SYNTHETIC AND MECHANISTIC STUDIES OF SILA-ALKYL/PLATINUM(II).

By
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For my Family.

"So it goes...."

Slaughterhouse 5

K. Vonnegut Jr.

Abstract.

A series of complexes *cis*-$L_2Pt(CH_2SiMe_2Ph)_2$ [L = py, py-d^5, Bu^{t}py, Phpy, pyd, PMe_3, PEt_3, PMe_2Ph, PPh_2Me, PPh_3, P*p*-tol_3, PPh_2-*o*-tol, $PPh_2C_6H_4$-2-CF_3; L_2 = tmed, bipy, Me_2bipy, Bu$^t_2$bipy, bipyz, bipym, phen, Ph_2phen, Me_4phen, Me_2Ph_2phen, dppm, dppe, dppp, dppb, dppf] has been synthesised by metathetical displacement of the diene from (cod)$Pt(CH_2SiMe_2Ph)_2$ or (nbd)$Pt(CH_2SiMe_2Ph)_2$, or by displacement of the thioether from $[Pt(CH_2SiMe_2Ph)_2(\mu\text{-dms})]_2$. These complexes have been extensively characterised by infra-red, ^1H, ^{13}C N.M.R. and where appropriate ^{31}P N.M.R. and electronic spectroscopy. The sila-neophyl ligand exerts a weaker *trans*-influence than neophyl, which on N.M.R. evidence, has the stronger Pt-C bond. A crystallographic study comparing (cod)$Pt(CH_2SiMe_2Ph)_2$ with (cod)$Pt(CH_2CMe_2Ph)_2$ indicates very little difference between bond lengths in the two complexes, suggesting that the difference between the two alkyl groups is steric in origin. The dependence of the ^1H N.M.R. with temperature has been studied for (dppf)$Pt(CH_2SiMe_2Ph)_2$ and a conformational equilibrium proposed.

Toluene solutions of $L_2Pt(CH_2SiMe_2Ph)_2$, rearrange thermolytically by different pathways depending on the ligand. $(Py)_2Pt(CH_2SiMe_2Ph)_2$ undergoes δ-C-H transfer yielding a platinasila-indan, $(py)_2\overline{Pt(CH_2SiMe_2C_6H_4)}$ and trimethylphenylsilane. In general though, complexes with monodentate phosphines (L = PMe_3, PMe_2Ph, PPh_2Me, PPh_3, P-*p*-tol_3, $PPh_2C_6H_4$-2-CF_3) undergo an isomerisation reaction, affording *cis*-$L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$. Detailed studies of this reaction by N.M.R. show first order kinetics. Kinetic isotope effects and activation parameters for the rearrangement are presented and mechanistic implications discussed. Prerequisite dissociation of an ancillary ligand is followed by regiospecific β-aryl transfer, most plausibly *via* an η^2-silene intermediate. Migratory insertion of the silene intermediate into the remaining Pt-CH_2 bond generates the observed product. $(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$ reacts similarly generating *trans*-$(PEt_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.

$(PPh_2$-*o*-$tol)_2Pt(CH_2SiMe_2Ph)_2$ selectively undergoes δ-aliphatic C-H activation of the phosphine *ortho*-tolyl group affording a platinacyclophosphapentene, *cis*-$(PPh_2$-*o*-tol$)(2\text{-}\overline{CH_2C_6H_4Ph_2P)Pt(CH_2SiMe_2Ph)}$ and trimethylphenylsilane. The reaction conforms to first order kinetics and has been studied by ^{31}P N.M.R.. A mechanism describing the transformation has been proposed.

The preparation of a series of *cis-bis*-$L_2Pt(CH_2SiMe_2R)_2$ [L_2 = cod; R = C_6H_4-2-CH_3, C_6H_4-3-CH_3, C_6H_4-4-CH_3, C_6H_4-4-OCH_3, C_6H_4-4-Bu^t, C_6H_4-4-F, C_6H_4-2-CF_3, C_6H_4-3-CF_3, C_6H_4-4-CF_3, C_6H_4-4-NMe_2, C_6F_5, CH_2Ph, CH_2 C_6H_4-4-CH_3: L_2 = nbd; R = C_6H_4-2-CH_3, C_6H_4-3-CH_3, C_6H_4-4-CH_3: L = Py; R = C_6H_4-3-CH_3, C_6H_4-4-CH_3, C_6H_4-4-OCH_3, C_6H_4-4-Bu^t, C_6H_4-4-F, CH_2Ph: L = PPh_3; R = C_6H_4-2-CH_3, C_6H_4-3-CH_3, C_6H_4-4-CH_3, C_6H_4-4-OCH_3, C_6H_4-4-Bu^t, C_6H_4-4-F, C_6H_4-2-CF_3, C_6H_4-3-CF_3, C_6H_4-4-CF_3, C_6H_4-4-NMe_2,

C_6F_5, CH_2Ph, $CH_2C_6H_4$-4-CH_3] is described and their ^1H, ^{13}C, ^{31}P and where appropriate ^{19}F N.M.R. characteristics discussed.

A study of the effect of aromatic substitution on the rearrangement of $(PPh_3)_2Pt(CH_2SiMe_2R)_2$ reveals that electron-withdrawing substituents accelerate the rate of rearrangement and electron-releasing groups retard isomerisation. *Ortho* substituents imbue greater lability than their *meta* and *para* counterparts for steric reasons. *Meta*-substituted sila-neophyl complexes are not less reactive than corresponding *para*-substituted derivatives, indicating that inductive effects are more important than resonance contributions. The rearrangement was confirmed to be regiospecific.

Thermolysis of $(PPh_3)Pt(CH_2SiMe_2CH_2Ar)_2$ [Ar = Ph, C_6H_4-4-Me] results in more complex behaviour. Preliminary evidence suggests that competitive β-alkyl transfer and aromatic C-H activation occurs.

Cis-$L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ [L = PEt_3, PPh_3] undergo aromatic C-H transfer, exclusively on the hydrocarbyl ligand giving 3,3-dimethylplatinaindan with concurrent formation of *tert*-butylbenzene. Detailed kinetic measurement and mechanistic interpretation is presented.

Toluene solutions of $(PPh_3)_2Pt(CH_2SiMe_3)_2$ undergo rearrangement to $(PPh_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_3)$. Activation parameters and kinetic isotope effects for the reaction are discussed and a mechanism proposed, in which β-methyl transfer follows preliminary dissociation of one ligand *via* an η^2-silene intermediate. Thermolytic rearrangement of $L_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ [L = PEt_3, PPh_3] and $(PPh_3)_2Pt(CH_2SiMe_3)(C_6H_4$-4-$CH_3)$ are also discussed.

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Abbreviations.

ADEPT	-	Automatic analysis of distortionless enhancement by polarisation transfer.
Ar	-	aryl
bipy	-	2,2'-bipyridyl
bipym	-	2,2'-bipyrimidyl
bipyz	-	2,2'-bipyrazyl
Bu^t_2bipy	-	4,4'-di-*tert*-butyl-2,2'-bipyridyl
^tBu	-	*tert*-butyl
^tBupy	-	4-*tert*-butylpyridine
cod	-	cycloocta-1,5-diene
Cp	-	cyclopentadienyl
Cp^*	-	pentamethylcyclopentadienyl
dcpe	-	*bis*-(1,2-dicyclohexylphosphino)ethane
dms	-	dimethyl sulphide
dppb	-	*bis*-(1,4-diphenylphosphino)butane
dppe	-	*bis*-(1,2-diphenylphosphino)ethane
dppf	-	*bis*-(1,1'-diphenylphosphino)ferrocene
dppm	-	*bis*-(diphenylphosphino)methane
dppp	-	*bis*-(1,3-diphenylphosphino)propane
ether	-	diethylether
Et_2O	-	diethylether
HOMO	-	highest occupied molecular orbital
HPLC	-	high pressure liquid chromatography
IR	-	infrared
LFE	-	linear free energy
LUMO	-	lowest unoccupied molecular orbital
M^+	-	molecular ion
Mass Spec.	-	mass spectrometry
Me_2bipy	-	4,4'-dimethyl-2,2'-bipyridyl
MLCT	-	metal-ligand charge transfer
MO	-	molecular orbital
Me_4phen	-	3,4,7,8-tetramethyl-1,10-phenanthroline
Me_2Ph_2phen	-	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
nbd	-	[2.2.1]bicyclohepta-2,5-diene
neopentyl	-	2,2-dimethylpropyl
neophyl	-	2-methyl-2-phenylpropyl
N.M.R.	-	nuclear magnetic resonance
O^tBu	-	*tert*-butoxide
P^tBu_3	-	tri-*tert*butylphosphine

PCy_3	-	tricyclohexylphosphine
PEt_3	-	triethylphosphine
Ph	-	phenyl
phen	-	1,10-phenanthroline
Ph_2phen	-	4,7-diphenyl-1,10-phenanthroline
Phpy	-	4-phenylpyridine
PMe_3	-	trimethylphosphine
PMe_2Ph	-	dimethylphenylphosphine
$PPh_2C_6H_4$-2-CF_3	-	diphenyl-*o*-trifluoromethylphenylphosphine
PPh_3	-	triphenylphosphine
PPh_2Me	-	diphenylmethylphosphine
PPh_2-*o*-tol	-	diphenyl-*o*-tolylphosphine
PPr^i_3	-	tri-*iso*-propylphosphine
Pr	-	propyl
P-*p*-tol_3	-	tri-*para*-tolylphosphine
py	-	pyridine
py-d^5	-	pyridine-d^5
pyd	-	pyridazine
QALE	-	quantitative analysis of ligand effects
sila-neopentyl	-	trimethylsilylmethyl
sila-neophyl	-	dimethyl(phenyl)silylmethyl
styrene	-	2-phenylethene
tmed	-	N,N,N,N-tetramethylethylenediamine

Chapter One :

INTRODUCTION.

Introduction.

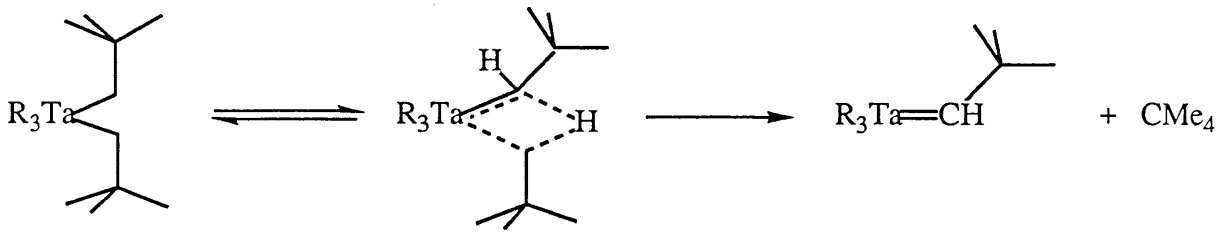
Organotransition metal complexes play crucial rôles in various organic reactions mediated by transition metals. Understanding the behaviour of transition metal alkyl (or aryl) complexes, which are also believed to resemble closely intermediates formed at metal surfaces[1], is therefore fundamental to the elucidation of such metal-promoted processes[2]. Early attempts to isolate transition metal alkyl complexes were not very successful and led to the proposition that metal-carbon bonds were weak and that their complexes were thermodynamically unstable. It was soon generally accepted that the M-C bond was not inherently weak, typically 160-350 kJ mol^{-1} (*vide infra*) and that the facile decomposition of such species was not thermodynamic but kinetic in origin.

The most common reaction pathway for many alkyl-metals is "β-hydrogen transfer". A hydrogen atom is abstracted usually, by the metal from a β-carbon site, forming a hydrido-olefin complex. Further decomposition due to subsequent loss of olefin and hydrogen may then occur. The reverse reaction - the insertion of an alkene into a metal-hydrogen bond - is also well documented[3].

Inhibition of this pathway has been achieved by the development of a variety of "β-elimination stabilised" alkyl groups[3b]. Complexes of this type have no β-hydrogens available consequently, other thermolytic pathways operate, including H-migration from more remote sites[4]. Perhaps the most studied alkyl fragments have been the neopentyl group ($-CH_2CMe_3$) and its silicon analogue, trimethylsilylmethyl ($-CH_2SiMe_3$).

1.1. C-H Activations of Neopentyl and Trimethylsilylmethyl Groups.

Reaction preferences may vary. For example, neopentyl complexes of the early transition metals (Nb, Ta, W) may undergo α-H abstraction to form metal-alkylidene complexes with concomitant loss of neopentane[5]. The reaction proceeds through a concerted pathway in which the α-hydrogen is transferred to the leaving group with no net change in metal oxidation state throughout the course of the reaction. A four-centre transition state can be postulated, in which metal-carbon and carbon-hydrogen bonds are both being broken and formed (Scheme. 1.1).



Scheme. 1.1 : *Formation of a metal alkylidene species.*

Trimethylsilylmethyl complexes also undergo reactivity of this type, although they appear to be more inert and often form alkylidene bridged polynuclear species[6].

On the other hand, low valent late d-block elements undergo γ-C-H transfer yielding metallacycles[7]. A thorough mechanistic investigation into the thermal reactivity of *cis-bis*-(neopentyl)-*bis*-(triethylphosphine)platinum(II) has been made by Whitesides and co-workers[7b]. The proposed mechanism involves initial dissociation of triethylphosphine, followed by oxidative addition of the neopentyl methyl C-H bond, forming a metallacyclic hydrido-platinum(IV) intermediate. Subsequent loss of neopentane generates a 3,3-dimethylplatinacyclobutane. The observation of a large positive deuterium isotope effect and a substantial positive entropy of activation led to the suggestion that reductive elimination of neopentane was the "rate-limiting step" (Scheme. 1.2).

This pattern of reactivity is not uncommon, but the neopentylmetal parent complexes are not always isolable. Treatment of $RhCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)$ with either an excess of $LiCH_2CMe_3$ or the corresponding Grignard reagent afforded *ortho*-metallation of the triphenylphosphine group as well as γ-H abstraction from the neopentyl ligand. The mechanism of this reaction is not clear; both oxidative addition of a distal C-H bond forming a rhodium(V) species or a four-centred transition state would be possible[7d], though the authors favour the former proposition.

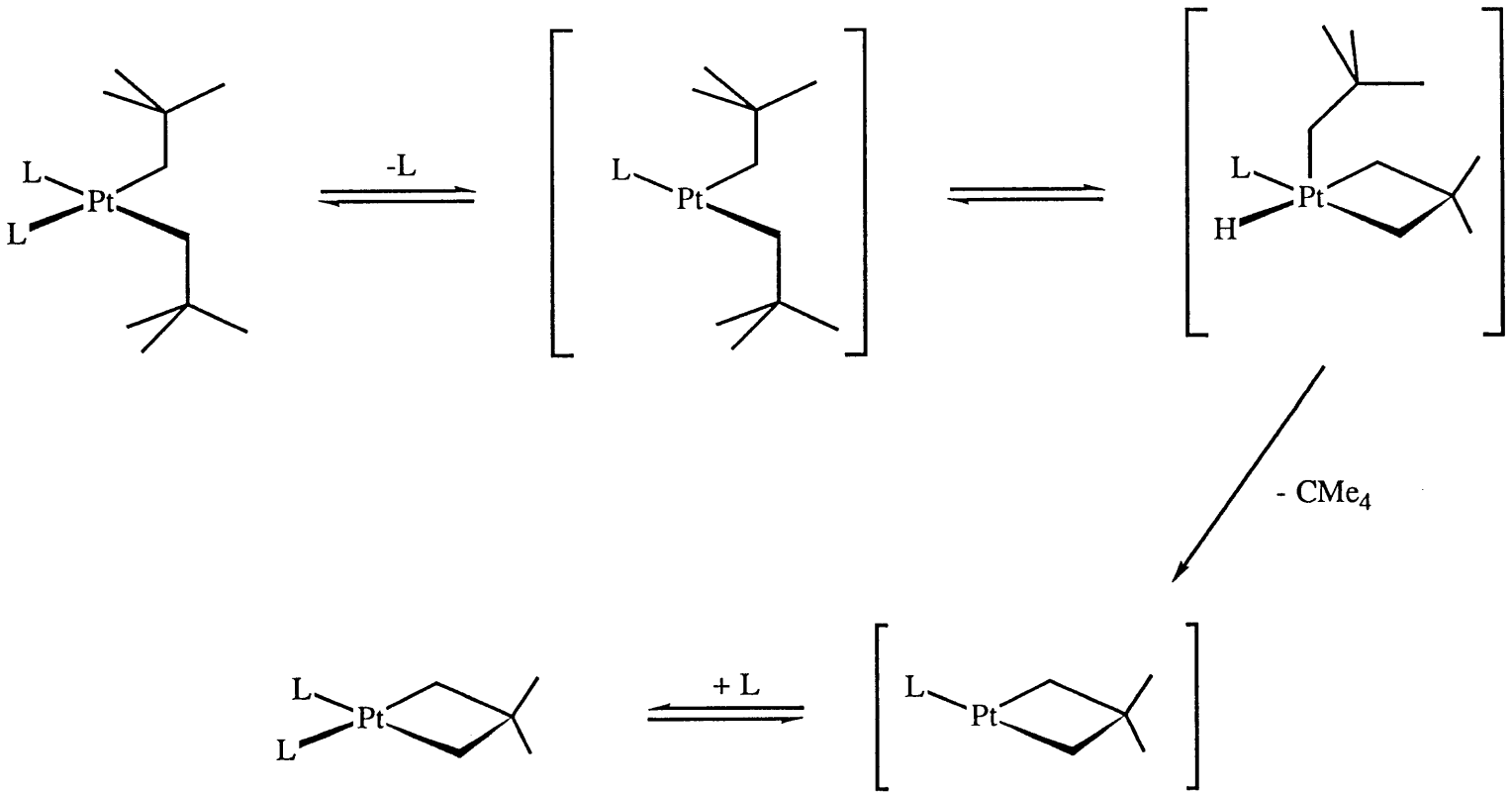
Greater inertness of the trimethylsilylmethyl group is again apparent, although metallacyclisation has been observed. Interaction of $Mo_2(O_2CMe)_4$[8a] with an excess of $Mg(CH_2SiMe_3)_2$ in the presence of PMe_3 generates a complex with a five membered ring containing two molybdenum atoms linked by a metal-metal bond and bridged by a trimethylsilylmethylene group, derived by γ-C-H activation of a Mo-CH_2SiMe_3 group. Treatment of $Rh_2(O_2CMe_4)_4$[8a] with dialkylmagnesium and trimethylphosphine produces a monomeric species with a sila-cyclobutane ring and a σ-bonded trimethylsilyl group. Similarly, $(PMe_3)_4\overline{Os(CH_2SiMe_2CH_2)}$ can be isolated from the reaction of $(PMe_3)_4Os(O_2CMe)_2$ with $Mg(CH_2SiMe_3)_2$[8b].

1-Metalla-3-sila-cyclobutanes of early transition metals were obtained by reaction of $Cp^*_2MX_2$ with $[Mg(CH_2)_2SiMe_2]_n$ [M = Ti, Zr, Nb; X = Cl]. X-ray diffraction studies of several compounds demonstrated the metallacyclic ring to be planar[9].

1.2. Comparative Neopentyl and Trimethylsilylmethyl Systems.

Thermolysis of homoleptic transition metal alkyls MR_4, [M = Ti, Zr, Hf; R = CH_2CMe_3, CH_2SiMe_3] were found to form a black solid and CMe_4 or $SiMe_4$ respectively. It was postulated that the complexes decomposed by binuclear elimination of alkane with concomitant formation of a bridging alkylidene species[10].

At moderate temperatures, $(PMe_3)_4Os(H)R$ undergo γ-C-H transfer forming the corresponding metallacyclobutane, $(PMe_3)_3\overline{Os(H)_2(CH_2EMe_2CH_2)}$ [E = C or Si], though the trimethylsilylmethyl complex was clearly less reactive. The reaction proposedly



Scheme. 1.2 : *Proposed Mechanism for the Thermolytic Rearrangement of* $(PEt_3)_2Pt(CH_2CMe_3)_2$.

involves initial loss of PMe_3 affording $(PMe_3)_3Os(H)(CH_2EMe_3)$ as an intermediate, which is followed by reversible oxidative addition of an γ-C-H bond to form the observed metallacycle[11].

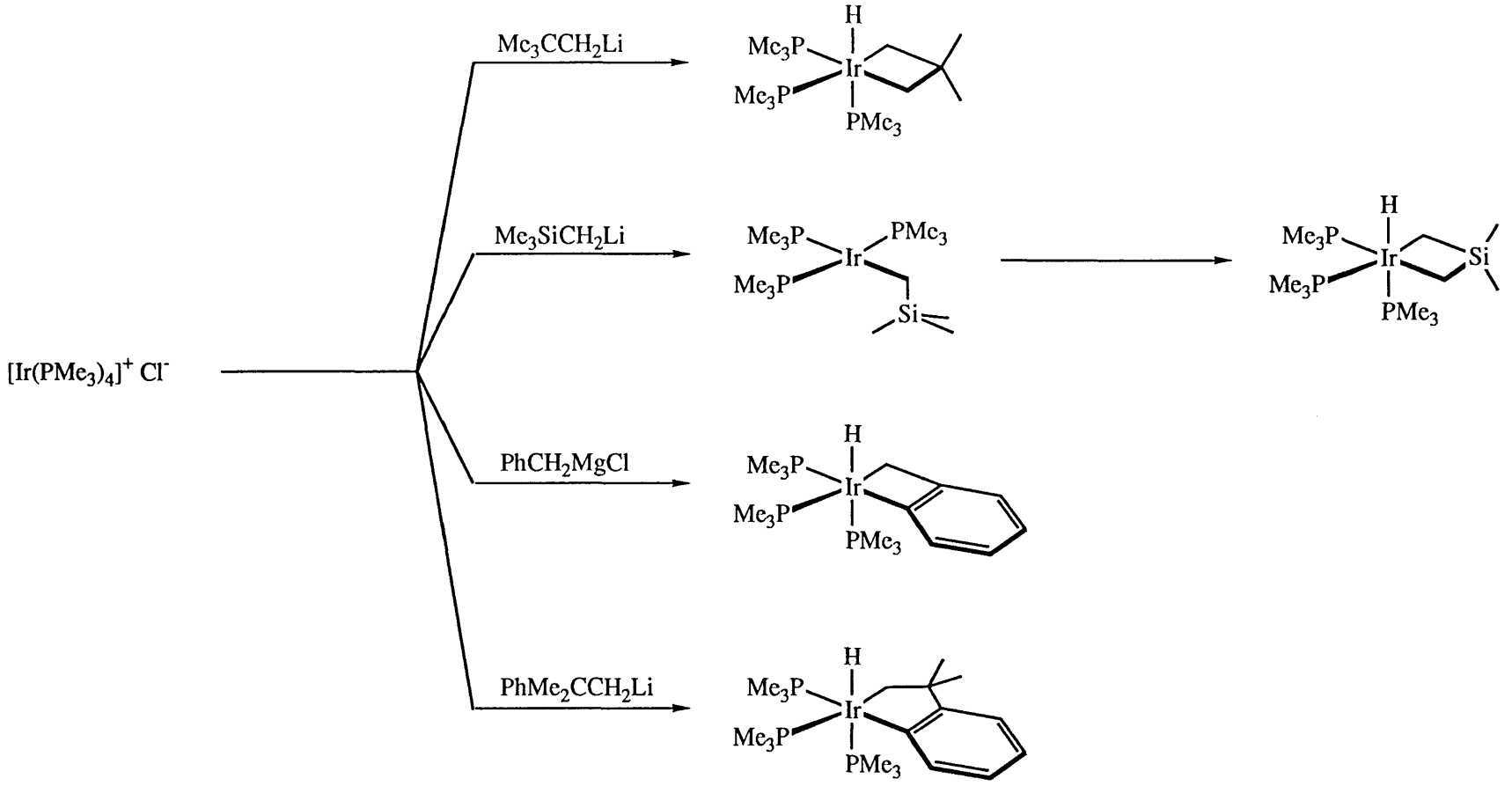
Support for the proposition of alkyl-metal hydrido species as intermediates in such reactions has been provided by the isolation of an iridium(III) hydride complex from the reaction of $[Ir^I(PMe_3)_4]^+ Cl^-$ and neopentyllithium[12]. Although the iridium(I) alkyl precursor could not be isolated in this case; reaction of $[Ir^I(PMe_3)_4]^+ Cl^-$ with $LiCH_2SiMe_3$ afforded the iridium(I) alkyl complex, which was shown to form the corresponding hydrido-1-irida-3-sila-cyclobutane on heating (Scheme. 1.3). This difference in reactivity was ascribed to the lesser steric demands of the trimethylsilylmethyl group as opposed to the neopentyl moiety[13].

Very few systematic comparisons have been made between neopentyl and trimethylsilylmethyl derivatives. One notable exception features the f-block metal, thorium. Marks *et. al.* have studied the intramolecular C-H activation in thorium alkyls of the type $Cp^*_2ThR_2$ (R = CH_2CMe_3, CH_2SiMe_3), which, on thermolysis, quantitatively form the corresponding metallacycles[14]. Mechanistic investigations led to the proposition of a sterically constrained, electrophilic, "four-centre" transition state. From selective deuterium labelling studies it was shown that γ-C-H activation was the predominant reaction pathway for the neopentyl complex, but in the case of the trimethylsilylmethyl group, a secondary competing mechanism was also operating. Rate-limiting abstraction of a hydrogen from a Cp^* ligand, followed by intramolecular opening of the ring-metallated $[Th(\eta^6\text{-}C_5Me_4)Cp^*(CH_2SiMe_3)]$ intermediate also afforded the thoracyclobutane (Scheme. 1.4). At 70°C this pathway was 20 times slower than the corresponding γ-C-H activation route. Also, at a given temperature, neopentyl rearranges 20 times faster than the trimethylsilylmethyl group. Additionally, $Cp^*_2\overline{Th(CH_2CMe_2CH_2)}$ will undergo facile ring-opening C-H activation with saturated hydrocarbons. Again a four-centred transition state is invoked[15].

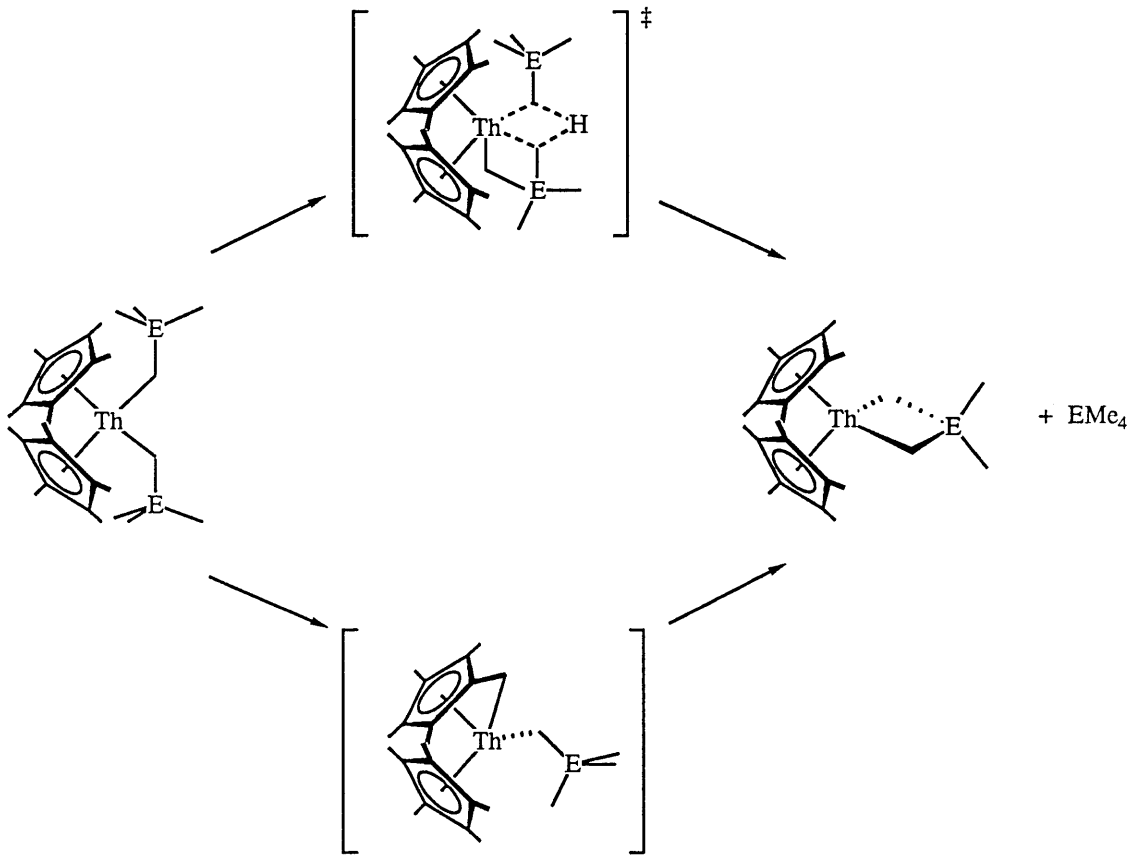
Recently a detailed study of the thermal behaviour of $(PR_3)_2Pt(CH_2SiMe_3)_2$ has revealed a contrast with that of $(PR_3)_2Pt(CH_2CMe_3)_2$ - a metallacycle is not formed. Instead, linkage isomerisation, involving β-Si-CH_3 scission and transfer - most plausibly *via* an η^2-silene intermediate - affording methylplatinum(II) products, $(PR_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$ is observed (*vide infra*)[16].

1.3. C-H Activations at more Remote Sites.

Although the most studied reaction has been γ-C-H activation, aliphatic C-H activations at more remote sites have been observed. Platinum(II) and ruthenium(II) complexes with a 2-methylbenzyl group undergo δ-C-H abstraction to form the corresponding metallacyclopentene[17] or η^4-xylidene complexes, while replacement of one of the β-methyl groups in neopentylplatinum complexes by higher alkyls, such as ethyl



Scheme. 1.3 : *Formation of Hydridoiridacycles by C-H Activation.*



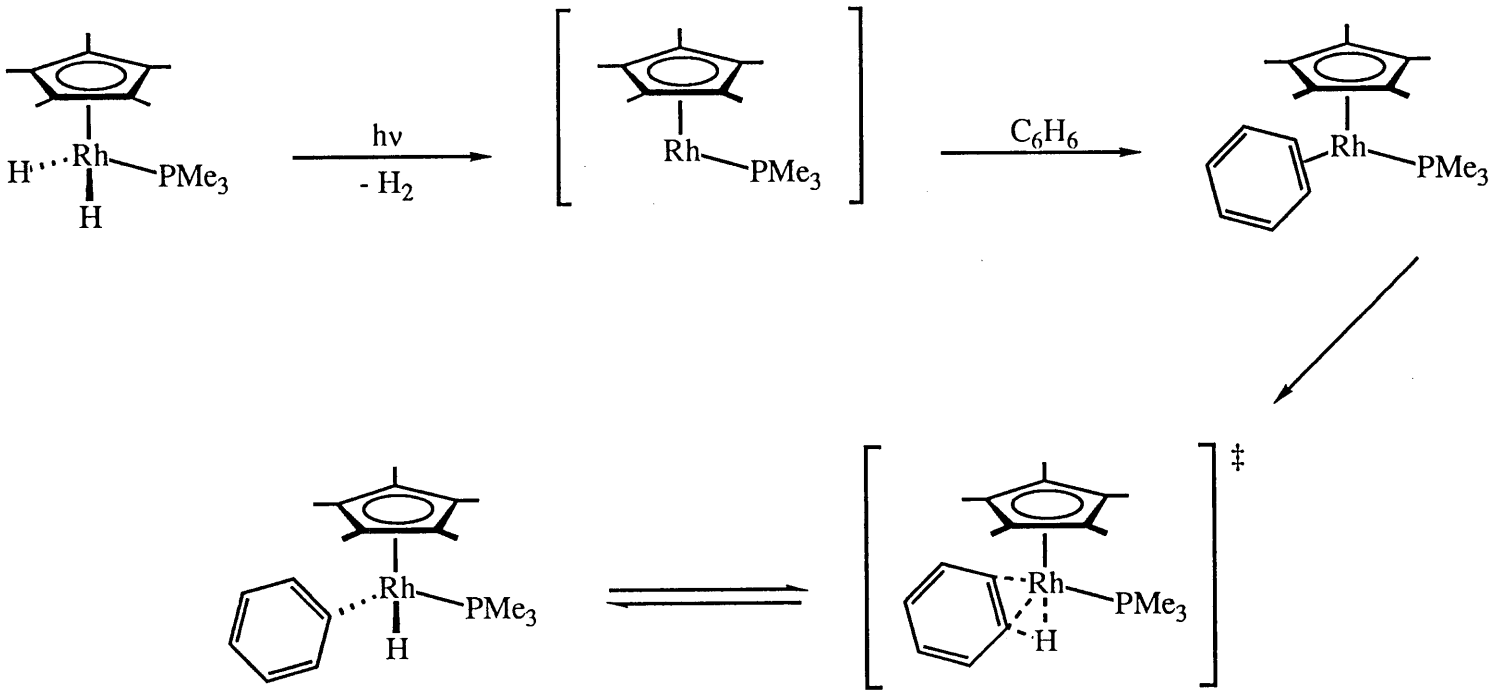
Scheme. 1.4 : *Proposed Mechanisms for Cyclometallation of $Cp^*_2ThR_2$ Complexes.*

and neopentyl, affords the corresponding 5- and 6-membered platinacycles respectively[18]. From the latter study it was shown that very little ring strain was involved in the formation of these rings.

1.4. Intermolecular C-H Transfer.

It is interesting to note, that although there are numerous examples of intramolecular aliphatic C-H activation, until recently few examples of intermolecular alkane activation had been observed[19]. By contrast, several examples of intermolecular arene activation have been reported[2k,20,21].

A thorough study of the reactivity of the coordinatively unsaturated complex, [$RhCp^*(PMe_3)$], by Jones and Feher revealed that initial arene pre-coordination in an η^2-fashion prior to C-H activation was rate limiting. This η^2-arene species rapidly and reversibly undergoes intramolecular oxidative addition to produce a relatively stable aryl hydride[22] (Scheme. 1.5). Further studies enabled comparisons to be made between *intra* and *inter*molecular activation of the same type of bond and of *inter*molecular aromatic *versus* aliphatic C-H bond cleavage[23].

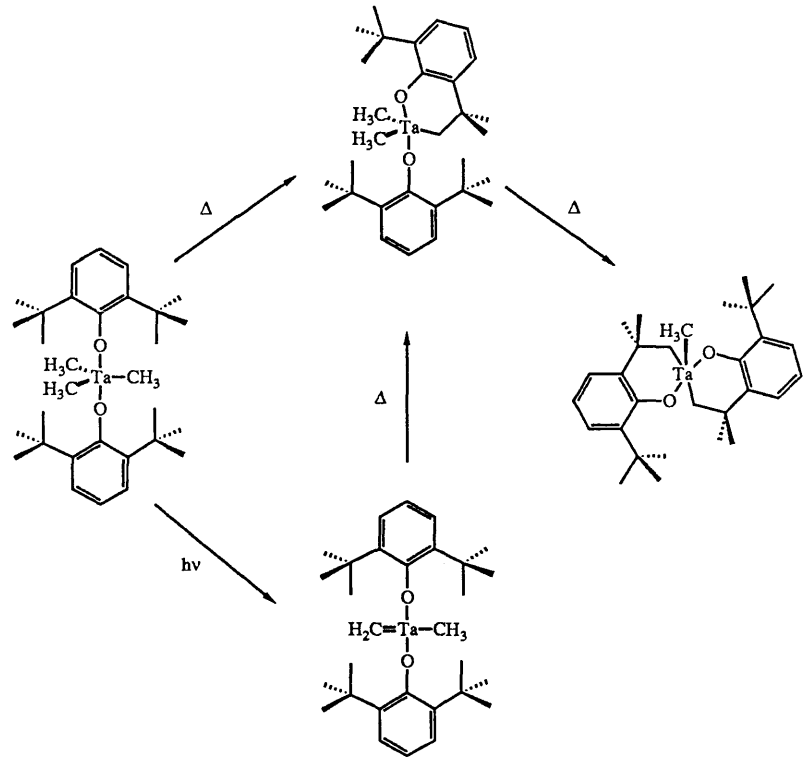


Scheme. 1.5 : *An η^2-arene Complex as a Possible Intermediate During Intermolecular C-H Activation of Benzene by [RhCp*(PMe$_3$)].*

1.5. Cyclometallation of Heteroatomic Donor Ligands.

Activation of C-H bonds of heteroatomic ligands have until recently been relatively scarce. Sterically bulky ligands such as $N(SiMe_3)_2$ form metallacyclic products by γ-C-H transfer from a Si-CH_3 group. For example, reaction of $Cp^*_2TiCl_2$ with two equivalents of $LiN(SiMe_3)_2$ results in formation of $Cp^*_2Ti[N(SiMe)_3SiMe_2CH_2]$, a four membered ring containing four different elements[24].

Recently Rothwell has shown that early transition metal compounds ligated to bulky aryloxides of the type $M(OAr)_2R_3$ (M = Nb, Ta; OAr = 2,6-^{t}Bu$_2$C$_6$H$_3$O$^-$, 2,6-^{t}Bu$_2$-4-$CH_3C_6H_2O^-$, 2,6-^{t}Bu$_2$-4-$OMeC_6H_2O^-$; R = CH_3, CH_2SiMe_3, CH_2Ph, Ph) have a rich and interesting chemistry[25]. Their reactivity is demonstrated, for example, by $Ta(OAr)_2Me_3$ (OAr = 2,6-^{t}Bu$_2$C$_6$H$_3$O$^-$) which undergoes clean thermolytic cyclometallation of one of the CH_3 groups, forming an isolable derivative containing a 6-membered ring, $Ta(OAr)(OC_6H_3\text{-}2\text{-}CMe_2CH_2\text{-}6\text{-}^t\text{Bu})Me_2$, with the concomitant loss of methane. From deuterium labelling studies it was found that photolysis of the parent compound proceeded by a different mechanism. A methylmethylidene complex, $Ta(OAr)_2(=CH_2)(CH_3)$, due to α-H abstraction from one methyl group was initially obtained. This compound is thermolytically labile and readily gives rise to the *mono*-metallated species (Scheme. 1.6). The *mono*-metallated derivative can undergo subsequent thermolytic rearrangement to yield the *bis*-cyclometallated complex, $Ta(OC_6H_3\text{-}2\text{-}CMe_2CH_2\text{-}6\text{-}^t\text{Bu})_2Me$.

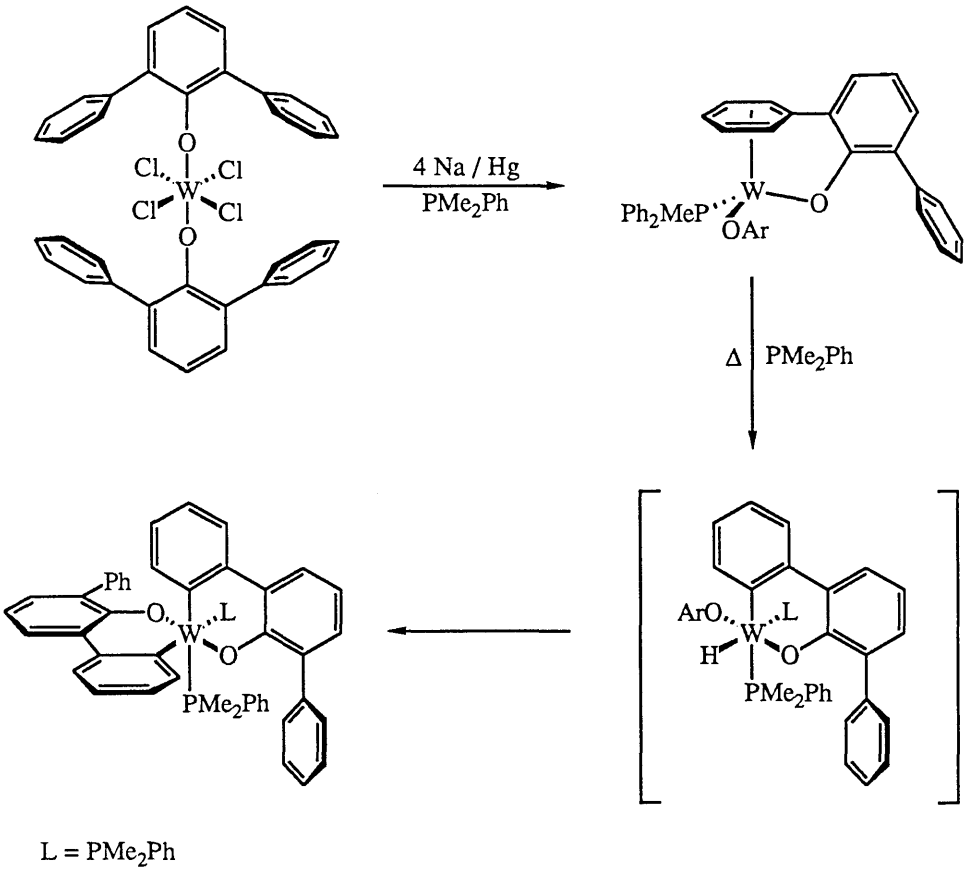


Scheme. 1.6 : *Cyclometallation of* $Ta(OC_6H_3\text{-}2,6\text{-}^t\text{Bu}_2)_2Me_3$.

When R = Ph a *mono*-cyclometallated diphenyl complex is formed. This again rearranges by two distinct pathways; either by direct activation of a *tert*-butyl C-H proton with loss of benzene or *via* a benzyne intermediate. Ultimately the reaction yields the analogous *bis*-cyclometallated derivative. As with the work of Marks, a four-centre, four-electron transition state is proposed for the C-H activation of this series of compounds.

