H, quart, CH$_2$CH$_3$, J(HH) = 7.0 Hz] $\delta$ 7.00-8.00 (30H, m, Ph). $^{31}$P $^1$H NMR spectrum (121.94 MHz, C$_6$D$_6$, 295 K): $\delta$ 6.2 (br d, PO, $^3$J(PtP) = 3790 Hz), $\delta$ 16.6 (d, P$^N$, $^2$J(PP) = 23 Hz, J(PtP) = 3166 Hz). IR (KBr): v(CO, CN) 1610, 1621, 1629, 1648, 1668 cm$^{-1}$.

6.2.3 Preparation of Pt(PMe$_3$)$_2$(PhOCNOCOPh) 3

This complex was prepared by the same procedure as 1 using cis-Pt(PMe$_3$)$_2$Cl$_2$ (0.2 g, 0.5 mmol). The product was recrystallised by addition of hexane to a benzene solution until precipitation began. The benzene/hexane mixture gave light yellow crystals (Yield 0.20 g, 68 %) (Found: C, 40.3; H, 4.5; N 4.5. Calc. for C$_{20}$H$_{28}$N$_2$O$_2$Pt: C, 41.0; H, 4.8; N, 4.9). Mass spectrum (FAB): $m/z$ 584 ($M^+$, $^{194}$Pt, 55 %), $m/z$ 585 ($M^+$, $^{195}$Pt and [$M + H$]$^+$, $^{194}$Pt, 100 %). $^1$H NMR spectrum (300.13 MHz, CDCl$_3$, 295 K): $\delta$ 1.80 [9H, d, PCH$_3$, $^2$J(PH) = 11.0 Hz], $\delta$ 1.90 [9H, d, PCH$_3$, $^2$J(PH) = 11.3 Hz], $\delta$ 7.00-8.00 (10H, m, Ph). $^{13}$C $^1$H NMR spectrum (75.47 MHz, CDCl$_3$, 295 K): $\delta$ 16.6 [d, PCH$_3$, J(PC) = 38 Hz, J(PtC) = 33 Hz], $\delta$ 19.7 [dd, PCH$_3$, J(PC) = 44 Hz, $^2$J(PC) = 2 Hz, J(PtC) = 43 Hz], $\delta$ 124.2-131.8 (Ph), $\delta$ 163.4 [dd, CO, J(PC) = 9, 3 Hz], $\delta$ 174.6 [d,
\[ \text{CO, } J(\text{PC}) = 4]. \] ²³¹P \{¹H\} NMR spectrum (121.94 MHz, CDCl₃, 295 K): \( \delta -20.1 \) [d, P², \( J(\text{PP}) = 26 \) Hz, \( J(\text{PtP}) = 3435 \) Hz], \( \delta -10.9 \) [d, P², \( J(\text{PP}) = 26 \) Hz, \( J(\text{PtP}) = 3028 \) Hz]. ¹⁹⁵Pt \{¹H\} NMR spectrum (107.52 MHz, CD₂Cl₂, 300 K): \( \delta -4257 \) [dd, \( J(\text{PtP}) = 3028 \) Hz, 3458 Hz]. IR (KBr): \( \nu(\text{CO, CN}) \) 1561, 1586 cm⁻¹.

6.2.4 Preparation of Pt(PMe₃)₂(MeOCNNCOMe) ⁴

This complex was prepared by a procedure similar to that of ¹ using cis-Pt(PMe₃)₂Cl₂ (0.2 g, 0.5 mmol). The product was recrystallised by addition of hexane to a benzene solution of ⁴ until precipitation began. The benzene/hexane mixture yielded light brown crystals (Yield 0.15 g, 65 %) (Found: C, 26.3; H, 5.4; N, 6.1. Calc. for C₁₀H₂₄N₂O₂P₂Pt:C, 26.0; H, 5.2; N, 6.1). Mass spectrum (FAB): \( m/z \) 460, (\( M^+ \), ¹⁹⁴Pt, 53 %), \( m/z \) 461 \( (M^+ \), ¹⁹⁵Pt and \( [M + H]^+ \), ¹⁹⁵Pt, 100%). ¹H NMR spectrum (75.47 MHz, CDCl₃, 295 K): \( \delta 1.70 \) [9H, d, \( J(\text{PH}) = 10.7 \) Hz], \( \delta 1.80 \) [9H, d, \( J(\text{PH}) = 11.2 \) Hz], \( \delta 2.01 \) [3H, d, COCH₃, \( J(\text{PH}) = 0.9 \) Hz], \( \delta 2.23 \) [3H, COCH₃]. ¹³C \{¹H\} NMR spectrum (75.47 MHz, CDCl₃, 295 K): \( \delta 16.3 \) [d, \( J(\text{PC}) = 38 \) Hz, \( J(\text{PtC}) = 33 \) Hz], \( \delta 16.5 \) [d, \( J(\text{PC}) = 5 \) Hz, \( J(\text{PtC}) = 45 \) Hz, \( J(\text{PC}) = 2 \) Hz, \( J(\text{PtC}) = 45 \) Hz], \( \delta 22.1 \) [d, \( J(\text{PC}) = 5 \) Hz, \( J(\text{PtC}) = 45 \) Hz], \( \delta 22.1 \) [d, \( J(\text{PC}) = 9 \), \( J(\text{PtC}) = 4 \) Hz], \( \delta 175.4 \) [d, CO, \( J(\text{PC}) = 3 \), \( J(\text{PtC}) = 67 \) Hz]. ³¹P \{¹H\} NMR spectrum (121.94 MHz, CDCl₃, 295 K): \( \delta -38.0 \) [d, \( J(\text{PC}) = 5 \) Hz, \( J(\text{PtC}) = 26 \) Hz, \( J(\text{PtP}) = 3435 \) Hz], \( \delta -29.0 \) [d, \( J(\text{PC}) = 26 \) Hz, \( J(\text{PtP}) = 3028 \) Hz]. IR (KBr): \( \nu(\text{CO, CN}) \) 1561, 1586 cm⁻¹.