1.6 C-H Transfer at Distant Aromatic Sites.

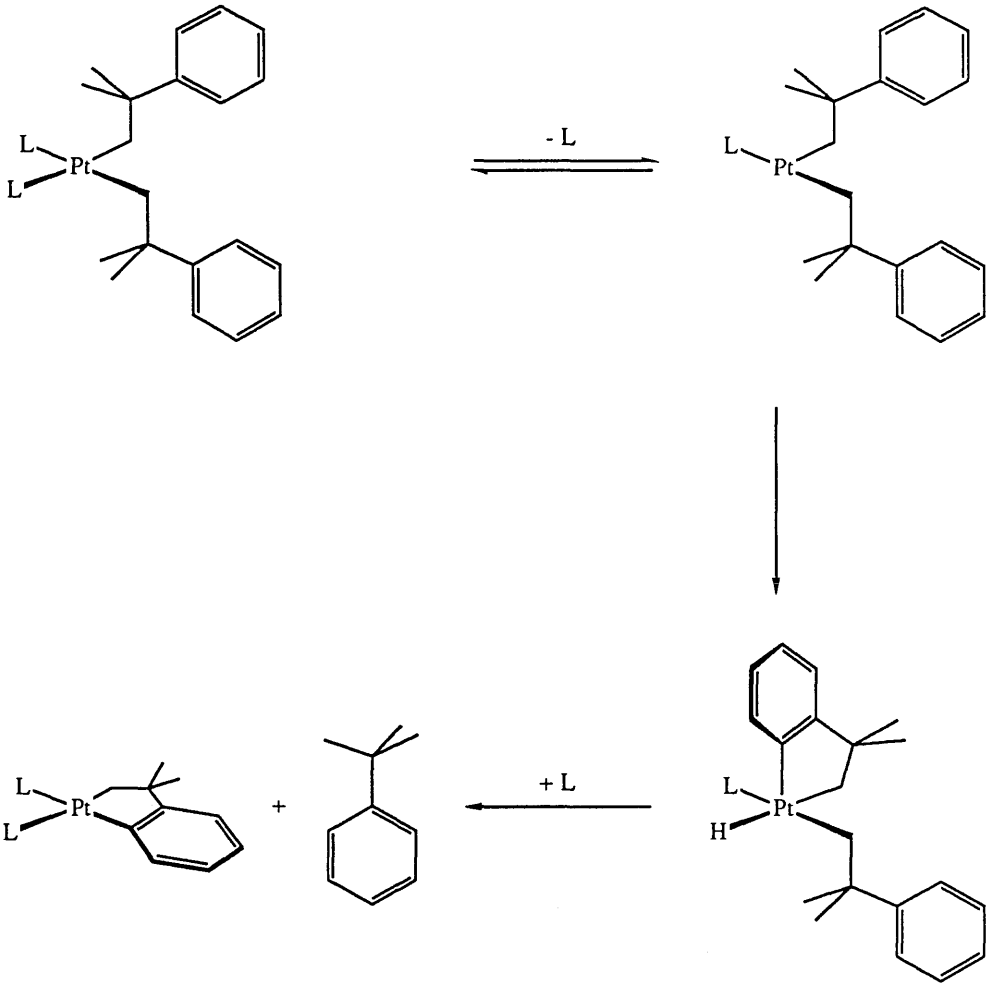
Aromatic C-H activation of hydrogens at remote sites has also proved fruitful. Early work by Tulip and Thorn, showed that alkylation of $[Ir^{I}(PMe_3)_4]^+ Cl^-$ with benzyl or neophyl reagents afforded hydrido-metallacycles. These species were formed by γ- and δ-C-H activation of an *ortho*-phenyl proton respectively[12] (see Scheme. 1.3). More recently $Ta(OAr)_3Cl_2$ (OAr = 2,6-$Ph_2C_6H_3O^-$) cleanly undergoes cyclometallation of one phenyl ring on two phenoxide ligands affording *bis*-cyclometallated $Ta(OC_6H_3PhC_6H_4)_2(OAr)$ in high yield[26]. Related group six analogues, $W(OAr)_2Cl_4$ in the presence of PR_3, react similarly forming a *bis*-cyclometallated species, $W(OC_6H_3PhC_6H_4)_2(PR_3)_2$. The reaction proposedly proceeds by a metal η^6-arene intermediate[27] (Scheme. 1.7).



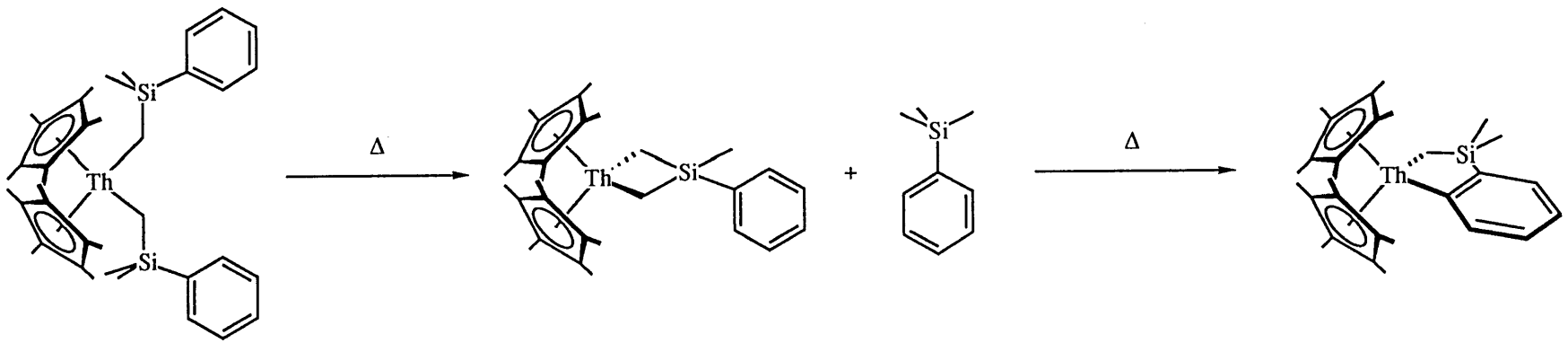
Scheme. 1.7 : *Aromatic C-H Activation via an η^6-arene Intermediate.*

The neophyl ligand, also "β-elimination stabilised" and capable of more remote hydrogen transfer has also been studied in recent years. This group can undergo aromatic δ-C-H transfer forming a five-membered metallacycle and loss of an equivalent of *tert*-butylbenzene. Original attempts to isolate the metallacycle from the interaction of nickel halides with appropriate alkylating agents proved unsuccessful[28] but several well characterised complexes have now emerged[29].

A systematic study of platinum(II) dineophyl derivatives with a variety of donor ligands were shown to undergo facile rearrangement, which occurs almost exclusively at an *ortho*-aromatic carbon site[30-32]. The reaction proceeds by δ-C-H oxidative addition, generating a platinum(IV) hydrido intermediate, followed by reductive C-H elimination (Scheme. 1.8). The intimate mechanism of the reaction depends on the nature of the ancillary ligand (*vide infra*).



Scheme. 1.8 : *Aromatic C-H Transfer Generating Platinaindans.*



Scheme. 1.9 : *Thermolytic Rearrangement of* $Cp^*_2Th(CH_2SiMe_2Ph)_2$.

Although many transition metal compounds of the trimethylsilylmethyl group are known[33], complexes of the related sila-neophyl group have received scant attention[14,34,35]. To data, only one instance - in an f-block metal complex - of the reactivity of a sila-neophyl group has been reported. $Cp^*_2Th(CH_2SiMe_2Ph)_2$ was found to undergo initial γ-C-H transfer affording a thoracyclobutane, which on further heating yielded a 5-membered metallacycle, proposedly *via* δ-aromatic C-H activation[14] (Scheme. 1.9), though the precise nature of this unusual isomerisation remains unclear.

Following from the studies of neophylplatinum(II) derivatives, a series of complexes, $L_2Pt(CH_2SiMe_2Ph)_2$ was prepared in order to explore in more detail the reactivity controls on aromatic C-H activation and to further the understanding of the relative inertness of β-sila-alkyl groups. It was recognised that substituents on the aromatic ring may greatly effect the controls of the reaction pathway. Suitable substituted neophyl derivatives proved difficult to synthesise[36], however, corresponding substituted sila-neophyl groups were obtained relatively easily. To this end, a series of ring substituted *bis*-sila-neophylplatinum(II) complexes was also studied.

Chapter Two :

SYNTHETIC AND SPECTROSCOPIC STUDIES OF *BIS*-[DIMETHYL(PHENYL)SILYLMETHYL] PLATINUM(II) COMPLEXES WITH DIENE AND NITROGEN DONOR LIGANDS.

2.1. Synthesis of *bis*-[dimethyl(phenyl)silylmethyl]platinum(II) complexes with diene and nitrogen donor ligands[37].

A variety of *bis*-(sila-neophyl)platinum (II) compounds has been isolated in good yields using methods similar to those previously employed for analogous *bis*-alkyl and *bis*-aryl platinum (II) complexes[30, 38-43]. Thus, the synthesis of (cod)Pt(CH_2SiMe_2Ph)$_2$ has been achieved in >85% by the interaction of excess sila-neophylmagnesium chloride with (cod)$PtCl_2$, affording the product as a colourless crystalline solid. Related (nbd)Pt(CH_2SiMe_2Ph)$_2$ was prepared analogously, also in good yield (83%). Attempts to prepare dieneplatinum*mono*alkyl*mono*chloride complexes by a variety of methods all failed. Using stoichiometric amounts of Grignard reagent and/or shortening the reaction time led to mixtures of the parent complex, the desired product and the dialkyl derivative. Treatment of either (cod) or (nbd)Pt(CH_2SiMe_2Ph)$_2$ with HCl or CH_3COCl afforded, mainly, a derivative with one platinum-bound chlorine and a chloro(dimethyl)silylmethyl group (from cleavage of the silicon-phenyl bond).

Reaction of (dms)$_2PtCl_2$ with $LiCH_2SiMe_2Ph$ resulted in the formation of [Pt(CH_2SiMe_2Ph)$_2$(μ-dms)]$_2$ in moderate yield. However, this compound is thermally labile; even solid samples decompose in a few days forming unidentified products. Using Grignard reagent in place of alkyllithium predominantly produces the *mono*alkylated species, [Pt(CH_2SiMe_2Ph)$_2$Cl(μ-dms)]$_2$, although contamination with the dialkyl is inevitable.

Metathetical displacement of diene from (cod)Pt(CH_2SiMe_2Ph)$_2$ or (nbd)Pt(CH_2SiMe_2Ph)$_2$, or displacement of the thioether from [Pt(CH_2SiMe_2Ph)$_2$(μ-dms)]$_2$ by nitrogen donor ligands produces L_2Pt(CH_2SiMe_2Ph)$_2$. With the diene complexes substitutions are characteristically slow; sila-neophyl complexes are qualitatively more inert to diene displacement than their neophyl analogues. Conversion is generally complete in 5-30 days at 60°C in toluene; nbd is more labile than cod, due presumably to the greater strain imposed on the former. Dms is clearly the most labile of the three; replacement by ligands takes place at ambient temperature in 2-4 days. Excess of the nitrogen donor ligand (2-15 fold) accelerates the reactions. Usually, residual free ligand can be separated readily from the organometallic product by extraction into aqueous ferrous sulphate solution as $[Fe(L)_3]^{2+}$.

With the exception of (tmed)Pt(CH_2SiMe_2Ph)$_2$, which was isolated as a colourless liquid, all of the complexes L_2Pt(CH_2SiMe_2Ph)$_2$ are air-stable and, unlike pale yellow (py)$_2$Pt(CH_2SiMe_2Ph)$_2$ and pale orange (^{t}Bupy)$_2$Pt(CH_2SiMe_2Ph)$_2$, are brightly coloured crystalline solids. Most of these compounds rapidly decompose in toluene solutions exposed to air. In addition, they react with chlorocarbon solvents. Chloroform and dichloromethane were avoided as crystallisation solvents. All have satisfactory elemental analyses (Table 2.1).

Table 2.1 : *Analytical Data for* bis-*(sila-neophyl)platinum(II) complexes with Diene, N- and S-Donor Ligands.*

Compound	Colour	Found (Calculated)		
		C %	H %	N %
$(cod)Pt(CH_2SiMe_2Ph)_2$	Colourless	51.67 (51.89)	6.30 (6.36)	-
$(nbd)Pt(CH_2SiMe_2Ph)_2$	White	51.12 (51.26)	5.93 (5.85)	-
$[Pt(CH_2SiMe_2Ph)_2(\mu\text{-dms})]_2$	White	42.95 (43.22)	5.72 (5.80)	-
$[Pt(CH_2SiMe_2Ph)Cl(\mu\text{-dms})]_2$	White	29.55 (29.89)	4.63 (4.33)	-
$(py)_2Pt(CH_2SiMe_2Ph)_2$	Pale Yellow	51.80 (51.59)	5.58 (5.57)	4.28 (4.29)
$(Bu^tpy)_2Pt(CH_2SiMe_2Ph)_2$	Pale Orange	56.43 (56.59)	6.67 (6.86)	3.86 (3.67)
$(Phpy)_2Pt(CH_2SiMe_2Ph)_2$	Lemon Yellow	60.11 (59.75)	5.77 (5.52)	3.26 (3.48)
$(pyd)_2Pt(CH_2SiMe_2Ph)_2$	Yellow	47.30 (47.59)	4.89 (5.24)	8.79 (8.57)
$(bipy)Pt(CH_2SiMe_2Ph)_2$	Orange	51.71 (51.75)	5.29 (5.27)	4.30 (4.31)
$(bipy)Pt(CH_2SiMe_2Ph)Cl \cdot CH_2Cl_2$	Amber	38.48 (38.69)	3.66 (3.73)	4.74 (4.51)
$(Me_2bipy)Pt(CH_2SiMe_2Ph)_2$	Orange	53.08 (53.15)	5.54 (5.65)	4.15 (4.13)
$(Bu^t_2bipy)Pt(CH_2SiMe_2Ph)_2$	Orange	57.08 (56.74)	6.68 (6.61)	3.65 (3.68)
$(bipym)Pt(CH_2SiMe_2Ph)_2$	Maroon	48.17 (47.91)	4.89 (4.95)	8.57 (8.59)

Table 2.1 : (continued)

(bipyz)Pt(CH_2SiMe_2Ph)$_2$	Magenta	48.02 (47.91)	4.87 (4.95)	8.95 (8.60)
[Pt_2(CH_2SiMe_2Ph)$_4$(μ-bipym)]	Dark green	46.14 (46.14)	5.09 (5.10)	4.82 (4.89)
(phen)Pt(CH_2SiMe_2Ph)$_2$	Red	53.47 (53.47)	5.00 (5.09)	4.13 (4.16)
(Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$	Vermillion	61.18 (61.07)	5.02 (5.12)	3.37 (3.39)
(Me_4phen)Pt(CH_2SiMe_2Ph)$_2$	Orange	55.86 (55.94)	5.85 (5.80)	3.75 (3.84)
(Me_2Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$	Vermillion	62.53 (62.63)	5.91 (5.71)	3.35 (3.18)

2. 2. Spectroscopic Studies of *bis*-(sila-neophyl)platinum(II) Complexes.

2.2.1. Conventions.

The numbering system follows that for the neophyl and platinaindan analogues (Fig. 2.1)[30b]. The phenyl carbon attached (or potentially attached) to the platinum is labelled C_2, while the alkyl-substituted carbon is designated C_1. Also shown in Fig. 2.1 are the numerical conventions for the diene and nitrogen donor ligands.

Throughout the discussion, peaks which show a coupling to ^{195}Pt ($I = \frac{1}{2}$, 34% abundant) are denoted by δ(J); where δ is the chemical shift (ppm) and J is the observed coupling constant (Hz) to ^{195}Pt. Such multiplets are termed "triplets" ("t") to distinguish them from binomial 1:2:1 triplets.

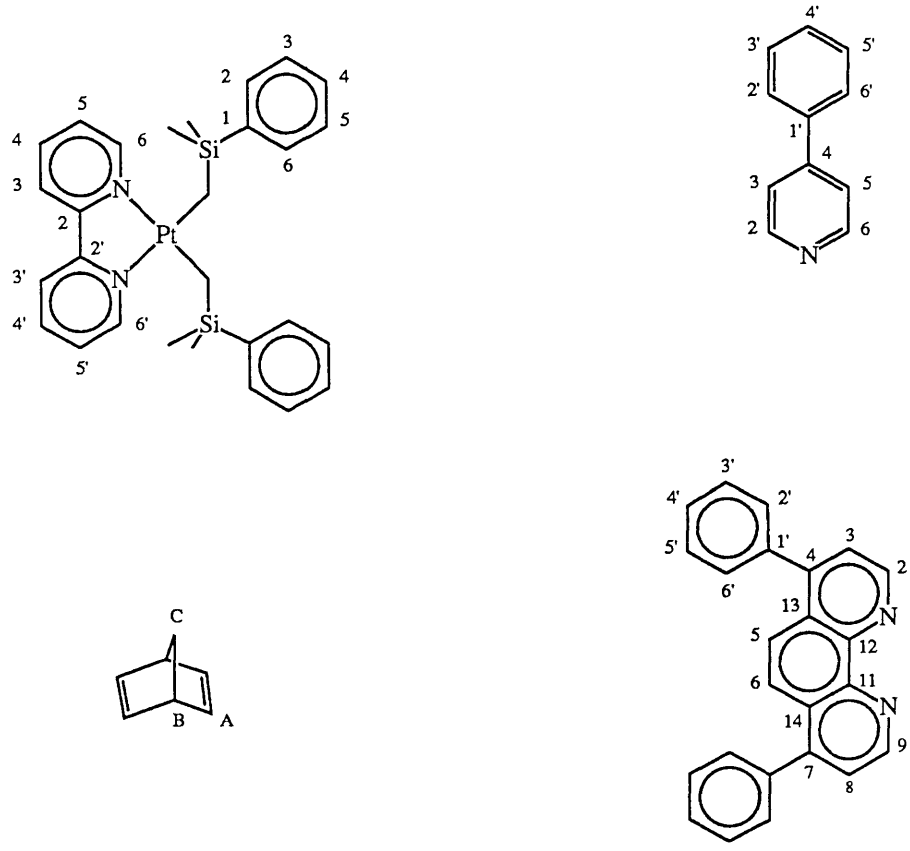


Fig. 2.1 : N.M.R. Numbering Conventions for Diene and N-Donor Ligands.

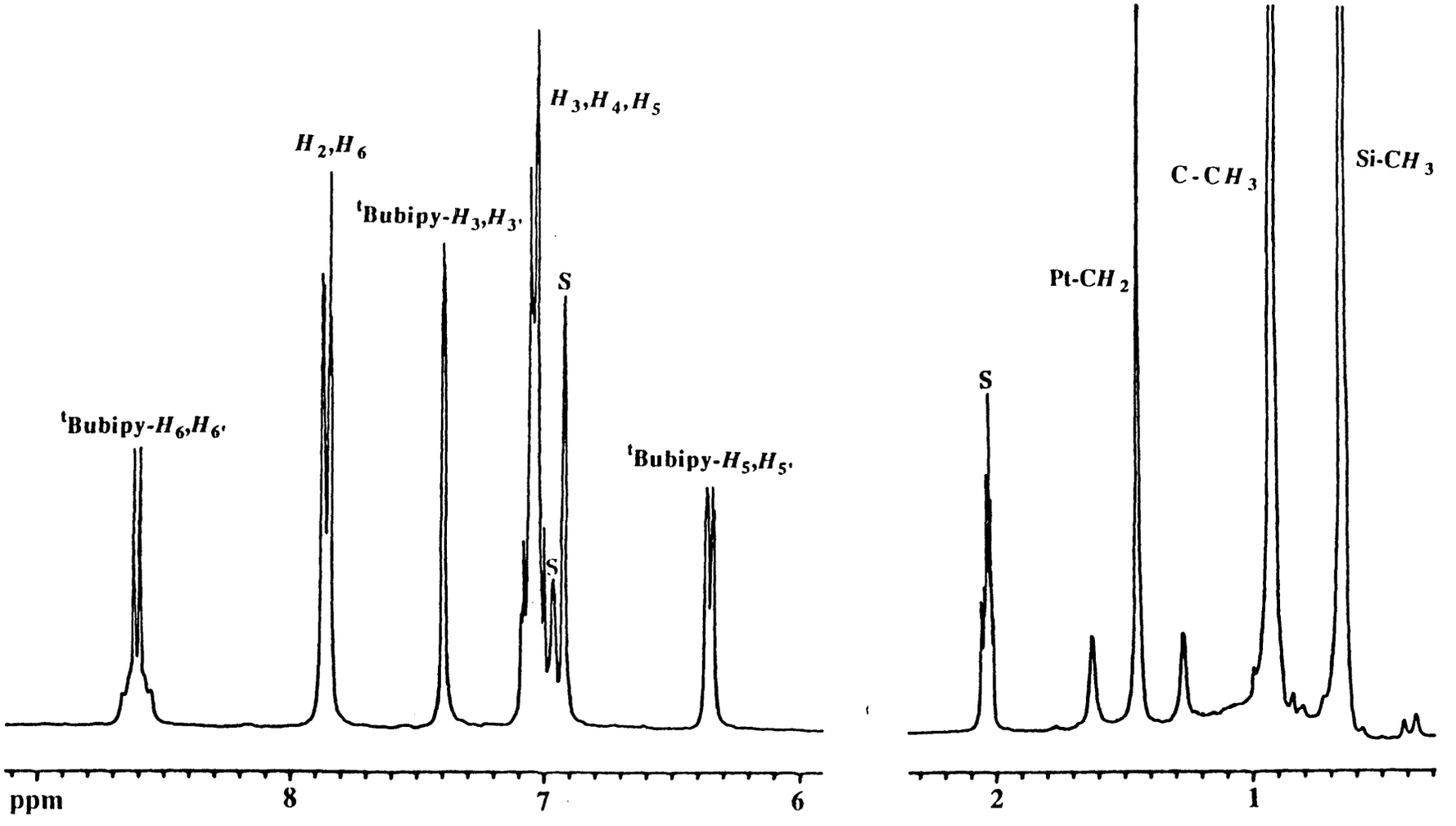


Fig. 2.2 : *^{1}H N.M.R. of (Bu^t_2bipy)Pt($CH_2SiMe_2Ph)_2$.*

2.2.2. *^1H N.M.R. Spectroscopy.*

The ^1H N.M.R. characteristics of the sila-neophyl complexes are shown in Table 2.2. Particularly diagnostic of the coordinated sila-neophyl skeleton are the high field singlet (δ 0.26-0.70 ppm) for the silicon-bound methyl groups and a doubled doublet at low field (δ 7.6-7.9 ppm), due to the *ortho*-phenyl protons (Fig. 2.2). The platinum-bound methylene hydrogens generate 1:4:1 "triplets"; $^2J_{Pt-H}$ for these protons is in the range 82.0-102.0 Hz, depending on the *trans* ligand. The ^{195}Pt "satellites" of these signals are noticeably broader in complexes with nitrogen-donor ligands in comparison with (cod) or (nbd)Pt(CH_2SiMe_2Ph)$_2$ (Fig. 2.3). This phenomenon appears more pronounced for phenanthroline ligands than for those of the bipyridyl family and is a general feature of dialkylplatinum complexes of this type[41, 42]. It is attributed to enhanced relaxation of the ^{195}Pt nuclei by quadrupolar ^{14}N. A related effect has been observed in the ^1H N.M.R. spectrum of H_3CHgI, in which $^2J_{Hg-H}$ is not observed due to rapid relaxation of ^{199}Hg by ^{127}I[44]. General broadening of the ^1H N.M.R. signals has been noted occasionally as a characteristic of N-coordination[45] but although some effect can be detected for the central resonance, it is not as pronounced as that in the Pt-satellites.

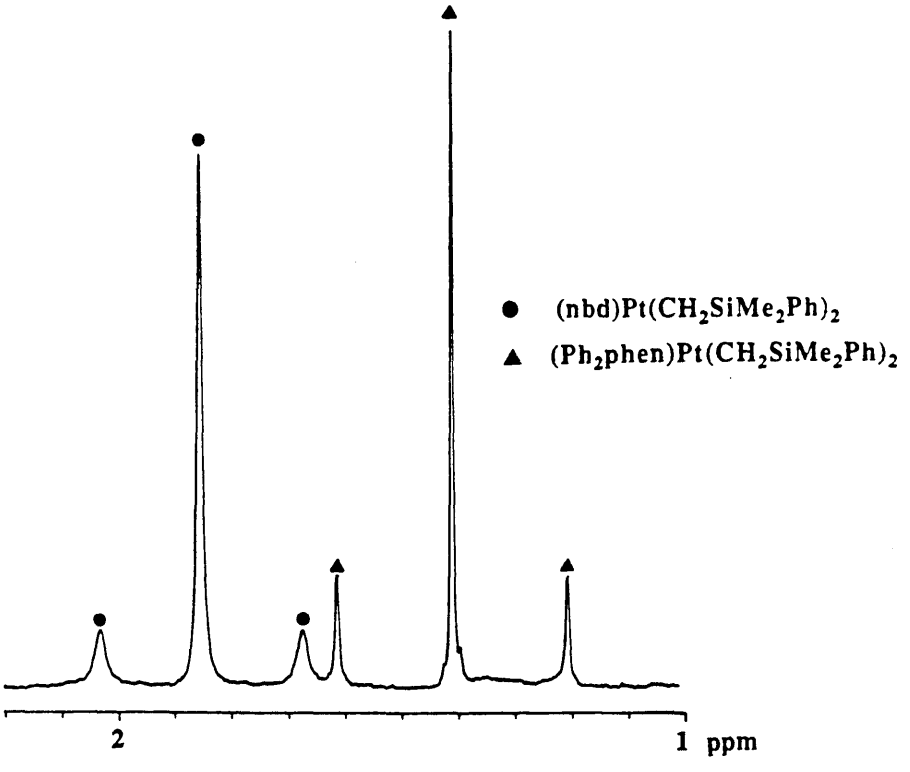


Fig. 2.3 : *Satellite broadening in $L_2Pt(CH_2SiMe_2Ph)_2$.*

Table 2.2 : *^{1}H N.M.R. Characteristics of* bis-*(sila-neophyl)platinum(II) Complexes with Diene, N- and S-Donor Ligands.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]			δ ^{1}H ppm : Neutral donor ligands (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Aromatic ($J_{H_2-H_3}$) / Hz	
(cod)Pt(CH_2SiMe_2Ph)$_2$[a]	1.15 (**92.2**)	0.43	7.13-7.21 m, [H_3, H_4, H_5]; 7.60 dd, [H_2, H_6] (**6.4**)	1.46-1.59 m, [CH_2]; 4.14 "t", (**42.7**) [CH]
(nbd)Pt(CH_2SiMe_2Ph)$_2$[b]	1.09 (**98.2**)	0.26	7.21-7.33 m, [H_3, H_4, H_5]; 7.59 dd, [H_2, H_6] (**8.0**)	1.28-1.29 m, [H_C]; 3.54-3.58 m, [H_B]; 4.41 "t", (**41.3**) [H_A]
[Pt(CH_2SiMe_2Ph)$_2$(μ-dms)]$_2$[c]	0.66 (**101.1**)	0.55	7.25-7.35 m, [H_3, H_4, H_5]; 7.85 dd, [H_2, H_6] (**7.5**)	1.62 "t", (**20.0**) [S-CH_3]
[Pt(CH_2SiMe_2Ph)Cl(μ-dms)]$_2$[b]	0.89 (**84.6**)	0.28	7.02-7.08 m, [H_3, H_4, H_5]; 7.59 dd, [H_2, H_6] (**7.6**)	1.90 "t", (**19.1, 52.5**) [S-CH_3];
(tmed)Pt(CH_2SiMe_2Ph)$_2$[c]	0.42 (**101.8**)	0.56	7.13-7.20 m, [H_3, H_4, H_5]; 7.97 dd, [H_2, H_6] (**7.5**)	1.38 "t", (**11.6**) [N-CH_2]; 1.81 "t", (**21.6**) [N-CH_3]

Table 2.2 : (continued)

$(py)_2Pt(CH_2SiMe_2Ph)_2$[d]	0.87 (**88.4**)	0.42	6.96-7.06 m, [H_3, H_4, H_5]; 7.63 dd, [H_2, H_6] (**6.2**)	6.13 m, [H_3, H_5] ($J_{H_2-H_3}$=6.4 Hz); 6.66 m, [H_4] ($J_{H_3-H_4}$=7.6 Hz); 8.06 dd, (**20.7**) [H_2, H_6] ($J_{H_2-H_4}$=1.5 Hz)
$(py\text{-}d^5)_2Pt(CH_2SiMe_2Ph)_2$[a]	0.95 (**90.2**)	0.37	7.24-7.31 m, [H_3, H_4, H_5]; 7.78 dd, [H_2, H_6] (**7.8**)	-
$(^tBupy)_2Pt(CH_2SiMe_2Ph)_2$[c]	1.08 (**89.3**)	0.59	7.17-7.09 m, [H_3, H_4, H_5]; 7.80 dd, [H_2, H_6] (**7.8**)	0.83 s, [*C-CH*$_3$]; 6.38 d, [H_3, H_5] ($J_{H_2-H_3}$=6.7 Hz); 8.22 dd, (**23.8**) [H_2, H_6]
$(Phpy)_2Pt(CH_2SiMe_2Ph)_2$[c]	1.08 (**85.9**)	0.60	7.00-7.06 m, [H_3, H_4, H_5]; 7.71 dd, [H_2, H_6] (**7.4**)	6.46 d, [H_3, H_5]; ($J_{H_2-H_3}$=6.6 Hz); 7.00-7.06 m, [*Phenyl group*]; 8.19 d, [H_2, H_6]
$(pyd)_2PtPt(CH_2SiMe_2Ph)_2$[c]	1.21 (**86.8**)	0.55	7.02-7.22 m, [H_3, H_4, H_5]; 7.83 dd, [H_2, H_6] (**7.5**)	6.05 dd, [H_4] ($J_{H_3-H_4}$=5.3 Hz); 6.10 dd, [H_5] ($J_{H_4-H_5}$=7.9 Hz); 7.88 m, [H_6] ($J_{H_5-H_6}$= 4.9 Hz); 9.01 dt, [H_3] (**21.7**) ($J_{H_3-H_5}$= 1.4 Hz)
$(bipy)Pt(CH_2SiMe_2Ph)_2$[a]	1.41 (**89.5**)	0.57	6.97-7.15 m, [H_3, H_4, H_5]; 7.81 dd, [H_2, H_6] (**7.7**)	6.26 m, [H_5] ($J_{H_5-H_6}$=5.6 Hz); 6.71 dd, [H_3] ($J_{H_3-H_5}$=1.2 Hz); 6.95 dd, [H_4] ($J_{H_3-H_4}$=7.5 Hz); 8.68 dd, (**22.8**) [H_6] ($J_{H_4-H_6}$=1.4 Hz)

Table 2.2 : (continued)

(bipy)Pt(CH_2SiMe_2Ph)Cl[e]	1.36 (**82.1**)	0.31	7.12-7.17 m, [H_3, H_4, H_5]; 7.62 dd, [H_2, H_6] (**6.5**)	7.37 m, [$H_{5'}$] ($J_{H_{5'}-H_{6'}}$=6.6 Hz); 7.78 m, [H_5] ($J_{H_5-H_6}$=6.2 Hz); 8.27 dd, [$H_{3'}$] ($J_{H_{3'}-H_{5'}}$=1.6 Hz); 8.32 dd, [H_3] ($J_{H_3-H_5}$=1.6 Hz); 8.37 dd, [$H_{4'}$] ($J_{H_{3'}-H_{4'}}$=7.0 Hz); 8.44 dd, [H_4] ($J_{H_3-H_4}$=8.0 Hz); 8.85 dd, (**57.1**) [$H_{6'}$] ($J_{H_{4'}-H_{6'}}$=0.6 Hz); 9.84 dd, (**13.8**) [H_6] ($J_{H_4-H_6}$=0.8 Hz)
(Me_2bipy)Pt(CH_2SiMe_2Ph)$_2$[a]	1.37 (**89.0**)	0.59	7.04-7.16 m, [H_3, H_4, H_5]; 7.86 dd, [H_2, H_6] (**7.7**)	1.53 s, [CH_3]; 6.11 dd, [H_5]; 6.74 d, [H_3] ($J_{H_3-H_5}$=0.8 Hz); 8.58 dd, (**22.2**) [H_6] ($J_{H_5-H_6}$=5.6 Hz)
(Bu^t_2bipy)Pt(CH_2SiMe_2Ph)$_2$[a]	1.44 (**88.9**)	0.65	6.97-7.09 m, [H_3, H_4, H_5]; 7.85 dd, [H_2, H_6] (**7.5**)	0.92 s, [CH_3]; 6.36 dd,[H_5] ($J_{H_5-H_6}$=5.9 Hz); 7.39 d, [H_3] ($J_{H_3-H_5}$=1.9 Hz); 7.60 dd, (**24.0**) [H_6] ($J_{H_3-H_6}$=0.6 Hz)
(bipyz)Pt(CH_2SiMe_2Ph)$_2$[a]	1.64 (**90.8**)	0.51	6.97-7.04 m, [H_3, H_4, H_5]; 7.64 dd, [H_2, H_6] (**6.1**)	7.63 d, [H_5] ($J_{H_5-H_6}$=3.1 Hz); 8.00 s, [H_3]; 8.28 dd, (**21.3**) [H_6] ($J_{H_3-H_6}$=1.0 Hz)
(bipym)Pt(CH_2SiMe_2Ph)$_2$[a]	1.37 (**90.0**)	0.57	6.90-7.05 m, [H_3, H_4, H_5]; 7.68 dd, [H_2, H_6] (**7.0**)	5.86 dd, [H_5] ($J_{H_5-H_6}$=5.5 Hz); 8.17 dd, [H_4] ($J_{H_4-H_5}$=4.6 Hz); 8.36 dd, (**20.7**) [H_6] ($J_{H_4-H_6}$=2.2 Hz)

Table 2.2 : (continued)

$[Pt_2(CH_2SiMe_2Ph)_4(\mu\text{-bipym})]$[a]	1.44 (**92.9**)	0.50	6.95-7.03 m, [H_3, H_4, H_5]; 7.62 dd, [H_2, H_6] (**6.6**)	5.52 m, [H_5] ($J_{H_5\text{-}H_6}$=5.4 Hz); 8.30 d, (*ca.* **22.0**) [H_4, H_6]
$(phen)Pt(CH_2SiMe_2Ph)_2$[a]	1.60 (**90.3**)	0.62	6.99-7.05 m, [H_3, H_4, H_5]; 7.82 dd,[H_2, H_6] (**6.5**)	6.51 m, [H_3, H_8] ($J_{H_2\text{-}H_3}$=5.2 Hz); 6.87 s, [H_5,H_6]; 7.36 dd, [H_4, H_7]; 8.89 dd, (**22.1**) [H_2, H_9] ($J_{H_2\text{-}H_4}$=1.3 Hz)
$(Ph_2phen)Pt(CH_2SiMe_2Ph)_2$[a]	1.70 (**89.7**)	0.70	6.99-7.06 m, [H_3, H_4, H_5]; 7.89 dd, [H_2, H_6] (**7.4**)	6.62 d, [H_3, H_8] ($J_{H_2\text{-}H_3}$=5.4 Hz); 7.08-7.19 m, [C_6H_5]; 7.32 s, [H_5, H_6]; 9.02 d, (**22.4**) [H_2, H_9]
$(Me_4phen)Pt(CH_2SiMe_2Ph)_2$[a]	1.54 (**89.7**)	0.67	6.94-7.04 m, [H_3, H_4, H_5]; 7.86 dd, [H_2, H_6] (**8.0**)	1.72 s, [*4,7-*CH_3]; 1.74 s, [*3,8-*CH_3]; 7.80 s, [H_5, H_6]; 8.71 "t", (**23.1**) [H_2, H_9]
$(Me_2Ph_2phen)Pt(CH_2SiMe_2Ph)_2$[a]	1.62 (**97.6**)	0.50	6.90-7.11 m, [H_3, H_4, H_5]; 7.84 dd, [H_2, H_6] (**7.6**)	2.64 s, [CH_3]; 6.72 s, [H_3, H_8]; 7.12-7.23 m, [C_6H_5]; 7.30 s, [H_5, H_6]

a :- toluene-d^8

b :- chloroform-d^1

c :-benzene- d^6

d :- pyridine-d^5

e :-acetone- d^6

Resonances assigned to the neutral ligands are largely as expected and the values of $^3J_{Pt-H}$ for the protons adjacent to the nitrogen atoms are about 20 Hz. The bridging nature of the dimethyl sulphide group in $[Pt(CH_2SiMe_2Ph)_2(\mu\text{-dms})_2]$ is shown by the resonance of the sulphide methyl protons. They appear as an approximately 1:8:18:8:1 "quintet" caused by spin-spin coupling to two ^{195}Pt nuclei.

Compared with *bis*-(neophyl)platinum(II) complexes[30b], hydrogens in both the Si-bound methyl groups and the Pt-bound methylene groups resonate, as expected, at higher fields due to the proximal silicon. Among the aromatic hydrogens the doubled doublet of H_2 is generally downfield of that in the corresponding *bis*-(neophyl) complex. In addition, the values of $^2J_{Pt-H}$ are marginally higher than those of the *bis*-(neophyl) compounds, in accord with greater s-character in the Pt-C-H skeleton (See 2.2.3).

2.2.3. ^{13}C N.M.R. Spectroscopy.

Detailed in Table 2.3 are the $^{13}C\{^1H\}$ N.M.R. characteristics of *bis*-(sila-neophyl) complexes. Most are very complicated by the number and variety of aromatic carbons present. Assignments are based on comparison with the free ligands[46, 47] (Table 2.4), with analogous *bis*-alkylplatinum(II) complexes, on platinum-carbon coupling constants and on signal intensities[30, 41, 42]. Carbon atoms with attached hydrogen(s) experience nuclear Overhauser enhancement due to the decoupling radiation; quaternary carbon atoms appear as low intensity resonances. Thus, the peaks due to C_2 and C_3 of the sila-neophyl phenyl group are generally twice as intense as that of C_4 (Fig. 2.4). In addition, the resonances observed for $(bipy)Pt(CH_2SiMe_2Ph)_2$ have been assigned unequivocally by phase-modulated spin-echo measurements.

The compounds $L_2Pt(CH_2SiMe_2Ph)_2$ all show marked coordination shifts for both Si-CH_3 and aryl carbon atoms relative to Me_3SiPh[48] (Tables 2.5 and 2.6). In accord with the general trends observed previously for $PhMe_2Si(X)$, magnitudes of coordination shifts ($\Delta\delta$) are in the order $C_1 > C_4 > C_2 > C_3$; the chemical shifts of *meta*-carbon atoms in monosubstituted benzenes are least affected by changing the substituents. In all cases C_1 and C_2 are shifted downfield relative to Me_3SiPh and C_3 and C_4 upfield. A downfield shift for C_1 indicates that LPt(R) is more electron withdrawing (relative to H). The silicon bound methyl carbons also display downfield co-ordination shifts, again reflecting that $LPt(R)CH_2^-$ is more electron withdrawing than a methyl group. In general though, the coordination shifts do not display a marked variation with changing L, suggesting that the inductive properties of the metal fragment is rather insensitive to L. Relatedly, $^3J_{Pt-C}$ for the sila-neophyl group changes little as L varies.

The magnitude of $^1J_{Pt-C}$ for the sila-neophyl derivatives is characteristically *ca.* 200 Hz smaller than that for the neophyl analogue[30, 49] but of comparable magnitude to that observed for corresponding trimethylsilylmethyl[41, 50] and ethenyldimethylsilylmethylplatinum(II) complexes[42, 51]. With the exception of

Table 2.3 : *^{13}C N.M.R. Characteristics of* bis-*(sila-neophyl)platinum(II) Complexes with Diene and Nitrogen Donor Ligands.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*]			δ ^{13}C ppm : Ancillary ligands (J_{Pt-C}) / Hz [*Assignment*]
	Pt-***C***H_2	Si-***C***H_3	Aromatic	
(cod)Pt(CH_2SiMe_2Ph)$_2$[a]	12.34	2.14	127.77 [C_3, C_5]; b [C_4];	29.78 [CH_2]; 97.89 (**64.7**) [*CH*]
	(**710.0**)	(**31.8**)	134.12 [C_2, C_6]; 144.50 (**26.4**) [C_1]	
(nbd)Pt(CH_2SiMe_2Ph)$_2$[c]	14.28	1.56	127.40 [C_3, C_5]; 128.02 [C_4];	48.77 (**40.6**) [C_B]; 72.54 (**53.5**) [C_C];
	(**752.5**)	(**33.4**)	133.62 [C_2, C_6]; 144.52 (**25.4**) [C_1]	85.45 (**54.3**) [C_A]
[Pt(CH_2SiMe_2Ph)$_2$(μ-dms)]$_2$[c]	14.22	1.77	127.32 [C_3, C_5]; 127.96 [C_4];	29.73 (**39.1**) [*S-CH*$_3$]
	(**785.5**)	(**37.7**)	134.05 [C_2, C_6]; 144.23 (**20.8**) [C_1]	
(py)$_2$Pt(CH_2SiMe_2Ph)$_2$[d]	-13.16	1.55	127.21 [C_3, C_5]; 127.64 [C_4];	124.92 [C_3, C_5]; 134.71 [C_4];
	(**739.8**)	(**27.4**)	133.88 [C_2, C_6]; 146.29 (**29.7**) [C_1]	150.50 (**33.7**) [C_2, C_6]
(^{t}Bupy)$_2$Pt(CH_2SiMe_2Ph)$_2$[a]	-13.43	1.79	127.19 [C_4]; 127.31 [C_3, C_5];	29.83 [*C-**C**H*$_3$]; 34.46 [***C**-CH*$_3$];
	(**741.2**)	(**35.2**)	137.07 [C_2, C_6]; 146.60 (**25.9**) [C_1]	121.98 (**19.8**) [C_3, C_5];
				150.46 (**30.1**) [C_2, C_6]; 159.17 [C_4]

Table 2.3 : (continued)

$(Phpy)_2Pt(CH_2SiMe_2Ph)_2$[d]	-12.56 (**734.3**)	1.81 (**36.0**)	127.12 [C_4]; 127.32 [C_3, C_5]; 133.97 [C_2, C_6]; 146.34 (**26.1**) [C_1]	122.54 (**19.2**) [C_3, C_5]; 126.62 [$C_{3'}$, $C_{5'}$]; b [$C_{4'}$]; 129.40 [$C_{2'}$,$C_{6'}$]; b [C_4]; 146.77 [$C_{1'}$]; 150.80 (**16.4**) [C_2, C_6]
$(bipy)Pt(CH_2SiMe_2Ph)_2$[a]	-8.26 (**745.4**)	1.79 (**35.0**)	127.35 [C_3, C_5]; 128.29 [C_4]; 134.62 [C_2, C_6]; 145.82 (**29.7**) [C_1]	121.53 (**11.2**) [C_5]; 125.98 (**20.4**) [C_3]; 134.62 [C_4]; 147.35 (**32.4**) [C_6]; 155.85 (**10.3**) [C_2]
$(bipy)Pt(CH_2SiMe_2Ph)Cl$[e]	-10.78 (**687.1**)	1.33 (**18.5**)	127.96 [C_3, C_5]; 129.05 [C_4]; 134.78 [C_2, C_6]; 144.87 (**25.8**) [C_1]	123.69 (**11.1**) [C_5]; 124.46 (**31.5**) [$C_{5'}$]; 128.28 [C_4]; 128.47 [$C_{4'}$]; 138.59 [C_3]; 139.23 [$C_{3'}$]; 149.34 (**44.4**) [$C_{6'}$]; 149.74 (**29.6**) [C_6]; 155.85 [$C_{2'}$]; 158.41 [C_2]
$(Me_2bipy)Pt(CH_2SiMe_2Ph)_2$[a]	-9.16 (**743.7**)	1.89 (**34.3**)	127.38 [C_3, C_5]; b [C_4]; 134.61 [C_2, C_6]; 146.17 (**31.4**) [C_1]	21.07 [CH_3]; 122.44 (**11.0**) [C_5]; 126.85 (**21.3**) [C_3]; 146.40 [C_4]; 146.94 (**32.8**) [C_6]; 155.94 (**10.3**)[C_2]
$(Bu^t_2bipy)Pt(CH_2SiMe_2Ph)_2$[a]	-8.69 (**742.3**)	1.93 (**35.9**)	127.32 [C_3, C_5]; b [C_4]; 134.73 [C_2, C_6]; 146.11 (**28.3**) [C_1]	29.78 [C-$\boldsymbol{CH_3}$]; 35.07 [$\boldsymbol{C}$-CH_3]; 118.09 [C_5]; 123.47 (**20.0**) [C_3]; 147.28 (**32.4**) [C_6]; 156.29 [C_2]; 159.26 [C_4]
$(bipyz)Pt(CH_2SiMe_2Ph)_2$[a]	-5.21 (**750.5**)	1.50 (**37.4**)	127.40 [C_3, C_5]; 128.68 [C_4]; 134.55 [C_2, C_6]; 144.74 (**23.2**) [C_1]	140.14 (**29.5**) [C_6]; 143.68 (**12.5**) [C_5]; 148.76 [C_2]; 149.05 (**16.1**)[C_3]

Table 2.3 : (continued)

(bipym)Pt(CH_2SiMe_2Ph)$_2$[a]	-7.81	1.53	127.32 [C_4]; 127.86 [C_3, C_5];	122.75 (**16.4**) [C_5]; 152.42 (**27.6**) [C_6];
	(**759.3**)	(**39.0**)	134.68 [C_2, C_6]; 145.09 (**27.7**) [C_1]	155.00 [C_4]; 162.36 [C_2]
[Pt_2(CH_2SiMe_2Ph)$_4$(μ-bipym)][a]	-8.63	1.40	127.90 [C_3, C_5]; 128.68 [C_4];	127.51 (**15.7**) [C_5]; 151.64 (**26.0**) [C_4, C_6];
	(**767.1**)	(**37.3**)	135.02 [C_2, C_6]; 145.23 (**25.7**) [C_1]	166.28 [C_2]
(phen)Pt(CH_2SiMe_2Ph)$_2$[a]	-9.03	1.84	127.30 [C_3, C_5]; 128.14 [C_4];	125.05 (**20.8**) [C_3, C_8]; 126.39 [C_5, C_6];
	(**749.5**)	(**36.1**)	134.64 [C_2, C_6]; 145.91 (**29.2**) [C_1]	130.15 (**11.3**) [C_{13}, C_{14}]; 133.94 [C_4, C_7];
				147.15 (**32.6**) [C_2, C_9] ;147.99 [C_{11}, C_{12}];
(Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$[a]	-8.36	1.93	127.33 [C_3, C_5]; 128.29 [C_4];	124.56 [$C_{4'}$]; 125.71 (**20.8**) [C_3, C_8];
	(**744.2**)	(**36.4**)	134.73 [C_2, C_6]; 146.06 (**28.8**) [C_1]	127.06 [C_5, C_6]; 128.91 [$C_{3'}$, $C_{5'}$];
				129.16 [$C_{2'}$, $C_{6'}$]; 129.46 [C_{13}, C_{14}];
				137.80 [C_4, C_7]; 146.76 (**33.4**) [C_2, C_9];
				147.01 [$C_{1'}$]; 148.53 [C_{11}, C_{12}]
(Me_4phen)Pt(CH_2SiMe_2Ph)$_2$[a]	-9.30	1.99	127.21 [C_3, C_5]; 127.33 [C_4];	14.25 [*4,7-*CH_3]; 17.10 [*3,8-*CH_3];
	(**744.4**)	(**37.9**)	134.64 [C_2, C_6]; 146.32 (**26.1**)[C_1]	122.32 [C_5, C_6]; 128.78 [C_{13}, C_{14}];
				133.18 (**22.2**) [C_3, C_8]; 140.56 [C_4, C_7];
				146.79 [C_{11}, C_{12}]; 148.46 (**32.9**) [C_2, C_9]

Table 2.3 : (continued)

$(Me_2Ph_2phen)Pt(CH_2SiMe_2Ph)_2$[d]	-17.30 (**749.2**)	2.11 (**31.8**)	125.70 [C_4]; 127.34 [C_3, C_5]; 134.34 [C_2, C_6]; 146.00 (**30.6**) [C_1]	27.87 (**18.8**) [2,9-CH_3]; 123.13 [$C_{4'}$]; 125.56 (**23.2**) [C_3, C_8]; 125.91 [C_5, C_6]; 128.71 [$C_{3'}$, $C_{5'}$]; 129.23 [$C_{2'}$, $C_{6'}$]; 133.76 (**34.3**) [C_2, C_9]; 137.57 [C_4, C_7]; 146.45 [$C_{1'}$]; 149.32 (**30.4**) [C_{11}, C_{12}]; 159.35 (**23.6**) [C_{13}, C_{14}];

a :- benzene-d^6

b :- obscured by solvent

c :- chloroform-d^1

d :- toluene-d^8

e :- acetone-d^6

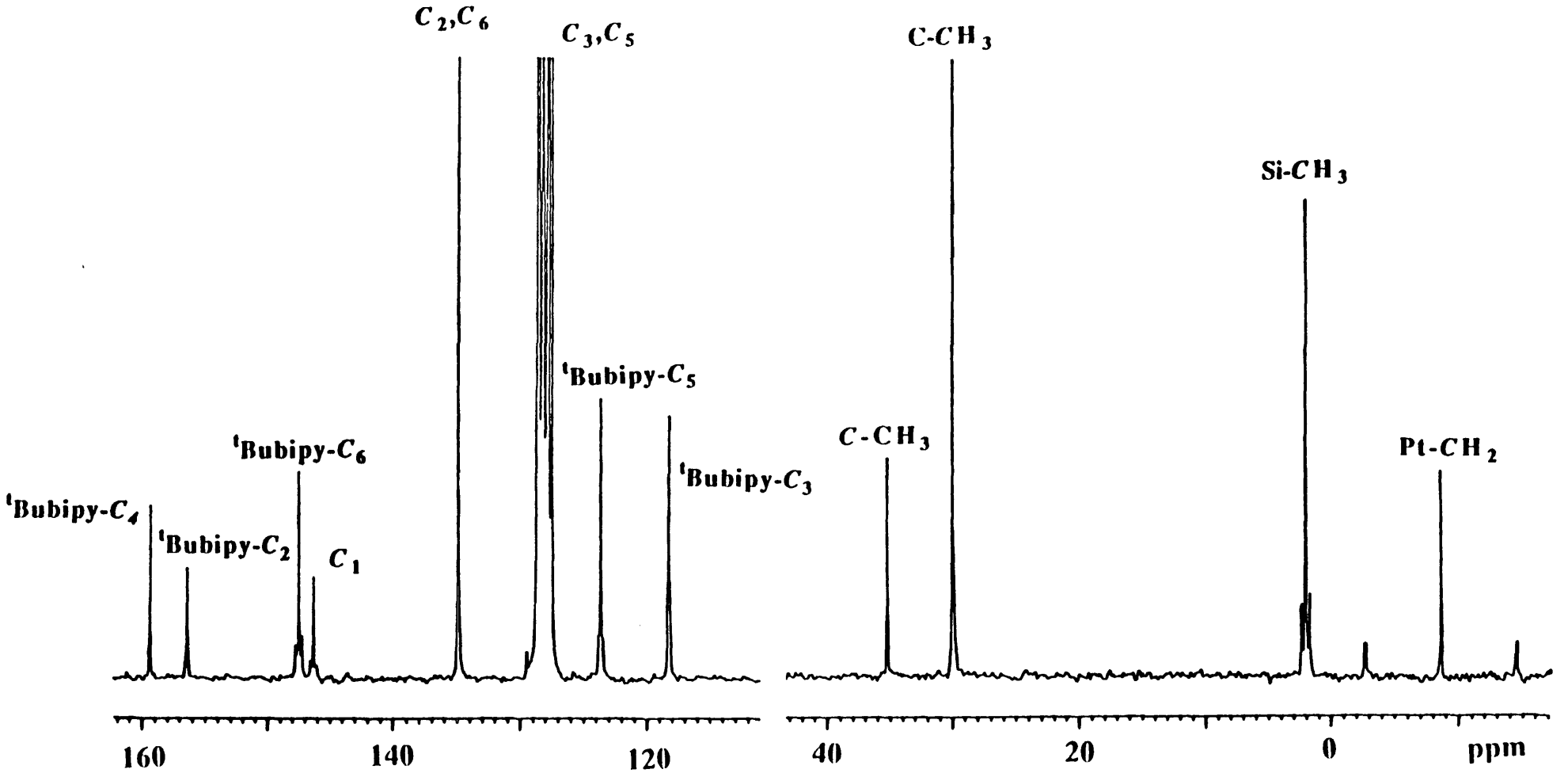


Fig. 2.4 : ^{13}C *N.M.R. of* $(Bu^t_2bipy)Pt(CH_2SiMe_2Ph)_2$.

Table 2.4 : *^{13}C N.M.R. Characteristics of Nitrogen Donor Ligands.*

Ligand	δ / ppm [*Assignment*]
2,2'-bipyridine	121.34 [C_5]; 124.15 [C_3]; 137.40 [C_4]; 149.65 [C_6]; 156.80 [C_2]
2,2'-bipyrimidine	120.3 [C_5]; 156.7 [C_4, C_6]; 161.0 [C_2]
1,10-phenanthroline	122.9 [C_3, C_8]; 126.4 [C_5, C_6]; 128.5 [C_{13}, C_{14}]; 135.9 [C_4, C_7]; 146.1 [C_{11}, C_{12}]; 150.1 [C_2, C_9]
4,7-diphenyl-1,10-phenanthroline	123.4 [C_3, C_8]; 123.9 [$C_{3'}$, $C_{5'}$]; 126.4 [C_{13}, C_{14}]; 128.4 [C_5, C_6]; 128.5 [$C_{4'}$]; 129.5 [$C_{2'}$, $C_{6'}$]; 138.0 [C_4, C_7]; 146.8 [$C_{1'}$]; 148.4 [C_{11}, C_{12}]; 149.8 [C_2, C_9]

Table 2.5 : *^{13}C N.M.R. Chemical Shifts of Trimethylphenylsilane in a Variety of Solvents.*

Solvent	δ ^{13}C ppm : Trimethylphenylsilane				
	Si-CH_3	C_1	C_2	C_3	C_4
benzene-d^6	-1.02	140.33	133.62	128.06	129.10
toluene-d^8	-1.12	140.09	133.44	127.88	128.92
acetone-d^6	-0.96	140.76	133.99	128.55	129.59
chloroform-d	-1.13	140.35	133.27	127.72	128.76

Table 2.6 : *Coordination Shifts of* bis-*(sila-neophyl)platinum(II) Complexes with Nitrogen Donor Ligands.*

Complex	Δδ ^{13}C ppm : Hydrocarbyl ligand[a,b]				
	Si-CH_3	C_1	C_2	C_3	C_4
(cod)Pt(CH_2SiMe_2Ph)$_2$	+3.16	+4.17	+0.50	-0.29	c
(nbd)Pt(CH_2SiMe_2Ph)$_2$	+2.69	+4.17	+0.35	-0.32	-0.74
[Pt(CH_2SiMe_2Ph)$_2$(μ-dms)]$_2$	+2.90	+3.88	+0.78	-0.40	-0.80
(py)$_2$Pt(CH_2SiMe_2Ph)$_2$	+2.67	+6.20	+0.44	-0.67	-1.28
(^{t}Bupy)$_2$Pt(CH_2SiMe_2Ph)$_2$	+2.91	+6.51	+3.08	-0.57	-1.73
(Phpy)$_2$Pt(CH_2SiMe_2Ph)$_2$	+2.93	+6.25	+0.53	-0.56	-1.80
(bipy)Pt(CH_2SiMe_2Ph)$_2$	+2.81	+5.49	+1.00	-0.71	-0.81
(bipy)Pt(CH_2SiMe_2Ph)Cl	+2.29	+4.52	+0.51	-0.59	-0.54
(Me_2bipy)Pt(CH_2SiMe_2Ph)$_2$	+2.91	+5.84	+0.99	-0.68	c
(Bu^t_2bipy)Pt(CH_2SiMe_2Ph)$_2$	+2.95	+5.78	+1.11	-0.74	c
(bipyz)Pt(CH_2SiMe_2Ph)$_2$	+2.52	+4.41	+0.93	-0.66	c
(bipym)Pt(CH_2SiMe_2Ph)$_2$	+2.55	+4.76	+1.06	-0.20	-1.78
[Pt_2(CH_2SiMe_2Ph)$_4$(μ-bipym)]	+2.36	+4.47	+1.03	-0.65	-0.91

Table 2.6 : (continued)

(phen)Pt(CH_2SiMe_2Ph)$_2$	+2.86	+5.58	+1.02	-0.76	-0.96
(Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$	+2.95	+5.73	+1.11	-0.73	-0.81
(Me_4phen)Pt(CH_2SiMe_2Ph)$_2$	+3.01	+5.99	+1.02	-0.85	-1.77
(Me_2Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$	+3.23	+5.91	+0.90	-0.54	-3.22

a :- positive sign indicates downfield shift

b :- negative sign indicates upfield shift

c :- obscured by solvent

$(py)_2Pt(CH_2SiMe_2Ph)_2$ and $(bipy)Pt(CH_2SiMe_2Ph)Cl$, $^3J_{Pt\text{-}C}$ for silicon-methyl groups is larger than that of the Si-aryl carbons reflecting greater 2s-character in the Si-CH_3 bond, assuming, that Fermi contact contributions to J predominate[52].

It is generally accepted that $^1J_{Pt\text{-}C}$ arises mainly from the Fermi contact contribution to coupling[53]. A convenient molecular orbital approximation, describing ^1J magnitudes is the Pople-Santry expression[54], which has previously been employed in the rationalisation of $^1J_{Pt\text{-}P}$[53, 55] and $^1J_{Pt\text{-}C}$[41, 42, 51] values. It is given by the equation :-

$$^1J_{Pt\text{-}C} = C[^3\Delta E]^{-1} |S_{Pt}(0)|^2 |S_C(0)|^2 [P'S_{Pt}S_C]^2$$

The constant C contains the gyromagnetic ratios of ^{195}Pt and ^{13}C, $^3\Delta E$ is an average singlet-triplet MO excitation energy. $S_{Pt}(0)$ and $S_C(0)$ are the s-electron densities evaluated at ^{195}Pt and ^{13}C nuclei respectively and $P'S_{Pt}S_C$ is the MO bond order between the s-orbitals of Pt and C. This last term increases in proportion to α^2_{Pt} and α^2_C, the s-characters of the platinum acceptor and carbon donor orbitals. In complexes where coordination geometry, oxidation state and ancillary ligands remain constant, there is likely to be little variation in $^3\Delta E$ or $S_{Pt}(0)$[53b].

Comparison of $(cod)Pt(CH_2SiMe_2Ph)_2$ with $(cod)Pt(CH_2CMe_2Ph)_2$ suggests that the effect derives in part from changes in α^2_{Pt}, *ie.* the extent to which platinum commits its 6s orbital to its two mutually *trans* bonds to carbon. While $^1J_{Pt\text{-}C}$ for the alkyl group increases from 710 Hz to 897 Hz from the silicon to the carbon analogue, $^1J_{Pt\text{-}C}$ for the η^2-alkene decreases correspondingly from 43 Hz to 65 Hz (Fig. 2.5). Neophyl in effect, exercises a stronger bond-weakening *trans*-influence[56] than sila-neophyl; platinum is diverting less 6s character towards its η^2-M-C bond and more to its η^1-M-C interaction. Presumably this is in response to a greater 2s contribution (α^2_{Pt}) to Pt-C bonding by the metal-bound carbon of neophyl. One possible explanation invokes Bent's proposition of isovalent hybridisation, which imply that increasing electronegativity of one substituent on carbon will direct more s-character into the remaining three bonds[57]. Carbon is more electronegative than silicon and platinum is clearly the least electronegative of the remaining substituents, so the Pt-C bond will be most affected.

It has been argued that the less effective 3s-2s overlap in the Si-C bond can have the effect of diverting 2s character to the other substituents[58] but this contribution is evidently outweighed by electronegativity considerations in this case. Notably $^1J_{Pt\text{-}C}$ for $(cod)PtMe_2$ has the intermediate value of 773 Hz and H has electronegativity intermediate between C and Si. $^2J_{Pt\text{-}H}$ varies in the same sense as $^1J_{Pt\text{-}C}$ in accord with these propositions. There is no evidence for a π-mesomeric effect of Si *via* hyperconjugative or $d\pi$-$p\pi$ interactions with neighbouring carbon[59]; this would lead to an increase in α^2_C and greater $^1J_{Pt\text{-}C}$. There could, on the other hand, be a steric explanation (*vide infra*).

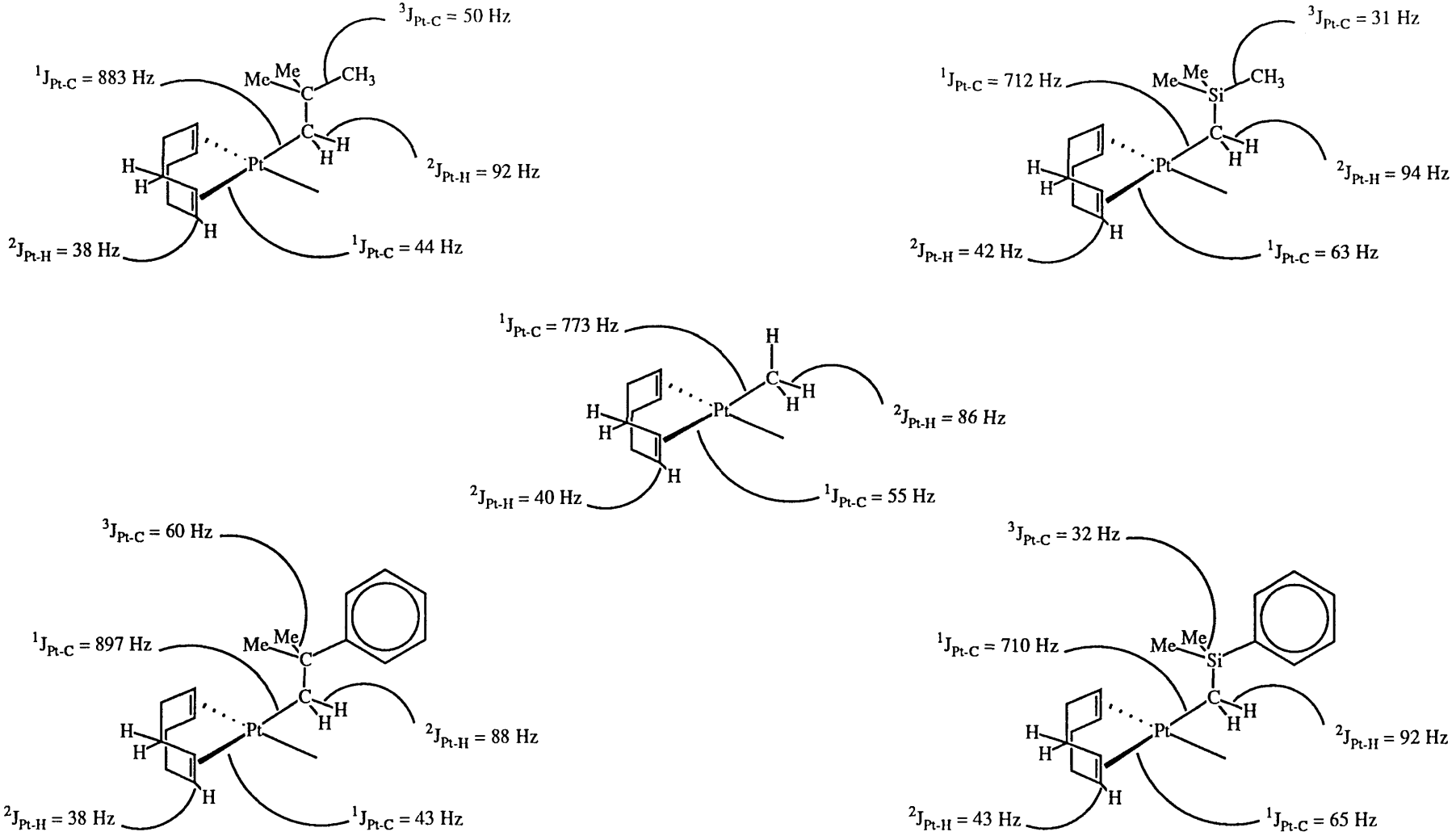


Fig. 2.5 : *Comparison of Spin-Spin Couplings in (cod)PtR$_2$ [R = Me, CH$_2$CMe$_3$, CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$SiMe$_2$Ph].*

These ^1J data seem to imply that the platinum-carbon bond is stronger in neophyl than in sila-neophyl complexes. This observation contradicts previous thermochemical measurements of bond strengths. Although no direct comparison of neophyl and sila-neophyl-metal bond strengths have been undertaken, comparative thermochemical studies of a series of homoleptic MR_4 complexes (M = Ti, Zr; R = CH_2CMe_3, CH_2SiMe_3) have shown that the mean bond dissociation enthalpies for the silicon containing compounds are greater by *ca.* 80 kJ mol^{-1} [60]. In the first instance, the weaker M-CH_2CMe_3 bond was attributed to a steric effect, but later work with linear ZnR_2 also proved that the metal-trimethylsilylmethyl bond was stronger by 38 kJ mol^{-1}[61]. Clearly in this case silicon electronic effects may also be important. Similar trends have been noted in a study of organo-f block compounds[62]; complexes of the type $Cp^*_2ThR_2$, $Cp^*_2ThR(O^tBu)$ and Cp^*_3ThR all exhibited weaker Th-CH_2CMe_3 bonds. The differences here were attributed to steric effects.

Measurement of Pt-C bond strengths has received scant attention[63]. Recent comparative thermochemical studies of Pt-C bond energies in *trans*-$(PMe_3)_2PtRCl$ (R = CH_2CMe_3, CH_2SiMe_3) gave values of bond enthalpies of 317 and 268 kJ mol^{-1} for neopentyl and trimethylsilylmethyl respectively[64]. In the above system, the trimethylsilylmethyl-metal bond is marginally weaker than the M-CH_2CMe_3 bond. This surprising result, although at odds with previous thermochemical studies, is in accord with N.M.R. evidence. Measurement of Pt-C bond lengths of these complexes by X-ray diffraction is currently underway.

In an effort to establish any geometrical differences between neophyl and sila-neophyl, suitable crystals of $(cod)Pt(CH_2CMe_2Ph)_2$ and $(cod)Pt(CH_2SiMe_2Ph)_2$ were studied by X-ray diffractometry (Fig. 2.6). Selected bond lengths and angles are found in Tables 2.7 and 2.8. From these it can be noted that the Pt-C bond of neophyl is only marginally longer than that of the silicon analogue. There are correspondingly small variations in Pt-C η^2-alkene bonds, which are slightly longer when *trans* to a sila-neophyl group. Both complexes show only minor deviations from ideal planarity around platinum.

The main difference between these analogues is, not surprisingly, the bond lengths and angles around the β-substituent. The mean C-Si bond of 1.893Å is as expected much longer than the C-C bond, which has a value of 1.555Å. This is also reflected in the Pt-C-E (E = C or Si) bond angles which have values of 115.0° and 120.3° for sila-neophyl and neophyl respectively. Since the $SiMe_2Ph$ group is further away from the metal than the CMe_2Ph moiety, sila-neophyl does not exert as great steric demands around platinum as does neophyl.

The greater 2s contribution (α^2_{Pt}) to Pt-C bonding by the methylene carbon in neophyl (and neopentyl) complexes may in fact have an important steric as well as electronic derivation. This phenomenon is clearly observed when one neophyl (or neopentyl) group is replaced by a silicon-containing analogue. Thus, in $(cod)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ $^1J_{Pt\text{-}C}$ for the methylene carbon of neophyl

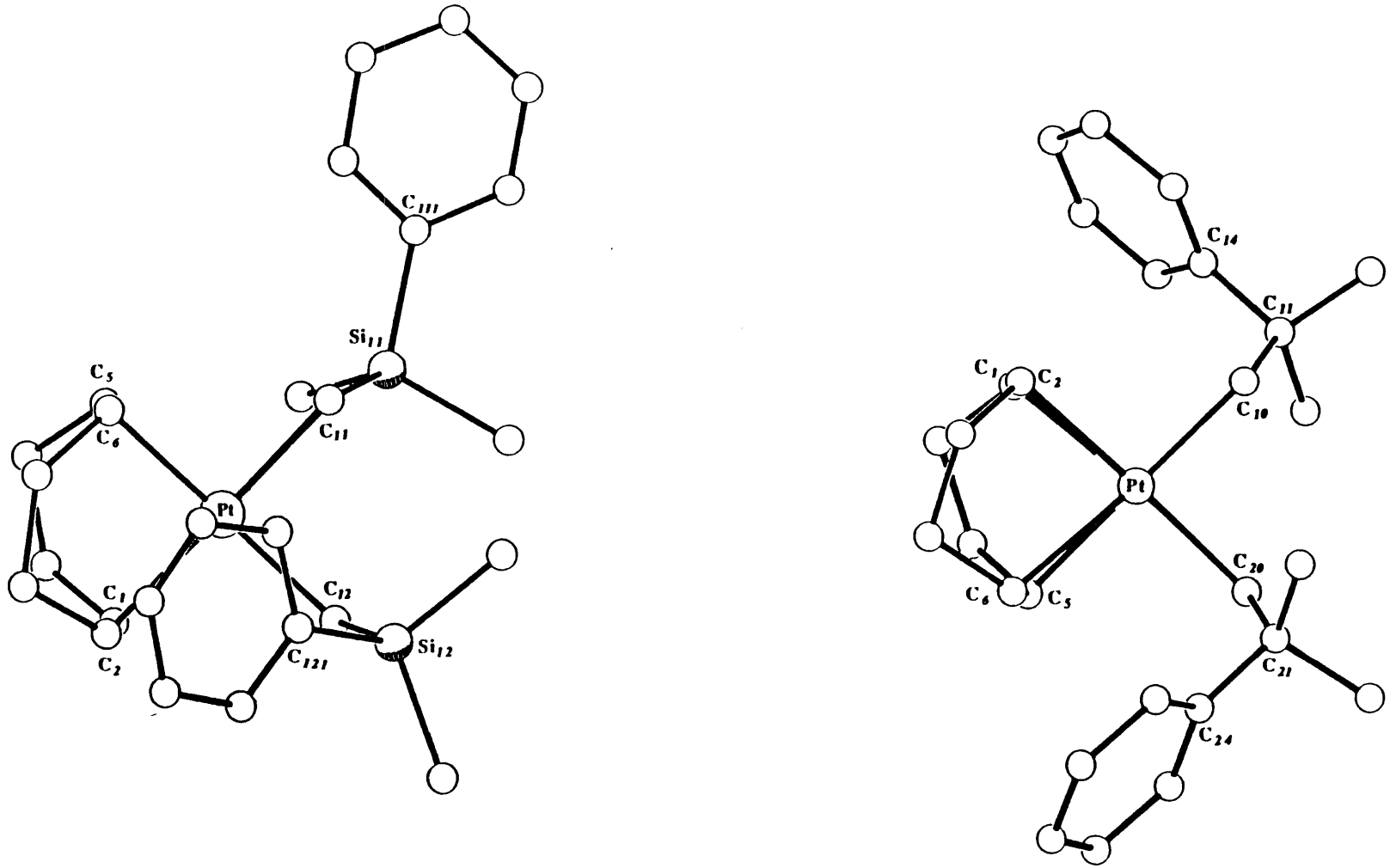


Fig. 2.6 : *X-ray Structures of* $(cod)Pt(CH_2EMe_2Ph)_2$ *[E = C, Si].*

Table 2.7 : *Selected Bond Lengths for (cod)Pt(CH_2EMe_2Ph)$_2$ [E = C, Si].*

R	Bond	Length / Å
CH_2SiMe_2Ph	Pt - C_{11}	2.060 (12)
	Pt - C_{12}	2.053 (10)
	Pt - C_1	2.227 (14)
	Pt - C_2	2.260 (12)
	Pt - C_5	2.231 (12)
	Pt - C_6	2.231 (13)
	Si_{11} - C_{11}	1.881 (12)
	Si_{12} - C_{12}	1.904 (14)
	Si_{11} - C_{111}	1.852 (11)
	Si_{12} - C_{121}	1.885 (13)
CH_2CMe_2Ph	Pt - C_{10}	2.110 (09)
	Pt - C_{20}	2.084 (08)
	Pt - C_1	2.245 (10)
	Pt - C_2	2.311 (10)
	Pt - C_5	2.270 (09)
	Pt - C_6	2.286 (10)
	C_{11} - C_{10}	1.543 (14)
	C_{21} - C_{20}	1.566 (14)
	C_{11} - C_{14}	1.534 (13)
	C_{21} - C_{24}	1.512 (13)

decreases from 897 to 855 Hz, whilst sila-neophyl shows an increase in $^1J_{Pt-C}$ from 710 to 746 Hz. As a result, the magnitude of $^1J_{Pt-C}$ for the η^2-alkene would be expected to increase when *trans* to neophyl and decrease for sila-neophyl. In fact, a small increase is observed for $^1J_{Pt-C}$ of the η^2-alkene carbon atoms when R = CH_2SiMe_2Ph and neophyl shows a complementary decrease. Similar variations are observed in $^2J_{Pt-H}$.

This trend is also reflected in the magnitude of $^3J_{Pt-C}$ to the methyl groups and C_1 of the aromatic ring. In the case of sila-neophyl, the value of $^3J_{Pt-C}$ for the methyl groups is only slightly larger (5 Hz) than that of the quaternary carbon of the aromatic ring, suggesting that there is little difference in the 2s character of these bonds. However, there is a significant difference in the magnitude of $^3J_{Pt-C}$ of 29 Hz in the neophyl group,

Table 2.8 : *Selected Bond Angles for (cod)Pt(CH_2EMe_2Ph)$_2$ [E = C, Si].*

R	Bonds	Angle / Degrees
CH_2SiMe_2Ph	C_{11} - Pt - C_{12}	89.8
	C_{12} - Pt - C_1	92.3
	C_{12} - Pt - C_2	91.9
	C_{11} - Pt - C_5	92.1
	C_{11} - Pt - C_6	91.1
	C_1 - Pt - C_5	94.6
	C_2 - Pt - C_6	90.3
	Pt - C_{11} - Si_{11}	115.8
	Pt - C_{12} - Si_{12}	114.1
CH_2CMe_2Ph	C_{10} - Pt - C_{20}	87.4
	C_{20} - Pt - C_5	93.9
	C_{20} - Pt - C_6	96.4
	C_{10} - Pt - C_1	92.1
	C_{10} - Pt - C_2	96.4
	C_1 - Pt - C_5	92.9
	C_2 - Pt - C_6	83.9
	Pt - C_{10} - C_{11}	119.4
	Pt - C_{20} - C_{21}	121.2

implying there is greater s-character in the C-CH_3 bonds than in the C-C_1 bond. Since the geometry of the alkene is little affected by replacement of a hydrocarbyl group by a sila-alkyl group, $^1J_{Pt\text{-}C}$ and $^3J_{Pt\text{-}C}$ must reflect modifications of the steric demands of neophyl by the sila-neophyl group.

2.2.4. Infrared Spectroscopy.

Selected I.R. data for this series of compounds are listed in the experimental section. Absorptions characteristic of *bis*-(sila-neophyl) complexes arise mainly from the phenyl and silicon-carbon vibrations. Those at *ca.* 1600 cm^{-1} and 1470-1430 cm^{-1} are aryl C-C vibrations. The strong peaks at 760-750 cm^{-1} and 710-700 cm^{-1} are out of plane C-H bending modes typical of five adjacent phenyl hydrogens. The peak at 1240-1230 cm^{-1} is a symmetric CH_3 deformation and the two strong bands at 860-830 cm^{-1} and

815-810 cm^{-1} are assigned to Si-C stretching modes. The strong band at 1110-1105 cm^{-1} is a characteristic X-sensitive band. In addition, the band near 580 cm^{-1} may be attributed to a Pt-C stretching mode.

2.2.5. Electronic Spectroscopy.

The electronic spectra of $L_2Pt(CH_2SiMe_2Ph)_2$ (where L = neutral nitrogen donor ligand) (Table 2.9) are particularly characterised by two absorptions attributed to metal-ligand charge transfer (MLCT) $d\pi \rightarrow \pi^*$ transitions and have been employed as a measure of relative electronic effects of such ligands[40, 65, 66]. The more energetic of the two is often obscured by the more intense ligand $\pi \rightarrow \pi^*$ transitions in the near UV. The lower energy absorption can always be observed and hence has been a gauge of the energy difference between the ($d\pi$) HOMO on the metal and the (π^*) LUMO of the ligand. The energy of λ_1 increases in the order:

μ-bipym < bipyz < Ph_2phen < Me_2Ph_2phen < phen ≡ bipy < Me_2bipy ≡ Bu^t_2bipy < Me_4phen.

The lower MLCT energies for the bipyz and bipym complexes relative to the bipy analogue is consistent with the generally observed reduction in complexes of N-bonded heteroaromatic ligands with electronegative ring atoms or substituents[67]. The LUMO for bipym is proposedly lower in energy than for bipy, resulting in a smaller separation from the $d\pi$ orbitals of platinum. Similarly the higher energy of this absorption for Me_2bipy and Bu^t_2bipy complexes (relative to bipy) is explained by the electron releasing substituent raising the energy of the LUMO. The phenanthroline ligands, with their increased conjugation, might be expected to exhibit lower energy absorption relative to bipy. Ph_2phen in which conjugation can be further augmented by suitable orientation of the phenyl substituents (though CPK molecular models suggest this is highly unfavourable), does give rise to a relatively minor reduction in energy of the π^* orbitals but phen and bipy exhibit similar absorption energies. For the dinuclear complex, $[Pt_2(CH_2SiMe_2Ph)_4(\mu\text{-bipym})]$, the absorption occurs at considerably longer wavelength than for the mononuclear analogue. This phenomenon, which has been noted previously[40], is believed to be due to the presence of a relatively high energy, largely non-bonding HOMO, spanning both metals in the binuclear complex.

The energy of the MLCT bands exhibited solvatochromatism as observed for related complexes[40]. On changing from acetone to dichloromethane, fairly small bathochromic shifts were observed for the bipy and various phenanthroline complexes, while bipym (both *mono* and *bis*-bidentate) and bipyz complexes displayed significant energetic lowering of the absorption (15-18 nm). In toluene, on the other hand, all the complexes displayed significant shifts. The energy of the λ_1 absorption, in general, was lowered by 15-25 nm with the exception of (bipyz)$Pt(CH_2SiMe_2Ph)_2$, where a smaller

Table 2.9 : *Electronic Spectroscopy of* bis-*(sila-neophyl)platinum(II) Complexes with Nitrogen Donor Ligands.*

Complex	λ_{max} (nm)		
	Acetone	CH_2Cl_2	Toluene
(bipy)Pt(CH_2SiMe_2Ph)$_2$	475.5	478.0	504.0
(bipy)Pt(CH_2SiMe_2Ph)Cl	432.0	435.0	467.2
(Me_2bipy)Pt(CH_2SiMe_2Ph)$_2$	467.5	468.0	497.5
(Bu^t_2bipy)Pt(CH_2SiMe_2Ph)$_2$	465.5	468.5	497.0
(bipyz)Pt(CH_2SiMe_2Ph)$_2$	525.0	541.0	548.0
(bipym)Pt(CH_2SiMe_2Ph)$_2$	487.5	505.5	528.5
[Pt_2(CH_2SiMe_2Ph)$_4$(μ-bipym)]	591.5	616.5	624.0
(phen)Pt(CH_2SiMe_2Ph)$_2$	475.0	475.0	500.5
(Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$	485.0	489.5	506.0
(Me_4phen)Pt(CH_2SiMe_2Ph)$_2$	429.0	432.5	468.5
(Me_2Ph_2phen)Pt(CH_2SiMe_2Ph)$_2$	479.0	482.0	504.0

shift (7 nm) was observed. It has been suggested that direct interaction with the metal centre is responsible for the solvatochromic shifts of MLCT bands of closely related *bis*-dialkylplatinum(II) complexes[66].

Comparing the electronic spectra of corresponding *bis*-(neophyl) complexes revealed no significant differences in the relative electronic effects of the ligands, suggesting that the ligands confer similar electronic environments in both types of complexes. Thus, the differing reactivity of sila-neophyl and neophyl derivatives probably do not originate with the electronic influence of the ancillary ligand.

2.3. Thermolytic Behaviour of *bis*(sila-neophyl)platinum(II) Complexes.

Qualitatively, *bis*-(sila-neophyl) complexes are more substitution inert than the related dineophyl analogues, higher temperatures are required for displacement of the diolefin by the nitrogen donor ligand. Preliminary investigations indicate that sila-neophyl complexes with bidentate N-donor ligands are more thermolytically inert than the

corresponding neophyl complexes, as no detectable rearrangement occurs in toluene solutions up to 150°C. Toluene solutions of $(py)_2Pt(CH_2SiMe_2Ph)_2$ at ambient temperature (or above) do rearrange to the corresponding platinasila-indan (See 5.2.4).

2.4. Experimental.

2.4.1. General.

Elemental analyses were by Imperial College Microanalytical Laboratories. N.M.R. spectra were recorded on Brüker WM250 (^{1}H, 250.13 MHz; ^{13}C, 62.9 MHz), Jeol GSX270 (^{1}H, 270.17 MHz; ^{13}C, 67.9 MHz) and Jeol FX90Q (^{1}H, 89.55 MHz) spectrometers. IR. data were collected on a Perkin-Elmer 683 instrument as 4% KBr dispersions and electronic spectra were recorded on a Shimadzu UV-160 spectrometer.

All reactions were carried out under argon, using standard anaerobic techniques. All apparatus was flame-dried before use[68]. Solvents were distilled under nitrogen prior to use: diethyl ether and *n*-hexane from sodium/benzophenone; toluene from sodium.

Chloromethyldimethylphenylsilane (sila-neophyl chloride) and 2,2'-bipyrimidyl were used as supplied by Lancaster synthesis. Chloromethyldimethylchlorosilane supplied by Lancaster synthesis was stored under argon but used without further purification. Tetramethylethylenediamine, 4-^{t}butylpyridine, 4-phenylpyridine, pyridazine, 2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, cycloocta-1,5-diene, [2.2.1]bicyclohepta-2,5-diene and dimethyl sulphide were all used as supplied by Aldrich Chem. Co.. Pyridine was supplied by Rose Chemicals and distilled under argon from sodium hydroxide prior to use. A sample of 4,4'-di-*tert*-butyl-2,2'-bipyridyl was synthesised by modification of a published procedure[69]. The precursors (cod)$PtCl_2$[2b], (nbd)$PtCl_2$[70] and $(dms)_2PtCl_2$[71] were prepared using published methods.

2.4.2. Syntheses.

Preparation of chloromethyldimethylphenylsilane [72].

A solution of PhMgBr (167 mmol) in diethyl ether (200 cm^3) was added slowly dropwise to $ClCH_2SiMe_2Cl$ (22 cm^3, 167 mmol) in diethyl ether (50 cm^3). Upon stirring the initially colourless solution gradually turned pale yellow and a white precipitate of magnesium halides was produced. After addition of PhMgBr was complete, the mixture was refluxed for 24 hours. The resulting stirred suspension was cooled to -15°C and hydrolysed by dropwise addition of degassed, saturated aqueous ammonium chloride solution (100 cm^3). The pale yellow ethereal layer was separated and the aqueous phase washed with diethyl ether (3 x 20 cm^3). The ether extracts were combined, dried over magnesium sulphate and decolourised with activated charcoal to give an almost colourless solution. Removal of the diethyl ether *in vacuo* afforded a pale yellow oil of the crude product. Distillation under reduced pressure gave sila-neophyl chloride as a colourless liquid (b.p. 114°C / 10 mmHg).