6.2.5 Preparation of Pt(PPh₃)₂(Pr¹O₂CNNCO₂Pr¹) ⁵

This complex was prepared as for ² using cis-Pt(PPh₃)₂Cl₂ (0.2 g, 0.2 mmol). The product was recrystallised from THF giving orange crystals (Yield 0.12 g, 70 %) (Found: C, 57.3; H, 4.8; N, 3.0. Calc. for C₄₄H₄₄N₂O₄P₂Pt: C, 57.3; H, 4.8; N, 3.0). Mass spectrum (FAB): \( m/z \) 920 (\( M^+ \), ¹⁹⁴Pt, 12 %), \( m/z \) 921 (\( M^+ \), ¹⁹⁵Pt and \( [M + H]^+ \), ¹⁹⁵Pt, 73 %). ¹H NMR spectrum (300.13 MHz, CDCl₃, 295 K): \( \delta 0.75 \) [6H, d, \( J(\text{HH}) = 6.2 \) Hz], \( \delta 1.06 \) [6H, d, \( J(\text{HH}) = 6.2 \) Hz], \( \delta 4.08 \) [1H, d, \( J(\text{HH}) = 6.2 \) Hz], \( \delta 7.00-8.00 \) (30H, m, Ph). ¹³C \{¹H\} NMR spectrum (75.47 MHz, \( ^{2}[^{3}H] \) THF, 295 K): \( \delta 23.8 \) (s, \( \text{CH}_{3} \)), \( \delta 24.1 \) (s, \( \text{CH}_{3} \)), \( \delta 67.6 \) (s, \( \text{CH} \)), \( \delta 128.8-136.6 \) (Ph). ³¹P \{¹H\} NMR spectrum (121.94 MHz, \( ^{2}[^{3}H] \) THF, 295 K): \( \delta 5.8 \) [d, \( J(\text{PP}) = 23 \) Hz, \( J(\text{PtP}) = 3859 \) Hz], \( \delta 16.5 \) [d, \( J(\text{PP}) = 23 \) Hz, \( J(\text{PtP}) = 3158 \) Hz]. ¹⁹⁵Pt \{¹H\} NMR spectrum (107.51 MHz, \( ^{2}[^{3}H] \) THF, 300 K): \( \delta -4168 \) [dd, \( J(\text{PtP}) = 3118 \) Hz, 3871 Hz]. IR (KBr): \( \nu(\text{CO, CN}) \) 1613, 1635 cm⁻¹.
6.2.6 Preparation of Pt(dppe)(EtO$_2$CNNCO$_2$Et) 6

Pt(dppe)(EtO$_2$CNNCO$_2$Et) 6 was prepared in situ by reacting Pt(PPh$_3$)$_2$-(EtO$_2$CNNCO$_2$Et) 2 with excess dppe in C$_6$D$_6$ in an NMR tube. $^1$H NMR spectrum (300.13 MHz, C$_6$D$_6$, 295 K): δ 0.97 [3H, t, CH$_2$CH$_3$, J(HH) = 7.2 Hz], δ 1.35 [3H, t, CH$_2$CH$_3$, J(HH) = 7.2 Hz], δ 4.00 [2H, br, CH$_2$CNN, J(HH) = 7.2], δ 4.57 [2H, quart, CH$_2$CH$_3$, J(HH) = 7.2 Hz], δ 7.00-8.00 (30H, m, Ph). $^{31}$P {$^1$H} NMR spectrum (121.94 MHz, C$_6$D$_6$, 295 K): δ 31.1 [d, P$^0$, $^2$J(PtP) = 11 Hz, J(PtP) = 3839 Hz], δ 38.1 [d, P$^N$, $^2$J(PtP) = 11 Hz, J(PtP) = 3041 Hz].

6.2.7 Preparation of Pt(dppe)(Pr$_2$O$_2$CNNCO$_2$Pr$^r$) 7

This complex was prepared by reacting Pt(PPh$_3$)$_2$(Pr$_2$O$_2$CNNCO$_2$Pr$^r$) 5 with excess dppe in situ in C$_6$D$_6$, in an NMR tube. $^1$H NMR spectrum (300.13 MHz, C$_6$D$_6$, 295 K): δ 1.10 [6H, d, CH(CH$_3$)$_2$, J(HH) = 6.2 Hz], δ 1.36 [6H, d, CH(CH$_3$)$_2$, J(HH) = 6.2 Hz], δ 4.79 [1H, sept, CH(CH$_3$)$_2$, J(HH) = 6.2 Hz], δ 5.40 [1H, sept, CH(CH$_3$)$_2$, J(HH) = 6.2 Hz], δ 7.00-8.00 (30H, m, Ph). $^{31}$P {$^1$H} NMR spectrum (121.94 MHz, C$_6$D$_6$, 295 K): δ 31.0 [d, P$^0$, $^2$J(PtP) = 12 Hz, J(PtP) = 3843 Hz], δ 38.1 [d, P$^N$, $^2$J(PtP) = 12 Hz, J(PtP) = 3023 Hz].

6.2.8 X-ray crystallographic study of 5

Crystals of compound 5 were grown at ambient temperature by the slow evaporation of a 2:1 THF/benzene solution. The resulting crystal was cut to size and mounted on a glass fibre using epoxy cement. The structure of compound 5 was solved using Patterson methods with SAPI91 and expanded using Fourier techniques with DIRDIF. Full-matrix least squares refinement on $F^2$ was carried out with SHELXL 93. Programs.$^{5,7}$ All non hydrogen atoms were refined anisotropically. The hydrogen atoms were refined on all structures using a riding model with isotropic temperature factors 1.2 times that of their carrier atoms (1.5 times for methyl groups). The crystal data of 5 were collected, solved and refined by Leroy Cronin at the University of York.