(Yield : 22.6g, 122 mmol, 77%)

[^{1}H NMR ($CDCl_3$) : $\delta \equiv$ 0.32 ppm - CH_3, 2.85 ppm - CH_2, 7.14-7.47 ppm - C_6H_5].

Preparation of phenyl(dimethyl)silylmethylmagnesiumchloride.

A solution of $ClCH_2SiMe_2Ph$ (2.5g, 13.5 mmol) in diethyl ether (20 cm^3) was added to magnesium shot (2.5g, 103 mmol) in Et_2O (10 cm^3) previously activated by introduction of 1,2-dibromoethane (0.25 cm^3). After 16 hours stirring at room temperature, the resulting solution of $ClMgCH_2SiMe_2Ph$ was filtered and was ready for use.
(Yield : 13.5 mmol, 100%).

Preparation of phenyl(dimethyl)silylmethyllithium[14].

Immediately before use, sufficient lithium sand (25% wt. dispersion in mineral oil) to ensure stoichiometric excess in the following reaction was mixed with dry *n*-hexane (30 cm^3), filtered and then washed several times with *n*-hexane (5 x 30 cm^3) to remove residual oil. After drying the lithium sand *in vacuo*, *n*-hexane (80 cm^3) was added. A solution of $ClCH_2SiMe_2Ph$ (2.5g, 13.5 mmol) was added dropwise: upon addition the mixture was refluxed for 7 days. After this time the reaction was cooled to room temperature, filtered and the lithium residues washed with *n*-hexane (3 x 15 cm^3). The clear, colourless combined filtrate was concentrated to 10 cm^3 *in vacuo* and cooled to -20°C to give large colourless crystals. These were filtered and dried *in vacuo* to give the product.
(Yield : 1.41g, 9.1 mmol, 67%).

Preparation of bis-*(sila-neophyl)(1,5-cyclooctadiene)platinum(II)*

To a stirred suspension of (cod)$PtCl_2$ (1.85g, 4.94 mmol) in diethyl ether (30 cm^3) at -25°C was added dropwise a solution of $PhMe_2SiCH_2MgCl$ (16 mmol) in diethyl ether (30 cm^3). The mixture was allowed to reach room temperature and stirred for a further 16 hours, during which time magnesium chloride was precipitated from the dark yellow solution. The stirred suspension was cooled to -25°C and hydrolysed dropwise with degassed, saturated aqueous ammonium chloride solution (30 cm^3). On reaching ambient temperature the yellow ethereal layer was separated and the aqueous phase washed with diethyl ether (3 x 10 cm^3). The ether extracts were combined, dried over magnesium sulphate and decolourised with activated charcoal to give a colourless solution. Removal of the solvent *in vacuo* gave a white crystalline solid which was recrystallised from the minimum amount of *n*-hexane (10 cm^3) to afford large colourless prisms of the product.
(Yield : 2.38g, 4.40 mmol, 89%).

IR. : 1475w, 1460w, 1428m, 1375vs, 1262m, 1242s, 865m, 810vs,br, 780s, 765s, 740s, 730s, 700s, 550m.

Preparation of bis-*(sila-neophyl)([2.2.1]bicylcohepta-2,5-diene)platinum(II).*

A solution of $PhMe_2SiCH_2MgCl$ (14 mmol) in diethyl ether (40 cm^3) was added dropwise at -78°C to a stirred suspension of $(nbd)PtCl_2$ (1.6g, 4.5 mmol) in diethyl ether (20 cm^3). The mixture was gradually warmed to room temperature and then stirred for a further 16 hours. The stirred suspension was then cooled to -25°C and hydrolysed with saturated ammonium chloride solution (20 cm^3). The ethereal layer was separated and the aqueous phase washed with diethyl ether (5 x 20 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with activated charcoal to give an almost colourless solution. Filtration, washing the $MgSO_4$ with diethyl ether (2 x 20 cm^3) and removal of the solvent *in vacuo* gave an off-white solid, which was recrystallised from the minimum amount of *n*-hexane (3 cm^3) to give pale yellow needles of the product.
(Yield 1.85g, 3.74 mmol, 83%).

N.B. Even as a solid, $(nbd)Pt(CH_2SiMe_2Ph)_2$ decomposes slowly at room temperature over a period of several days, hence all samples were stored at -20°C.

IR. : 1422m, 1258m, 1239m, 1104s, 832s, 808s,br, 790m, 753m, 748m, 736m, 715m, 698s, 560wm.

Preparation of tetrakis-*(sila-neophyl)*-bis- *(μ-dimethyl sulphide)diplatinum(II)*[73].

A solution of sila-neophyl lithium (3.9 mmol) in *n*-hexane (30 cm^3) was added, dropwise to a stirred suspension of $(dms)_2PtCl_2$ (0.51g, 1.3 mmol) in diethyl ether (30 cm^3) at -20°C. The mixture was gradually warmed to room temperature and stirred for a further 8 hours. The stirred suspension was cooled to -20°C and hydrolysed with saturated ammonium chloride solution (30 cm^3). The ethereal layer was separated and the aqueous phase washed with diethyl ether (2 x 15 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with charcoal. Filtration followed by removal of the solvents *in vacuo* gave a yellow-brown oily residue. Trituration with either *n*-hexane or toluene afforded the product as a white powder.
(Yield : 0.4g, 0.36 mmol, 55%).

N.B. The solid decomposes at room temperature over a period of several hours and was stored at -20°C.

IR. : 1422m, 1408wm, 1237m, 1106s, 981s, 825s,br, 803s,br, 768m, 732s, 699s, 552wm.

*Preparation of (dichloro)*bis-*(sila-neophyl)*-bis- *(μ-dimethyl sulphide)diplatinum(II).*

To a stirred suspension of $(dms)_2PtCl_2$ (0.49g, 1.2mmol) in diethyl ether (20 cm^3) at -20°C was added a solution of $ClMgCH_2SiMe_2Ph$ (2.5 mmol) in ether (20 cm^3). The

mixture was warmed to ambient temperature and stirred for a further 6 hours. With continued stirring, the suspension was cooled to -78°C and hydrolysed with saturated, aqueous ammonium chloride solution (25 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (2 x 10 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with charcoal. Filtration followed by removal of the solvents *in vacuo* afforded an off-white oil. Recrystallisation from ether (2 cm^3) gave the product as an off-white powder.
(Yield : 0.35g, 0.40 mmol, 66%).

Preparation of bis-*(sila-neophyl)(tetramethylethylenediamine)platinum(II).*

(nbd)Pt(CH_2SiMe_2Ph)$_2$ (0.2g, 0.34 mmol) was dissolved in tmed (10 cm^3) and heated at 60°C for 21 days. Excess tmed was removed *in vacuo* to give the product as a colourless oil.
(Yield : 0.2g, 0.34 mmol, 100%)

Preparation of bis-*(sila-neophyl)*-bis-*(pyridine)platinum(II).*

(cod)Pt(CH_2SiMe_2Ph)$_2$ (0.2g, 0.33 mmol) was dissolved in excess pyridine (15 cm^3, *ca.* 186 mmol) and stirred at 60°C for 24 hours to give a pale yellow solution. Excess pyridine was removed *in vacuo* to give a pale yellow semi-crystalline solid, which was dissolved in diethyl ether (2 cm^3) and *n*-hexane added dropwise (0.5 cm^3). Cooling the solution to -20°C afforded small yellow plates of the product.
(Yield : 0.19g, 0.28 mmol, 85%).

IR. : 1482m, 1448s, 1428m, 1264wm, 1238m,br, 1109s, 838s, 813vs, 786m, 760s, 732vs, 700vs, 580wm.

Preparation of bis-*(sila-neophyl)*-bis-*(4-tert-butylpyridine)platinum(II).*

(nbd)Pt(CH_2SiMe_2Ph)$_2$ (0.2g, 0.34 mmol) was dissolved in excess *tert*-butylpyridine (10 cm^3, *ca.* 68 mmol) and stirred at 60°C for 24 hours. Excess *tert*-butylpyridine was removed by distillation to give a pale orange solid residue, which was recrystallised from diethyl ether (2 cm^3) and *n*-hexane (1 cm^3) to give the product as pale orange crystals.
(Yield : 0.21g, 0.28 mmol, 81%).

IR : 1465m, 1418m, 1261m, 1241m, 1233m, 829vs, 813vs, 794vs, 778m, 766wm, 745wm.

Preparation of bis-*(sila-neophyl)*-bis-*(4-phenylpyridine)platinum(II).*

[$Pt_2(CH_2SiMe_2Ph)_4(\mu\text{-dms})_2$] (0.14g, 0.13 mmol) and 4-phenylpyridine (0.04g, 0.26 mmol) were dissolved in toluene (10 cm^3) and stirred at ambient for 3 days. Removal

of the solvent *in vacuo* and recrystallisation of the oily residue from diethyl ether (2 cm^3) and *n*-hexane (1 cm^3) afforded the product as a lemon yellow solid.
(Yield : 0.20g, 0.12 mmol, 96%)

IR : 1479m, 1426wm, 1410wm, 1258m, 1241wm, 1234 m, 837vs, 826s, 802vs, 780m, 763vs, 724s, 694s.

Preparation of bis-*(sila-neophyl)*-bis-*(pyridazine)platinum(II).*

(nbd)Pt(CH_2SiMe_2Ph)$_2$ (0.2g, 0.34 mmol) was dissolved in toluene (6 cm^3), excess pyridazine (0.15g, 1.87 mmol) added and then stirred at ambient temperature for 14 days. Excess pyridazine was removed by washing with saturated aqueous $FeSO_4$ solution (2 x 10 cm^3). The organic layer was dried over $MgSO_4$, filtered and subsequent removal of the toluene *in vacuo* gave an amber solid.
(Yield : 0.21g, 0.32 mmol, 94%)

IR : 1477m, 1448wm, 1430m, 1411s, 1240m, 835s, 818s, 802s, 770m, 751s, 742s, 717m, 701s.

Preparation of bis-*(sila-neophyl)(2,2'-bipyridyl)platinum (II).*

2,2'-Bipyridyl (0.5g, 3.2 mmol) and (cod)Pt(CH_2SiMe_2Ph)$_2$ (0.2g, 0.32mmol) were dissolved in the minimum amount of toluene (15 cm^3) and the solution stirred at 60°C for 5 days. Excess ligand was removed by washing with saturated aqueous $FeSO_4$ solution. The toluene extracts were dried over $MgSO_4$ and filtered. Concentration of the solution to *ca.* 2 cm^3, dropwise addition of *n*-hexane (1 cm^3) to effect crystallisation and cooling to -20°C afforded large orange needles of the product.
(Yield : 0.22g, 0.25 mmol, 78%).

IR. : 1469m, 1444m, 1426m, 1238m, 1108s, 833s, 812s, 756s, 739m, 723m, 702s, 577wm.

Preparation of (chloro)(sila-neophyl)(2,2'-bipyridyl)platinum(II).

[Pt(CH_2SiMe_2Ph)Cl(μ-dms)]$_2$ (0.15g, 0.17 mmol) was dissolved in diethyl ether (8 cm^3) and bipy (0.03g, 0.17 mmol) added. The mixture was then stirred at ambient temperature for 10 days. Removal of the ether *in vacuo* yielded an amber solid, which was recrystallised from the minimum amount of ether (2 cm^3).
(Yield : 0.17 g, 0.14 mmol, 85%).

IR : 1471m, 1448m, 1262m, 1236m, 857s, 833vs, 819s, 774m, 760vs, 741m, 717s, 702m, 371m.

Preparation of bis-*(sila-neophyl)(4,4'-dimethyl-2,2'-bipyridyl)platinum(II).*

(nbd)Pt($CH_2SiMe_2Ph)_2$ (0.2g, 0.32 mmol) and Me_2bipy (0.063g, 0.34 mmol) were dissolved in toluene (10 cm^3) and stirred at 60°C for 21 days to give an orange-red solution. Concentration of the resulting solution to *ca.* 2 cm^3, followed by dropwise addition of *n*-hexane (1 cm^3) and cooling to -20°C gave orange needles of the product. (Yield : 0.2g, 0.30 mmol, 87%).

IR. : 1427m, 1406s, 1238m, 1109s, 832s, 816s, 803s, 750s, 740s, 719s, 704s, 576wm.

Preparation of bis-*(sila-neophyl)(4,4'-di-tert-butyl-2,2'-bipyridyl)platinum(II).*

[Pt($CH_2SiMe_2Ph)_2$(μ-dms)]$_2$ (0.16g, 0.14 mmol) and Bu^t_2bipy (0.08g, 0.3 mmol) were dissolved in toluene (10 cm^3) and left at ambient temperature for 4 days giving a deep orange-red solution. Excess Bu^t_2bipy was removed by washing with aqueous $FeSO_4$ solution. Concentration of the solution to *ca.* 2 cm^3, followed by dropwise addition of *n*-hexane (0.1 cm^3) and cooling to -20°C yielded orange crystals of the product.
(Yield : 0.21g, 0.13 mmol, 96%).

IR. : 1478s, 1423m, 1418s, 1259m, 1234s, 1104s, 830vs, 810s, 769s, 734s, 717s, 698s,577wm.

Preparation of bis-*(sila-neophyl)(2,2'-bipyrimidyl)platinum(II).*

(cod)Pt($CH_2SiMe_2Ph)_2$ (0.34g, 0.56 mmol) and 2,2'-bipyrimidyl (0.2g, 1.26 mmol) were dissolved in toluene (15 cm^3) and stirred at 60°C for 10 days to give a dark red solution. Excess bipym was removed by washing with aqueous $FeSO_4$ solution. Concentration to *ca.* 2 cm^3, followed by dropwise addition of *n*-hexane (2 cm^3) and cooling to -20°C afforded wine red hexagonal crystals of the product.
(Yield : 0.28g, 0.43 mmol, 77%).

IR. : 1427m, 1406s, 1238m, 1109s, 832s, 816s, 803s, 750s, 740s, 704s, 576wm.

Preparation of tetrakis-*(sila-neophyl)(μ-2,2'-bipyrimidyl)diplatinum(II).*

[Pt($CH_2SiMe_2Ph)_2$(μ-dms)]$_2$ (0.2g, 0.18 mmol) and 2,2'-bipyrimidyl (0.03g, 0.18 mmol) were dissolved in toluene (8 cm^3) and allowed to stand at ambient temperature for 4 days. The initially colourless solution turned dark red after 5 minutes and dark green after 15 minutes. After 1 hour fine needles began to precipitate. The solid was filtered and recrystallised from acetone (15 cm^3) to give dark green needles of the product.
(Yield : 0.19g, 0.17 mmol, 97%).

IR. : 1425m, 1265wm, 1240m, 1106s, 829vs, 85vs,br, 738m, 728s, 698s, 577wm.

Preparation of bis-*(sila-neophyl)(2,2'-bipyrazyl)platinum(II).*

$[Pt(CH_2SiMe_2Ph)_2(\mu\text{-dms})]_2$ (0.13g, 0.12 mmol) and bipyz (0.04g, 0.25 mmol) were dissolved in toluene (8 cm^3) and left at room temperature for four days to give a purple solution. Excess ligand was removed by washing with aqueous $FeSO_4$ solution. Concentration of the solution to *ca.* 2 cm^3, addition of *n*-hexane (1 cm^3) dropwise and cooling to -20°C gave magenta rods of the product.
(Yield : 0.13g, 0.21 mmol, 87%).

IR. : 1422s, 1403s, 1237s, 1106s, 829vs, 805vs,br, 738m, 728s, 717m, 698s, 581wm.

Preparation of bis-*(sila-neophyl)(1,10-phenanthroline)platinum(II).*

(cod)$Pt(CH_2SiMe_2Ph)_2$ (0.25g, 0.42 mmol) and 1,10-phenanthroline (0.15g, 0.83 mmol) were dissolved in toluene (10 cm^3) and stirred at 60°C for 8 days forming an intense orange-red solution. Excess phen was removed by washing with freshly prepared $FeSO_4$ solution (5 x 30 cm^3) until the washings were colourless. Concentration of the organic layer to *ca.* 2 cm^3 and addition of *n*-hexane (2 cm^3) yielded large red plates of the product.
(Yield : 0.23g, 0.34 mmol, 82%).

IR. : 1425m, 1240m, 1110s, 840s, 815s, 740s, 722s, 705m, 577wm.

Preparation of bis-*(sila-neophyl)(3,4,7,8-tetramethyl-1,10-phenanthroline)platinum(II).*

(cod)$Pt(CH_2SiMe_2Ph)_2$ (0.35g, 0.58 mmol) and 3,4,7,8-tetramethyl-1,10-phenanthroline (0.2g, 0.85 mmol) were dissolved in toluene (20 cm^3) and stirred at 60°C for 14 days. The resulting orange solution was washed with aqueous $FeSO_4$ solution, concentrated to *ca.* 2 cm^3 and *n*-hexane added to give long orange needles of the product.
(Yield : 0.32g, 0.44 mmol, 76%).

IR. : 1428s, 1268m, 1240s, 1112s, 839vs, 813vs, 772s, 743s, 726s, 703s, 572wm.

Preparation of bis-*(sila-neophyl)(4,7-diphenyl-1,10-phenanthroline)platinum(II).*

(cod)$Pt(CH_2SiMe_2Ph)_2$ (0.23g, 0.38 mmol) and 4,7-diphenyl-1,10-phenanthroline (0.235g, 0.71 mmol) were dissolved in toluene (20 cm^3) and stirred for 28 days at 60°C to give a dark orange-red solution. Excess ligand was removed by washing with aqueous $FeSO_4$ solution. Concentration of the solution to ca. 3 cm^3 and addition of *n*-hexane (1 cm^3) gave vermillion red rods of the product.
(Yield : 0.31g, 0.38 mmol, 99%).

IR. : 1423m, 1262m, 1242m, 1237m, 1100s, 848s, 831s, 812s, 770s, 765s, 740s, 703s, 571wm.

Preparation of bis-*(sila-neophyl)(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) platinum(II).*

$[Pt(CH_2SiMe_2Ph)_2(\mu\text{-dms})]_2$ (0.15g, 0.13 mmol) was dissolved in toluene (10 cm^3) and Me_2Ph_2phen (0.1g, 0.27 mmol) was added. The mixture was left at room temperature for 3 hours and then the solvent removed *in vacuo* to give an orange-red oily residue, which was extracted into *n*-hexane (3 x 15 cm^3). Evaporation of the solvent yielded a dark orange microcrystalline solid of the product. This may be further recrystallised from toluene (1 cm^3) and *n*-hexane (0.5 cm^3). Cooling to -20°C affords vermillion crystals of the product. (Yield : 0.18g, 0.21 mmol, 80%).

IR. : 1438m, 1425m, 1262s, 1104s,br, 806vs,br, 729m, 700s, 577wm.

Chapter Three :

SYNTHETIC AND SPECTROSCOPIC STUDIES OF *BIS*-[DIMETHYL(PHENYL)SILYLMETHYL] PLATINUM(II) COMPLEXES WITH PHOSPHORUS DONOR LIGANDS.

3.1. Synthesis of *bis*-[dimethyl(phenyl)silylmethyl]platinum(II) complexes with phosphorus donor ligands.

Reaction of the diene complexes with stoichiometric amounts of tertiary phosphines, yielded a series of *cis-bis*-(phosphine)platinum(II) dialkyls in essentially quantitative yields in most cases. With the exception of (dppf)Pt(CH_2SiMe_2Ph)$_2$ which is yellow, the remainder are colourless crystalline solids. Where L = PEt_3 and PPh_2Me, some problems were encountered in obtaining crystalline samples. Substitution was generally complete within 14 days at either 60°C or ambient temperature, depending on the diene complex and solvent employed. These air inert solids do not decompose in deoxygenated hydrocarbons. They do react slowly with chlorocarbon solvents, affording *cis-bis*-(PR_3)$_2$$PtCl_2$; the reaction is accelerated at higher temperatures and in the presence of oxygen. All have satisfactory elemental analyses (Table 3.1), except ($PPh_2C_6H_4$-2-CF_3)$_2$Pt(CH_2SiMe_2Ph)$_2$ which was not isolated pure.

3.2. Spectroscopic studies of *bis*-[dimethyl(phenyl)silylmethyl] platinum(II) complexes with phosphorus donor ligands.

3.2.1. ^1H N.M.R.

The numbering conventions used for phosphorus ligands for ensuing discussions is shown in Fig. 3.1.

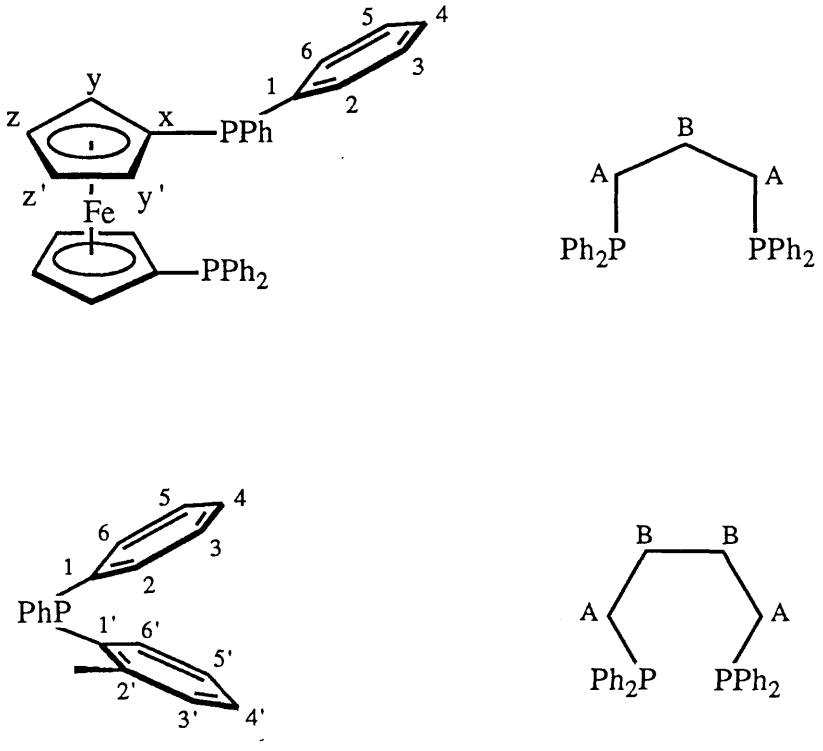


Fig. 3.1 : *N.M.R. Numbering Conventions for P-Donor Ligands.*

Table 3.1 : *Analytical Data for* bis-*(sila-neophyl)platinum(II) Complexes with P-Donor Ligands.*

Complex	Colour	Found (Calculated) %	
		C	H
$(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$	White	44.51 (44.63)	6.93 (6.87)
$(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$	White	49.51 (49.36)	7.81 (7.78)
$(PMe_2Ph)_2Pt(CH_2SiMe_2Ph)_2$	White	52.98 (53.04)	6.28 (6.31)
$(PPh_2Me)_2Pt(CH_2SiMe_2Ph)_2$	White	59.35 (59.37)	6.04 (5.84)
$(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$	White	63.82 (63.70)	5.53 (5.54)
$(P\text{-}p\text{-}tol_3)_2Pt(CH_2SiMe_2Ph)_2 \cdot \frac{1}{2} C_6H_6$	White	66.25 (66.29)	6.31 (6.27)
$(PPh_2\text{-}o\text{-}tol)_2Pt(CH_2SiMe_2Ph)_2$	White	63.97 (64.28)	5.69 (5.78)
$(dppm)Pt(CH_2SiMe_2Ph)_2$	White	58.62 (58.82)	5.47 (5.51)
$(dppe)Pt(CH_2SiMe_2Ph)_2$	White	59.05 (59.24)	5.48 (5.65)
$(dppp)Pt(CH_2SiMe_2Ph)_2 \cdot \frac{1}{2} CH_2Cl_2$	White	57.77 (57.61)	5.84 (5.63)
$(dppb)Pt(CH_2SiMe_2Ph)_2$	White	59.95 (60.05)	5.92 (5.96)
$(dppf)Pt(CH_2SiMe_2Ph)_2$	Amber	59.65 (59.59)	5.00 (5.19)

A common feature of all these spectra, detailed in Table 3.2 is the multiplet obtained from the hydrogens of the methylene group bound to platinum, typified by $(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$ (Fig. 3.2). This second-order resonance is attributed to an $A_2A_2'MRR'X_9X_9'$ spin system, where A = $^1H_{CH_2}$, M = ^{195}Pt, R = ^{31}P and X = $^1H_{P\text{-}CH_3}$. In practice though, it appears as an apparent quartet with platinum satellites. In addition, this multiplet is considerably broadened in several of the complexes at 250 MHz but a quartet is observed if the spectrum is measured at lower field. This phenomenon has been attributed to more efficient relaxation of the ^{195} Pt nucleus by increasing field gradient anisotropy[76]. The broadening of this signal may also be due to an unresolved coupling between the diastereotopic hydrogen atoms and the phosphorus nuclei.

Similar observations have been noted for related L_2PtR_2 [R = neophyl, trimethylsilylmethyl, ethenyldimethylsilylmethyl; L = PEt_3, PPh_3, dppe)[30b, 50, 51, 77]. Comparisons with *bis*-(neophyl) analogues show that $^2J_{Pt\text{-}H}$ values are 5-15 Hz larger for sila-neophyl derivatives. Also, the magnitude of $^2J_{Pt\text{-}H}$ coupling constants are consistently *ca.* 10 Hz smaller for phosphine complexes than for corresponding nitrogen donor derivatives, implying less s-orbital contribution in the Pt-C-H bond and reflecting the generally stronger *trans* influence of P-donor ligands[56].

A characteristic pattern is also observed for the hydrogens co-ordinated to phosphine. These appear as a doublet of "triplets" due to coupling to both ^{31}P and ^{195}Pt nuclei. The exception is $(dppf)Pt(CH_2SiMe_2Ph)_2$, where H_2 and H_6 of the phenyl group generates a very broad singlet at room temperature and the four cyclopentadienyl protons H_Y, $H_{Y'}$, H_Z, $H_{Z'}$ display slightly broadened but unresolved resonances (Fig. 3.3). Lowering the temperature initially broadens each of these signals, then subsequently they become resolved into doublets. Rate constants (k_c) for the processes responsible for this exchange can be determined from the linewidths at half-height ($\Delta\upsilon$) at each coalescence point according to the formula[78] :-

$$k_c = \frac{\pi(\Delta\nu)}{\sqrt{2}}$$

These rate constants were used to determine the free energies of activation ($\Delta G_c^{\ddagger}$) (Table 3.3) at the coalescence temperature, T_c, from the Eyring equation :-

$$k_c = (k_B / h)T_c e^{-\Delta G^{\ddagger}/RT}$$

where :-

k_B	=	Boltzmann's constant
h	=	Planck's constant
R	=	ideal gas constant

Table 3.2 : *^{1}H-N.M.R. Characteristics of* bis-*sila-neophylplatinum(II) complexes with P-donor ligands.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligand (J_{Pt-H}) / Hz [*Assignment*]			δ ^{1}H ppm : Ancillary ligand (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Aromatic ($J_{H_2-H_3}$) / Hz	
$(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$[a]	0.50 (**72.3**)	0.19	7.17-7.22 m, [H_3, H_4, H_5]; 7.62 dd, [H_2, H_6] (**7.6**)	1.14 m, (**20.2**) [P-CH_3] (J_{P-H} = 7.8 Hz)
$(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$[a]	0.64 (**79.5**)[b]	0.46	7.15-7.19 m, [H_3, H_4, H_5]; 7.78 dd, [H_2, H_6] (**7.8**)	0.73 m, (**14.8**) [P-CH_2CH_3] (J_{P-H} = 14.5 Hz); 1.36 m, (**15.1**) [P-CH_2CH_3] (J_{P-H} = 15.0 Hz)
$(PMe_2Ph)_2Pt(CH_2SiMe_2Ph)_2$[c]	1.15 (**76.3**)	0.66	7.20-7.32 m, [H_3, H_4, H_5]; 7.91 dd, [H_2, H_6] (**7.7**)	0.91 m, (**19.8**) [P-CH_3] (J_{P-H} = 7.6 Hz); 6.98-7.03 m, [H_3, H_4, H_5]; 7.27[b] [H_2, H_6]

Table 3.2 : (continued)

$(PMePh_2)_2Pt(CH_2SiMe_2Ph)_2$[a]	0.75 (**79.8**)	0.13	d [H_3, H_4, H_5]; 7.45 dd, [H_2, H_6] (**7.5**)	1.43 m, (**20.1**) [P-CH_3] (J_{P-H} = 7.2 Hz); 7.16-7.26 m, [H_3, H_4, H_5]; 7.29 dd, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$[e]	1.18 (**81.7**)[f]	0.37	7.15-7.18 m, [H_3, H_4, H_5]; 7.60 dd, [H_2, H_6] (**7.8**)	6.80-6.85 m, [H_3, H_4, H_5]; 7.37 td, [H_2, H_6]
$(P\text{-}tol_3)_2Pt(CH_2SiMe_2Ph)_2$[a]	0.80 (**81.3**)[f]	0.03	7.13-7.19 m, [H_3, H_4, H_5]; 7.30 dd, [H_2, H_6] (**7.5**)	2.23 s, [Ar-CH_3]; 6.79 d, [H_3, H_5]; 7.12 d, [H_2, H_6]
$(PPh_2\text{-}o\text{-}tol)_2Pt(CH_2SiMe_2Ph)_2$[e]	0.89[g]	0.39[g]	7.11-7.18 m, [H_3, H_4, H_5]; 7.47, dd [H_2, H_6] (**7.5**)	1.92 s, [Ar-CH_3]; 6.67-6.89 m, [H_3, H_4, H_5]; 6.96-7.05 m, [H_2, H_6]; 7.33[g] [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.88[g] [$H_{6'}$]
$(PPh_2Ar\text{-}2\text{-}CF_3)_2Pt(CH_2SiMe_2Ph)_2$[e]	0.91[g]	0.29 (**70.4**)	7.21-7.28 m, [H_3, H_4, H_5]; 7.61 dd, [H_2, H_6] (**7.9**)	6.79-6.84 m, [H_3, H_4, H_5]; 6.88-7.00 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.40-7.44 m, [H_2, H_6]; 7.65 m, [$H_{6'}$]
$(dppm)Pt(CH_2SiMe_2Ph)_2$[c]	1.16 (**86.6**)	0.01	7.12-7.21 m, [H_3, H_4, H_5]; 7.45 dd, [H_2, H_6] (**7.9**)	4.19 m, (**18.8**) [P-CH_2] (J_{P-H} = 20.4 Hz); 7.22-7.37 m, [H_3, H_4, H_5]; 7.50 m, [H_2, H_6]

Table 3.2 : (continued)

(dppe)Pt(CH_2SiMe_2Ph)$_2$[c]	1.32 (**81.1**)	0.20	7.17-7.21 m, [H_3, H_4, H_5]; 7.52 dd, [H_2, H_6] (**6.9**)	1.75 m, [P-CH_2]; 7.00-7.15 m, [H_3, H_4, H_5]; 7.43 m, [H_2, H_6]
(dppp)Pt(CH_2SiMe_2Ph)$_2$[a]	0.74 (**80.3**)	0.08	d [H_3, H_4, H_5]; 7.52 dd, [H_2, H_6] (**6.3**)	1.85[g] m, [C_BH_2]; 2.42[g] m, [C_AH_2, C_CH_2]; 7.17-7.33 m, [H_3, H_4, H_5]; 7.42 m, [H_2, H_6]
(dppb)Pt(CH_2SiMe_2Ph)$_2$[c]	1.16 (**79.2**)	0.40	7.19-7.26 m, [H_3, H_4, H_5]; 7.65 dd, [H_2, H_6] (**7.4**)	1.44[g] m, [C_BH_2, C_CH_2]; 2.09[g] m, [C_AH_2, C_DH_2]; 7.04[g] [H_3, H_4, H_5]; 7.45[g] [H_2, H_6]
(dppf)Pt(CH_2SiMe_2Ph)$_2$[c]	1.12[g]	0.33	7.10-7.17 m, [H_3, H_4, H_5]; 7.56 dd, [H_2, H_6] (**7.9**)	3.71 s, [H_Y, $H_{Y'}$]; 3.99 s, [H_Z,$H_{Z'}$]; 7.05[g] m, [H_3, H_4, H_5]; 7.70[g] m, [H_2, H_6]

a :- chloroform-d[1]
b :- partially obscured by ligand resonances
c :- benzene-d[6]
d :- obscured
e :- toluene-d[8]
f :- obtained at 90 MHz
g :- broad resonance

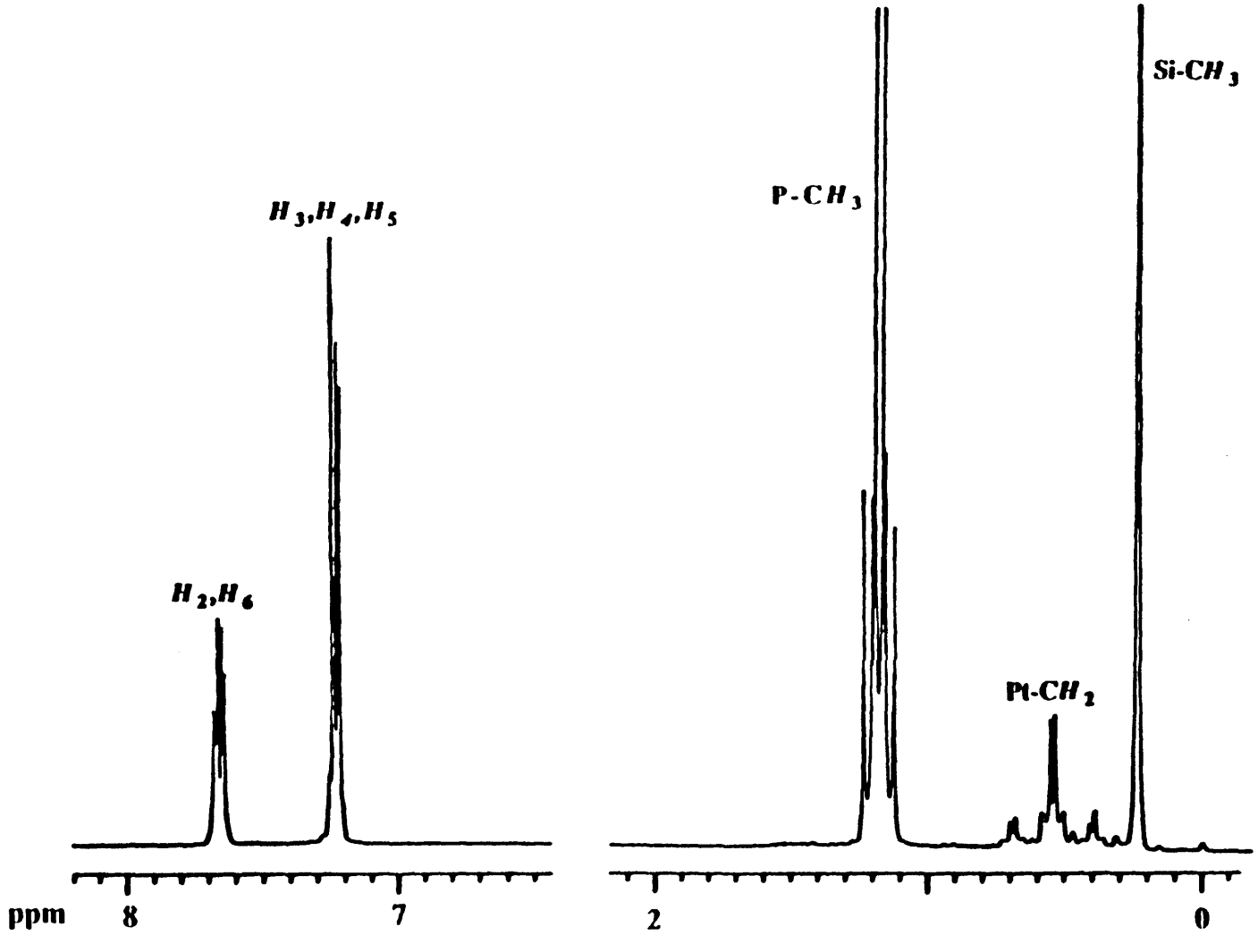


Fig. 3.2 : ^{1}H *N.M.R. of* $(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$.

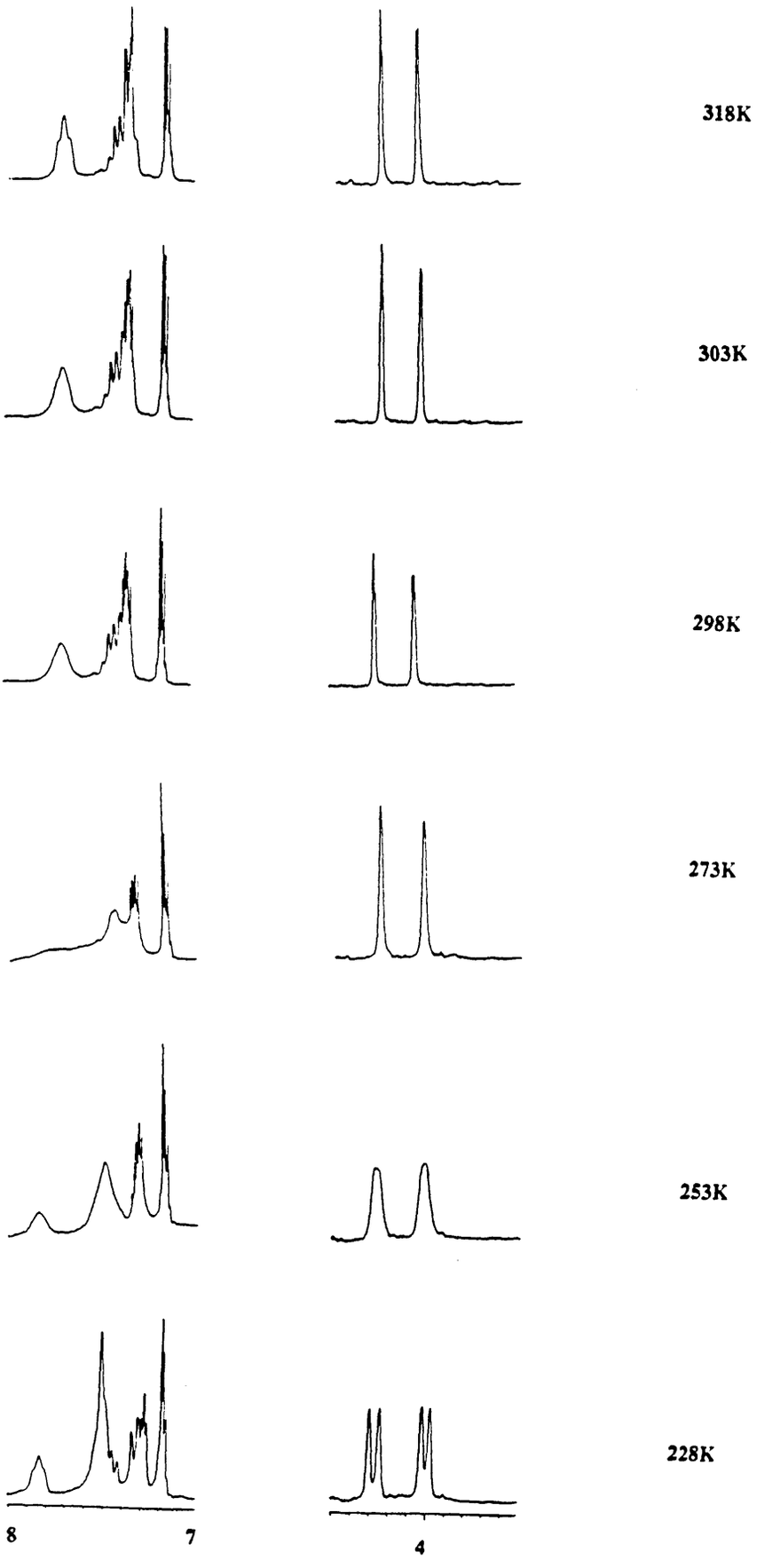


Fig. 3.3 : *Temperature Dependent ^1H N.M.R. Spectra of (dppf)Pt($CH_2SiMe_2Ph)_2$.*

Table 3.3 : *Variable Temperature ^1H N.M.R. Data for (dppf)Pt(CH_2SiMe_2Ph)$_2$.*

Resonance	T_c/K^a	$\Delta\upsilon/Hz^b$	k_c/s^{-1c}	$\Delta G_c^{\ddagger}/kJ\ mol^{-1d}$
H_2, H_6	275	102.3	227.2	54.76
H_Y, $H_{Y'}$	253	17.8	39.3	53.88
H_Z, $H_{Z'}$	251	16.2	38.2	53.66

a :- Error ± 1K
b :- Error ± 2%
c :- Error ± 2%
d :- Error ± 1%

The complex lacks a plane of symmetry unless the phosphine adopts a *syn*-eclipsed conformation on chelation[79], resulting in conformers which are enantiomeric (Fig. 3.4). H_Y and $H_{Y'}$ are now magnetically inequivalent, as are H_Z and $H_{Z'}$, and generate distinct resonances. Assuming that there is negligible coupling between hydrogens on different Cp rings, the observed low temperature spectrum (representing ideally an $A_2B_2C_2D_2$ system) may be explained by slow exchange of these conformers. At higher temperatures, rapid exchange gives rise to a time-averaged spectrum ($A_2A_{2'}B_2B_{2'}$) in which H_Y, $H_{Y'}$ and H_Z, $H_{Z'}$ exhibit single resonances. Similarly the two phenyl

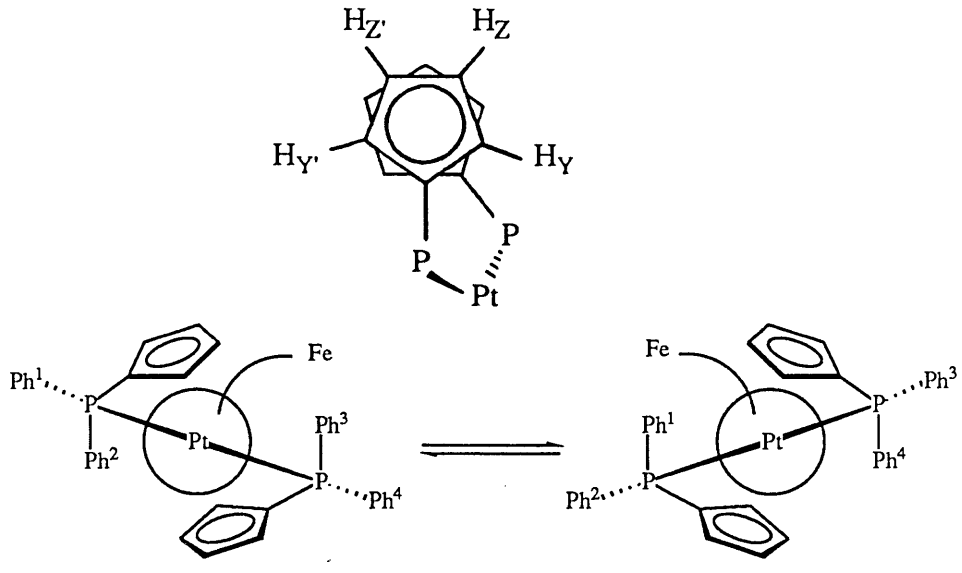


Fig. 3.4 : *Conformational Projections for (dppf)Pt(CH_2SiMe_2Ph)$_2$.*

substituents on each phosphorus are magnetically non-equivalent. Although all the phenyl hydrogens exhibit this type of behaviour, it is most prominent in the resonances due to H_2 and H_6 which collapse forming a broadened triplet at higher temperatures[80]. Assuming that the values of $\Delta G_c^{\ddagger}$ derive from the same process, then $\Delta H_c^{\ddagger}$ is estimated at 43.0 (± 1.0) kJ mol^{-1} and $\Delta S_c^{\ddagger}$ at -43.4 (± 2.0) JK^{-1} mol^{-1}. These values are very similar to those observed previously for related systems[77] indicating that the process is essentially independent of the nature of the alkyl group.