6.2.9 Photolysis of Pt(PPh$_3$)$_2$(PhOCNNCOPh) 1, Pt(PMe$_3$)$_2$(PhOCNNCOPh) 3 and Pt(PMe$_3$)$_2$(MeOCNNCOMe) 4 with ethene or diphenylacetylene in C$_6$D$_6$

NMR samples of 1, 3 and 4 were photolysed in C$_6$D$_6$ with either excess diphenyl acetylene or under an 1 atmosphere of ethene. Photolysis of these samples was stopped periodically and checked by $^1$H and $^{31}$P {$^1$H} NMR spectroscopy for signs of reaction. No signs of reaction were detected after 4 days of irradiation.
6.2.10 Photolysis of Pt(PPh$_3$)$_2$(PhOCNOCOPh) 1, Pt(PMe$_3$)$_2$(PhOCNOCOPh) 3 and Pt(PMe$_3$)$_2$(MeOCNOCOMe) 4 with ethene or diphenylacetylene in CDCl$_3$

NMR samples of 1, 3 and 4 were photolysed in CDCl$_3$ with either excess diphenylacetylene or under 1 atmosphere of ethene. Photolysis of these samples was stopped periodically and checked by $^1$H and $^{31}$P {$^1$H} NMR spectroscopy for signs of reaction. After two days of photolysis, the major product formed with 1 was cis-Pt(PPh$_3$)$_2$Cl$_2$, and for 3 and 4 was cis-Pt(PMe$_3$)$_2$Cl$_2$.

6.2.11 Photolysis of Pt(PPh$_3$)$_2$(EtO$_2$CNNCO$_2$Et) 2 and Pt(PPh$_3$)$_2$(PrO$_2$CNNCO$_2$Pr) 5 with ethene or diphenylacetylene in C$_6$D$_6$

NMR samples of 2 and 5 were photolysed with excess diphenylacetylene or under an atmosphere of ethene. After two days of photolysis, either Pt(PPh$_3$)$_2$(η$_2$-C$_2$H$_4$) or Pt(PPh$_3$)$_2$(η$_2$-PhC≡CPh) was formed as determined by their $^1$H and $^{31}$P {$^1$H} NMR spectra.

6.2.12 Thermal reaction of Pt(PPh$_3$)$_2$(EtO$_2$CNNCO$_2$Et) 2 and Pt(PPh$_3$)$_2$(PrO$_2$CNNCO$_2$Pr) 5 with ethene or diphenylacetylene in C$_6$D$_6$

NMR samples of 2 and 5 were heated at 60 °C with excess diphenylacetylene or under an atmosphere of ethene. The samples were shielded from light with aluminium foil. After 1 day, either Pt(PPh$_3$)$_2$(η$_2$-C$_2$H$_4$) or Pt(PPh$_3$)$_2$(η$_2$-PhC≡CPh) was formed as determined by their $^1$H and $^{31}$P {$^1$H} NMR spectra.

6.3 SYNTHESIS AND REACTIONS OF AZO INHIBITED PLATINUM HYDROSILATION CATALYSTS

6.3.1 Synthesis of [(Pt{η$_4$-(CH$_2$=CHSiMe$_2$)O})$_2$($µ$-(CH$_2$=CHSiMe$_2$)O)] 8

The synthesis of 8 follows the procedure reported by Lappert and co-workers, with minor modifications. H$_2$PtCl$_6$ (5.0 g) was added to a 250 mL round bottom flask. To this degassed water (0.6 g) and (CH$_2$=CHSiMe$_2$)O (50.0 g) was also added, the mixture was stirred and refluxed under a nitrogen atmosphere for 10 h. The reaction vessel was then allowed to cool to room temperature and the volatiles removed under vacuum to yield a yellow oil. The yellow oil was dissolved in hexane and NaHCO$_3$ (0.8 g) was added in small portions with continuous stirring. The mixture was then filtered through Celite, using hexane as an eluant. A majority of the oligomeric siloxanes and free (CH$_2$=CHSiMe$_2$)O can be removed by eluting a hexane solution of 8 through a
column of silica. Complex 8 was removed from the silica by eluting with acetone. The yield of 8 was calculated to be 74%, via quantitative $^{29}\text{Si} \, ^{1}\text{H}$ NMR spectroscopy using an inverse gated pulse sequence. The preparation of 8 was carried out in minimal lighting.

6.3.2 Synthesis of $\text{PtCl}_2(\text{CH}_2=\text{CHPh})_2$

$\text{PtCl}_2(\text{CH}_2=\text{CHPh})_2$ was prepared as described by Pregosin and co-workers. A 250 mL round bottom flask was charged with $\text{PtCl}_2$ (3.0 g), and styrene (60 mL) and stirred for 4 days at room temperature. An intensely red solution and a yellow precipitate was formed over this period. The yellow precipitate was collected and washed with toluene (2 x 10 mL) and then hexane (2 x 10 mL). The yellow solid of $\text{PtCl}_2(\text{CH}_2=\text{CHPh})_2$ was dried under vacuum for 2 h (yield 50%).

6.3.3 Synthesis of 8 with $\text{PtCl}_2(\text{CH}_2=\text{CHPh})_2$

This was prepared as described in Section 6.3.1, using $\text{PtCl}_2(\text{CH}_2=\text{CHPh})_2$ instead of $\text{H}_2\text{PtCl}_6$ reluxed in toluene.

6.3.4 Inhibition of 8 with $\text{R}_2\text{CNNC}_2\text{R}$ to form 9 ($\text{R}=\text{Et}$), 10 ($\text{R}=\text{Pr}$) and 11 ($\text{R}=\text{Bu}$)

Typically a two-fold excess of the azo dicarboxylate inhibitor, $\text{R}_2\text{CNNC}_2\text{R}$, is stirred with 8 (0.5 g) in toluene (10 mL). The mixture was then eluted through a column of silica with toluene to remove excess vinylsiloxanes, oligomers and free azo inhibitors. Azo inhibited 8 was then obtained by eluting the silica column with a 50:50 acetone:toluene mixture. Removal of solvent under vacuum yielded a yellow/brown oil which precipitated a light brown solid upon addition of hexane (10 mL). The light brown solid was collected, washed with hexane and dried under vacuum (yield 10-15%).

6.3.5 Model hydrosilation system using 1-octene and 1,1,1,3,5,5,5,-heptamethyl-trisiloxane and azo inhibited 8

A typical model hydrosilation involved dissolving 8 in 1-octene (12.2 g) (1 % wt. Pt). To this solution a 40 fold excess, relative to platinum, of the azo dicarboxylate inhibitor $\text{R}_2\text{CNNC}_2\text{R}$ was added. Equal molar quantities of 1,1,1,3,5,5,5-heptamethyl-trisiloxane (24.2 g), relative to 1-octene, was then added to the rest of the reaction mixture. The reaction mixture was left at room temperature for up to 4 h and
checked by GC to ensure no hydrosilation has taken place. Equal quantities (ca. 2 mL) of the reaction mixture were then transferred into two Pyrex sample tubes, one of which was shielded with foil. The sample tubes were immersed in water and photolysed for a measured amount of time (up to 5 minutes). Once photolysis had finished, 1 μL samples were taken from the photolysed and the control reaction mixture and were then subsequently monitored by GC. Further GC samples were taken at regular intervals and the progress of the increase in hydrosilation product was monitored with respect to time.

GC conditions employed: oven temperatures were at 100-250 °C at 20 °C / min, injection temperature and detector temperature were at 300 °C. A 1 m long OV 101 packed column was used.

6.4 SYNTHESIS AND REACTIONS OF PLATINUM BIS(PHOSPHINE) CARBOXYLATES COMPLEXES

The compounds cis-Pt(PMe3)2Cl2,3 Pt(dppe)Cl2,12 Pt(COD)Cl2,13 Ag2(O2CCH2CO2)14 and Ag2[O2C(C6H4)CO2]14 were prepared according to literature procedures.

6.4.1 Preparation of Pt(dppe)(O2CCH2CO2) 12

The complex Pt(dppe)(O2CCH2CO2) was prepared with minor modifications to the procedure reported by Anderson and co-workers.15 Pt(dppe)Cl2 (1.00 g, 2 mmol) was dissolved in a minimum amount of dichloromethane or chloroform. An excess of the silver malonate salt, Ag2(O2CCH2CO2) (3.0 g, 6 mmol), was then added to the solution. The reaction mixture was left stirring for 72 h at room temperature, whilst shielded from light. The mixture was then filtered and the resultant solution concentrated under reduced pressure to ca. 5 mL. Addition of ether at this point precipitated the white complex Pt(dppe)(O2CCH2CO2) 12. The complex was collected, washed with ether and dried under vacuum (Yield 1.2 g, 83 %). Mass spectrum (FAB): m/z 696 [M+, [195Pt + H]+ and [M + 2H]+, 194Pt, 100 %].1H NMR spectrum (300.13 MHz, CD3CN, 295 K): δ 2.58 [d, PCH2, 2J(PH) = 17.3 Hz], δ 3.34 (s, O2CCH2CO2), δ 7.60-7.50 (m, Ph). 13C {1H} NMR spectrum (75.47 MHz, CD2Cl2, 295 K) δ 27.5 [d, PCH2, J(PC) = 51 Hz], δ 51.1 (s, O2CCH2CO2), δ 126.4-133.7 (Ph), δ 174.0 (s, O2CCH2CO2). 31P {1H} NMR spectrum (121.94 MHz, CD3CN, 295 K): δ 32.7 [s, J(PtP) = 3665 Hz]. IR (KBr): ν(C=O) 1649 cm⁻¹, ν(C–O) 1354 cm⁻¹.
6.4.2 Preparation of Pt(PMe$_3$)$_2$[O$_2$C(1,2-C$_6$H$_4$)CO$_2$] 

Complex 13 was prepared from cis-Pt(PMe$_3$)$_2$Cl$_2$ (1.0 g, 2.4 mmol) and Ag$_2$[O$_2$C(1,2-C$_6$H$_4$)CO$_2$] using the same procedure as for complex 12 (Yield 0.73 g, 60 %). (Found: C, 32.7; H, 4.3. Calc. for C$_{14}$H$_{22}$O$_4$P$_2$Pt: C, 32.9; H, 4.3). Mass spectrum (FAB): m/z 512 [M$^+$, [195Pt + H]$^+$ and [M + 2H]$^+$, 194Pt, 100 %]. $^1$H NMR spectrum (300.13 MHz, CD$_3$CN, 295 K): δ 1.51 [d, PC$CH_3$, $^2$J(PH) = 11.7 Hz, J(PtH) = 36.2], δ 7.35-7.50 [m, O$_2$C(C$_6$H$_4$)CO$_2$]. $^{31}$C [$^1$H] NMR spectrum (75.47 MHz, CD$_2$Cl$_2$, 295 K) δ 14.6 (m, P$CCH_3$), δ 127.4-139.2 [m, O$_2$C(o,m-C$_6$H$_4$)CO$_2$], δ 175.3 [s, O$_2$C(o,m-C$_6$H$_4$)CO$_2$]. $^{31}$P [$^1$H] NMR spectrum (121.94 MHz, CD$_3$CN, 295 K): δ -27.4 [s, J(PtP) = 3564 Hz]. 

6.4.3 Preparation of Pt(COD)(O$_2$CCH$_2$CO$_2$) 14

Complex 14 was prepared from Pt(COD)Cl$_2$ (1.0 g, 2.7 mmol) and Ag$_2$(O$_2$CCH$_2$CO$_2$) using the same procedures as for complexes 12 and 13 (Yield 0.9 g, 81 %). Mass spectrum (FAB): m/z 406 [M$^+$, [195Pt + H]$^+$ and [M + 2H]$^+$, 194Pt, 100 %]. $^1$H NMR spectrum (300.13 MHz, CD$_2$Cl$_2$, 295 K): δ 2.30, 2.73 [br. m, CH$_2$CH$_2$(COD)], δ 3.37 (s, O$_2$CCH$_2$CO$_2$), δ 5.39 (br. s, CH=CH(COD), J(PtH) = 66.5 Hz). IR (CH$_2$Cl$_2$): v(C=O) 1674 cm$^{-1}$, v(C-O) 1340 cm$^{-1}$. 