3.2.2. ^{31}P N.M.R.

The $^{31}P\{^1H\}$-N.M.R. data for *bis*-(sila-neophyl)*bis*-(phosphine)platinum(II) complexes are listed in Table 3.4. Spin-spin coupling of ^{31}P to ^{195}Pt results in the

Table 3.4 : *^{31}P N.M.R. Characteristics for* bis-*(sila-neophyl)platinum(II) Complexes with P-donor Ligands.*

Complex	δ^a / ppm	$J_{Pt\text{-}P}$ / Hz
$(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$ [b]	-28.1	1987.2
$(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$ [c]	2.6	2015.9
$(PMe_2Ph)_2Pt(CH_2SiMe_2Ph)_2$ [b]	-16.9	2020.4
$(PMePh_2)_2Pt(CH_2SiMe_2Ph)_2$ [b]	0.9	2029.2
$(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$ [c]	23.3	2033.7
$(P\text{-}p\text{-}tol_3)_2Pt(CH_2SiMe_2Ph)_2$ [d]	21.7	2053.6
$(PPh_2\text{-}o\text{-}tol)_2Pt(CH_2SiMe_2Ph)_2$ [d]	22.3	1976.1
$(PPh_2C_6H_4\text{-}o\text{-}CF_3)_2Pt(CH_2SiMe_2Ph)_2$ [d]	34.0	2029.2 ($J_{P\text{-}F}$ = 4.4 Hz)
(dppm)$Pt(CH_2SiMe_2Ph)_2$ [b]	-43.5	1615.0
(dppe)$Pt(CH_2SiMe_2Ph)_2$ [c]	40.8	1953.9
(dppp)$Pt(CH_2SiMe_2Ph)_2$ [d]	-1.3	1922.9
(dppb)$Pt(CH_2SiMe_2Ph)_2$ [b]	11.5	1996.0
(dppf)$Pt(CH_2SiMe_2Ph)_2$ [b]	18.1	2060.3

a :- referenced to 85% H_3PO_4 / D_2O

b :- chloroform-d^1

c :- toluene-d^8

d :- benzene-d^6

expected "triplet" observed for all these complexes. For L = $PPh_2C_6H_4$-2-CF_3 a "triplet" of quartets due to coupling of three ^{19}F nuclei to ^{31}P was anticipated, instead, a broad "triplet" was observed. The ^{19}F N.M.R. however, showed the expected doublet with $^4J_{P\text{-}F} = 4.4$ Hz. With the exception of (dppm)Pt($CH_2SiMe_2Ph)_2$, the $^1J_{Pt\text{-}P}$ coupling constants are in the range 1950-2065 Hz, typical for *cis-bis*-(phosphine)platinum(II) dialkyl compounds[30b, 41, 77]. The especially low value of 1615 Hz for (dppm)Pt($CH_2SiMe_2Ph)_2$ is a general feature of this ligand and can be ascribed to angular constraints around Pt and P due to formation of the four-membered ring[81].

Phosphorus nuclei incorporated in chelate rings display a ring contribution , Δ_R, to their chemical shift change upon co-ordination. The magnitude and direction of Δ_R depend on ring substitution and size[82]. The ring contribution, defined as $\Delta_R = \Delta - \Delta_{R^\circ}$ [where Δ is the difference in the chemical shift upon coordination ($\delta P - \delta F$) and Δ_{R° is a standard ring contribution] has been determined for the series of bidentate phosphine complexes (Table 3.5). From this it can be noted that the four-membered ring has a shielding effect relative to ($PPh_2Me)_2$Pt($CH_2SiMe_2Ph)_2$, whilst the five-membered ring has a deshielding effect. These values are in good agreement with those obtained for other L_2PtR_2 compounds (L = dppm, dppe, dppp, dppb; R = Me, $CH_2SiMe_2CH_2$:CH_2, CH_2SiMe_3)[41, 77, 82].

Table 3.5 : *Ring Contributions for $L_2Pt(CH_2SiMe_2Ph)_2$ Complexes*[a].

L	δP/ppm	δF/ppm	Δ/ppm	Δ_R/ppm	Chelate ring size
dppm[b]	-43.5	-22.7	-20.8	-57.9	4
dppe[c]	40.8	-13.2	+54.0	+16.9	5
dppp[d]	-1.3	-17.3	+16.0	-12.1	6
dppb[b]	11.5	-15.0	+26.5	-0.6	7
dppf[b]	18.1	-28.1	+29.0	-8.1	(7)
PPh_2Me[b]	0.9	-28.1	+37.1	0.0	-

a :- free phoshine chemical shifts obtained from Ref. 82

b :- chloroform-d^1

c :- toluene-d^8

d :- benzene-d^6

Also noteworthy is the magnitude of $^1J_{Pt-P}$, which is consistently *ca.* 300 Hz greater in sila-neophyl than in neophyl analogues. The same trend has been observed in comparison of analogous neopentyl and trimethylsilylmethyl derivatives[50]. In both cases, the data suggest that β-sila-alkyl ligands exert a weaker *trans*-influence than their carbon analogues (*vide supra*).

3.2.3. ^{13}C N.M.R.

$^{13}C\{^1H\}$ N.M.R. characteristics of sila-neophyl complexes are presented in Table 3.6. Assignments have been made by comparison with the free ligand, by the magnitude of Pt-C coupling constants and peak intensities and are in accord with those noted elsewhere[30b, 41, 51, 77]. Typically (Fig. 3.5), carbon atoms on coordinated phosphine show coupling to both ^{31}P and ^{195}Pt producing a doublet of "triplets". $^3J_{Pt-C}$ coupling is observed to the silicon bound methyl groups and C_1 of the aromatic ring. The magnitude of this coupling constant is 20-30 Hz. It can be noted that for unhindered monodentate phosphines, the values of $^3J_{Pt-C}$ for Si-CH_3 groups is noticeably larger than for Si-C_1. As the steric bulk of the ligand is increased, a decrease in $^3J_{Pt-C_{methyl}}$ and a corresponding increase in J_{Pt-C_1} is observed; presumably reflecting changes in the magnitude of Pt-CH_2-Si skeleton. Similarly a corresponding increase in the magnitude of $^1J_{Pt-C}$ from PMe_3 (524 Hz) to $PPh_2C_6H_4$-2-CF_3 (587 Hz) is observed.

The magnitude of $^1J_{Pt-C}$ for sila-neophyl derivatives is characteristically *ca.* 160 Hz smaller than that for the neophyl analogues and are very similar to those for corresponding $L_2Pt(CH_2SiMe_3)_2$ and $L_2Pt(CH_2SiMe_2CH_2{:}CH_2)_2$. For instance, in (dppe)$Pt(CH_2SiMe_2Ph)_2$ the reduction of 133 Hz in $^1J_{Pt-C}$ is matched by an increase in $^1J_{Pt-P}$ of 370 Hz. The extent of change in $^1J_{Pt-C}$ (23.5%) is comparable and typical for analogues for which comparative data are available (Fig. 3.6). This may be attributed to a greater carbon 2s contribution to Pt-C bonding for the more electronegative neophyl group and has been discussed extensively elsewhere (*vide supra*). As mentioned previously sila-neophyl appears to exert a lesser *trans*-influence than neophyl. Ancillary ligand dislocation is often a prerequisite for thermolytic rearrangements of this type, so such a difference in ground state energies may have a kinetic influence on lability and contribute to the usually readier reactivity of neophyl complexes relative to silicon-bearing analogues. As emerges, however, the patterns of reactivity for sila-neophyl and neophylplatinum(II) analogues may differ completely (See Chapter 5).

3.2.4. Infrared Spectroscopy.

Selected infrared data are listed in the experimental section. These complexes show the same characteristic vibrations in the sila-neophyl skeleton as those previously described (See 2.2.5). Additionally, the band at 1090 cm^{-1} is a characteristic P-Ph X-sensitive band and bands occurring at 545-520 cm^{-1} are out of plane C-H bending modes typical of phosphine bound phenyl groups.

Table 3.6 : *^{13}C N.M.R. Characteristics of* bis-*(sila-neophyl)platinum(II) Complexes with Phosphorus Donor Ligands.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*]			δ ^{13}C ppm : Ancillary ligands (J_{Pt-C}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Aromatic	
$(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$[a]	5.97, 8.63	2.32	126.97 [C_3, C_5];	17.17 (**29.4**) [P-CH_3]
	(**524.6**)	(**28.4**)	127.34 [C_4];	(J_{C-P} = 31.4 Hz)
	($J_{C-P_{Trans}}$=94.3 Hz)		134.29 [C_2, C_6];	
	($J_{C-P_{Cis}}$ = 8.8 Hz)		146.37 (**21.8**) [C_1]	
$(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$[a]	3.12, 4.62	2.80	127.13 [C_3, C_5];	8.28 [P-CH_2-CH_3]
	(**540.7**)	(**28.6**)	127.31 [C_4];	(J_{C-P} = 17.9 Hz);
	($J_{C-P_{Trans}}$=94.0 Hz)		133.85 [C_2, C_6];	16.92 (**24.1**) [P-CH_2CH_3]
	($J_{C-P_{Cis}}$ = 8.0 Hz)		146.55 (**23.1**) [C_1]	(J_{C-P} = 27.2 Hz)
$(PMe_2Ph)_2Pt(CH_2SiMe_2Ph)_2$[a]	4.22, 5.70	2.51	127.15 [C_3, C_5];	14.83 (**28.7**) [P-CH_3]
	(**536.2**)	(**27.5**)	127.45 [C_4];	(J_{C-P} = 31.5 Hz);
	($J_{C-P_{Trans}}$=93.6 Hz)		134.20 [C_2, C_6];	128.02 (**13.8**) [C_3, C_5]
	($J_{C-P_{Cis}}$ = 8.3 Hz)		146.19 (**23.6**) [C_1]	(J_{C-P} = 8.3 Hz); 129.21 [C_4];

Table 3.6 : (continued)

$(PMe_2Ph)_2Pt(CH_2SiMe_2Ph)_2$[a]				130.87 (**13.9**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.6 Hz); 138.96 (**17.2**) [C_1] ($J_{C\text{-}P}$ = 45.0 Hz)
$(PPh_2Me)_2Pt(CH_2SiMe_2Ph)_2$[a]	5.28, 6.75 (**551.6**) ($J_{C\text{-}P_{Trans}}$=92.5 Hz) ($J_{C\text{-}P_{Cis}}$ = 7.4 Hz)	2.44 (**26.8**)	127.02 [C_3, C_5]; 127.31 [C_4]; 134.08 [C_2, C_6]; 146.05 (**25.8**) [C_1]	14.24 (**22.7**) {*P-CH*$_3$] ($J_{C\text{-}P}$ = 31.3 Hz); 127.84 (**12.9**) [C_3, C_5] ($J_{C\text{-}P}$ = 9.4 Hz); 129.26 [C_4]; 132.86 (**13.5**) [C_3, C_5] ($J_{C\text{-}P}$ = 10.1 Hz); 136.08 (**19.6**) [C_1] ($J_{C\text{-}P}$ = 44.6 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$[a]	6.38, 7.84 (**575.9**) ($J_{C\text{-}P_{Trans}}$=92.2 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.1 Hz)	2.66 (**24.4**)	126.87 [C_3, C_5]; 127.17 [C_4]; 134.16 [C_2, C_6]; 145.80 (**28.1**) [C_1]	127.40 (**7.0**) [C_3, C_5] ($J_{C\text{-}P}$ = 8.3 Hz); 129.16 [C_4]; 133.48 (**18.9**) [C_1] ($J_{C\text{-}P}$ = 44.2 Hz); 134.77 (**11.8**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.8 Hz)

Table 3.6 : (continued)

(P-*p*-tol$_3$)$_2$Pt(CH$_2$SiMe$_2$Ph)$_2$[a]	5.53, 7.13 (**573.9**) ($J_{C\text{-}P_{Trans}}$=92.7 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.5 Hz)	2.75 (**23.4**)	126.76 [C_3, C_5]; 126.99 [C_4]; 134.08 [C_2, C_6]; 146.26 (**29.6**) [C_1]	21.16 [*Ar-CH$_3$*]; 128.00 (**14.5**) [C_3, C_5] ($J_{C\text{-}P}$ = 8.6 Hz); 130.60 (**18.7**) [C_1] ($J_{C\text{-}P}$ = 46.33 Hz); 134.73 (**12.3**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.9 Hz); 138.91 [C_4]
(PPh$_2$-*o*-tol)$_2$Pt(CH$_2$SiMe$_2$Ph)$_2$[a]	4.97, 6.44 (**587.3**) ($J_{P\text{-}C_{Trans}}$=92.1 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.1 Hz)	2.22 (**22.1**)	126.85 [C_3, C_5]; 127.14 [C_4]; 133.87 [C_2, C_6]; 145.78 (**31.0**) [C_1]	23.15 [*Ar-CH$_3$*]; 125.05 [$C_{5'}$] ($J_{C\text{-}P}$ = 10.8 Hz); 127.38 [$C_{3'}$]; 127.49 [C_3, C_5]; 128.85 [C_4]; 130.08 [$C_{4'}$]; 131.33 [$C_{6'}$] ($J_{C\text{-}P}$ = 4.9 Hz); 134.94 (**12.3**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.9 Hz); 135.24 [$C_{2'}$]; 138.00 [C_1] ($J_{C\text{-}P}$ = 14.0 Hz); 142.75 [$C_{1'}$]
(dppm)Pt(CH$_2$SiMe$_2$Ph)$_2$[b]	2.74, 4.34 (**571.2**) ($J_{C\text{-}P_{Trans}}$=94.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 7.0 Hz)	2.62 (**27.9**)	127.47 [C_3, C_5]; c [C_4]; 134.32 [C_2, C_6]; 146.33 (**29.1**) [C_1]	48.55 (**10.6**) [*P-CH$_2$-P*]; ($J_{C\text{-}P}$ = 50.7 Hz); 128.79 (**10.3**) [C_3, C_5] ($J_{C\text{-}P}$ = 9.9 Hz); 130.35 [C_4];

Table 3.6 : (continued)

(dppm)Pt(CH_2SiMe_2Ph)$_2$[b]				132.67 (**26.5**) [C_1] (J_{C-P} = 19.6 Hz); 133.18 (**13.8**) [C_2, C_6] (J_{C-P} = 12.1 Hz)
(dppe)Pt(CH_2SiMe_2Ph)$_2$[a]	-0.04, 1.38 (**548.6**) ($J_{C-P_{Trans}}$=89.7 Hz) ($J_{C-P_{Cis}}$ = 5.1 Hz)	1.76 (**36.5**)	126.89 [C_3, C_5]; 127.04 [C_4]; 133.71 [C_2, C_6]; 146.55 (**34.6**) [C_1]	27.70 m, [*P*-CH_2-CH_2-*P*]; 128.28 [C_3, C_5] (J_{C-P} = 9.7 Hz); 130.13 [C_4]; 132.91 (**26.3**) [C_1] (J_{C-P} = 45.2 Hz); 133.50 [C_2, C_6] (J_{C-P} = 11.0 Hz)
(dppp)Pt(CH_2SiMe_2Ph)$_2$[a]	4.47, 5.94 (**551.4**) ($J_{C-P_{Trans}}$=92.5 Hz) ($J_{C-P_{Cis}}$ = 9.5 Hz)	2.47 (**25.7**)	126.79 [C_3, C_5]; 127.47 [C_4]; 134.17 [C_2, C_6]; 146.26 (**25.4**) [C_1]	20.05 [C_BH_2]; 26.74 m, [C_AH_2]; 127.88 (**9.3**) [C_3, C_5] (J_{C-P} = 8.3 Hz); 128.23 [C_4]; 133.46 (**12.7**) [C_2, C_6] (J_{C-P} = 14.2 Hz); 135.00 (**19.3**) [C_1] (J_{C-P} = 30.6 Hz)

Table 3.6 : (continued)

(dppb)Pt(CH_2SiMe_2Ph)$_2$[b]	5.84, 7.29 (**552.8**) ($J_{C\text{-}P_{Trans}}$=90.9 Hz) ($J_{C\text{-}P_{Cis}}$ = 7.3 Hz)	2.68 (**26.8**)	127.32 [C_3, C_5]; 127.42 [C_4]; 134.61 [C_2, C_6]; 146.38 (**25.5**) [C_1]	27.47 [C_BH_2]; 27.69 m, [C_AH_2]; 128.30 [C_3, C_5] ($J_{C\text{-}P}$ = 4.8 Hz); 129.62 [C_4]; 133.97 d, [C_2, C_6]; 135.65 (**22.6**) [C_1] ($J_{C\text{-}P}$ = 44.8 Hz)
(dppf)Pt(CH_2SiMe_2Ph)$_2$[a,e]	5.42, 6.91 (**559.4**) ($J_{C\text{-}P_{Trans}}$ = 93.8 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.1 Hz)	2.36 d	126.80 [C_3, C_5]; 127.14 [C_4]; 133.93 [C_2, C_6]; 146.03 (**29.3**) [C_1]	71.93 [C_Z, $C_{Z'}$]; 74.85 [C_Y, $C_{Y'}$] ($J_{C\text{-}P}$ = 3.1 Hz); 77.79 (**51.6**) [C_X]; 127.66 [C_3, C_5]; ($J_{C\text{-}P}$ = 7.0 Hz); 128.31 [C_4]; 134.27 d, [C_1]; 134.98 d,[C_2, C_6]

a :- chloroform-d^1

b :- benzene-d^6

c :- obscured

d :- broad resonance

e :- run at -10°C

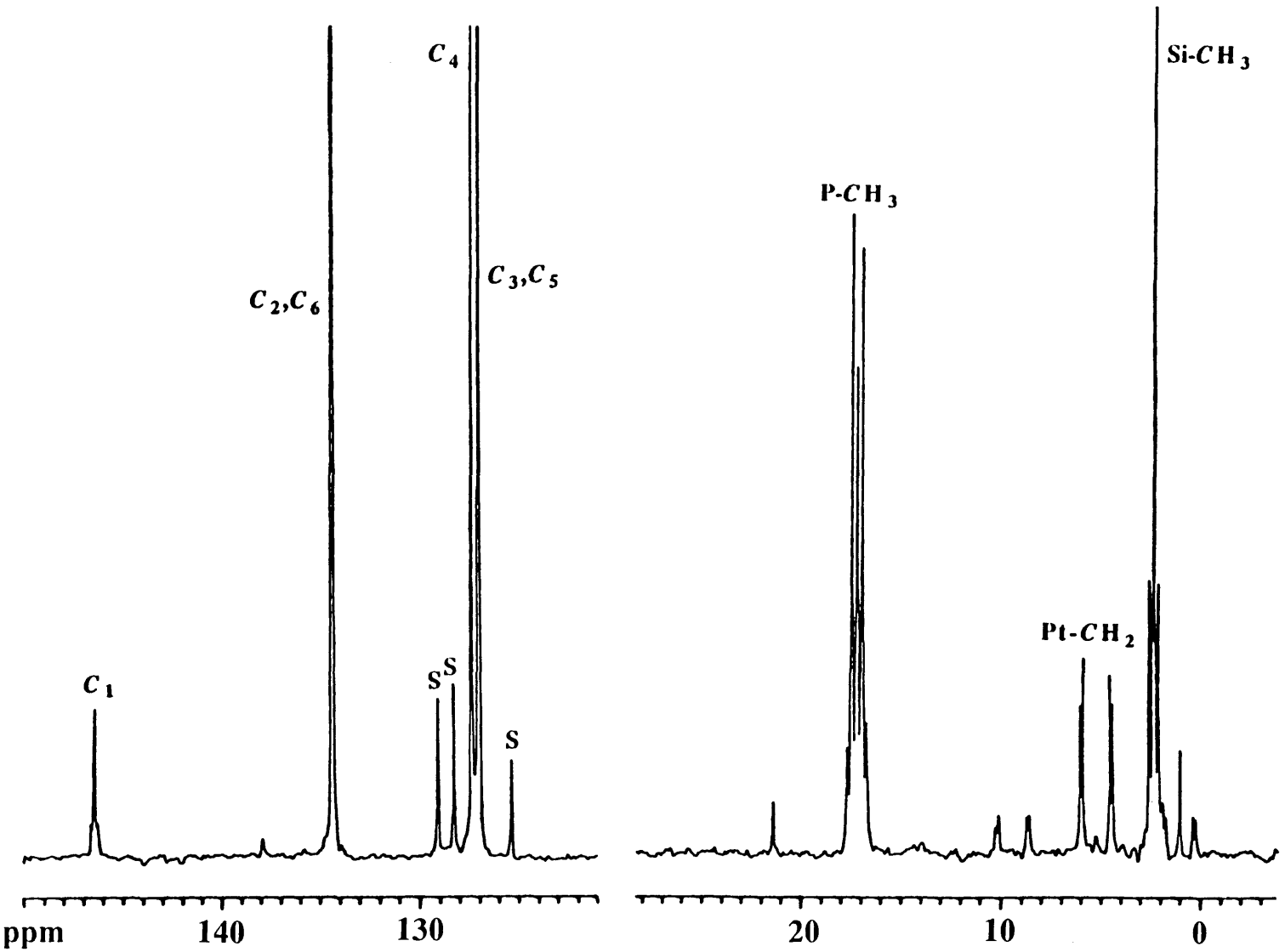


Fig. 3.5 : ^{13}C *N.M.R. of* $(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$.

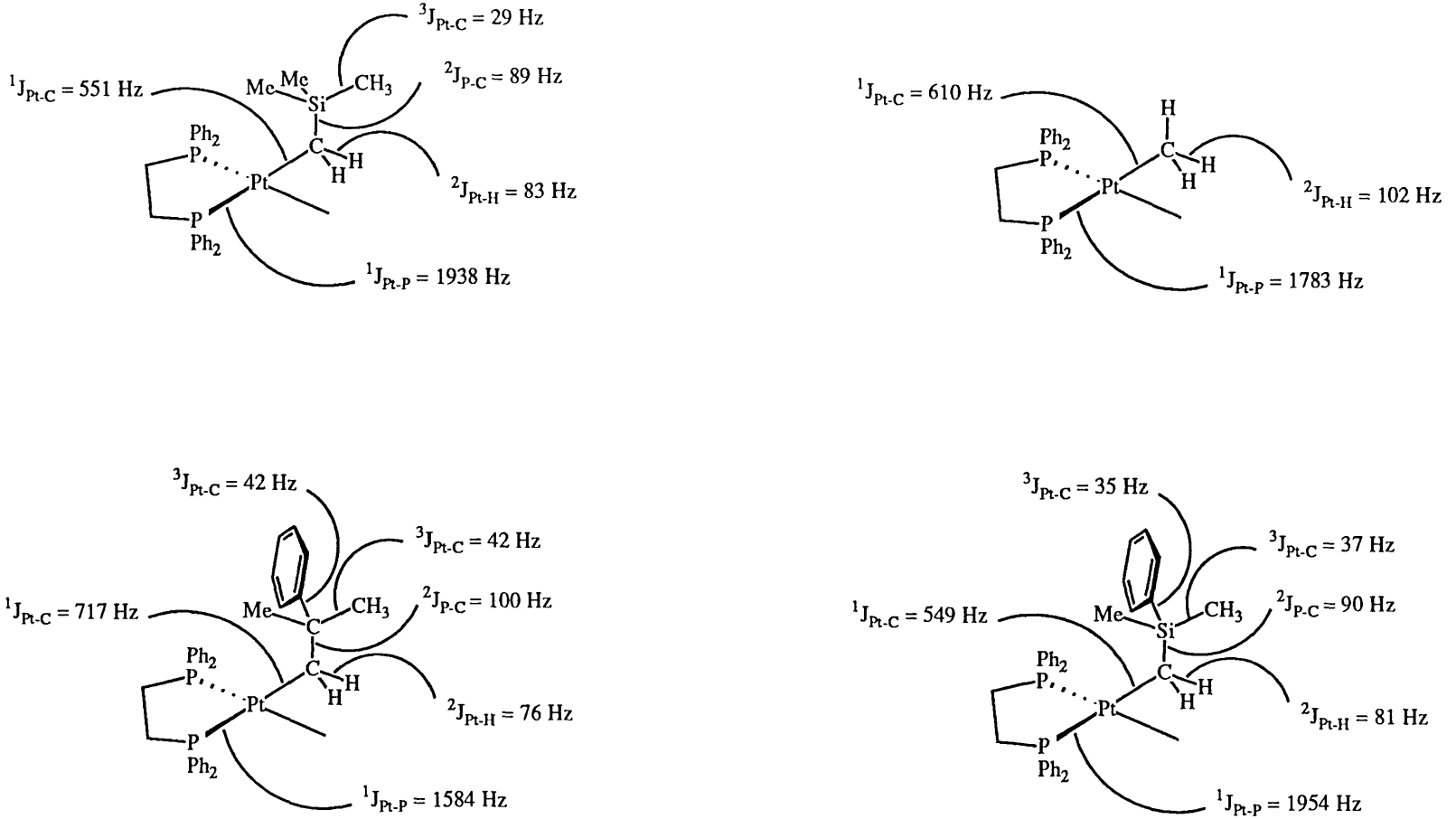


Fig 3.6 : *Comparative N.M.R. Data for (dppe)PtR_2 [R = Me, CH_2SiMe_3, $CH_2CH_2CMe_2Ph$, CH_2SiMe_2Ph].*

3.3. Experimental.

3.3.1. General.

Elemental analyses were determined by Imperial College Microanalytical Laboratories. N.M.R. spectra were recorded on Brücker WM250 (^{1}H, 250.13 MHz; ^{13}C, 62.9 MHz), Jeol GSX270 (^{1}H, 270.17 MHz; ^{13}C, 67.9 MHz) and Jeol FX90Q (^{1}H, 89.55 MHz; ^{31}P, 36.21 MHz) spectrometers. IR. data were collected on a Perkin-Elmer 683 or Perkin-Elmer 1720 FT instruments as 4% KBr dispersions.

All reactions were carried out under argon, using standard anaerobic techniques. All apparatus was flame dried before use[68]. Solvents were distilled under nitrogen prior to use: diethyl ether and *n*-hexane from sodium/benzophenone; toluene from sodium.

Cycloocta-1,5-diene, [2.2.1] bicyclohepta-2,5-diene, phosphorus trichloride, diphenylchlorophosphine, triphenylphosphine, *bis*-(1,2-diphenylphosphino)ethane, *bis*-(1,3-diphenylphosphino)propane, and *bis*-(1,1'-diphenylphosphino)ferrocene were all used as supplied by Aldrich Chem. Co.. Trimethylphosphine, triethylphosphine, dimethylphenylphosphine and diphenylmethylphosphine, supplied by Strem Chemicals were stored under argon but used without further purification.
Bis-(diphenylphosphino)methane and *bis*-(1,4-diphenylphosphino)butane were used as supplied by Strem Chemicals.

3.3.2. Syntheses.

Preparation of tri-p-*tolylphosphine*[83].

A solution of $BrMgC_6H_4$-4-CH_3 (50 mmol) in diethyl ether (15 cm^3) was added to a stirred solution of PCl_3 (2.00g, 14.6 mmol) in Et_2O (40 cm^3). The mixture, which had turned cloudy, was refluxed for 24 hours, then cooled to -20°C and quenched with saturated ammonium chloride solution (30 cm^3). The organic layer was separated and the aqueous phase washed with Et_2O (2 x 10 cm^3). The combined ether extracts were dried over $MgSO_4$, decolourised with charcoal and filtered. Removal of the diethyl ether *in vacuo* yielded a pale yellow solid, which was recrystallised from the minimum amount of hot ethanol (7 cm^3) affording colourless crystals of tri-*p*-tolylphosphine.
(Yield : 2.93g, 9.6mmol, 66%).

[^{31}P : $\delta \equiv$ -6.90 ppm, s]

Preparation of diphenyl-o-*tolylphosphine*[83].

To a stirred solution of PPh_2Cl (2.00g, 9.1 mmol) in Et_2O (15 cm^3) cooled to 0°C was added dropwise a solution of $BrMgC_6H_4$-2-CH_3 in diethyl ether (50 cm^3). Upon addition, the reaction mixture was stirred vigorously for 24 hours then cooled to -25°C and quenched with saturated ammonium chloride solution (30 cm^3).The organic layer was separated and the aqueous phase repeatedly washed with diethyl ether (3 x 15 cm^3) until

the washings were colourless. The ether extracts were combined, dried over $MgSO_4$, decolourised with activated charcoal, filtered and evaporated to dryness *in vacuo*, yielding a pale yellow crystalline solid. The solid was dissolved in hot ethanol (10 cm^3) and cooled slowly to ambient temperature. The white crystalline solid was filtered, washed with cold ethanol (2 x 4 cm^3) and dried *in vacuo*.
(Yield : 2.26g, 8.2 mmol, 90%).

[^{31}P : $\delta \equiv$ -14.1 ppm, s]

*Preparation of diphenyl-*o*-trifluoromethylphenylphosphine*[84].

Diphenyl-*o*-trifluoromethylphenylphosphine was prepared as a white crystalline solid by the reaction of excess LiC_6H_4-2-CF_3 and PPh_2Cl by a method analogous to that used for diphenyl-*o*-tolylphosphine.
(Yield : 2.12g, 6.4 mmol, 71 %).

[^{31}P : $\delta \equiv$ -11.4 ppm, q; J_{P-F}=53.2 Hz]

Preparation of -cis-bis-*(trimethylphosphine)*-bis-*(sila-neophyl)platinum(II).*

(cod)Pt($CH_2SiMe_2Ph)_2$ (0.20g, 0.33 mmol) was dissolved in toluene (10 cm^3) and trimethylphosphine (100 µl, 0.76 mmol) added by microsyringe. The reaction mixture was heated to 60°C for 14 days.The toluene was removed *in vacuo* to give a white solid, which was recrystallised from toluene (1 cm^3) and *n*-hexane (0.5 cm^3) and cooled to -20°C to give colourless crystals of $(PMe_3)_2Pt(CH_2SiMe_2Ph)_2$.
(Yield : 0.19g, 0.29 mmol, 89%).

I.R. : 1421m, 1283m, 1258wm, 1250m, 1233s, 1102s, 967s, 961s, 946vs, 936s, 809vs, 763s, 729s, 714s, 539m.

Preparation of cis-bis-*[(diphenylphosphino)methane*-bis-*(sila-neophyl)platinum(II).*

(nbd)Pt($CH_2SiMe_2Ph)_2$ (0.20g, 0.34 mmol) was dissolved in toluene (8 cm^3) and dppm (0.131g, 0.34 mmol) added. After 10 days at 60°C, the toluene was removed *in vacuo* affording a pale yellow crystalline solid. Recrystallisation from dichloromethane (2 cm^3) and methanol (1 cm^3) gave the product as a white crystalline solid.
(Yield : 0.27g, 0.31 mmol, 91%)

I.R. : 1485wm, 1438s, 1426 wm, 1265m, 1242m, 1109s, 1031m, 831vs, 819vs, 729vs, 702vs, 694vs, 585 m, 502s, 478m.

Prepared according to the same procedure were :-

cis-bis-*[(1,4-diphenylphosphino)butane*-bis-*(sila-neophyl)platinum(II).*
Product : White crystalline solid from dichloromethane and *n*-hexane.
(Yield : 0.16g, 0.17 mmol, 85%)

I.R. : 1485wm, 1438s, 1426m, 1265m, 1238m, 1109s, 1097s, 1031m, 839s, 811vs, 745s, 729s, 702 vs, 533m, 506s.

cis-bis-*[(1,3-diphenylphosphino)propane]*-bis-*(sila-neophyl)platinum(II).*
Product : White crystalline solid from dichloromethane and methanol.
(Yield : 0.26g, 0.29 mmol, 85%)

I.R. : 1489wm, 1438s, 1426m, 1265m, 1241m, 1109s, 839vs, 815vs, 718m, 737s, 702vs, 666m, 518vs.

Preparation of cis-bis-*(dimethylphenylphosphine)*-bis-*(sila-neophyl)platinum(II).*
(nbd)Pt($CH_2SiMe_2Ph)_2$ (0,20g, 0.34 mmol) was dissolved in diethyl ether (6 cm^3), dimethylphenylphosphine (120 µl, 0.70 mmol) added and the solution allowed to stand at ambient temperature for 7 days. The solvent was removed *in vacuo*, dissolved in the minimum of benzene (1 cm^3) and *n*-hexane (0.5 cm^3) added. Cooling to -20°C produced colourless crystals of the product.
(Yield : 0.25g, 0.32 mmol, 95%)

I.R. : 1440m, 1302m, 1240s, 942s, 917s, 906m, 837vs, 815vs, 765s, 753s, 543s, 504s, 489m, 430s.

Prepared according to an analogous procedure were :-

cis-bis-*(diphenylmethylphosphine)*-bis-*(sila-neophyl)platinum(II).*
Product : Colourless crystals from *n*-hexane.
(Yield : 0.23g, 0.26 mmol, 76%)

I.R. : 1433m, 1330m, 1236s, 939s, 910s, 904s, 839s, 831vs, 811vs, 762s, 747s, 726s, 706m, 539s, 494m, 424s.

cis-bis-*(triethylphosphine)*-bis-*(sila-neophyl)platinum(II).*
Product : Colourless crystals from *n*-hexane.
(Yield : 0.23g, 0.315 mmol, 93%)

I.R. : 1575m, 1457m, 1426m, 1379m, 1265m, 1242m, 1113s, 1038s, 1031s, 835s, 819vs, 772vs, 741vs, 721s, 709vs, 635m, 475m.

cis-bis-*(triphenylphosphine)*-bis-*(sila-neophyl)platinum(II).*
Product : White crystalline solid from benzene and *n*-hexane.
(Yield : 0.34g, 0.33 mmol, 98%)

I.R. : 1482m, 1476m, 1431s, 1247m, 1103m, 1092s, 828s, 806s, 763m, 737s, 722s, 692vs, 544m.

cis-bis-*(tri*-p-*tolylphosphine)*-bis-*(sila-neophyl)platinum(II).*
Poduct : White crystalline solid from benzene and *n*-hexane.
(Yield : 0.42g, 0.38 mmol, 89%)

I.R. : 1504s, 1430m, 1402wm, 1242m, 1191m, 1113s, 1101s, 831s, 806vs, 726s, 680s, 628s, 524vs, 514vs, 499m, 448m.

cis-bis-*(diphenyl*-o-*tolylphosphine)*-bis-*(sila-neophyl)platinum(II).*
Product : White crystalline solid from benzene and *n*-hexane.
(Yield : 0.28g, 0.27 mmol, 79%)

I.R. : 1481wm, 1438s, 1246m, 1113s, 1101s, 829s, 805vs, 747s, 728s, 698vs, 540m, 529s, 499m, 473s.

cis-bis-*[(1,2-diphenylphosphino)ethane]*-bis-*(sila-neophyl)platinum(II).*
Product : White solid from toluene and *n*-hexane.
(Yield : 0.31g, 0.35 mmol, 93%)

I.R. : 1432m, 1402wm, 1259wm, 1236m, 1102s, 828m, 803vs, 762m, 748s, 741m, 730m, 699vs, 524s.

cis-bis-*[(1,1'-diphenylphosphino)ferrocene]*-bis-*(sila-neophyl)platinum(II).*
Product : Amber crystalline solid from toluene and *n*-hexane.
(Yield : 0.28g, 0.27 mmol, 78%)

I.R. : 1485m, 1438s, 1430m, 1265m, 1242m, 1109s, 1101s, 1042m, 1031s, 835s, 811vs, 749m, 733s, 702vs, 643m, 553m, 498s, 471s.

Preparation of cis-bis-*(diphenyl*-o-*trifluoromethylphenylphosphine)*-bis-*(sila-neophyl)platinum(II).*

To (nbd)Pt(CH_2SiMe_2Ph)$_2$ (0.20g, 0.34 mmol) dissolved in diethyl ether (7 cm^3) was added excess diphenyl-*o*-trifluoromethylphenylphosphine (0.45g, 1.36 mmol). The solution was allowed to remain at ambient temperature for 21 days. After this time, the

reaction had reached 75% completion as established by ^{31}P N.M.R.. Unreacted (nbd)Pt($CH_2SiMe_2Ph)_2$ and excess phosphine were removed by column chromatography at 0°C (neutral alumina, 30 cm) using *n*-hexane as eluent. The product was then obtained using toluene as the eluent. Removal of the solvent *in vacuo* afforded a white solid. ^{31}P N.M.R. showed that the sample was 30% contaminated with the rearranged species. The desired product is very labile and rearranges quickly at ambient temperature in non-polar solvents.

Chapter Four :

SYNTHESIS AND SPECTROSCOPIC STUDIES OF *BIS*-[DIMETHYL(ARYL)SILYLMETHYL] AND *BIS*-[DIMETHYL(BENZYL)SILYLMETHYL] PLATINUM(II) COMPLEXES WITH DIENE, NITROGEN AND PHOSPHORUS DONOR LIGANDS.

4.1. Synthesis of *bis*-[dimethyl(aryl)silylmethyl]platinum(II) and *bis*-[dimethyl(benzyl)silylmethyl]platinum(II) complexes with diene, nitrogen and phosphorus donor ligands.

4.1.1. Synthesis of chloromethyl(dimethyl)arylsilanes and chloromethyl(dimethyl)benzylsilanes.

A series of chloromethyl(dimethyl)arylsilanes and chloromethyl(dimethyl)benzylsilanes has been prepared by modifications of a published procedure[72]. In general, *para*-substituted derivatives could be prepared in moderately good yields by the interaction of chloromethyl(dimethyl)chlorosilane with the appropriate arylmagnesium bromide, generated *in situ* by the reaction of magnesium shot and aryl bromide.

Although *meta*- and *ortho*-substituted arylsilanes could also be prepared analogously, yields were poor. Improved yields were obtained by reacting chloromethyl(dimethyl)chlorosilane with the corresponding aryllithium reagent. Silanes with N,N-dimethylamino or trifluoromethyl group substituents on the aromatic ring were also synthesised by this route. In these cases corresponding Grignard reagents could only be obtained in poor yields, due to intermolecular coupling reactions.

With the exception of chloromethyl(dimethyl)(4-*tert*-butylphenyl)silane and chloromethyl(dimethyl)(4-N,N-dimethylaminophenyl)silane, which are low melting point white solids, all are high boiling, colourless liquids.

4.1.2. Synthesis of diene and pyridine complexes.

The synthesis of diene complexes has been achieved in >70% yield by treatment of either (cod)$PtCl_2$ or (nbd)$PtCl_2$ with the appropriate Grignard reagent. These colourless or white solids are air inert; (nbd)$Pt(CH_2SiMe_2C_6H_4R)_2$ were stored at -20°C to prevent thermolytic decomposition, and have satisfactory analyses (Table 4.1).

Subsequent replacement of the diene by pyridine or 4-*tert*-butylpyridine yielded mostly pale yellow or orange crystalline solids. $(py)_2Pt(CH_2SiMe_2C_6H_4R)_2$ [R = 3-CH_3, 4-F] could only be isolated as pale yellow liquids. Elemental analyses are detailed in Table 4.2. Diene displacement is generally complete in 24 hours in neat ligand solution. Although stable as solids, at room temperature benzene or toluene solutions rapidly undergo rearrangement forming, in most cases, a platinasila-indan and liberating trimethylarylsilane (*vide infra*). $(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$ could not be isolated but has been characterised by ^1H N.M.R. spectroscopy as its pyridine-d^5 analogue.