6.4.4 Photolysis of Pt(dppe)(O$_2$CCH$_2$CO$_2$) 12

Photolysis of 12 in CD$_3$CN for up to 4 days with either diphenylacetylene or ethene (1 atm) resulted in low conversion to an unidentified yellow compound A4. $^{31}$P [$^1$H] NMR spectrum (121.94 MHz, CD$_3$CN, 295 K): δ 47.6 [J(PtP) = 3625 Hz]. 

6.4.5 Photolysis of Pt(PMe$_3$)$_2$(PMe$_3$)$_2$[O$_2$C(C$_6$H$_4$)CO$_2$] 13

Prolonged photolysis of 13 in CD$_3$CN with either diphenylacetylene or ethene (1 atm) yielded small amounts of two products, Pt(PMe$_3$)$_2$[O$_2$C(C$_6$H$_4$)CO$_2$] B4 and the unassigned product C4. $^1$H NMR spectrum (300.13 MHz, CD$_3$CN, 295 K) of B4: δ$_H$ 1.78 [d, PC$CH_3$, J(PH) = 11.2 Hz], δ 1.86 [d, PC$CH_3$, J(PH) = 11.0 Hz]. $^{31}$P [$^1$H] NMR spectrum (121.94 MHz, CD$_3$CN, 295 K) of B4: δ -11.2 [d, P$^C$, J(PP) = 19 Hz, J(PtP) = 1849 Hz], δ -29.7 [d, P$^O$, J(PP) = 19 Hz, J(PtP) = 3712 Hz]. $^1$H NMR spectrum (300.13 MHz, CD$_3$CN, 295 K) of C4: δ 1.62 [d, PC$CH_3$, J(PH) = 9.8 Hz]. $^{31}$P [$^1$H] NMR spectrum (121.94 MHz, CD$_3$CN, 295 K) of C4: δ -28.2 [s, J(PtP) = 3960 Hz].
6.5 SYNTHESIS AND REACTIONS OF PLATINUM BIS(PHOSPHINE) SILYL HYDRIDE COMPLEXES

6.5.1 Preparation of Pt(PCy₃)₂

Pt(PCy₃)₂ was prepared with a slight variation to the procedure described in the literature.²⁶ Crude trans-Pt(PCy₃)₂Cl₂ (2.22 g, 2.69 mmol), PCy₃ (0.02 g) and a magnetic stirrer bar were placed in a 100 mL Schlenk tube. To this a 0.33 M tetrahydrofuran solution of sodium naphthalene solution [prepared from sodium (0.5 g) and naphthalene (2.2 g) in THF (50 mL)] was added dropwise with stirring under an atmosphere of argon. The mixture gradually changed colour to red-brown and addition of the sodium naphthalene solution was stopped when the reaction mixture sustained a brown-green colour. The mixture was then stirred for a further 1-2 h, and the solvent was removed under vacuum leaving a brown-green residue. The brown-green residue was extracted with hexane (2 x 25 mL) and filtered under argon to give a yellow solution. The yellow hexane solution was concentrated under vacuum leaving behind the yellow complex of Pt(PCy₃)₂ which was contaminated with naphthalene. The unwanted naphthalene was removed by sublimation. Pt(PCy₃)₂ was used without further purification, since attempts on recrystallisation in hexane often resulted in the formation of phosphine oxide and the platinum oxygen complex Pt(PCy₃)(O₂) (Yield 0.86 g, 42 %).¹³H NMR spectrum (500.13 MHz, C₆D₆, 300 K): δ 1.30-2.40 (m, C₆H₁₁).³¹P {¹H} NMR spectrum (202.46 MHz, C₆D₆, 300 K): δ 61.5 [s, J(PtP) = 4163 Hz].

6.5.2 Preparation of trans-Pt(PCy₃)₂(H)₂

The complex trans-Pt(PCy₃)₂(H)₂ was prepared by N. Jasim at York, using the following procedures. Pt(PCy₃)₂ (0.50 g, 0.66 mmol) was dissolved in hexane, then carbon dioxide and oxygen were bubbled simultaneously through the solution. The white platinum peroxy carbonato complex precipitated out of solution and was collected and dried under reduced pressure. The platinum peroxy carbonato complex was stirred with excess NaBH₄ in ethanol for 10 min to give trans-platinum bis(phosphine) dihydride trans-Pt(PCy₃)₂H₂. Excess solvent was removed under vacuum. The platinum dihydride complex was extracted from the solid with benzene and recrystallised from a 1:1 methanol/benzene solution (Yield 0.2 g, 45 %).¹³H NMR spectrum (500.13 MHz, [²H₈]toluene, 300 K): δ -3.08 [t, PtH, J(PH) = 17.2 Hz, J(PtH) = 793.1 Hz].³¹P {¹H} NMR spectrum (202.46 MHz, [²H₈]toluene, 300 K): δ 52.4 [s, J(PtP) = 2887 Hz].
6.5.3 Preparation of cis-Pt(PCy₃)₂(H)(SiPh₃) 15

Pt(PCy₃)₂ (0.10 g, 0.15 mmol) was dissolved in pentane or hexane (15 mL). To this triphenylsilane (0.07 g, 0.26 mmol) in pentane or hexane (10 mL) was added dropwise with stirring. The reaction mixture was then left stirring in an ice bath for 12 h and a white precipitate was formed. The white solid of cis-Pt(PCy₃)₂(H)(SiPh₃) 15 was collected and washed with 3 x 10 mL of cold pentane or hexane (Yield 0.70 g, 47 %) (Found: C, 63.8; H, 8.1. Calc. for C₃₅H₆₂P₅SiPt: C, 63.1; H, 8.1). Mass Spectrum (FAB): m/z 1014 {M⁺, ¹⁹⁴Pt, 18 %}, m/z 1015 {M⁺, ¹⁹⁵Pt and [M + H]⁺, ¹⁹⁴Pt, 79 %}. ¹H NMR spectrum (500.13 MHz, [¹H₈]toluene, 250 K): δ -3.95 [1H, dd, PtH, ²J(PH)ₜᵣᵢₙₙ = 23.3 Hz, ²J(PH)ᵣᵢₐₗ₁ = 141.8 Hz, J(PtH) = 784.2 Hz], δ 1.12-2. 50 (22H, m, PC₆H₆), δ 7.20-8.40 (10H, m, PC₆H₅). ³¹P {¹H} NMR spectrum (202.46 MHz, [¹H₈]toluene, 250 K): δ 37.3 [d, P, J(PP) = 13 Hz, J(PtP) = 2642 Hz], δ 41.1 [d, PSi, J(PP) = 13 Hz, J(PtP) = 1560 Hz]. ¹⁹⁵Pt {¹H} NMR spectrum: δ -5205 [dd, J(PtSi) = 1555 Hz, J(PtP) = 2650 Hz]. IR (KBr): v(Pt-H) 2078 cm⁻¹.

6.5.4 Preparation of cis-Pt(PCy₃)₂(H)(SiMe₂CH₂CH=CH₂) 16

Complex 16 was prepared using the same procedure as for cis-Pt(PCy₃)₂(H)(SiPh₃). Pt(PCy₃)₂ (0.43 g, 0.57 mmol) and HSiMe₂CH₂CH=CH₂ (0.33 μL, 2.27 mmol) was dissolved in hexane and left stirring in an ice bath for 5 h. The white solid formed was collected and wash with 3 x 10 mL of cold hexane (Yield 0.20g, 41 %) (Found: C, 56.3; H, 9.1. Calc. for C₄₁H₇₈P₅SiPt: C, 57.5; H, 9.2). Mass Spectrum (FAB): m/z 854 {M⁺, ¹⁹⁴Pt, 18 %}, m/z 855 {M⁺, ¹⁹⁵Pt and [M + H]⁺, ¹⁹⁴Pt, 79 %}. ¹H NMR spectrum (500.13 MHz, [¹H₈]toluene, 240 K): δ -3.46 [1H, dd, PtH, ²J(PH)ₜᵣᵢₙₙ = 26.1 Hz, ²J(PH)ᵣᵢₐₗ₁ = 144.1 Hz, J(PtH) = 853.3 Hz], δ 1.05 [6H, d, SiCH₃], ³¹P {¹H} NMR spectrum (202.46 MHz, [¹H₈]toluene, 240): δ 37.3 [d, P, J(PP) = 13 Hz, J(PtP) = 2677 Hz], δ 42.8 [d, PSi, J(PP) = 12 Hz, J(PtP) = 1420 Hz]. IR (KBr): v(Pt-H) 2085 cm⁻¹.

6.5.5 Preparation of cis-Pt(PCy₃)₂(H)(SiMe₂Et) 17

Complex 17 was prepared in situ in an NMR tube by reacting Pt(PCy₃)₂ with an excess amount of HSiMe₂Et in [¹H₈]toluene at -77 °C. Attempts to obtain a solid by reacting Pt(PCy₃)₂ and HSiMe₂Et in hexane only resulted in an oily residue. ¹H NMR spectrum (500.13 MHz, [¹H₈]toluene, 240 K): δ -3.54 [1H, dd, PtH, ²J(PH)ₜᵣᵢₙₙ = 25.8 Hz, ²J(PH)ᵣᵢₐₗ₁ = 144.0 Hz, J(PtH) = 858.3 Hz], δ 0.85 [6H, d, SiCH₃], ³¹P {¹H} NMR spectrum (202.46 MHz, [¹H₈]toluene, 240): δ 41.6 [d, P, J(PP) = 12 Hz, J(PtP) = 2677 Hz], δ 42.8 [d, PSi, J(PP) = 12 Hz, J(PtP) = 1420 Hz]. IR (KBr): v(Pt-H) 2085 cm⁻¹.
\[3J(PtH) = 26.7 \text{ Hz}], \delta 1.10 \text{ - } 2.40 [27H, m, PC\text{e}_6H_{11}, \text{ SiCH}_2\text{CH}_3]. \text{ }^{31}P \{^1H\} \text{ NMR spectrum (202.46 MHz, } ^2\text{H}_8\text{toluene, 240): } \delta 42.2 \text{ [d, P}^H, J(PP) = 12 \text{ Hz, } J(PtP) = 2704 \text{ Hz}], \delta 43.1 \text{ [d, P}^Si, J(PP) = 12 \text{ Hz, } J(PtP) = 1387 \text{ Hz].}

6.5.6 Preparation of HSiMe_2OCH_2C(Me)=CH_2

CH_2=C(Me)CH_2OH (5.4 mL, 64.0 mmol) and NEt_3 (9.0 mL, 63.0 mmol) were added to 175 mL of ether in a 1 L two necked round bottom flask and cooled in an ice bath. HSiMe_2Cl (7.4 mL, 66.6 mmol) was added dropwise to the mixture with vigorous stirring over the course of 20 minutes, whereupon a white precipitate of ammonium chloride was formed. The mixture was left stirring for 15 h and then filtered through Celite. Volatiles were removed under vacuum leaving an opaque liquid. The product was collected in a liquid nitrogen trap on a high vacuum line. Small amounts of ether were detected as impurities in the final product. \(^1H\) NMR spectrum (300.13 MHz, C\text{e}_6D_6, 295 K): \(\delta 0.11 \text{ (6H, d, SiCH}_3, \ 3J(HH) = 2.9 \text{ Hz), } \delta 1.58 \text{ [3H, m, CH}_2\text{C}(CH_3)=CH_2\), \(\delta 3.93 \text{ [2H, m, CH}_2\text{C}(CH_3)=CH_2\), \(\delta 4.82 \text{ [1H, m, CH}_2\text{C}(CH_3)=CH_2\), \(\delta 4.84 \text{ [1H, sept, SiH, } 3J(HH) = 2.9 \text{ Hz), } \delta 5.10 \text{ [1H, m, CH}_2\text{C}(CH_3)=CH_2\).}