4.1.3. Synthesis of phosphine complexes.

The majority of complexes were synthesised by displacement of cod by triphenylphosphine at 60°C in diethyl ether. Substitution of diene is characteristically slow,

Table 4.1 : *Analytical Data for* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Diene Ligands.*

Complex	Found (Calculated) %		
	C	H	N
(cod)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2$	53.38 (53.39)	6.76 (6.70)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-3-Me)$_2$	52.97 (53.39)	6.68 (6.70)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2$	53.14 (53.39)	6.71 (6.70)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-4-OMe)$_2$	50.62 (50.81)	6.43 (6.40)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-4-^{t}Bu)$_2$	56.89 (57.19)	7.63 (7.62)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-4-F)$_2$	49.27 (48.96)	5.73 (5.69)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-2-CF_3)$_2$	45.56 (45.58)	4.90 (4.92)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-3-CF_3)$_2$	45.31 (45.58)	4.86 (4.92)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-4-CF_3)$_2$	45.37 (45.58)	4.89 (4.92)	-
(cod)Pt($CH_2SiMe_2C_6H_4$-4-NMe_2)$_2$	52.53 (52.37)	7.25 (7.03)	4.07 (4.04)
(cod)Pt($CH_2SiMe_2C_6F_5$)$_2$	39.80 (39.95)	3.62 (3.61)	-
(cod)Pt($CH_2SiMe_2CH_2Ph$)$_2$	53.19 (53.39)	6.79 (6.70)	-

Table 4.1 : (continued)

(cod)Pt($CH_2SiMe_2CH_2C_6H_4$-4-Me)$_2$	54.81 (54.76)	6.91 (7.05)	-
(nbd)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2$	52.61 (52.83)	6.13 (6.24)	-
(nbd)Pt($CH_2SiMe_2C_6H_4$-3-Me)$_2$	52.72 (52.83)	6.38 (6.24)	-
(nbd)Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2$	52.88 (52.83)	6.29 (6.24)	-

Table 4.2 : *Analytical Data for* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Nitrogen Donor ligands.*

Complex	Colour	Found (Calculated)		
		C %	H%	N%
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Pale Yellow	52.99 (52.92)	5.89 (5.93)	4.06 (4.12)
$(^tBupy)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Pale Orange	57.42 (57.62)	7.23 (7.13)	3.54 (3.54)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$	Pale Yellow	50.81 (50.61)	5.72 (5.66)	3.98 (3.93)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$	Pale Yellow	56.77 (56.59)	6.91 (6.86)	3.72 (3.67)
$(py)_2Pt(CH_2SiMe_2CH_2Ph)_2$	Pale Yellow	52.88 (52.92)	5.81 (5.93)	4.09 (4.12)

Table 4.3 : *Analytical Data for* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Phosphorus Donor ligands.*

Complex	Found (Calculated) %		
	C	H	N
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$	64.34 (64.28)	5.87 (5.78)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$	64.37 (64.28)	5.45 (5.78)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	64.00 (64.28)	5.57 (5.78)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2 \cdot \frac{2}{3} C_6H_6$	63.68 (63.75)	5.87 (5.71)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$	65.94 (65.87)	6.54 (6.42)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$	61.29 (61.52)	5.17 (5.07)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$	58.24 (58.27)	4.62 (4.72)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$	58.17 (58.27)	4.69 (4.72)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$	58.54 (58.27)	4.77 (4.72)	-
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$	62.84 (63.08)	6.83 (7.18)	2.74 (2.54)
$(PPh_3)_2Pt(CH_2SiMe_2CH_2Ph)_2$	63.94 (64.28)	5.86 (5.78)	-
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$	65.09 (64.84)	6.07 (6.00)	-
$(Dppf)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	60.57 (60.29)	5.47 (5.43)	-

often taking *ca.* 28 days for completion. Displacement of nbd was more facile, generally complete within 14 days at 60°C. Norbornadiene was displaced by phosphine at ambient temperature in the case of (nbd)Pt($CH_2SiMe_2C_6H_4$-2-CH_3)$_2$ to preclude any thermolytic rearrangement of the dialkyl complex.

These complexes are air-stable, white crystalline solids with satisfactory microanalytical characteristics (Table 4.3). Only (PPh_3)$_2$Pt($CH_2SiMe_2C_6F_5$)$_2$ was not isolated, although it was observed by ^{1}H and ^{31}P N.M.R. spectroscopy. They do not decompose at room temperature in deoxygenated hydrocarbon solvents but do react slowly with chlorocarbons affording *cis-bis*-(PPh_3)$_2$$PtCl_2$.

4.2. Spectroscopic characteristics of *bis*-[dimethyl(aryl)silyl methyl]platinum(II) and *bis*-[dimethyl(benzyl)silylmethyl] platinum(II) complexes.

4.2.1. Conventions.

The numerical conventions employed for the aromatic ring are shown in Fig. 4.1. In all cases, the silicon-bound carbon of the aromatic ring is designated C_1, while the substituents are attached either to C_2, C_3 or C_4.

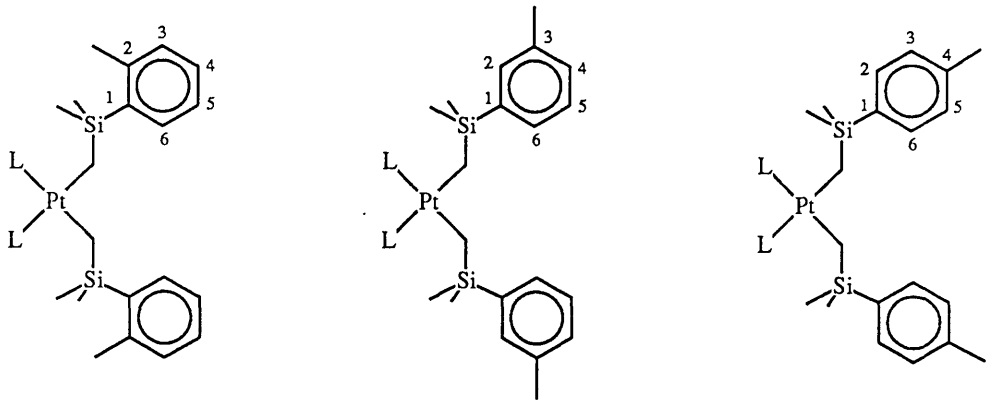


Fig. 4.1 : *N.M.R. Numbering Conventions for Substituted Sila-neophyl Groups.*

4.2.2. ^{1}H N.M.R. Spectroscopy.

Common features in all these spectra detailed in Tables 4.4 - 4.6 are the characteristic singlet near 0.0 ppm for the Si-(CH_3)$_2$ hydrogens and a 1:4:1 "triplet" for the methylene hydrogens [L = diene or py], as a result of spin-spin coupling to ^{195}Pt. An apparent quartet with satellites is observed for L = PPh_3. The magnitude of this coupling is generally of the order 84-102 Hz, depending on the *trans* ligand and increases in the

Table 4.4 : *^1H N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Diene Ligands.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*] (J_{H-F}) / Hz				δ ^{1}H ppm : Diene ligands (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Substituent	Aromatic	
(cod)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2$[a]	1.15 (**92.3**)	0.59	2.57 [CH_3]	7.09-7.25 m, [H_3, H_4, H_5]; 7.70 dd, [H_6] ($J_{H_2-H_3}$=7.0 Hz)	1.46-1.71 m[b], [CH_2]; 4.26 "t", (**42.3**) [CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-3-Me)$_2$[a]	1.37 (**92.0**)	0.60	2.26 [CH_3]	7.10 dd, [H_4] ($J_{H_4-H_5}$=7.7 Hz); 7.27 t, [H_5] ($J_{H_5-H_6}$=7.1 Hz); 7.61 dd, [H_6]; 7.66 dd, [H_2]	1.55-1.67 m[b], [CH_2]; 4.31 "t", (**41.7**) [CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2$[c]	1.19 (**92.2**)	0.44	2.13 [CH_3]	7.01 d, [H_3, H_5]; 7.53 d, [H_2, H_6] ($J_{H_2-H_3}$=7.6 Hz)	1.39-1.63 m[b], [CH_2]; 4.19 "t", (**41.9**) [CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-OMe)$_2$[a]	1.38 (**97.6**)	0.60	3.40 [OCH_3]	6.96 d, [H_3, H_5]; 7.70 d, [H_2, H_6] ($J_{H_2-H_3}$=8.5 Hz)	1.50-1.74 m[b], [CH_2]; 4.36 "t", (**42.0**) [CH]

Table 4.4 : (continued)

(cod)Pt($CH_2SiMe_2C_6H_4$-4-$^tBu)_2$[a]	1.49 (**85.8**)	0.62	1.31 [*C-CH₃*]	7.41 d, [*H₃, H₅*]; 7.77 d, [*H₂, H₆*] ($J_{H_2-H_3}$=7.9 Hz)	1.51-1.74 m[b], [*CH₂*]; 4.33 "t", (**40.7**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-F)$_2$[a]	1.05 (**93.0**)	0.35	-	6.85 m, [*H₃, H₅*] (***9.3***); 7.43 m, [*H₂, H₆*] (***6.4***) ($J_{H_2-H_3}$=8.5 Hz)	1.41-1.63 m[b], [*CH₂*]; 4.11 "t", (**39.4**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-2-$CF_3)_2$[d]	1.07 (**92.5**)	0.36	-	7.34-7.46 m, [*H₄,H₅*]; 7.62 dd, [*H₃*] ($J_{H_3-H_4}$=7.5 Hz); 7.73 dd, [*H₆*] ($J_{H_5-H_6}$=7.1 Hz)	2.03 "t", (**17.0**) [*CH₂*]; 4.49 "t", (**42.1**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-3-$CF_3)_2$[d]	0.96 (**92.6**)	0.31	-	7.40 t, [*H₅*]; 7.53 d, [*H₄*] ($J_{H_4-H_5}$=7.8 Hz); 7.71 d, [*H₆*]; ($J_{H_5-H_6}$=7.4 Hz); 7.79 d, [*H₂*]	1.96-2.04 m[b], [*CH₂*]; 4.45 "t", (**42.6**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-$CF_3)_2$[d]	0.97 (**92.4**)	0.30	-	7.52 d, [*H₃,H₅*]; 7.69 d, [*H₂, H₆*] ($J_{H_2-H_3}$=7.7 Hz)	2.02 "t", (**17.3**) [*CH₂*]; 4.45 "t" (**42.4**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-$NMe_2)_2$[d]	1.05 (**92.3**)	0.26	2.92 [*N-CH₃*]	6.71 d, [*H₃, H₅*]; 7.43 d, [*H₂, H₆*] ($J_{H_2-H_3}$=8.6 Hz)	1.97-2.05 m[b], [*CH₂*]; 4.48 "t", (**42.2**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6F_5)_2$[d]	0.98 (**91.6**)	0.40 (***3.6***)	-	-	2.19-2.26 m[b], [*CH₂*]; 4.68 "t", (**42.4**) [*CH*]

Table 4.4 : (continued)

$(cod)Pt(CH_2SiMe_2CH_2Ph)_2$[d]	0.81	0.02	2.06	6.98-7.04 m, [H_3, H_4, H_5];	2.11-2.24 m[b], [CH_2];
	(**93.5**)		[CH_2]	7.18 m, [H_2, H_6]	4.51 "t", (**42.0**) [CH]
$(cod)Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$[d]	0.92	0.09	2.12	6.99 d, {H_3, H_5];	2.18-2.31 m[b], [CH_2];
	(**93.5**)		[CH_2]	7.08 d, [H_2, H_6]	4.63 "t", (**41.4**) [CH]
			2.36	($J_{H_2\text{-}H_3}$=8.0 Hz)	
			[CH_3]		
$(nbd)Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$[d]	1.15	0.33	2.51	7.09-7.16 m, [H_4, H_5];	1.31 m, [H_C];
	(**102.0**)		[CH_3]	7.20 dd, [H_3] ($J_{H_3\text{-}H_4}$=7.4 Hz);	3.61 m[b], [H_B];
				7.52 dd, [H_6] ($J_{H_5\text{-}H_6}$=7.1 Hz)	4.42 "t", (**41.1**) [H_A]
$(nbd)Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[d]	1.11	0.27	2.36	7.11 d, [H_4] ($J_{H_4\text{-}H_5}$=7.6 Hz);	1.33 m, [H_C];
	(**101.2**)		[CH_3]	7.22 t, [H_5] ($J_{H_5\text{-}H_6}$=7.2 Hz);	3.59 m[b], [H_B];
				7.41 d, [H_6]; 7.43 d, [H_2]	4.44 "t", (**42.4**) [H_A]
$(nbd)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[d]	1.11	0.26	2.34	7.15 d, [H_3, H_5];	1.34 m, [H_C];
	(**101.2**)		[CH_3]	7.50 d, [H_2, H_6]	3.62 m[b], [H_B];
				($J_{H_2\text{-}H_3}$=8.0 Hz)	4.48 "t", (**42.4**) [H_A]

a :- benzene-d^6

b :- broad resonance

c :- toluene-d^8

d :- chloroform-d^1

Table 4.5 : *^{1}H N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Nitrogen Donor Ligands.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*] (J_{F-H}) / Hz				δ ^{1}H ppm : Pyridine ligands (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Substituent	Aromatic	
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[a,b]	0.95 (**88.8**)	0.49	2.11 [CH_3]	6.88 d, [H_3, H_5]; 7.63 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.7 Hz)	6.05 m, {H_3, H_5] ($J_{H_2\text{-}H_3}$=6.2 Hz); 6.60 m, [H_4] ($J_{H_3\text{-}H_4}$=7.6 Hz); 8.05 dd, (**22.6**)[H_2, H_6] ($J_{H_2\text{-}H_4}$=1.3 Hz)
$(^tBupy)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[a,b]	1.17 (**89.1**)	0.68	2.18 [CH_3]	7.03 d, [H_3, H_5]; 7.80 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.8 Hz)	0.86 s, [CH_3]; 6.39 d, [H_3, H_5]; 8.28 d, (**22.6**) [H_2, H_6] ($J_{H_2\text{-}H_3}$=6.9 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[c]	1.10 (**84.2**)	0.62	2.17 [CH_3]	6.99 dd, [H_4] ($J_{H_4\text{-}H_5}$=7.9 Hz); 7.18 m, [H_5];	6.18 m, [H_3, H_5] ($J_{H_2\text{-}H_3}$=6.4 Hz); 6.69 m, [H_4] ($J_{H_3\text{-}H_4}$=7.6 Hz) 8.19 dd, (**21.7**) [H_2, H_6]

Table 4.5 : (continued)

$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[c]				7.62 d, [H_2]; 7.71 dd, [H_6] ($J_{H_5\text{-}H_6}$= 7.3 Hz)	($J_{H_2\text{-}H_4}$=1.5 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$[a,b]	0.94 (**88.2**)	0.48	3.29 [OCH_3]	6.67 d, [H_3, H_5]; 7.61 d [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.4 Hz)	6.12 m, [H_3, H_5] ($J_{H_2\text{-}H_3}$=6.4 Hz); 6.65 m, [H_4] ($J_{H_3\text{-}H_4}$=7.5 Hz); 8.09 dd, (**21.4**)[H_2, H_6] ($J_{H_2\text{-}H_4}$=1.2 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$[a,b]	0.97 (**89.5**)	0.50	1.19 [$C\text{-}CH_3$]	7.11d, [H_3, H_5]; 7.63 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.2 Hz)	6.11 m, [H_3, H_5] ($J_{H_2\text{-}H_3}$=6.3 Hz); 6.63 m, [H_4] ($J_{H_3\text{-}H_4}$=7.6 Hz); 8.09 dd, (**22.8**) [H_2, H_6] ($J_{H_2\text{-}H_4}$=1.5 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[a]	0.76 (**89.4**)	0.35	-	6.73 m, [H_3, H_5] (***10.1***); 7.48 m, [H_2, H_6] (***6.5***) ($J_{H_2\text{-}H_3}$=10.1 Hz)	6.30 m, [H_3, H_5] ($J_{H_2\text{-}H_3}$=6.6 Hz); 7.04 m, [H_4] ($J_{H_3\text{-}H_4}$=7.7 Hz); 8.07 dd, (**23.1**) [H_2, H_6] ($J_{H_2\text{-}H_4}$=1.5 Hz)
$(py\text{-}d^5)_2(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)$[d]	0.84 (**88.5**)	0.36	-	7.52 d, [H_3, H_5]; 7.81 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.0 Hz)	-

Table 4.5 : (continued)

$(py)_2Pt(CH_2SiMe_2CH_2Ph)_2$[a]	0.63 (**87.1**)	-0.04	2.19 [CH_2]	6.82-6.92 m, [H_3, H_4, H_5]; 7.06 d, [H_2, H_6] ($J_{H_2-H_3}$=4.6 Hz)	6.34 m, [H_3, H_5] ($J_{H_2-H_3}$=6.6 Hz); 6.70 m, [H_4] ($J_{H_3-H_4}$=7.1 Hz); 8.24 dd, (**23.1**) [H_2, H_6] ($J_{H_2-H_4}$=1.6 Hz)

a :- toluene-d^8

b :- run at -20°C

c :- benzene-d^6

d :-pyridine-d^5

Table 4.6 : *^1H N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Phosphorus Donor Ligands.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*] (J_{F-H}) / Hz				δ ^{1}H ppm : Phosphine ligand (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Substituent	Aromatic	
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$[a]	0.87 b	0.08	2.03 [CH_3]	6.92 t, [H_5]; 7.01 t, [H_4]; 7.16 dd, [H_3] ($J_{H_3\text{-}H_4}$=7.3 Hz); 7.23 dd, [H_6] ($J_{H_5\text{-}H_6}$=7.5 Hz)	7.02-7.07 m, [H_3, H_4, H_5]; 7.32 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[c]	0.91 b	0.17	2.37 [CH_3]	7.22-7.32 m, [H_4, H_5, H_6]; e [H_2]	7.11-7.19 m, [H_3, H_4, H_5]; 7.39 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[c]	0.89 b	0.11	2.37 [CH_3]	7.23 d, [H_3, H_5]; 7.36 d, [H_2, H_6]($J_{H_2\text{-}H_3}$=8.0 Hz)	7.06-7.14 m, [H_3, H_4, H_5]; 7.34 m, [H_2, H_6]
$(Dppf)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[a]	1.25 b	0.48	2.29 [CH_3]	7.09 d, [H_3, H_5]; 7.62 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.5 Hz)	3.78 s,[H_Y, $H_{Y'}$]; 4.08 s, [H_Z, $H_{Z'}$]; 6.96-7.08 m, [H_3, H_4, H_5]; 7.83[e] m, [H_2, H_6]

Table 4.6 : (continued)

$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$[a]	1.54	0.50	3.42	6.89 d, [H_3, H_5];	6.84-8.89 m, [H_3, H_4, H_5];
	b		[OCH_3]	7.67 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.5 Hz)	7.48 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$[a]	0.91	0.57	1.36	7.38 d, [H_3, H_5];	6.90-6.95 m, [H_3, H_4, H_5];
	b		[CH_3]	7.73 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.0 Hz)	7.51 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[a]	1.31	0.44	-	7.01 q, [H_3, H_5] (***17.7***);	6.89-6.96 m, [H_3, H_4, H_5];
	b			7.55 q, [H_2, H_6] (***14.2***)	7.52 m, [H_2, H_6]
				($J_{H_2\text{-}H_3}$=8.4 Hz)	
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$[c]	0.79	0.06	-	6.88-6.94 m, [H_3, H_5]; e [H_4];	7.00-7.07 m, [H_3, H_4, H_5];
	(**84.1**)			7.21 m, [H_6]	7.29 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$[c]	1.08	0.41	-	7.40[f] [H_5]; e [H_4]; 7.62 dd, [H_6]	6.82-6.97 m, [H_3, H_4, H_5];
	b			($J_{H_5\text{-}H_6}$=7.5 Hz); 7.92 d, [H_2]	7.47 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$[d]	1.10	0.35	-	7.32 d, [H_3, H_5];	6.76-6.87 m, [H_3, H_4, H_5];
	b			7.44 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.6 Hz)	7.35 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$[a]	1.43	0.57	2.63	6.74 d, [H_3, H_5];	6.89-7.01 m, [H_3, H_4, H_5];
	b		[$N\text{-}CH_3$]	7.74 d, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.6 Hz)	7.51 m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6F_5)_2$[c]	0.84	0.19	-	-	7.12-7.16 m, [H_3, H_4, H_5];
	b	(***3.4***)			7.39 m, [H_2, H_6,]
$(PPh_3)_2Pt(CH_2SiMe_2CH_2Ph)_2$[a]	1.05	0.26	2.13	7.01 m, [H_4] ($J_{H_3\text{-}H_4}$=5.3 Hz);	6.89-6.92 m, [H_3, H_4, H_5]
	(**84.4**)		[CH_2]	7.07 dd, [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.1 Hz);	7.58 m, [H_2, H_6]
				7.19 m, [H_3, H_5]	

Table 4.6 : (continued)

$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$[a]	1.06 **(92.1)**	0.25	2.13 $[CH_2]$ 2.23 $[CH_3]$	e $[H_3, H_5]$; 7.09 d, $[H_2, H_6]$ ($J_{H_2\text{-}H_3}$=7.9 Hz)	6.94-7.04 m, $[H_3, H_4, H_5]$; 7.61m, $[H_2, H_6]$

a :- benzene-d^6

b :- broad resonance

c :- chloroform-d^1

d :- toluene-d^8

e :- obscured

f :- partially obscured by ligand peak

order :-

$$PPh_3 < py < cod < nbd$$

This implies that there is more s-orbital character in the Pt-CH_2 skeleton of η^2-diene complexes, reflecting the weaker *trans*-influence[56] of diene relative to N- and P-donor ligands.

Within each series there is little variation in the magnitude of $^2J_{Pt-H}$ as the substituent is changed, indicating that the ring substituents are too distant to exert any appreciable steric and/or electronic effects at the metal. This is reflected in the magnitude of $^2J_{Pt-H}$ for olefinic hydrogens in the diene and $^2J_{Pt-H}$ for the *ortho*-protons in the pyridine ring, which also show a corresponding lack of variation.

The aromatic region of *para*-substituted derivatives appears as a set of two doublets, characteristic of 1,4-disubstituted benzenes. These resonances are readily assigned; the signal occurring at higher field is due to *meta*-hydrogens, the one at lower field due to *ortho*-hydrogens. These assignments were further verified in the case of $L_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$ (L_2 = cod; L = py, PPh_3) by comparison of the magnitudes of J_{F-H} coupling constants. Values of $^3J_{F-H}$, in the range 9-18 Hz, due to a spin-spin interaction of the ^{19}F nucleus ($I = \frac{1}{2}$, 100% abundant) with the *meta*-hydrogens were observed. Interaction of ^{19}F with the *ortho*-hydrogens gave $^4F_{F-H}$ between 6 and 14 Hz.

More complicated patterns were observed for *ortho* and *meta*-substituted arene rings. H_2 could usually be distinguished from H_6 in *meta*-substituted derivatives; the former appearing as a doublet, due to coupling of H_2 with H_4, and the latter as a doubled doublet. Often H_5 could also be assigned as the resonance which occurs furthest upfield. For complexes with *ortho*-substituted phenyl rings only H_6 could be assigned unequivocally, occurring as a doubled doublet at low field ($\delta \equiv 7.5$ - 7.7 ppm). The remaining protons appear as a complicated multiplet.

For complexes $L_2Pt(CH_2SiMe_2C_6H_4R)_2$ (R = 2-CF_3, 3-CF_3, 4-CF_3; L_2 = cod; L = PPh_3), no coupling was observed between the fluorine nuclei and protons on the aromatic ring, presumably the magnitude of $^4J_{F-H}$ is so small that it remains unresolved. However, $^5J_{F-H}$ *is* observed due to ^{19}F interacting with the silicon-methyl hydrogens in $L_2Pt(CH_2SiMe_2C_6F_5)_2$ (L_2 = cod; L = PPh_3).

4.2.3. ^{13}C N.M.R. Spectroscopy.

All isolated compouds have been characterised by $^{13}C\{^1H\}$ N.M.R. spectroscopy (Tables 4.7 - 4.9). Assignments are based on comparison with free ligands[85], with corresponding XCH_2SiMe_2Ar compounds (X = H or Cl)[48b, 86], platinum-carbon and/or fluorine-carbon coupling constants and on the intensity of the peaks. The two quaternary carbon atoms on the aromatic ring could be readily distinguished. The silicon-bound carbon, C_1, is coupled to ^{195}Pt, typically giving $^3J_{Pt-C}$ of 20-35 Hz, while the substituent-bearing carbon appears as a singlet. The remaining aromatic carbons were

Table 4.7 : *^{13}C N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Diene Ligands.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{C-F}) / Hz				δ ^{13}C ppm : Diene ligands (J_{Pt-C}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Substituent	Aromatic	
(cod)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2$[a]	12.31 (**713.4**)	3.04 (**32.6**)	23.63 [CH_3]	124.67 [C_5]; 128.33 [C_3]; 129.70 [C_4]; 134.42 [C_6]; 142.13 (**20.3**) [C_1]; 143.43 [C_2]	29.83 [CH_2]; 97.85 (**63.4**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-3-Me)$_2$[b]	12.51 (**711.4**)	2.17 (**32.1**)	21.61 [CH_3]	127.79 [C_5]; 129.12 [C_4]; 131.30 [C_6]; 134.85 [C_2]; 136.67 [C_3]; 144.41 (**22.6**) [C_1]	29.78 [CH_2]; 97.83 (**64.5**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2$[b]	12.64 (**710.5**)	2.25 (**31.7**)	21.40 [CH_3]	128.59 [C_3, C_5]; 134.23 [C_2, C_6]; 137.67[C_4]; 140.94 (**22.6**) [C_1]	29.78 [CH_2]; 97.77 (**64.3**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-OMe)$_2$[a]	12.04 (**710.4**)	1.88 (**31.0**)	55.04 [OCH_3]	113.26 [C_3, C_5]; 135.01 [C_2, C_6]; 135,41 (**25.4**) [C_1]; 159.82 [C_4]	29.80 [CH_2]; 97.64 (**64.1**) [*CH*]

Table 4.7 : (continued)

(cod)Pt($CH_2SiMe_2C_6H_4$-4-$^tBu)_2$[a]	11.78 (**710.4**)	1.66 (**29.6**)	31.36 [*C*-***C***H_3] 34.54 [***C***-CH_3]	124.26 [C_3, C_5]; 133.60 [C_2, C_6]; 140.84 (**25.9**) [C_1]; 150.78 [C_4]	29.69 [CH_2]; 97.65 (**64.6**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-F)$_2$[a]	11.59 (**711.0**)	1.83 (**30.5**)	-	114.36 [C_3, C_5] (***19.1***); 135.46 [C_2, C_6] (***7.4***); 139.78 (**26.1**) [C_1] (***3.6***); 163.55 [C_4] (***246.6***)	29.81 [CH_2]; 97.98 (**64.1**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-2-$CF_3)_2$[a]	12.97 (**713.5**)	3.29 (**27.0**)	125.32 [CF_3] (***274.0***)	125.75 [C_3] (***5.6***); 128.01 [C_5]; 130.32 [C_4]; 134.54 [C_2] (***30.7***); 136.29 [C_6]; 142.86 (**28.0**) [C_1]	29.82 [CH_2]; 97.97 (**63.9**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-3-$CF_3)_2$[a]	10.95 (**708.5**)	1.52 (**29.8**)	124.77 [CF_3] (***272.5***)	134.70 [C_4] (***3.2***);127.56 [C_5]; 129.68 [C_3] (***31.3***); 130.17 [C_2] (***2.6***);137.02 [C_6]; 145.76 (**26.3**) [C_1]	29.73 [CH_2]; 98.24 (**64.9**) [*CH*]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-$CF_3)_2$[a]	10.79 (**707.9**)	1.48 (**29.5**)	124.54 [CF_3] (***271.9***)	123.88 [C_3, C_5] (***3.0***); 129.69 [C_4] (***32.1***); 133.90 [C_2, C_6]; 149.45 (**26.3**) [C_1]	29.77 [CH_2]; 98.24 (**64.9**) [*CH*]

Table 4.7 : (continued)

(cod)Pt($CH_2SiMe_2C_6H_4$-4-NMe_2)$_2$[a]	12.58	1.99	40.42	112.25 [C_3, C_5]; 130.40 (**25.2**) [C_1];	29.85 [CH_2];
	(**713.1**)	(**31.0**)	[N-CH_3]	134.73 [C_2, C_6]; 150.80 [C_4];	97.52 (**63.8**) [CH]
(cod)Pt($CH_2SiMe_2C_6F_5$)$_2$[a]	10.33	3.01	-	114.47 (**36.7**) [C_1] (***67.3***);	29.95 [CH_2];
	(**701.3**)	(**26.1**)		137.22 m, [C_3, C_5]; 141.35 m, [C_4];	99.22 (**65.6**) [CH]
		(***7.3***)		148.73 m, [C_2, C_6]	
(cod)Pt($CH_2SiMe_2CH_2Ph$)$_2$[a]	10.79	1.16	30.29	123.43 [C_4]; 127.83 [C_3, C_5];	29.90 [CH_2];
	(**709.0**)	(**23.3**)	(**38.4**)	128.26 [C_2, C_6]; 141.84 [C_1]	97.46 (**64.3**) [CH]
			[CH_2]		
(cod)Pt($CH_2SiMe_2CH_2C_6H_4$-4-Me)$_2$[a]	11.04	1.13	20.83	128.15 [C_3, C_5]; 128.57 [C_2, C_6];	29.92 [CH_2];
	(**708.4**)	(**25.2**)	[CH_3]	132.56 [C_4]; 138.53 [C_1]	97.35 (**63.6**) [CH]
			29.63		
			(**36.5**)		
			[CH_2]		
(nbd)Pt($CH_2SiMe_2C_6H_4$-2-CH_3)$_2$[a]	15.22	2.90	23.55	124.75 [C_5]; 128.41 [C_3];	48.80 (**40.5**) [C_B];
	(**755.5**)	(**35.7**)	[CH_3]	129.69 [C_4]; 134.42 [C_6];	72.65 (**52.7**) [C_C];
				142.14 (**20.8**) [C_1]; 143.46 [C_2]	85.68 (**54.4**) [C_A]
(nbd)Pt($CH_2SiMe_2C_6H_4$-3-CH_3)$_2$[a]	14.36	1.62	21.60	127.34 [C_5]; 128.83 [C_4];	48.74 (**40.7**) [C_B];
	(**752.7**)	(**32.9**)	[CH_3]	130.66 [C_6]; 134.40 [C_2];	72.52 (**53.3**) [C_C];
				136.50 [C_3]; 144.39 (**24.8**) [C_1]	85.38 (**54.6**) [C_A]

Table 4.7 : (continued)

(nbd)Pt($CH_2SiMe_2C_6H_4$-2-CH_3)$_2$[a]	14.48 (**752.3**)	1.70 (**32.9**)	21.37 [CH_3]	128.23 [C_3, C_5]; 133.66 [C_2, C_6]; 137.61 [C_4]; 140.84 (**25.9**) [C_1]	48.74 (**40.7**) [C_B]; 72.53 (**53.2**) [C_C]; 85.35 (**54.9**) [C_A]

a :- chloroform-d[1]

b :- benzene-d[6]

Table 4.8. : *^{13}C N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Nitrogen Donor Ligands.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*]				δ ^{13}C ppm : Ancillary ligand (J_{Pt-C}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Substituent	Aromatic	
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[a]	-13.03 (**743.2**)	1.73 (**35.3**)	21.45 [CH_3]	128.21 [C_3, C_5]; 134.17 [C_2, C_6]; 136.32 [C_4]; 142.81 (**35.4**) [C_1]	127.68 (**20.8**) [C_3, C_5]; 134.51[C_4]; 150.74 (**24.8**) [C_2, C_6]
$(^tBupy)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[b]	-12.74 (**743.4**)	1.87 (**37.1**)	21.49 [CH_3]	128.06 [C_3, C_5]; 134.03 [C_2, C_6]; 135.79 [C_4]; 142.88 (**35.1**) [C_1]	29.74 [$C\text{-}CH_3$]; 34.40 [$C\text{-}CH_3$]; 121.71 (**18.5**) [C_3, C_5]; 158.73 [C_4]; 137.4 (**25.2**) [C_2, C_6]
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$[b,c]	-12.58 (**736.6**)	1.84 (**30.6**)	54.19 [OCH_3]	113.03 [C_3, C_5]; 135.13 [C_2, C_6]; 136.96 (**21.0**) [C_1]; 159.49[C_4]	124.68 [C_3, C_5]; 134.58 [C_4]; 150.61 d [C_2, C_6]

Table 4.8 : (continued)

$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$ [b,c]	-12.80 (**735.2**)	1.74 (**20.1**)	31.42 [*C*-***C****H*$_3$] 34.36 [***C***-*CH*$_3$]	124.63 [C_3, C_5]; 133.76 [C_2, C_6]; 135,41 (**27.5**) [C_1]; 149.13 [C_4]	124.14 [C_3, C_5]; 134.50 [C_4]; 150.60 d [C_2, C_6]
$(py)_2Pt(CH_2SiMe_2CH_2Ph)_2$ [b,c]	-13.06 (**742.1**)	1.55 (**28.7**)	30.43 (**41.8**) [CH_2]	123.27 [C_4]; 127.99 [C_3, C_5]; 128.58 [C_2, C_6]; 143.26 [C_1]	124.89 [C_3, C_5]; 134.95 [C_4]; 150.79 d [C_2, C_6]

a :- benzene-d^6

b :- toluene-d^8

c :- run at -25°C

d :- platinum satellites unresolved

Table 4.9 : *^{31}C N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl]platinum(II) and [dimethyl(benzyl)silylmethyl]platinum(II) Complexes with Phosphorus Donor ligands.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{C-F}) / Hz				δ ^{13}C ppm : Phosphine ligand (J_{Pt-C}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Substituent	Aromatic	
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$[a]	6.70, 8.16 (**577.8**) ($J_{C-P_{Trans}}$=91.4 Hz) ($J_{C-P_{Cis}}$ = 6.1 Hz)	3.26 (**27.1**)	15.23 [CH_3]	124.08 [C_5]; 127.32 [C_3]; 129.16 [C_4]; 134.19 [C_6]; 143.37 [C_2]; 143.90 (**22.5**) [C_1]	127.44 [C_3, C_5] (J_{C-P} = 4.0 Hz); 129.16 [C_4] 133.56 (**19.5**) [C_1] (J_{C-P} = 43.6 Hz); 134.69 (**21.2**) [C_2, C_6] (J_{C-P} = 10.8 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[a]	6.43, 7.89 (**575.5**) ($J_{C-P_{Trans}}$=92.2 Hz) ($J_{C-P_{Cis}}$ = 6.4 Hz)	2.69 (**24.7**)	21.60 [CH_3]	126.84 [C_5]; 128.00 [C_4]; 128.32 [C_3]; 131.26[C_6]; 135.67 [C_2]; 145.68 (**28.4**) [C_1]	127.38 (**8.6**) [C_3, C_5] (J_{C-P} = 8.6 Hz); 129.13 [C_4]; 133.55 (**18.3**) [C_1]; (J_{C-P} = 34.4 Hz);

Table 4.9 : (continued)

$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[a]					134.78 (**11.1**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.5 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$[a]	6.71, 8.18 (**576.9**) ($J_{C\text{-}P_{Trans}}$=92.2 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.0 Hz)	2.72 (**24.1**)	21.37 [CH_3]	127.73 [C_3, C_5]; 134.27 [C_2, C_6]; 136.55 [C_4]; 142.18 (**28.5**) [C_1]	127.38 (**8.6**) [C_3, C_5] ($J_{C\text{-}P}$ = 8.6 Hz); 129.13 [C_4]; 133.58 (**18.3**) [C_1] ($J_{C\text{-}P}$ = 44.5 Hz); 134.84 (**11.6**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.8 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$[a]	6.73, 8.19 (**566.1**) ($J_{C\text{-}P_{Trans}}$=92.2 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.9 Hz)	2.88 (**24.1**)	54.98 [OCH_3]	112.82 [C_3, C_5]; 135.51 [C_2, C_6]; 136.95 (**28.4**) [C_1]; 159.31 [C_4]	127.43 [C_3, C_5] ($J_{C\text{-}P}$ = 3.4 Hz); 129.17 [C_4]; 133.58 (**18.0**) [C_1] ($J_{C\text{-}P}$ = 44.4 Hz); 134.84 (**11.5**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.3 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$[a]	6.80, 8.26 (**601.1**) ($J_{C\text{-}P_{Trans}}$=100.3 Hz) ($J_{C\text{-}P_{Cis}}$ = 8.2 Hz)	2.79 (**28.0**)	31.87 [$C\text{-}CH_3$] 34.51 [$C\text{-}CH_3$]	124.97 [C_3, C_5]; 134.19 [C_2, C_6]; 142.27 (**21.4**) [C_1]; 149.79 [C_4]	127.51 (**12.7**) [C_3, C_5] ($J_{C\text{-}P}$ = 7.3 Hz); 129.17 [C_4]; 133.72 (**14.1**) [C_1] ($J_{C\text{-}P}$ = 35.9 Hz); 134.94 (**12.3**) [C_2, C_6] ($J_{C\text{-}P}$ = 8.7 Hz)

Table 4.9 : (continued)

$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[b]	6.84, 8.31 (**574.5**) ($J_{C\text{-}P_{Trans}}$=92.1 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.2 Hz)	3.39 (**24.5**)	-	114.31 [C_3, C_5] (***19.6***); 136.38 [C_2, C_6] (***7.0***); 141.40 (**27.0**) [C_1]; 163.65 [C_4] (***245.7***)	127.78 [C_3, C_5] ($J_{C\text{-}P}$ = 5.0 Hz); 129.59 [C_4]; 133.92 (**18.3**) [C_1] ($J_{C\text{-}P}$ = 44.7 Hz); 135.12 (**11.8**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.8 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$[a]	6.02, 7.37 (**577.5**) ($J_{C\text{-}P_{Trans}}$=91.9 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.3 Hz)	3.22 (**27.4**)	121.85 [CF_3] (***154.7***)	125.26 [C_3] (***5.2***); 127.06 [C_5]; 129.72 [C_4]; 134.15 [C_2] (***11.4***); 136.26 [C_6]; 144.31 (**30.6**) [C_1]	127.38 (**8.4**) [C_3, C_5] ($J_{C\text{-}P}$ = 9.4 Hz); 129.26 [C_4]; 133.19 (**18.7**) [C_1] ($J_{C\text{-}P}$ = 44.7 Hz); 134.53 (**12.5**) [C_2, C_6] ($J_{C\text{-}P}$ = 11.4 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$[a]	5.39, 6.86 (**583.4**) ($J_{C\text{-}P_{Trans}}$=92.4 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.7 Hz)	2.47 (**23.7**)	110.96 [CF_3] (***309.9***)	124.74 [C_3] (***125.8***); 123.95 [C_5]; 130.02 [C_4]; 137.21 [C_2] (***23.1***); 137.45 [C_6]; 147.38 (**31.0**) [C_1]	127.51 (**7.8**) [C_3, C_5] ($J_{C\text{-}P}$ = 8.4 Hz); 129.41 [C_4]; 133.24 (**18.2**) [C_1] ($J_{C\text{-}P}$ = 50.1 Hz); 134.70 (**10.7**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.7 Hz)

Table 4.9 : (continued)

$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$[a]	5.48, 7.98 (**567.7**) ($J_{C\text{-}P_{Trans}}$=92.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 7.1 Hz)	2.42 (**24.2**)	124.70 [CF_3] (***306.0***)	123.32 [C_3, C_5] (***4.5***); 129.30 [C_4] (***35.7***); 134.15 [C_2, C_6]; 151.09 (**27.0**) [C_1]	127.33 (**11.9**) [C_3, C_5] ($J_{C\text{-}P}$ = 11.0 Hz); 129.39 [C_4]; 133.18 (**21.0**) [C_1] ($J_{C\text{-}P}$ = 51.9 Hz); 134.68 (**11.2**) [C_2, C_6] ($J_{C\text{-}P}$ = 12.6 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$[a]	7.33, 8.80 (**581.5**) ($J_{C\text{-}P_{Trans}}$=91.9 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.2 Hz)	2.95 (**23.2**)	40.59 [$N\text{-}CH_3$]	112.02 [C_3, C_5]; 133.96 (**18.4**) [C_1]; 135.28 [C_2, C_6]; 150.69 [C_4];	127.35 (**16.2**) [C_3, C_5] ($J_{C\text{-}P}$ = 8.3 Hz); 129.04 [C_4]; 133.76 (**18.6**) [C_1] ($J_{C\text{-}P}$ = 44.0 Hz); 134.90 (**12.4**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.7 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2CH_2Ph)_2$[b]	7.56, 9.01 (**583.1**) ($J_{C\text{-}P_{Trans}}$=94.4 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.0 Hz)	2.10 (**23.3**)	31.32 (**36.1**) [CH_2]	123.57 [C_4]; 128.11[C_3, C_5]; 128.67 [C_2, C_6]; 142.82 [C_1]	127.82 [C_3, C_5] ($J_{C\text{-}P}$ = 4.5 Hz); 129.61 [C_4]; 134.22 (**18.3**) [C_1] ($J_{C\text{-}P}$ = 44.2 Hz); 135.20 (**10.6**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.7 Hz)

Table 4.9 : (continued)

$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$[a]	6.75, 8.21 (**574.8**) ($J_{C\text{-}P_{Trans}}$=91.7 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.8 Hz)	1.47 (**23.0**)	20.81 [CH_3] 30.07 (**36.0**) [CH_2]	128.05 [C_3, C_5]; 128.33 [C_2, C_6]; 128.55 [C_4]; 139.37 [C_1]	127.49 [C_3, C_5] ($J_{C\text{-}P}$ = 3.3 Hz); 129.29 [C_4]; 133.62 (**17.9**) [C_1] ($J_{C\text{-}P}$ = 43.2 Hz); 134.79 (**9.8**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.3 Hz)

a :- chloroform-d^1

b :- benzene-d^6

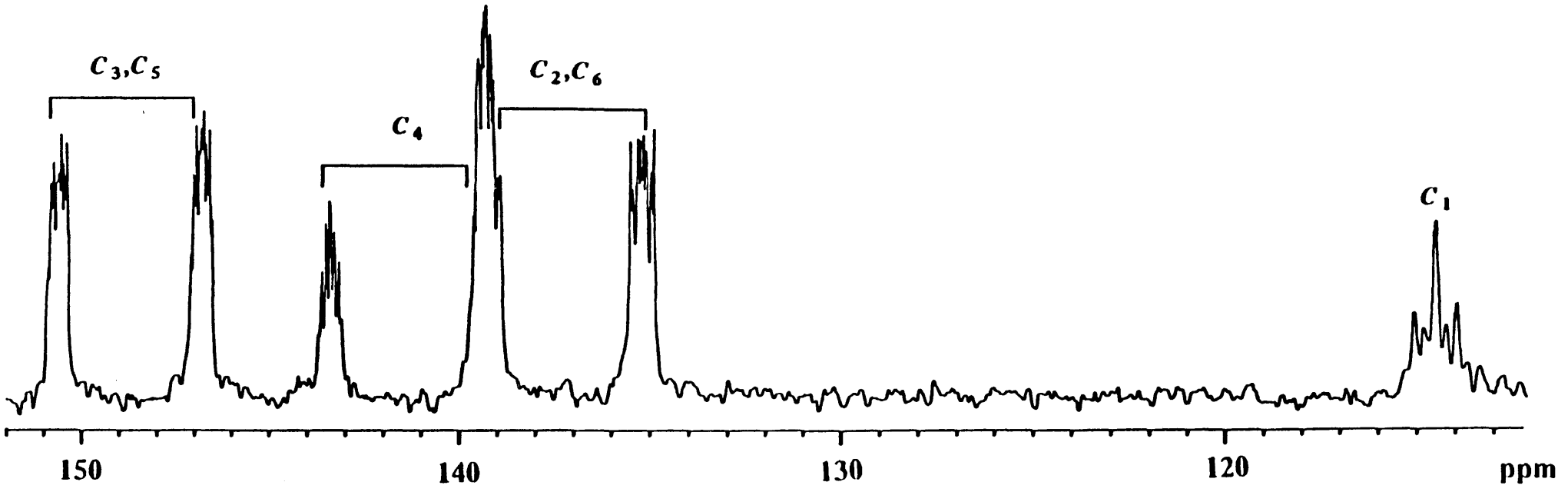


Fig. 4.2 : ^{13}C *N.M.R. of* $(cod)Pt(CH_2SiMe_2C_6F_5)_2$.

assigned on the basis that *meta*-carbon atoms are least affected by changing the substituent[48]. Hence lower frequency resonances were usually designated as C_3 and C_5; those at higher frequency C_2 and C_6.