6.5.7 Preparation of cis-Pt(PCY_3)_2(H)[SiMe_2OCH_2C(Me)=CH_2] 18

This complex was prepared by reacting Pt(PCY_3)_2 and excess HSiMe_2OCH_2C(Me)=CH_2 in \(^2\text{H}_8\)toluene in situ at \(-78 \text{ °C. Attempts at obtaining a solid product only yielded an oily residue. } ^1H\) NMR spectrum (500.13 MHz, \[^2\text{H}_8\]toluene, 250 K): \(\delta -4.15 \text{ [1H, dd, Pt}H, 2J(PH)_{\text{cis}} = 27.7 \text{ Hz, } 2J(PH)_{\text{trans}} = 140.5 \text{ Hz, } J(PtH) = 888.5 \text{ Hz}], \delta 1.16 \text{ [6H, s, SiCH}_3, \ 3J(PtH) = 29.9 \text{ Hz], } \delta 1.20-2.40 \text{ [25H, m, PC}_6\text{H}_{11}, \text{ CH}_2\text{C}(CH_3)=CH_2\), \(\delta 4.52 \text{ (2H, br., SiOC}CH=CH_2\), \(\delta 5.24, \delta 5.51 \text{ [2H, br., C(CH}_3)=CH_2\). \text{ }^{31}P \{^1H\} \text{ NMR spectrum (202.46 MHz, } ^2\text{H}_8\text{toluene, 250 K): } \delta 41.9 \text{ [d, P}^H, J(PP) = 13 \text{ Hz, } J(PtP) = 2658 \text{ Hz], } \delta 42.0 \text{ [br., P}^Si, J(PtP) = 1369 \text{ Hz].}

6.5.8 Preparation of cis-Pt(PCY_3)_2(H)[Si(OMe)_2CH_2CH=CH_2] 19

Complex 19 was prepared by reacting Pt(PCY_3)_2 and excess HSi(OMe)_2CH_2CH=CH_2 in C\text{e}_6D_6 in an NMR tube at room temperature. Attempts to isolate this product only produced an oily residue. \(^1H\) NMR spectrum (200.13 MHz, C\text{e}_6D_6, 295 K): \(\delta -4.00 \text{ [1H, dd, Pt}H, 2J(PH)_{\text{cis}} = 28.0 \text{ Hz, } 2J(PH)_{\text{trans}} = 141.8 \text{ Hz, } J(PtH) = 863.4 \text{ Hz}], \delta 0.80 \text{ - } 2.77 \text{ (22H, m, PC}_6\text{H}_{11}, \delta 2.40 \text{ [2H, d, SiCH}_2\text{CH}=CH_2, J(HH) = 8.9 \text{ Hz], } \delta 3.84 \text{ [6H, s, Si(OCH}_3\), \(\delta 5.13, \delta 5.30 \text{ (2H, m, SiCH}_2\text{CH}=CH_2\), \(\delta 6.50 \text{ (1H, m, SiCH}_2\text{CH}=CH_2\). \text{ }^{31}P \{^1H\} \text{ NMR spectrum (81.02 MHz, C\text{e}_6D_6, 295 K): } \delta 41.9 \text{ [d, P}^Si, J(PP) = 14 \text{ Hz, } J(PtP) = 1408 \text{ Hz], } \delta 42.4 \text{ [br. d, P}^H, J(PtP) = 2638 \text{ Hz].}
6.5.9 Preparation of cis-Pt(PCY₃)(H)(SiPh₂OSiPh₂) 20

Complex 20 was prepared by reacting Pt(PCY₃)₂ and HSiPh₂OSiPh₂H in a 1:1 ratio in C₆D₆ in an NMR tube at room temperature. ¹H NMR spectrum (200.13 MHz, C₆D₆, 295 K): δ -4.00 [1H, dd, PtH, 2J(PH)ₜₜ = 27.2 Hz, 2J(PH)ᵣᵣ = 140.7 Hz, J(PtH) = 851.4 Hz], δ 0.71 - δ 2.79 (22H, m, PC₆H₁₁). δ 6.06 [1H, s, SiH, J(SiH) = 213.0 Hz], δ 7.04-7.15 (20H, m, SiC₆H₄). ³¹P {¹H} NMR spectrum (81.02 MHz, C₆D₆, 295 K): δ 43.1 [d, Pᵣ, J(PP) = 15 Hz, J(PtP) = 1428 Hz], δ 43.4 [d, Pᵣ, J(PP) = 15 Hz, J(PtP) = 2612 Hz].

Using a 2:1 ratio of Pt(PCY₃)₂ and HSiPh₂OSiPh₂H in the reaction at room temperature only resulted in the formation of cis-Pt(PCY₃)(H)(SiPh₂OSiPh₂H) 20. Chelating disilyl complexes or dimeric species were not detected.

6.5.10 Reaction of Pt(PCY₃)₂ with HSiMe₂(C₆H₄)SiMe₂H

Pt(PCY₃)₂ and HSiMe₂C₆H₄SiMe₂H were reacted in [²H₈]toluene in an NMR tube at -77 °C to form an unidentified platinum hydride phosphine complex A₅. Attempts to isolate A₅ only resulted in an oily residue. ¹H NMR spectrum (500.13 MHz, [²H₈]toluene, 295 K): δ -1.89 [br, J(PtH) = 675.2 Hz], δ 0.94 [s, Si(CH₃)₂, J(PtH) = 28.3 Hz]. ¹H NMR spectrum (500.13 MHz, [²H₈]toluene, 200 K): δ -1.89 [d, J(PH) = , J(PtH) = 675.2 Hz], δ 0.94 [s, Si(CH₃)₂, J(PtH) = 28.3 Hz]. ³¹P {¹H} NMR spectrum (202.46 MHz, [²H₈]toluene, 295 K): δ 56.1 [br, J(PtP) = 1531 Hz]. ¹⁹⁵Pt {¹H} NMR spectrum (107.52 MHz, [²H₈]toluene, 200 K): δ -5700 [d, J(PtP) = 1538 Hz].

At room temperature, reaction of Pt(PCY₃)₂ and HSiMe₂C₆H₄SiMe₂H formed a new unidentified platinum species B₅, along with A₅ which was initially formed at low temperature. Warming a sample of A₅ to room temperature only resulted in gradual decomposition to the trans-platinum dihydride, no formation of B was detected. ³¹P {¹H} NMR spectrum (81.02 MHz, C₆D₆, 295 K) of B₅: δ 33.5 [s, J(PtP) = 1437 Hz].

6.5.11 Thermolysis of cis-Pt(PCY₃)(H)(SiMe₂CH₂CH=CH₂) 16

Complex 16 (ca. 30 mg) was dissolved in 5 mL of C₆D₆ under an argon atmosphere. Immediate GC analysis of this sample showed that only one volatile species was present which corresponded to HSiMe₂CH₂CH=CH₂ in C₆D₆. Over a period of 30 minutes, GC analysis of the sample showed the disappearance of HSiMe₂CH₂CH=CH₂ and the formation of three new products with retention times of 7.2, 19.0 and 33.9 minutes. GC/MS analysis of the three major products contains the following dominant mass spectral peaks: 7.2 min [m/z = 73 (15 %), 133 (100 %), 173 (33 %), 175 (23 %)]. 19.0 min [m/z = 41 (36 %), 55 (56 %), 81 (24 %), 83 (25 %), 115
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(25 %), 116 (27 %), 117 (100 %), 198 (89 %), 199 (36 %), 280 (25 %)]. 33.9 min [m/z = 41 (25 %), 55 (42 %), 132 (40 %), 133 (54 %), 214 (100 %)]. GC conditions employed: oven temperatures were at 40-200 °C at 15 °C / min, injection temperature and detection temperature were at 250 °C. A 12 m long methylsilicone packed column was used.

6.5.12 Photolysis of cis-Pt(PCy3)2(H)(SiR12R2) [R1 = R2 = Ph (15); R1 = Me, R2 = CH2CH=CH2 (16)]

NMR samples of complexes 15 and 16 in [2H8]toluene were photolysed for 4 h at -78 °C and partially yields trans-Pt(PCy3)2(H)(SiPh3)2 21 and trans-Pt(PCy3)2(H)(SiMe2CH2CH=CH2) 22. 1H NMR spectrum of 21 {500.13 MHz, [2H8]toluene, 250 K}: δ -3.00 [t, PtH, 2J(PH) = 16.6 Hz, J(PtH) = 584.2 Hz]. 31P {1H} NMR spectrum of 21 {202.46 MHz, [2H8]toluene, 250 K}: δ 37.5 [s, J(PtP) = 2656 Hz]. 1H NMR spectrum of 22 {500.13 MHz, [2H8]toluene, 250 K}: δ -2.64 [t, PtH, 2J(PH) = 18.1 Hz, J(PtH) = 584.2 Hz]. 31P {1H} NMR spectrum of 22 {202.46 MHz, [2H8]toluene, 250 K}: δ 37.5 [s, J(PtP) = 2747 Hz].

6.5.13 Photolysis of trans-Pt(PCy3)2(H) with HSiMe2Et

An excess amount of HSiMe2Et was added to an NMR sample of trans-Pt(PCy3)2(H)2 in C6D6 at room temperature. The sample was monitored by 1H and 31P{1H} NMR spectroscopy and no reaction was observed between the silane and the platinum dihydride complex. A small amount of trans-Pt(PCy3)2(H)(SiMe2Et) 23 was formed after 1 day of photolysis. 1H NMR spectrum of 23 {500.13 MHz, C6D6, 300 K}: δ -2.85 [t, PtH, 2J(PH) = 18.5 Hz, J(PtH) = 552.1 Hz]. 31P {1H} NMR spectrum of 23 {202.46 MHz, C6D6, 250 K}: δ 37.5 [s, J(PtP) = 2747 Hz].

An NMR sample of trans-Pt(PCy3)2(H)2 with an excess amount of HSiMe2Et in [2H8]toluene was prepared at room temperature. NMR spectroscopy of the sample with in situ photolysis, performed by John Lowe at the University of York, was carried out at 250 K. After 1 h of in situ photolysis, a small amount of cis-Pt(PCy3)2(H)(SiMe2Et) was detected in the 1H NMR spectrum.

6.5.14 Thermodynamic and kinetic measurements of dynamic processes in cis-Pt(PCy3)2(H)(SiR12R2) [R1 = R2 = Ph (15); R1 = Me, R2 = CH2CH=CH2 (16); R1 = Me, R2 = Et (17)]

NMR samples of complexes 15 and 16 were prepared by distillation of [2H8]toluene into a Pyrex NMR tube, using a liquid nitrogen trap, containing complexes
15 or 16 on a high vacuum line. NMR samples of complex 17 were prepared by distillation of a solution of HSiMe₂Et (1 equivalent relative to Pt) in [²H₅]toluene into a Pyrex NMR tube containing Pt(PCY₃)₂. All samples were kept cold in liquid nitrogen prior to NMR spectroscopy. For each complex, quantitative H and ³¹P {¹H} NMR spectra were recorded in the range of 250-300 K. Samples were left for 30 minutes at each temperature prior to obtaining the spectrum. The H NMR resonance of the Si–H group on the free silanes was found to have a long relaxation time of up to 8 seconds at room temperature. A 60 seconds delay between acquisition was therefore used to allow for reliable integration analysis of the proton spectrum. Quantitative ³¹P {¹H} NMR spectra were acquired using an inverse-gated pulse.

Integration values of the hydride and Si–H signals in the H NMR spectra, and the Pt(PCY₃)₂ and the Pt(PCY₃)₂(H)(SiR₃)₂ signals from the ³¹P {¹H} NMR spectra were used to determine the thermodynamic parameters for complexes 15-17. Kinetic data were obtained by simulation of the hydride resonance using the computer programme DNMR-SIM, see Chapter 5, Section 5.2.6.

6.6 REFERENCES

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