Complexes with either a fluorine or trifluoromethyl substituent all exhibited coupling to ^{19}F. For diene complexes the magnitude of $^1J_{F\text{-}C}$ to the quaternary carbon of the CF_3 group was *ca.* 280 Hz, while for $^2J_{F\text{-}C_4}$ a smaller value of 250 Hz was observed. The magnitude of $^2J_{F\text{-}C_4}$ is larger than expected and is in accord with more s-character deployed at an sp^2-carbon atom. Replacing the diene by triphenylphosphine in $L_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$, however, results in an anomalously low value of $^1J_{F\text{-}C}$ of 154.7 Hz; possibly explained by a lengthening of the carbon-fluorine bonds in response to a greater steric demand by triphenylphosphine (*cf.* 2.2.3).

A very complicated pattern for the aromatic region is observed for $(cod)Pt(CH_2SiMe_2C_6F_5)_2$, since each carbon atom experiences spin-spin coupling with more than one fluorine nucleus (Fig. 4.2). Six multiplets are observed; the two occurring at the lowest field may be attributed to C_2, C_6 and those furthest upfield correspond to C_3, C_5. The lowest intensity signal is due to C_1, which shows platinum satellites. In addition the signal due to the silicon-methyl groups is observed as a "triplet" of doublets with $^4J_{F\text{-}C} = 7.3$ Hz.

The magnitude of $^1J_{Pt\text{-}C}$ for these compounds varies from 565-755 Hz. Smaller values are obtained for the phosphine complexes, again reflecting their stronger *trans*-influence. A trend is also observed in the magnitude of $^3J_{Pt\text{-}C}$ to C_1 of the aromatic ring and to the silicon-bound methyl groups. When the ancillary ligand is a diene or pyridine, $^3J_{Pt\text{-}C_{Methyl}}$ is larger than $^3J_{Pt\text{-}C_1}$, indicating greater s-character in the $Si\text{-}CH_3$ bond. If the ligand is triphenylphosphine, the converse is true. These changes in $^3J_{Pt\text{-}C}$ presumably reflect modifications in the bonding around the silicon atom as the steric demand of the ancillary ligand changes.

Resonances due to the ancillary ligand are largely as expected, though $^2J_{Pt\text{-}C}$ to C_2 and C_6 of pyridine could not always be determined, as the ^{195}Pt satellites were not well enough resolved at -20°C due to chemical shift anisotropy[87].

4.2.4. ^{19}F N.M.R. Spectroscopy.

Most ^{19}F N.M.R. spectra (Table 4.10) display a single resonance at lower field relative to $CFCl_3$. A chemical shift of *ca.* +100.0 ppm was observed for complexes with trifluoromethyl groups, about +50.0 ppm at lower field than analogous *para*-fluoro derivatives. Three resonances were observed for $L_2Pt(CH_2SiMe_2C_6F_5)_2$ (L_2 = cod; L = PPh_3) and are similar to those observed previously for *trans*-$(PEt_3)_2Pt(C_6F_5)X$[88]. Both these complexes are thermolytically labile, readily rearranging to $L_2Pt(C_6F_5)(CH_2SiMe_2CH_2SiMe_2C_6H_5)$ (*vide infra*). The ^{19}F N.M.R. of these derivatives also consists of three distinct resonances. The multiplet at highest field is due to the *meta*-fluorine atoms. The signal due to F_4 appears as a triplet and that due to the

ortho-fluorine atoms as a doubled doublet with platinum satellites. The magnitudes of $J_{F_2\text{-}F_3}$ and $J_{F_3\text{-}F_4}$ are between 15-20 Hz and $^3J_{Pt\text{-}F}$ is *ca.*50 Hz .

Table 4.10 : *^{19}F N.M.R. Characteristics of* bis-*[dimethyl (aryl)silylmethyl]platinum(II) Complexes with Diene, Nitrogen and Phosphorus Donor Ligands*

Complex	δ^a ppm : ($J_{F\text{-}F}$) / Hz [*Assignment*]
$ClCH_2SiMe_2C_6H_4\text{-}4\text{-}F$[b]	51.3
$ClCH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3$[b]	104.0
$ClCH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3$[b]	99.4
$ClCH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3$[b]	99.0
$ClCH_2SiMe_2C_6F_5$[b]	1.3 m, [F_3, F_5]; 11.7 t, (**19.5**) [F_4]; 35.3 dd, (**14.7**) [F_2, F_6]
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[b]	48.1
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$[b]	104.8
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$[b]	100.1
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$[b]	99.9
$(cod)Pt(CH_2SiMe_2C_6F_5)_2$[b]	-0.2 m, [F_3, F_5]; 7.7 t, (**19.5**) [F_4]; 35.1 dd, (**19.5**) [F_2, F_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[c]	47.5
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$[b]	104.9
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$[b]	100.5
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$[d]	100.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6F_5)_2$[b]	-0.2 m, [F_3, F_5]; 8.5 t, (**19.5**) [F_4]; 35.6 dd, (**14.7**)[F_2, F_6]

a :- referenced to $CFCl_3$

b :- chloroform-d^1

c :- toluene-d^8

d :- benzene-d^6

4.2.5. ^{31}P N.M.R. Spectroscopy.

Detailed in Table 4.11 are the $^{31}P\{^{1}H\}$ N.M.R. data for the series of compounds $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4R)_2$. All complexes display the expected 1:4:1 "triplet" due to spin-spin coupling of the ^{31}P nucleus to ^{195}Pt. Since the ring substituents are so remote from both platinum and phosphorus nuclei, very little variation in either chemical shift or magnitude of $^{1}J_{Pt\text{-}P}$ is observed by changing the substituent.

Table 4.11 : *^{31}P N.M.R. Characteristics of* bis-*[dimethyl(aryl)silylmethyl] platinum(II) and* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with P-Donor Ligands.*

Complex	δ^a / ppm	$J_{Pt\text{-}P}$ / Hz
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$ [b]	24.5	2013.7
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$ [c]	25.2	2018.1
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$ [c]	24.1	2027.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$ [c]	25.0	2027.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^{t}Bu)_2$ [c]	23.3	2029.2
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$ [c]	23.1	2038.1
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$ [c]	24.0	2024.8
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$ [c]	24.7	2055.8
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$ [c]	24.8	2058.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$ [c]	24.7	2060.3
$(PPh_3)_2Pt(CH_2SiMe_2C_6F_5)_2$ [d]	23.6	2082.4
$(PPh_3)_2Pt(CH_2SiMe_2CH_2Ph)_2$ [c]	23.2	2022.6
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$ [c]	25.1	2018.1
$(dppf)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$ [b]	18.6	2044.7

a :- referenced to 85% H_3PO_4 / D_2O

b :- toluene-d^8

c :- benzene-d^6

d :- chloroform-d^1

4.3. Experimental.

4.3.1. General.

Elemental analyses were by Imperial College Microanalytical Laboratories and by Butterworth Laboratories Ltd. N.M.R. spectra were recorded on a Jeol GSX 270 (^{1}H, 270.17 MHz, ^{13}C, 67.94 MHz), Brüker WM250 (^{1}H, 250.13 MHz, ^{13}C, 62.9 MHz) and Jeol FX90Q (^{1}H, 89.55 MHz, ^{19}F, 84.27 MHz, ^{31}P, 36.21 MHz) spectrometers.

All reactions were carried out under argon using standard anaerobic techniques. Solvents were distilled under nitrogen prior to use (See 2.3).

Chloromethyl(dimethyl)chlorosilane supplied by Aldrich Chem. Co. was stored under argon but used without further purification. [2.2.1]Bicyclohepta-2,5-diene, cycloocta-1,5-diene, 2-bromotoluene, 4-bromobenzotrifluoride, 4-bromo-N,N-dimethylaniline, bromopentafluorobenzene, benzyl bromide, α-bromo-*p*-xylene, triphenylphosphine, *bis*-(1,1'-diphenylphosphino)ferrocene and 4-*tert*-butylpyridine were all used as supplied by Aldrich Chem. Co.. 3-Bromotoluene, 4-bromotoluene, 2-bromobenzotrifluoride, 3-bromobenzotrifluoride, 4-bromoanisole, 4-bromo-*tert*-butylbenzene and 4-bromofluorobenzene, supplied by Lancaster Synthesis, were used without further purification.

Most aryllithium reagents were prepared *in situ* by metal-halogen exchange of *n*-butyllithium with the corresponding aryl bromide in dithyl ether by an established route[89].

4.3.2. Syntheses.

Preparation of pentafluorophenylmagnesium bromide[90].

To a stirred solution of C_2H_5MgBr (60.8 mmol) at 0°C in THF (40 cm^3) was added dropwise a solution of C_6F_5Br (15.00g, 60.8 mmol) in THF (60 cm^3). The mixture was gradually warmed to ambient temperature and then stirred for a further 4 hours. Filtration of this solution afforded C_6F_5MgBr .
(Yield : 58.4 mmol, 96%)

Preparation of o-*tolyllithium.*

A solution of 2-bromotoluene (20.00g, 116.9 mmol) in *n*-hexane (60 cm^3) was added to a stirred solution of Bu^{t}Li (116.9 mmol) in *n*-hexane (60 cm^3) cooled to 0°C. A white precipitate formed immediately. After stirring for a further 16 hours, the mixture was filtered; the solid washed with *n*-hexane (4 x 30 cm^3) and dried *in vacuo*, yielding LiC_6H_4-2-CH_3 as a white powdery solid.
(Yield : 10.55g, 107.5 mmol, 92%)

*Preparation of chloromethyl(dimethyl)(4-*tert*-butylphenyl)silane.*

To a stirred solution of chloromethyl(dimethyl)chlorosilane (10.5 cm^3, 80.0 mmol) in Et_2O (50 cm^3) was added dropwise a solution of $BrMgC_6H_4$-4-^tBu (80.0 mmol) in diethyl ether (90 cm^3). Upon complete addition of alkylating reagent, the mixture was refluxed for 24 hours, then cooled to -20°C and quenched with aqueous ammonium chloride solution (80 cm^3). The organic layer was separated and the aqueous phase washed with Et_2O (2 x 20 cm^3). The combined ether extracts were dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* formed a pale yellow oil, which was distilled to afford chloromethyl(dimethyl)(4-*tert*-butylphenyl)silane as a low melting point, colourless crystalline solid (mp. 30-31°C).
(Yield : 13.36g, 53.0 mmol, 70%)

^1H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.21s - Si-CH_3; 1.13s - ^tBu; 2.59s - CH_2Cl; 7.14d, 7.72d - Aromatic.

Preparation of chloromethyl(dimethyl)(4-methoxyphenyl)silane.

Chloromethyl(dimethyl)(4-methoxyphenyl)silane was prepared as a colourless liquid from chloromethyl(dimethyl)chlorosilane and 4-$OCH_3C_6H_4MgBr$ according to a similar procedure described above.
(Yield : 9.58g, 45.1 mmol, 56%)

^1H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.38s - Si-CH_3; 2.90s - CH_2Cl; 3.80s - OCH_3; 6.91d, 7.45d - Aromatic.

Preparation of chloromethyl(dimethyl)(2-methylphenyl)silane.

Chloromethyl(dimethyl)(2-methylphenyl)silane was obtained as a colourless liquid by the interaction of chloromethyl(dimethyl)chlorosilane and 2-$CH_3C_6H_4Li$, following a procedure similar to the one described above.
(Yield : 7.89g, 39.7 mmol, 50%)

^1H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.52s - Si-CH_3; 2.51s - Ar-CH_3; 3.12s - CH_2Cl; 7.14- 7.53m - Aromatic.

Preparation of chloromethyl(dimethyl)(3-methylphenyl)silane.

Chloromethyl(dimethyl)(3-methylphenyl)silane, a colourless liquid, was prepared by an analogous procedure described above from chloro(dimethyl)chlorosilane and 3-$CH_3C_6H_4Li$.
(Yield : 13.26g, 66.7 mmol, 79%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.40s - Si-CH_3; 2.35s - Ar-CH_3; 2.91s - CH_2Cl;
7.17- 7.36m - Aromatic.

Preparation of chloromethyl(dimethyl)(4-methylphenyl)silane.

Chloromethyl(dimethyl)(4-methylphenyl)silane was prepared as a colourless liquid from chloro(dimethyl)chlorosilane and 4-$CH_3C_6H_4Li$ by a method essentially identical to that described above.
(Yield : 11.89g, 59.8 mmol, 75%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.23s - Si-CH_3; 2.17s - Ar-CH_3; 2.73s - CH_2Cl; 7.01d,
7.25d - Aromatic.

Preparation of chloromethyl(dimethyl)(2-trifluoromethylphenyl)silane.

Chloromethyl(dimethyl)(2-trifluoromethylphenyl)silane was obtained as a colourless liquid, according to a similar procedure described above, from chloromethyl(dimethyl)chlorosilane and 2-$CF_3C_6H_4Li$.
(Yield : 16.23g, 64.0 mmol, 77%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.49s - Si-CH_3; 3.07s - CH_2Cl; 7.49-7.75m - Aromatic.

Preparation of chloromethyl(dimethyl)(3-trifluoromethylphenyl)silane.

Chloromethyl(dimethyl)(3-trifluoromethylphenyl)silane, a colourless liquid, was prepared from chloromethyl(dimethyl)chlorosilane and 3-$CF_3C_6H_4Li$ by a similar method described above.
(Yield : 14.58g, 57.7 mmol, 72%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.42s - Si-CH_3; 2.93s - CH_2Cl; 7.31-7.50m - Aromatic.

Preparation of chloromethyl(dimethyl)(4-trifluoromethylphenyl)silane.

Chloromethyl(dimethyl)(4-trifluoromethylphenyl)silane was obtained as a colourless liquid from chloromethyl(dimethyl)chlorosilane and 4-$CF_3C_6H_4Li$ by a procedure similar to that outlined above.
(Yield : 12.33g, 48.8 mmol, 61%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.35s - Si-CH_3; 2.95s - CH_2Cl; 7.62d,
7.68d - Aromatic.

Preparation of chloromethyl(dimethyl)(4-fluorophenyl)silane.

Chloromethyl(dimethyl)(4-fluorophenyl)silane was prepared by an analogous procedure from chloromethyl(dimethyl)chlorosilane and 4-FC_6H_4MgBr and obtained as a

colourless liquid.
(Yield : 11.94g, 58.9 mmol, 68%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.35s - Si-CH_3; 2.84s - CH_2Cl; 6.96m, 7.44m - Aromatic.

Preparation of chloromethyl(dimethyl)(4-N,N-dimethylaminophenyl)silane.

Chloromethyl(dimethyl)(4-N,N-dimethylaminophenyl)silane was obtained by a method essentially identical to that described previously from the reaction of chloromethyl(dimethyl)chlorosilane with 4-$NMe_2C_6H_4Li$, affording a white low melting point solid (mp. 18-21°C).
(Yield : 14.82g, 65.1 mmol, 76%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 1.09s - Si-CH_3; 3.63s - CH_2Cl; 3.67s - NCH_3; 7.44d, 8.12d - Aromatic.

Preparation of chloromethyl(dimethyl)(pentafluorophenyl)silane.

Chloromethyl(dimethyl)(pentafluorophenyl)silane was prepared as a colourless liquid from chloromethyl(dimethyl)chlorosilane and C_6F_5MgBr by a procedure similar to that described above.
(Yield : 9.36g, 34.1 mmol, 71%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.51d - Si-CH_3; 3.08s - CH_2Cl.

Preparation of chloromethyl(dimethyl)(benzyl)silane.

Chloromethyl(dimethyl)(benzyl)silane, a colourless liquid, was obtained from chloromethyl(dimethyl)chlorosilane and $C_6H_5CH_2MgBr$ by an identical method described above.
(Yield : 18.77g, 94.4 mmol, 65%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.35s - Si-CH_3; 2.48s - Ar-CH_2; 2.96s - CH_2Cl; 7.23- 7.51m - Aromatic.

Preparation of chloromethyl(dimethyl)(4-methylbenzyl)silane.

Chloromethyl(dimethyl)(4-methylbenzyl)silane was prepared analogously to the procedure adopted above from chloromethyl(dimethyl)chlorosilane and 4-$CH_3C_6H_4CH_2MgBr$ and was obtained as a colourless liquid.
(Yield : 7.71g, 36.2 mmol, 67%)

^{1}H N.M.R. ($CDCl_3$) : δ (ppm) ≡ 0.13s - Si-CH_3; 2.19s - Ar-CH_2; 2.34s - Ar-CH_3; 2.74s - CH_2Cl; 6.91d, 7.06d - Aromatic.

Preparation of bis-*[(2-methylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene) platinum(II).*

A solution of 2-$CH_3C_6H_4SiMe_2CH_2MgCl$ (6.0 mmol) in Et_2O (40 cm^3) was added dropwise to a stirred suspension of (cod)$PtCl_2$ (0.69g, 1.84 mmol) in diethyl ether (20 cm^3) at -78°C. After complete addition of the Grignard reagent, the mixture was gradually warmed to ambient temperature and stirred for a further 16 hours. The stirred suspension was cooled to -25°C and hydrolysed dropwise with saturated aqueous ammonium chloride solution (30 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (2 x 10 cm^3). The combined ether extracts were dried over $MgSO_4$ and decolourised with activated charcoal to give a colourless solution after filtration. Removal of the solvent *in vacuo* gave a white crystalline solid, which was recrystallised from the minimum amount of *n*-hexane (5 cm^3) to afford colourless rhomboid crystals of the product.
(Yield : 1.01g, 1.60 mmol, 87%)

Prepared according to a similar procedure were :-

bis-*[(3-methylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II).*
Product : Colourless plates from *n*-hexane.
(Yield : 0.89g, 1.41 mmol, 78%)

bis-*[(4-methylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II).*
Product : Colourless crystalline solid from *n*-hexane.
(Yield : 1.44g, 2.29 mmol, 96%)

bis-*[(4-methoxyphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II).*
Product : Colourless rods from *n*-hexane.
(Yield : 0.98g, 1.48 mmol, 81%)

bis-*[(4-*tert*-butylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II).*
Product : White crystalline solid from *n*-hexane.
(Yield : 1.09g, 1.53 mmol, 84%)

bis-*[(4-fluorophenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II).*
Product : Colourless crystalline solid from *n*-hexane.
(Yield : 1.16g, 1.82 mmol, 97%)

bis-*[(2-trifluoromethylphenyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene)platinum(II).*
Prodict : Colourles rods from *n*-hexane.
(Yield : 1.81g, 2.46 mmol, 92%)

bis-*[(3-trifluoromethylphenyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene)platinum(II).*
Product : White crystalline solid from *n*-hexane
(Yield : 1.73g, 2.35 mmol, 88%)

bis-*[(4-trifluoromethylphenyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene)platinum(II).*
Product : Colourless crystalline solid from *n*-hexane.
(Yield : 1.30g, 1.76 mmol, 88%)

bis-*[(4-N,N-dimethylaminophenyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene) platinum(II).*
Product : Buff crystalline solid from *n*-hexane.
(Yield : 1.56g, 2,27 mmol, 85%)

bis-*[(pentafluorophenyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene)platinum(II).*
Product : White crystalline solid from chloroform.
(Yield : 1.52g, 1.94 mmol, 73%)

bis-*[(benzyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene)platinum(II).*
Product : Colourless blocks from *n*-hexane.
(Yield : 0.94g, 1.43 mmol, 80%)

bis-*[(4-methylbenzyl)(dimethyl)silylmethyl)](cycloocta-1,5-diene)platinum(II).*
Product : Colourless sticky solid.
(Yield : 1.16g, 1.76 mmol, 94%)

bis-*[(2-methylphenyl)(dimethyl)silylmethyl)]([2.2.1]bicyclohepta-2,5-diene)platinum(II).*
Product : White solid from *n*-hexane.
(Yield : 1.63g, 2.65 mmol, 95%)

bis-*[(3-methylphenyl)(dimethyl)silylmethyl)]([2.2.1]bicyclohepta-2,5-diene)platinum(II).*
Product : White crystalline solid from *n*-hexane.
(Yield : 1.32g, 2.14 mmol, 77%)

bis-*[(4-methylphenyl)(dimethyl)silylmethyl)]([2.2.1]bicyclohepta-2,5-diene)platinum(II).*
Product : White crystalline solid from *n*-hexane.
(Yield : 1.51g, 2.45 mmol, 88%)

Preparation of cis-bis-*[(4-methylphenyl)(dimethyl)silylmethyl]*-bis-*(pyridine)platinum(II).*

(cod)Pt($CH_2SiMe_2C_6H_4$-4-CH_3)$_2$ (0.21g, 0.33 mmol) was dissolved in pyridine (15 cm^3, 186.0 mmol) and the resulting solution stirred at 60°C for 24 hours. Unreacted pyridine was removed *in vacuo* and the yellow solid residue recrystallised from diethyl ether (3 cm^3) and *n*-hexane (1 cm^3) affording the product as a pale yellow-brown solid.
(Yield : 0.17g, 0.25 mmol, 76%)

Prepared according to an essentially identical method were :-

cis-bis-*[(3-methylphenyl)(dimethyl)silylmethyl]*-bis-*(pyridine)platinum(II).*
Product : Pale yellow liquid.
(Yield : 0.19g, 0.29 mmol, 100%)

cis-bis-*[(4-methoxyphenyl)(dimethyl)silylmethyl]*-bis-*(pyridine)platinum(II).*
Product : Pale yellow-brown crystalline solid from diethyl ether and *n*-hexane.
(Yield : 0.18g, 0.25 mmol, 84%)

cis-bis-*[(4-*tert*-butylphenyl)(dimethyl)silylmethyl]*-bis-*(pyridine)platinum(II).*
Product : Pale yellow crystalline solid from diethyl ether and *n*-hexane.
(Yield : 0.165g, 0.22 mmol, 75%)

cis-bis-*[(4-fluorophenyl)(dimethyl)silylmethyl]*-bis-*(pyridine)platinum(II).*
Product : Pale yellow liquid.
(Yield : 0.21g, 0.31 mmol, 100%)

cis-bis-*[(benzyl)(dimethyl)silylmethyl]*-bis-*(pyridine)platinum(II).*
Product : Pale yellow crystalline solid from diethyl ether and *n*-hexane.
(Yield : 0.16g, 0.23 mmol, 74%)

Preparation of cis-bis-*[(4-methylphenyl)(dimethyl)silylmethyl]*-bis-*(4-*tert*-butylpyridine) platinum(II).*

(cod)Pt($CH_2SiMe_2C_6H_4$-4-CH_3)$_2$ (0.18g, 0.29 mmol) was dissolved in excess 4-*tert*-butylpyridine (10 cm^3, 68.1 mmol) and the solution stirred for 24 hours at 60°C. Excess ligand was removed by vacuum distillation, during which the pale yellow solution turned orange. The oily residue was dissolved in Et_2O (2 cm^3), *n*-hexane (1 cm^3) added, then cooled to -20°C. Filtration of the solid and drying *in vacuo* afforded the product as a pale orange crystalline solid.
(Yield : 0.19g, 2.40 mmol, 83%)

Preparation of cis-bis-*[(2-methylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine) platinum(II).*

To a solution of (nbd)Pt($CH_2SiMe_2C_6H_4$-2-CH_3)$_2$ (0.42g, 0.68 mmol) in diethyl ether (6 cm^3) was added triphenylphosphine (0.36g, 1.36 mmol). After 15 minutes a white crystalline solid began forming. The solution was allowed to stand at ambient temperature for 5 days to ensure that the reaction was complete. The solvent was removed *in vacuo* giving white needles of the product as the etherate. The solid was dissolved in the minimum amount of cold toluene (60 cm^3) and flash evaporated to afford the product as a white microcrystalline solid.
(Yield : 0.70g, 0.67 mmol, 98%)

Preparation of cis-bis-*[(3-methylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine) platinum(II).*

Triphenylphosphine (0.17g, 0.66mmol) was added to a solution of (nbd)Pt($CH_2SiMe_2C_6H_4$-3-CH_3)$_2$ (0.20g, 0.33 mmol) in diethyl ether (6 cm^3), which was then heated to 60°C for 14 days. The solvent was removed *in vacuo* forming a white solid, which was recrystallised from benzene (2 cm^3) and *n*-hexane (1 cm^3) to afford the product as a white crystalline solid.
(Yield : 0.30g, 0.29 mmol, 88%)

cis-bis-*[(4-methylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine)platinum(II).*
cis-bis-[(4-methylphenyl)(dimethyl)silylmethyl]-bis-(triphenylphosphine)platinum(II) was prepared in an analogous fashion from (nbd)Pt($CH_2SiMe_2C_6H_4$-4-CH_3)$_2$ and triphenylphosphine, forming a white crystalline solid from benzene and *n*-hexane.
(Yield : 0.29g, 0.28 mmol, 85%)

Preparation of cis-bis-*[(2-trifluoromethylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine)platinum(II).*

To a solution of (cod)Pt($CH_2SiMe_2C_6H_4$-2-CF_3)$_2$ (0.20g, 0.28 mmol) in diethyl ether (7 cm^3) was added triphenylphosphine (o.14g, 0.56 mmol) and the solution heated to 60°C for 21 days. The colourless rods which had formed were filtered, washed with *n*-hexane (3 x 2 cm^3) and dried *in vacuo* to give analytically pure (PPh_3)$_2$Pt($CH_2SiMe_2C_6H_4$-2-CF_3)$_2$. A second crop of sample was obtained by recrystallising the filtrate from benzene (1 cm^3) and *n*-hexane (1 cm^3) as a white crystalline solid.
(Yield : 0.25g, 0.22 mmol, 82%)

Preparation of cis-bis-*[(4-*tert*-butylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine) platinum(II).*

Triphenylphosphine (0.14g, 0.56 mmol) was added to a solution of

(cod)Pt($CH_2SiMe_2C_6H_4$-4-$^tBu)_2$ (0.20g, 0.28 mmol) in diethyl ether (7 cm^3), which was then heated to 60°C for 28 days. Removal of the solvent *in vacuo* yielded a solid residue. Dissolution in benzene (2 cm^3), addition of *n*-hexane (1 cm^3), cooling to -20°C followed by filtration and drying *in vacuo*, afforded the product as a white crystalline solid.
(Yield : 0.26g, 0.23 mmol, 82%)

Prepared according to essentially an analogous procedure were :-

cis-bis-*[(3-trifluoromethylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine) platinum(II).*
Product : White crystalline solid from benzene and *n*-hexane.
(Yield : 0.23g, 0.20 mmol, 74%)

cis-bis-*[(4-trifluoromethylphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine) platinum(II).*
Product : Colourless plates from benzene and methanol.
(Yield : 0.26g, 0.23 mmol, 84%)

cis-bis-*[(4-methoxyphenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine)platinum(II).*
Product : Colourless aggregates from benzene and *n*-hexane.
(Yield : 0.29g, 0.27 mmol, 90%)

cis-bis-*[(4-fluorophenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine)platinum(II).*
Product : Colourless crystalline solid from benzene and *n*-hexane.
(Yield : 0.27g, 0.26 mmol, 83%)

cis-bis-*[(4-N,N-dimethylaminophenyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine) platinum(II).*
Product : White solid from benzene and *n*-hexane.
(Yield : 0.25g, 0.23 mmol, 78 %)

cis-bis-*[(benzyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine)platinum(II).*
Product : White crystalline solid from benzene and *n*-hexane.
(Yield : 0.32g, 0.30 mmol, 96%)

cis-bis-*[(4-methylbenzyl)(dimethyl)silylmethyl]*-bis-*(triphenylphosphine)platinum(II).*
Product : White solid from *n*-hexane.
(Yield : 0.26g, 0.24 mmol, 80%)

Preparation of cis-bis-*[(4-methylphenyl)(dimethyl)silylmethyl][(1,1'-diphenylphosphino) ferrocene]platinum(II).*

To a solution of (cod)Pt($CH_2SiMe_2C_6H_4$-4-CH_3)$_2$ (0.21g, 0.34 mmol) in toluene (6 cm^3) was added dppf (0.19g, 0.34 mmol) and the solution heated to 50°C for 21 days. Removal of the solvent *in vacuo* yielded an amber residue, which was dissolved in the minimum amount of toluene (2 cm^3), *n*-hexane added (2 cm^3) and cooled to -20°C. Filtration followed by drying *in vacuo* gave an amber microcrystalline powder of the product.

(Yield : 0. 26g, 0.28 mmol, 83%)

Chapter Five :

MECHANISTIC STUDIES OF THERMOLYTIC REARRANGEMENTS OF *CIS*-BIS-(PHOSPHINE)-*BIS*-[DIMETHYL(ARYL)SILYLMETHYL] PLATINUM(II) COMPLEXES.

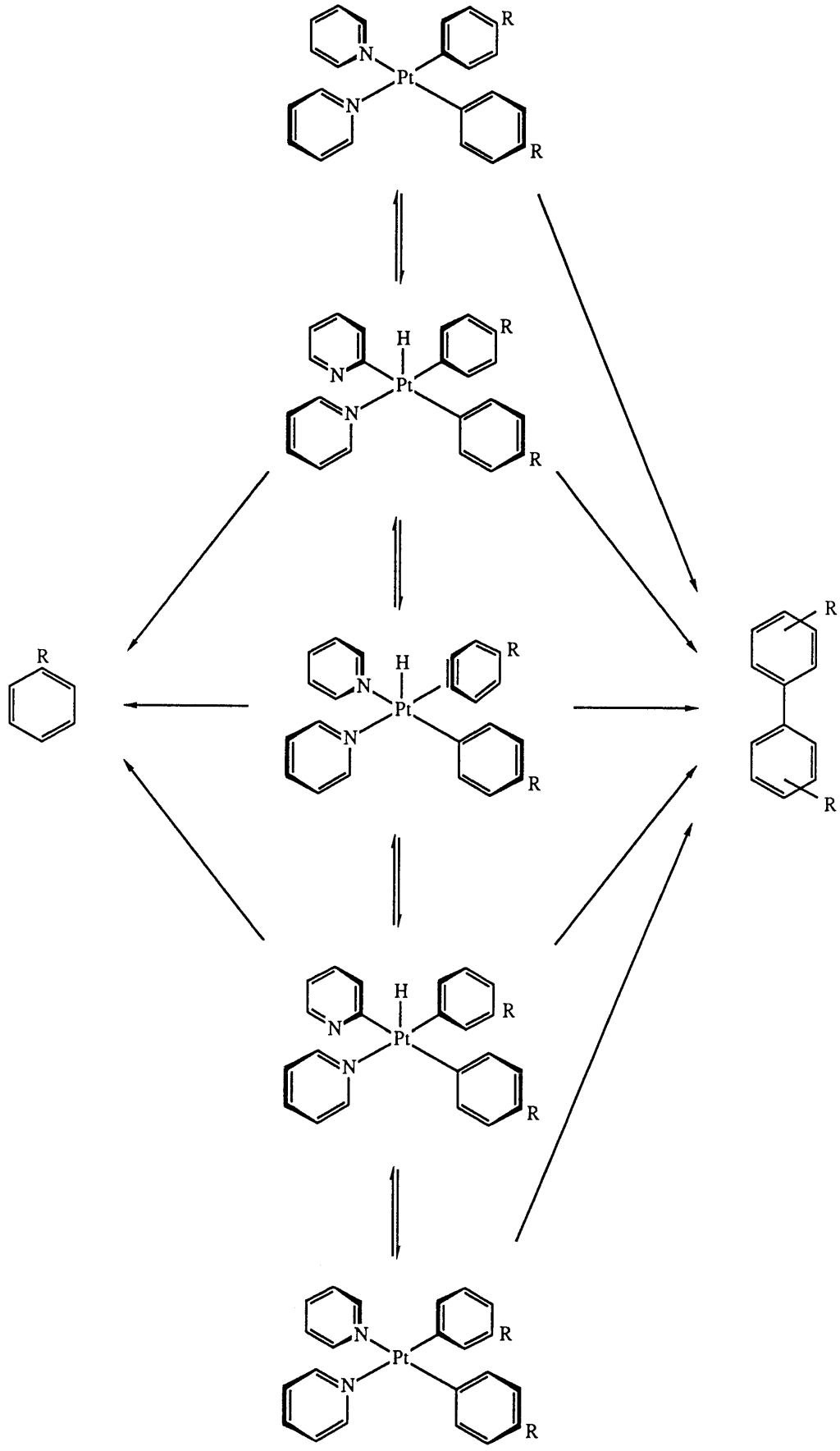
5.1. Introduction.

Most previous investigations of organometal-mediated transformations have focused on organophosphines as ancillary ligands. Tertiary phosphines have the capacity to act as strong Lewis bases and to participate in π-back bonding to low valent metal centres, accepting electron density from filled metal orbitals into empty, low lying d-orbitals on the phosphorus atom. The extent of σ and π-bonding, depends on the metal and the nature of substituents at the phosphorus atom. Changes in phosphine hydrocarbyl groups can cause differences in both electronic and steric environments at the metal centre, thus affecting the reactivity of the complex. As a result, variation of the phosphine ligand can provide much mechanistic information about a reaction. Numerous such studies have been conducted for a variety of reactions[91].

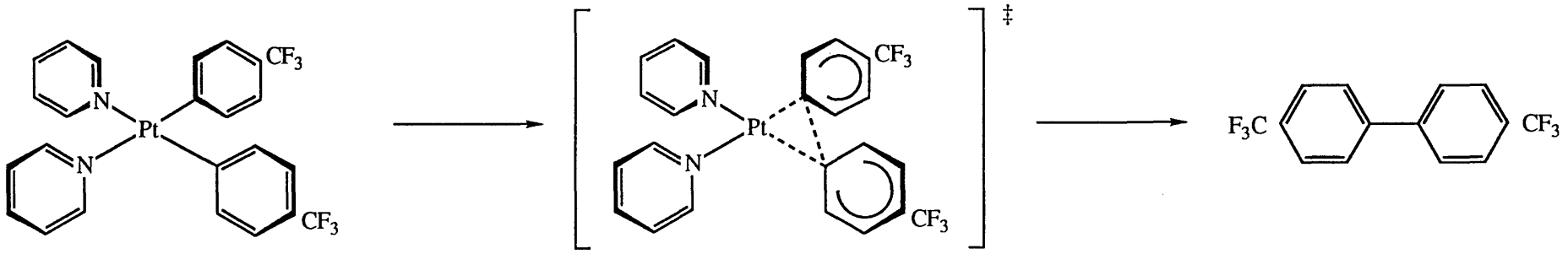
In contrast, few mechanistic studies of substituent effects on the "participating" hydrocarbyl fragment have been documented. Reductive elimination of biaryl from $(PPh)_3Pt(C_6H_4R)_2$ and $(py)_2Pt(C_6H_4R)_2$was enhanced by electron-releasing substituents on the aryl fragment, which stabilise the transition-state relative to the unsubstituted analogue[92, 93]. The converse was true for decelerating substituents. Similar trends have been observed for insertion of *para*-substituted styrenes into an R-H bond of $[RhH_2Cl(PPh_3)_2(\eta^2\text{-styrene})]$[94] and the Nb-H bond of $Cp^*_2Nb(CH_2{=}CHR)(H)$[95].

Variation of the substituent may also alter the intimate mechanism of a reaction[85, 96]. Thermolysis of *cis*-$(py)_2Pt(C_6H_4R)_2$ where R = ^{t}Bu, was found to generate biaryl *via* reductive elimination. Arene elimination, an important competitive reaction, was suppressed by deuteration of either aryl or pyridine ligands. A mechanism involving successive, reversible H-transfers from pyridine and aryl ligands - the latter resulting in aryl group isomerisation prior to elimination - was proposed (Scheme. 5.1). Intramolecular reductive elimination was the only significant pathway when the arene was substituted by an inductively electron-withdrawing group (R = CF_3). Significantly, the reaction was slowest in this case, in accord with an expected retarding effect on reductive elimination by an electron-withdrawing substituent (Scheme. 5.2). Lack of formation of arene indicated that C-H elimination was more susceptible to inhibition by electron-withdrawing substituents than concerted reductive elimination.

In view of such studies, thermolysis of a series of complexes, $L_2Pt(CH_2SiMe_2Ph)_2$ [L = monodentate phosphine] and $(PPh_3)_2Pt(CH_2SiMe_2Ar)_2$ [Ar = substituted aryl group] was conducted to assess the importance of steric and electronic effects on the rearrangement of such complexes. These complexes were anticipated to undergo δ-C-H activation, analogous to their neophyl cousins or else β-hydrocarbyl transfers by a process similar to trimethylsilylmethyl derivatives, it was planned that such an investigation would shed some light on the mechanistic controls of such transformations.



Scheme. 5.1 : *Mechanism of Arene and Biaryl Formation in* $(py)_2Pt(C_6H_4R)_2$.



Scheme. 5.2 : *Reductive Elimination of Biaryl from* $(py)_2Pt(C_6H_4\text{-}4\text{-}CF_3)_2$.

5.2. Results and Discussion.

5.2.1. *Mechanistic Studies of* cis-bis-*(phosphine)*-bis-*(sila-neophyl) platinum(II).*

5.2.1.1. Kinetic studies.

Thermolysis of $L_2Pt(CH_2SiMe_2Ph)_2$ [L = PMe_3, PEt_3, PMe_2Ph, PPh_2Me, PPh_3, P-*p*-tol_3, $PPh_2C_6H_4$-2-CF_3] in toluene results in rearrangement to a species, which contains two inequivalent phosphorus nuclei coupled to platinum. The magnitudes of the coupling constants suggest that one phosphorus is *trans* to an aryl group, while the second is *trans* to a β-sila-alkyl fragment. From this evidence alone it was impossible to discriminate whether aryl transfer or δ-C-H aromatic activation had occurred (Table 5.1).

A numbering convention based on designation of transferred phenyl group carbon atoms as C_n and the remaining carbon atoms as $C_{n'}$ is shown in Fig. 5.1. Ligand carbon atoms *trans* to the phenyl group and those *trans* to the sila-alkyl fragment are designated as C_n and $C_{n'}$ respectively.

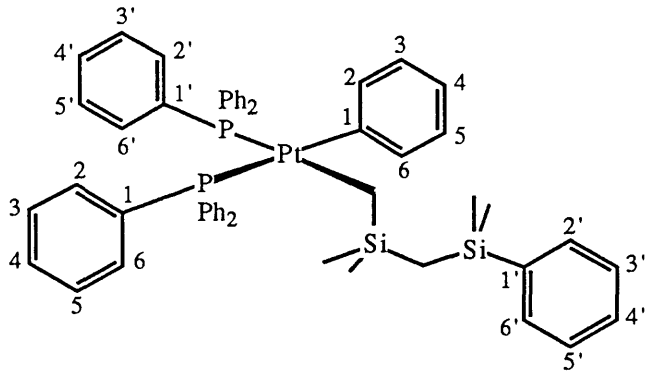


Fig. 5.1 : *N.M.R. Numbering Conventions for* $(PR_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.

^1H N.M.R. spectra (Table 5.2) of these products have several distinctive features, notably two silicon-methyl environments and a smaller singlet further upfield attributable to a silicon bound methylene group. A multiplet at *ca.* 1.00 ppm, coupled to platinum and ^{31}P, corresponds to a Pt-CH_2 group. The aromatic region, when not obscured by ancillary ligand peaks, exhibits three multiplets with integral ratios of 2:1:2; the resonance at lowest field displays coupling to both ^{195}Pt and ^{31}P, typical for a platinum coordinated aryl group. In addition, two further resonances, a doubled doublet and a higher field multiplet are observed with chemical shifts diagnostic of a phenyl ring attached to a β-sila-alkyl group (Fig. 5.2). Two distinct resonances are evident for each ligand environment, confirming their inequivalence. Comparison with data obtained for the products of thermolysis of *cis*-$L_2Pt(CH_2SiMe_3)_2$ (*vide infra*), show marked similarities in the aliphatic

Table 5.1 : *^{31}P N.M.R. Characteristics of $L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.*

Complex	δ^a / ppm	J_{Pt-P} / Hz	J_{P-P} / Hz	J_{P-F} / Hz
cis-$(PMe_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	-27.97, -24.49	1890.8, 1718.0	11.1	-
cis-$(PEt_3)_2Pt(Ph)(CH_2SiMe_2Ph)$[b]	4.22, 4.83	2002.6, 1736.8	13.3	-
cis-$(PMe_2Ph)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	-14.84, -13.25	1947.3, 1749.0	13.3	-
cis-$(PMe_2Ph)_2Pt(Ph\text{-}d^5)(CH_2SiMe_2CH_2SiMe_2Ph\text{-}d^5)$[b]	-14.84, -13.22	1945.1, 1746.8	11.1	-
cis-$(PPh_2Me)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	2.75, 4.61	1972.7, 1764.5	11.1	-
cis-$(PPh_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	23.95, 25.26	2082.4, 1670.4	11.1	-
cis-$(PPh_3)_2Pt(Ph\text{-}d^5)(CH_2SiMe_2CH_2SiMe_2Ph\text{-}d^5)$[b]	23.82, 25.04	2082.4, 1673.7	8.9	-
cis-$(PPh_3\text{-}d^{15})_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	23.44, 24.83	2083.6, 1664.6	8.9	-
cis-$(P\text{-}p\text{-}tol_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[c]	22.24, 23.15	2092.4, 1696.9	8.9	-
cis-$(PPh_2C_6H_4\text{-}2\text{-}CF_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[c]	28.59, 30.42	2036.3, 1725.7	11.1	13.3
trans-$(PMe)_3Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	-19.79	2782.5	-	-
trans-$(PEt_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	14.54	2800.1	-	-
trans-$(PMe_2Ph)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[c]	-9.22	2886.5	-	-
trans-$(PPh_2Me)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$[b]	8.74	2974.0	-	-

a :- referenced to 85% H_3PO_4 / D_2O b :- toluene-d^8 c :- benzene-d^6

Table 5.2 : *^1H N.M.R. Characteristics of $L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.*

Ligand *Geometry*	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]				δ ^{1}H ppm : Ancillary ligands [*Assignment*]
	Pt-CH_2	Si-CH_2	Si-CH_3	Aromatic	
PMe_3[a]	0.65	-0.09	0.08	6.93 m, [H_4];	0.76 m, [P-CH_3]; 0.98 m, [P'-CH_3]
cis	(**67.8**)		0.32	7.09-7.20 m, [H_3, $H_{3'}$, H_4, H_5, $H_{5'}$];	
				7.51 dd, [$H_{2'}$, $H_{6'}$];	
				7.56 t"t", (**64.4**) [H_2, H_6]	
PEt_3[a,b]	0.63		0.20	6.92 m, [H_4]; 6.73 m, [H_3, H_5];	0.72-0.83 m, [P-CH_2CH_3];
cis	(**81.7**)			7.15-7.23 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	0.73-0.84 m, [P'-CH_2CH_3];
				7.58 t"t", (**53.2**) [H_2, H_6];	1.23 m, [P-CH_2CH_3];
				7.77 dd, [$H_{2'}$, $H_{6'}$]	1.40 m, [P'-CH_2CH_3]
PEt_3[a]	0.34	-0.18	-0.08	6.83 m, [H_4]; 6.91 m, [H_3, H_5];	0.86 m, [P-CH_2CH_3];
trans	(**79.6**)		0.21	7.11-7.16 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	1.47 m, [P-CH_2CH_3]
				7.37 dd, [$H_{2'}$, $H_{6'}$];	
				7.42 t"t", (**56.7**) [H_2, H_6]	

Table 5.2 : (continued)

PMe_2Ph[c]	0.69	-0.18	-0.08	d [H_3, H_4, H_5]; d [$H_{3'}$, $H_{4'}$, $H_{5'}$];	0.83 m, [P-CH_3]; 1.12 m, [P'-CH_3];
cis	d		0.33	7.51 dd, [$H_{2'}$, $H_{6'}$];	6.89-6.98 m, [H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$];
				7.65 t"t", (**56.7**) [H_2, H_6]	7.12-7.22 m, [H_2, $H_{2'}$, H_6, $H_{6'}$]
PMe_2Ph[a,e]	0.74	-0.08	0.12	-	0.83 m, [P-CH_3]; 1.09 m, [P'-CH_3];
cis					6.90-6.96 m, [H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$];
					7.18-7.23 m, [H_2, H_6];
					7.25-7.34 m, [$H_{2'}$, $H_{6'}$]
PPh_2Me[a]	0.85	-0.39	-0.17	7.15-7.18 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; d [H_3, H_4, H_5];	1.11 m, (**24.7**) [P-CH_3];
cis	(**85.2**)		0.23	7.43 dd, [$H_{2'}$, $H_{6'}$];	1.25 m, (**20.3**)[P'-CH_3];
				7.48 t"t", (**50.5**) [H_2, H_6]	6.86-6.91 m, [H_3, H_4, H_5];
					6.96-6.99 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];
					7.35-7.37 m, [H_2, H_6];
					7.37-7.39 m, [$H_{2'}$, $H_{6'}$]
PPh_3[f]	0.41	-0.97	-0.72	6.36 m, [H_4]; 6.44 m, [H_3, H_5];	6.88-6.92 m, [H_2, H_6];
cis	(**81.1**)		-0.14	d [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.04 t"t", (**64.2**) [H_2, H_6];	6.96-7.00 m, [$H_{2'}$, $H_{6'}$];
				7.09 dd, [$H_{2'}$, $H_{6'}$];	7.11-7.15 m, [H_3, H_4, H_5];
					7.18-7.24 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]
PPh_3[a,e]	0.92	-0.58	-0.19	-	6.73-6.81 m, [H_3, H_4, H_5];
cis	(**83.4**)		0.19		6.82-6.88 m, [H_3, $H_{4'}$, $H_{5'}$];
					7.31-7.47 m, [H_2, $H_{2'}$, H_6, $H_{6'}$]

Table 5.2 : (continued)

PPh_3-d^{15}[a]	0.91	-0.58	-0.19	6.66 m, [H_4]; 6.75 m, [H_3, H_5];	-
cis	(**85.9**)		0.19	7.11-7.19 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	
				7.40 t"t", (**58.6**) [H_2, H_6];	
				7.43 dd, [$H_{2'}$, $H_{6'}$]	
P-*p*-tol_3[c]	1.05	-0.48	0.00	d [H_3, H_4, H_5]; d [$H_{3'}$, $H_{4'}$, $H_{5'}$];	2.06 s, [*Ar*-CH_3]; 2.07 s, [*Ar'*-CH_3];
cis	(**88.7**)		0.30	6.90 t"t", (**62.3**) [H_2, H_6];	6.76 d, [H_3, H_5]; 6.84 d, [$H_{3'}$, $H_{5'}$];
				7.24 dd, [$H_{2'}$, $H_{6'}$]	7.45 dd, [H_2, H_6] (J_{P-H} = 10.2 Hz);
					7.56 dd, [$H_{2'}$, $H_{6'}$] (J_{P-H} = 9.5 Hz)
$PPh_2C_6H_4$-2-CF_3[a]	0.95	-0.45	-0.15	6.60 m, [H_4]; 6.73 m, [H_3, H_5];	6.85-6.93 m, [H_3, H_4, H_5];
	(**88.7**)		0.26	7.12-7.17 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	6.99-7.02 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];
				7.52 dd, [$H_{2'}$, $H_{6'}$];	7.42-7.49 m, [$H_{2'}$, $H_{6'}$];
				8.02 t"t", (**125.9**) [H_2, H_6]	7.56-7.63 m, [H_2, H_6]

a :- toluene-d^8

b :- $(PEt_3)_2Pt(Ph)(CH_2SiMe_2Ph)$

c :- benzene-d^6

d :- obscured by ligand resonances

e :- $L_2Pt(Ph\text{-}d^5)(CH_2SiMe_2CH_2SiMe_2Ph\text{-}d^5)$

f :- chloroform-d^1

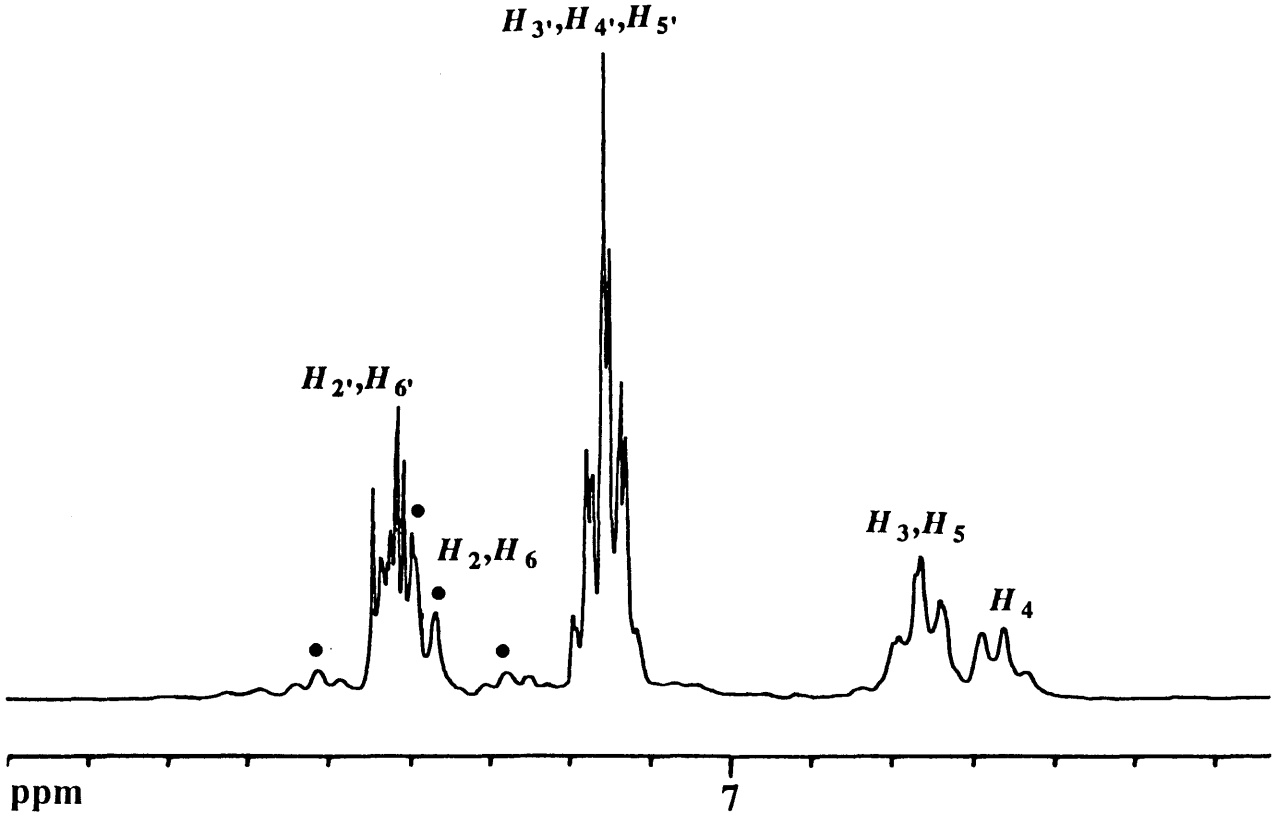


Fig. 5.2 : ^{1}H *N.M.R. of the Aromatic Region of* $(PPh_3\text{-}d^{15})_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.

region, suggesting that $L_2Pt(CH_2SiMe_2Ph)_2$ yield asymmetric (phenyl)[dimethyl(phenyl)silylmethyl]platinum(II) complexes (Fig. 5.3).

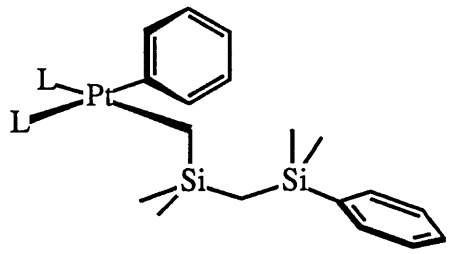


Fig. 5.3 : *Product formed During Thermolysis of* $L_2Pt(CH_2SiMe_2Ph)_2$.

Unequivocal assignment of the structure of these complexes is obtained from the $^{13}C-\{^1H\}$ N.M.R. spectra (Table 5.3). They display two Si-CH_3 carbons; one an intense resonance with no observed coupling and a second less intense signal with a $^3J_{Pt-C}$ coupling. An additional aliphatic carbon coupled to platinum but not to phosphorus due to a Si-CH_2-Si group and a Pt-CH_2 group are also evident. The aromatic region, in addition to resonances due to the asymmetric phosphines, show eight distinct aromatic resonances, three of which are coupled to platinum (Fig. 5.4). This observation effectively excludes the possibility of the metallacycle, since only six signals would be expected. The assignment of these carbons is relatively straightforward. Signals due to the free phenyl group display chemical shifts very similar to those observed for parent dialkyl complexes. C_1 of the coordinated group is characterised by its low field shift, diminished intensity and large coupling constant to platinum. C_4 occurs as a singlet, slightly upfield of its counterpart in the dialkyl.

The peak at *ca.* 127 ppm is assigned to C_3, C_5 on the basis of its chemical shift relative to related complexes[30b, 49, 85, 96]. The remaining signal, also coupled to platinum, is attributed to C_2, C_6. $^2J_{Pt-C}$ for C_2, C_6 is consistently smaller than $^3J_{Pt-C}$ of C_3, C_5. The latter carbon atoms also exhibit a coupling to phosphorus, whereas for the former no spin interaction with ^{31}P is observed. Though these coupling constants have unexpected values, similar trends have been noted elsewhere (See 5.2.4). The resonances of all aromatic carbon atoms experience considerable chemical shifts relative to analogues in the parent dialkyl. Most significantly, C_1 shows a downfield coordination shift of *ca.* 17 ppm and C_4 an upfield shift of 7 ppm relative to $L_2Pt(CH_2SiMe_2Ph)_2$.

The kinetics of this rearrangement have been investigated in some detail, using either ^{31}P, or where this was not possible, ^1H N.M.R. as a monitor. The reaction could be followed readily by ^1H N.M.R. by measuring the relative integrals of the silicon methyl groups in parent and product complexes, hence enabling calculation of the relative concentrations of the two species at a given time.

The reaction was first-order in platinum substrate for at least two half-lives; rate

Table 5.3 : *^{13}C N.M.R. Characteristics of* bis-*(phosphine)(phenyl){([dimethyl(phenyl)silylmethyl]dimethylsilyl}methyl)platinum(II) Complexes.*

L	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*]				δ ^{13}C ppm : Phosphine ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{P-C}) / Hz
	Pt-CH_2	Si-CH_2	Si-CH_3	Aromatic	
PPh_3	14.08, 15.40	5.45	0.02	120.56 [C_4]; 126.60 (**55.7**) [C_3, C_5]	127.33 [$C_{3'}$, $C_{5'}$] (***9.8***);
[$CDCl_3$]	(**567.5**)	(**27.7**)	3.30	(J_{C-P} = 6.6 Hz); 127.84 [$C_{4'}$];	127.61 [C_3, C_5] (***9.7***);
	($J_{C-P_{Trans}}$=83.0 Hz)		(**24.1**)	128.34 [$C_{3'}$, $C_{5'}$];133.40 [$C_{2'}$, $C_{6'}$];	128.90 [$C_{4'}$]; 129.90 [C_4];
	($J_{C-P_{Cis}}$ = 5.8 Hz)			138.41 (**32.4**) [C_2, C_6]; 143.34 [$C_{1'}$];	133.63 (**16.9**) [C_1, $C_{1'}$] (***39.0***);
				159.36 (**875.8**) [C_1] ($J_{C-P_{Trans}}$=114.9 Hz)	134.15 (**15.9**) [$C_{2'}$, $C_{6'}$] (***11.6***);
				($J_{C-P_{Cis}}$ = 11.8 Hz)	134.90 (**13.1**) [C_2, C_6] (**10.7**)
PPh_2Me	12.02, 13.35	5.64	-0.01	121.39 [C_4]; 126.80 (**64.5**) [C_3, C_5]	14.63 (**22.2**) [*P-*CH_3] (***22.2***);
[$CDCl_3$]	(**535.9**)	(**27.6**)	3.62	(J_{C-P} = 6.1 Hz); 126.95 [$C_{4'}$];	16.29 (**29.8**) [*P-*CH_3] (***35.1***);
	($J_{C-P_{Trans}}$=83.6 Hz)		(**25.5**)	127.21 [$C_{3'}$, $C_{5'}$]; 133.38 [$C_{2'}$, $C_{6'}$];	127.91 [$C_{3'}$, $C_{5'}$]; 128.06 [C_3, C_5];
	($J_{C-P_{Cis}}$ = 4.8 Hz)			138.17 (**30.9**) [C_2, C_6] (J_{C-P} = 2.1 Hz);	129.34 [$C_{4'}$]; 129.43 [C_4];
				143.20 [$C_{1'}$]; 160.96 (**807.6**) [C_1]	132.61 (**14.3**) [$C_{2'}$, $C_{6'}$] (***11.5***);
				($J_{C-P_{Trans}}$=117.4 Hz; $J_{C-P_{Cis}}$ = 12.4 Hz)	132.91 (**14.8**) [C_2, C_6] (***10.6***);
					134.90 (**16.5**) [C_1, $C_{1'}$] (***22.2***)

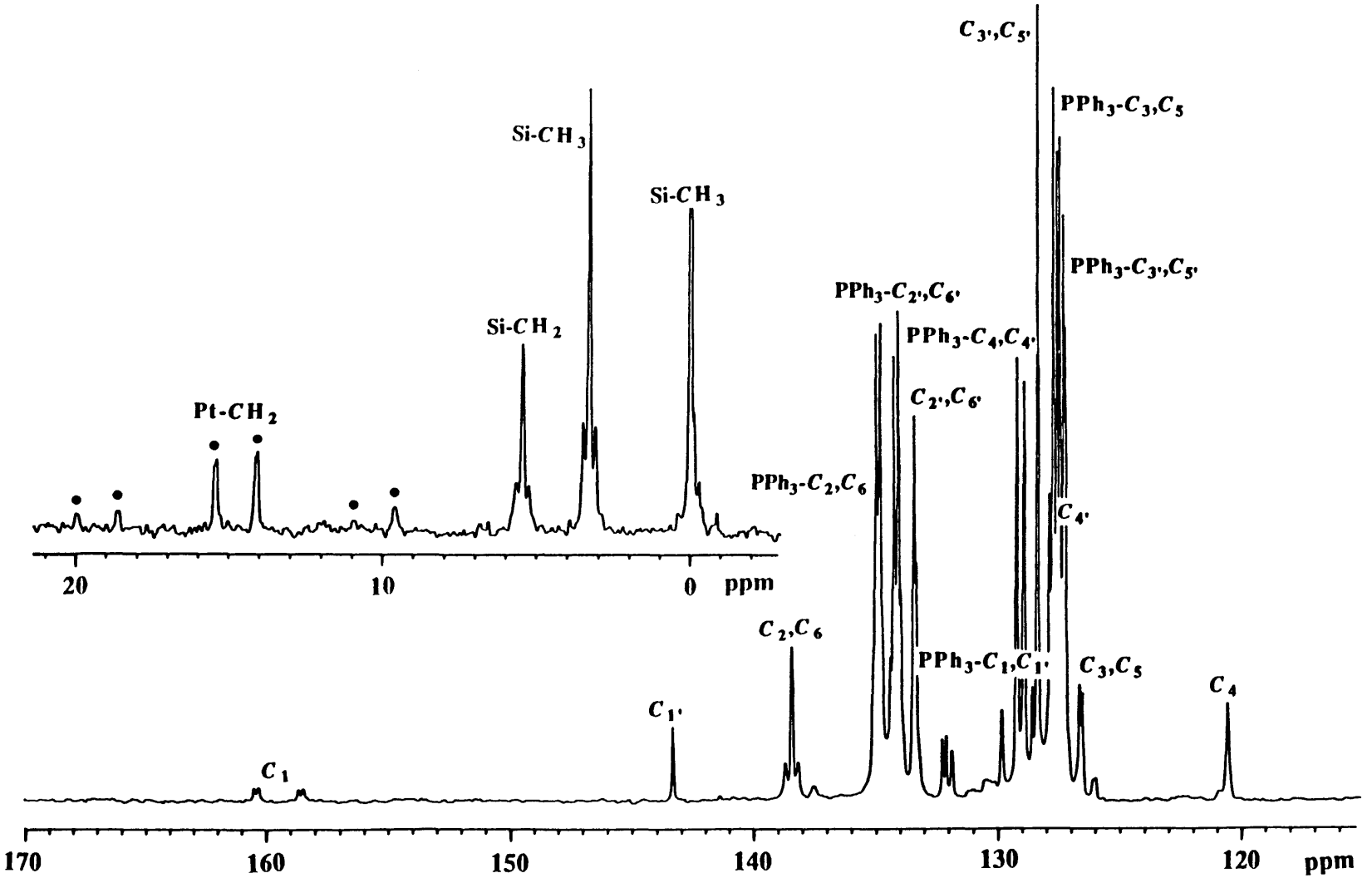


Fig. 5.4 : *^{13}C N.M.R. of $(PPh_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.*

Table 5.4 : *Kinetic Data for the Thermolysis of* $L_2Pt(CH_2SiMe_2Ph)_2$.

R	L	[L] / M	T / °C	$10^5 \times k_{obs}$ / s^{-1}
CH_2SiMe_2Ph	PMe_2Ph	0.0	115.0	1.75
CH_2SiMe_2Ph	PMe_2Ph	0.0	117.5	2.58
CH_2SiMe_2Ph	PMe_2Ph	0.0	120.0	3.44
CH_2SiMe_2Ph	PMe_2Ph	0.0	122.5	4.50
CH_2SiMe_2Ph	PMe_2Ph	0.0	125.0	6.85
CH_2SiMe_2Ph-d^5	PMe_2Ph	0.0	125.0	5.59
CH_2SiMe_2Ph	PPh_2Me	0.0	125.0	1.78
CH_2SiMe_2Ph	PPh_2Me	0.0	127.5	2.60
CH_2SiMe_2Ph	PPh_2Me	0.0	130.0	3.51
CH_2SiMe_2Ph	PPh_2Me	0.0	132.5	4.66
CH_2SiMe_2Ph	PPh_2Me	0.0	135.0	6.12
CH_2SiMe_2Ph	PPh_3	0.0	75.0	1.60
CH_2SiMe_2Ph	PPh_3	0.0	77.5	2.64
CH_2SiMe_2Ph	PPh_3	0.0	80.0	3.65
CH_2SiMe_2Ph	PPh_3	0.0	82.5	5.39
CH_2SiMe_2Ph	PPh_3	0.0	85.0	8.61
CH_2SiMe_2Ph-d^5	PPh_3	0.0	85.0	7.12
CH_2SiMe_2Ph	PPh_3-d^{15}	0.0	85.0	5.86
CH_2SiMe_2Ph	PPh_3	0.025	115.0	5.85
CH_2SiMe_2Ph	PPh_3	0.05	115.0	3.81
CH_2SiMe_2Ph	PPh_3	0.075	115.0	2.79
CH_2SiMe_2Ph	PPh_3	0.1	115.0	2.09
CH_2SiMe_2Ph	P-*p*-tol_3	0.0	85.0	1.36
CH_2SiMe_2Ph	P-*p*-tol_3	0.0	87.5	2.41
CH_2SiMe_2Ph	P-*p*-tol_3	0.0	92.5	4.91
CH_2SiMe_2Ph	P-*p*-tol_3	0.0	95.0	6.57
CH_2SiMe_2Ph	P-*p*-tol_3	0.0	97.5	9.84
CH_2SiMe_2Ph	PMe_3	0.0	130.0	3.53
CH_2SiMe_2Ph	PEt_3[a]	0.0	100.0	4.09
CH_2SiMe_2Ph	$PPh_2C_6H_4$-2-CF_3	0.15	25.0	0.33

a :- rearranges to the *trans* product

data appear in Table 5.4 and are presented graphically for $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$ in Fig. 5.5. $L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$ is the only product observed by ^1H and ^{31}P N.M.R. when the reactions are carried out under argon.

An investigation of the temperature variation of the first order rate constant conforms linearly to the Arrhenius relationship :-

$$k_{obs} = Ae^{-E_a/RT}$$

for the rearrangement of $L_2Pt(CH_2SiMe_2Ph)_2$ [L = PMe_2Ph, PPh_2Me, PPh_3, P-*p*-tol_3] (Figs. 5.6 and 5.7). From these plots values of the Arrhenius activation energy, E_a and the frequency factor, A can be obtained. Additionally, the enthalpy of activation ($\Delta H^{\ddagger}$) for a reaction in solution and entropy of activation ($\Delta S^{\ddagger}$), for each system, was calculated using the following expressions :-

$$\Delta H^{\ddagger} = E_a - RT \quad kJ\ mol^{-1} \ ^{97}$$

$$\Delta S^{\ddagger} = 19.155\ (\log_{10}A - 13.23) \quad JK^{-1}\ mol^{-1} \ ^{98}$$

Values of the same activation parameters obtained by application of the Eyring equation :-

$$k_{obs} = \frac{\kappa RT}{Nh}\ e^{\Delta S^{\ddagger}/R}\ e^{-\Delta H^{\ddagger}/RT}$$

where :-

κ = transmission coefficient
h = Planck's constant
N = Avogardo's constant
R = gas constant

were essentially identical to those calculated by the Arrhenius treatment; verifying the validity of the Arrhenius relationship over relatively small temperature ranges.

The activation parameters obtained for L = PMe_2Ph, PPh_2Me, PPh_3 and P-*p*-tol_3 are similar implying a common mechanism for the rearrangement (Table 5.5). The variation in $\Delta S^{\ddagger}$ across the series suggest that differences in reactivity are entropic in origin; the most labile of the systems studied is that where L = PPh_3, the least reactive is $(PPh_2Me)_2Pt(CH_2SiMe_2Ph)_2$. The reason for the relative inertness of the latter complex is not entirely clear, though differences in steric and electronic demands in the ground and transition state may be a significant factor (*vide infra*).

Isotopic substitution at selected sites can often give useful information about

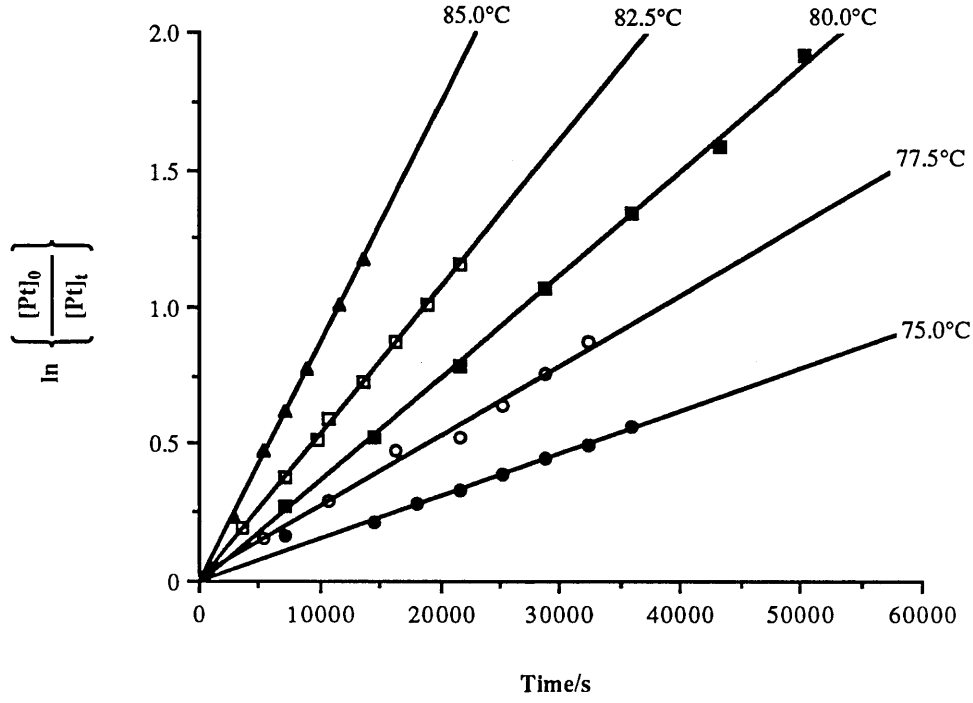


Fig. 5.5 : *Kinetic Data for the Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$.

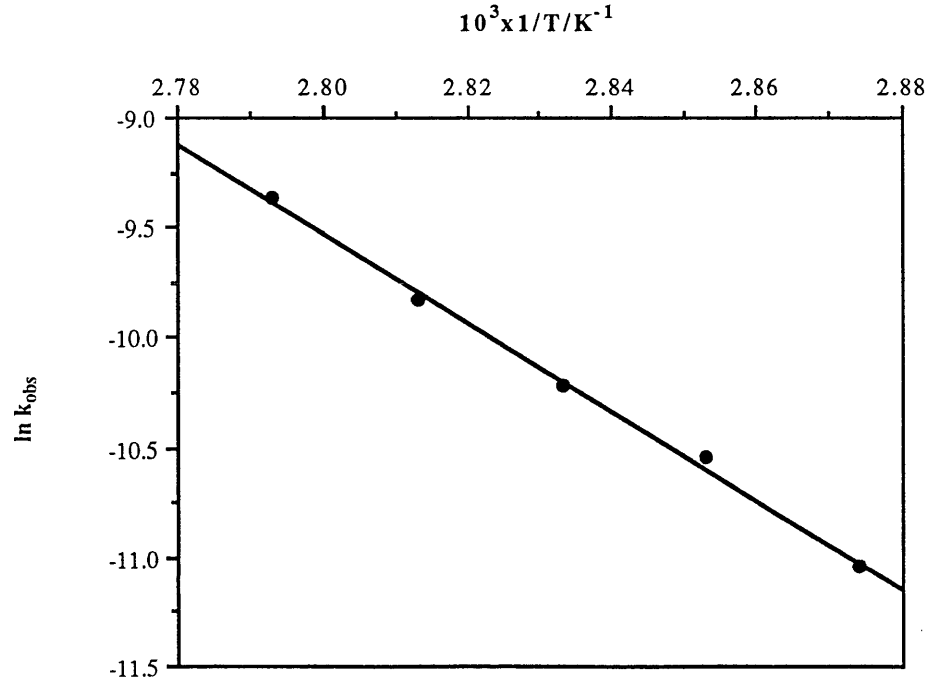


Fig. 5.6 : *Arrhenius Plot for the Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$.

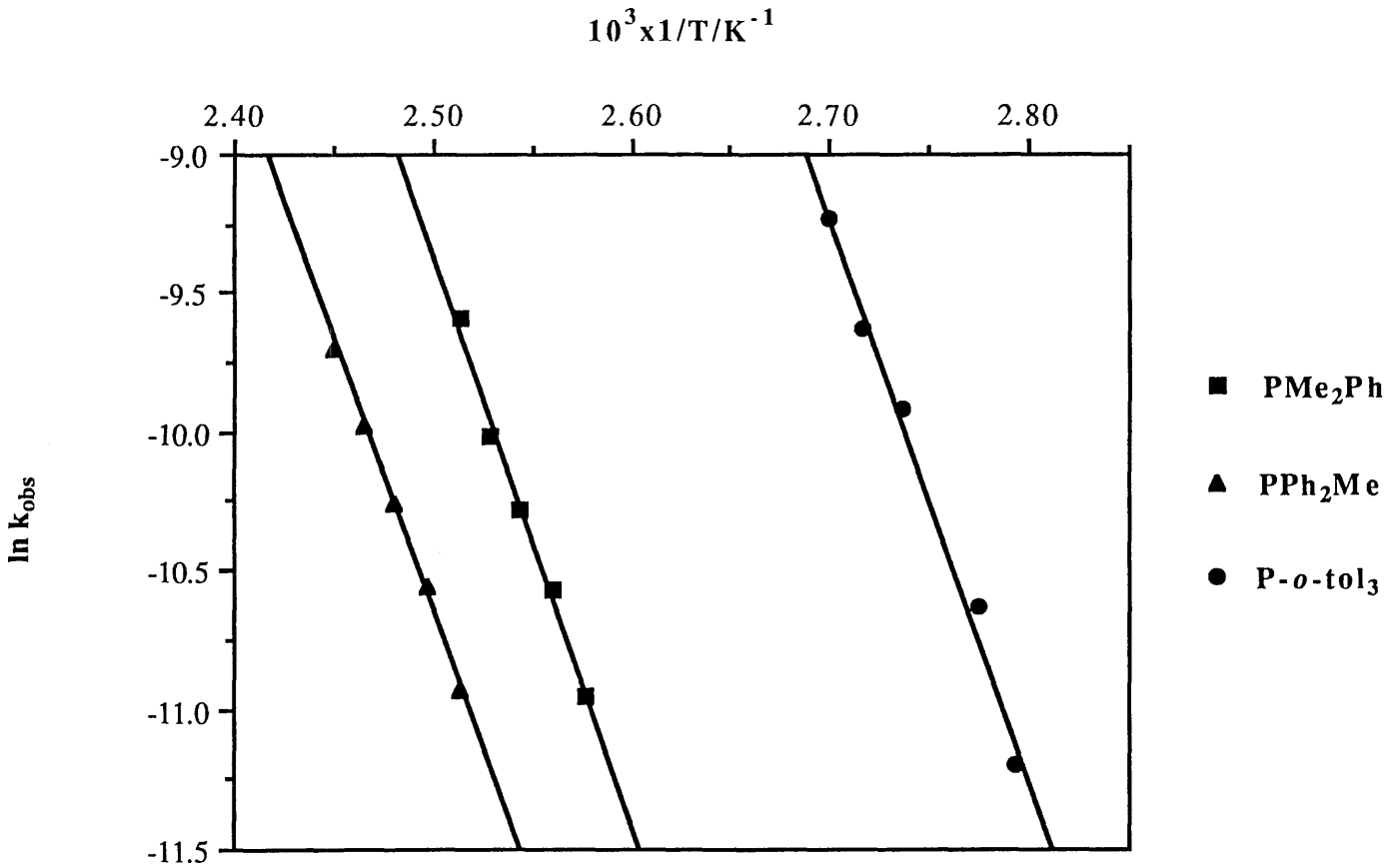


Fig. 5.7 : *Arrhenius Plot for the Thermolysis of* $L_2Pt(CH_2SiMe_2Ph)_2$ *[L =* PMe_2Ph, PPh_2Me, P-o-tol_3*].*

Table 5.5 : *Activation Parameters for the Rearrangement of* cis-$L_2Pt(CH_2SiMe_2Ph)_2$.

L	E_a kJ mol^{-1}	$\Delta H^{\ddagger}_{298}$ kJ mol^{-1}	Frequency factor, A	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$ kJ mol^{-1}
PMe_2Ph	169.2 (±3)	166.7 (±3)	1.05×10^{18}	91.8 (±7)	139.3 (±5)
PPh_2Me	163.9 (±1)	161.4 (±1)	5.98×10^{16}	68.0 (±3)	141.1 (±2)
PPh_3	168.1 (±2)	165.6 (±2)	2.84×10^{20}	138.4 (±6)	124.4 (±2)
P-*p*-tol_3	168.0 (±3)	165.5 (±3)	4.80×10^{19}	123.6 (±8)	128.7 (±3)

force-constant changes on the isotopically substituted atom in the transition state compared with those in the reactant (See 6.2.2.2)[99]. To deduce the importance of any such effects, rates of rearrangement were monitored for $L_2Pt(CH_2SiMe_2Ph\text{-}d^5)_2$ [L = PMe_2Ph, PPh_3] and $(PPh_3\text{-}d^{15})_2Pt(CH_2SiMe_2Ph)_2$ (Table 5.4 and Figs. 5.8 and 5.9). These measurements show a small but significant isotopic inhibition upon deuteration of the sila-neophyl ring sites ($k^H/k^D = 1.2$) and a slightly larger effect for triphenylphosphine-d^{15}; clearly indicating that C-H bond cleavage does not participate *en route* to the most energetic transition state.

Addition of PPh_3 to solutions of $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$, severely retards the reaction. The dependence of k_{obs} on phosphine concentration was obtained by plotting the reciprocal of the rate constant against phosphine concentration. The resultant straight line has a non-zero intercept (Fig. 5.10).

5.2.1.2. Mechanistic Implications.

Inhibition of the reaction in the presence of excess phosphine suggests that dissociation of L is a prerequisite for rearrangement. If the reaction is characterised by the following series of steps :-

$$L_2PtR_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LPtR_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \eta^2\text{-silene intermediate} \xrightarrow{k_3} \text{Product}$$

a first order rate-law of the form :-

$$\frac{-d[L_2PtR_2]}{dt} = \frac{k_1k_2k_3}{k_2k_3 + k_{-1}(k_{-2} + k_3)[L]}$$

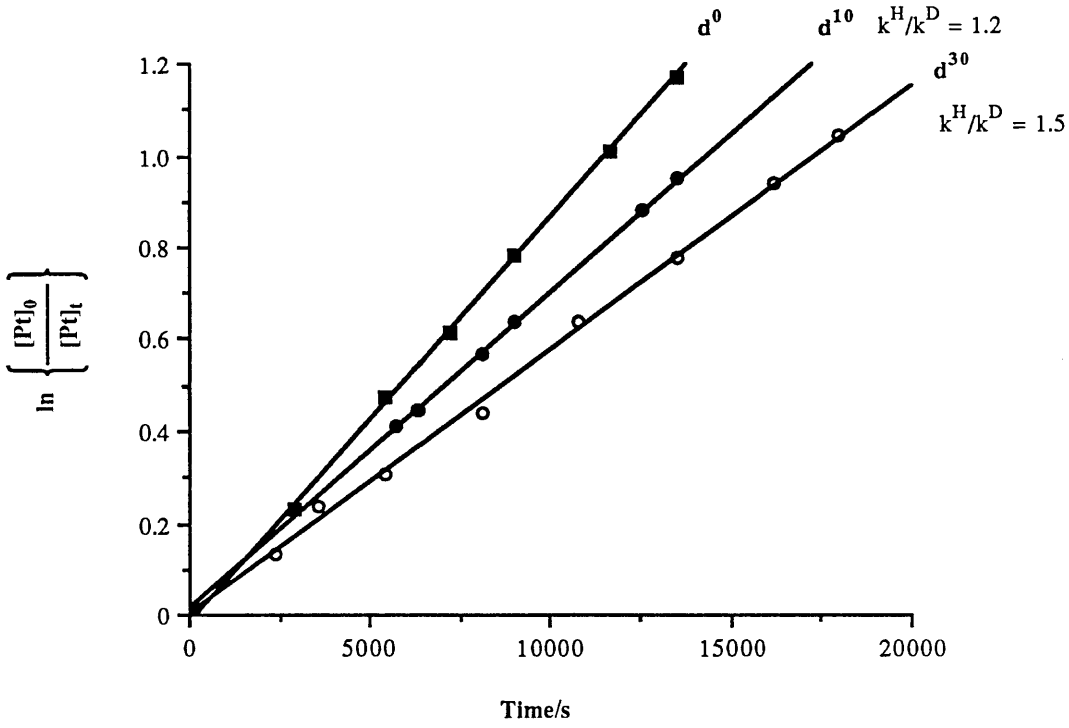


Fig. 5.8 : *Deuterium Isotope Studies for the Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$.

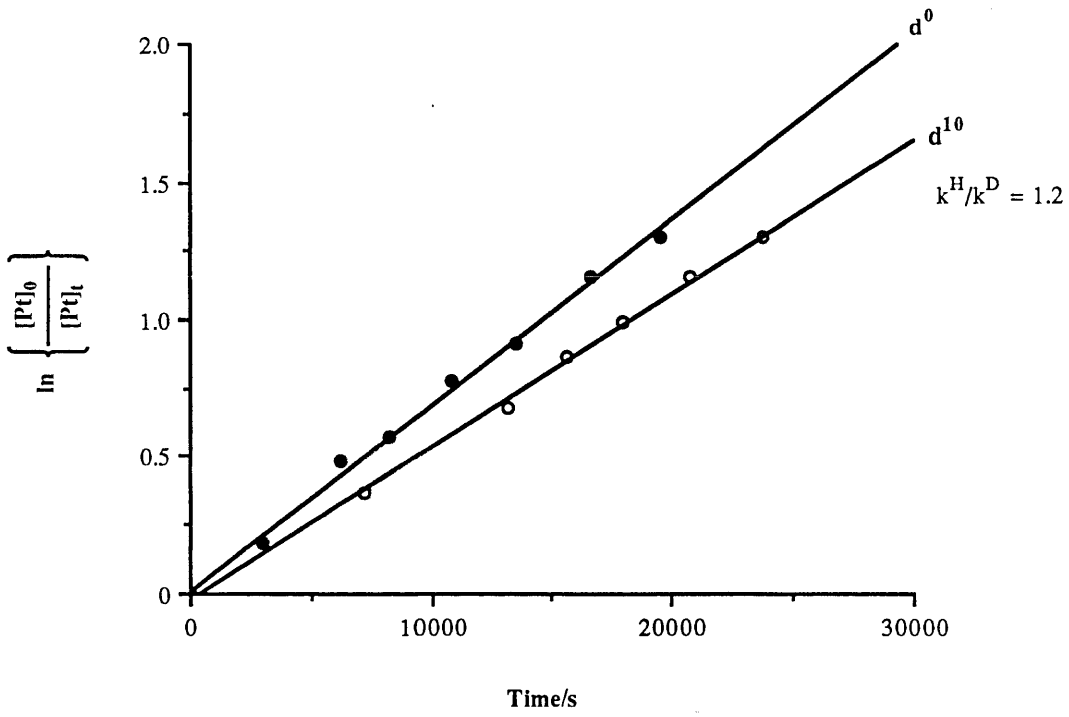


Fig. 5.9 : *Deuterium Isotope Studies for the Thermolysis of* $(PMe_2Ph)_2Pt(CH_2SiMe_2Ph)_2$.

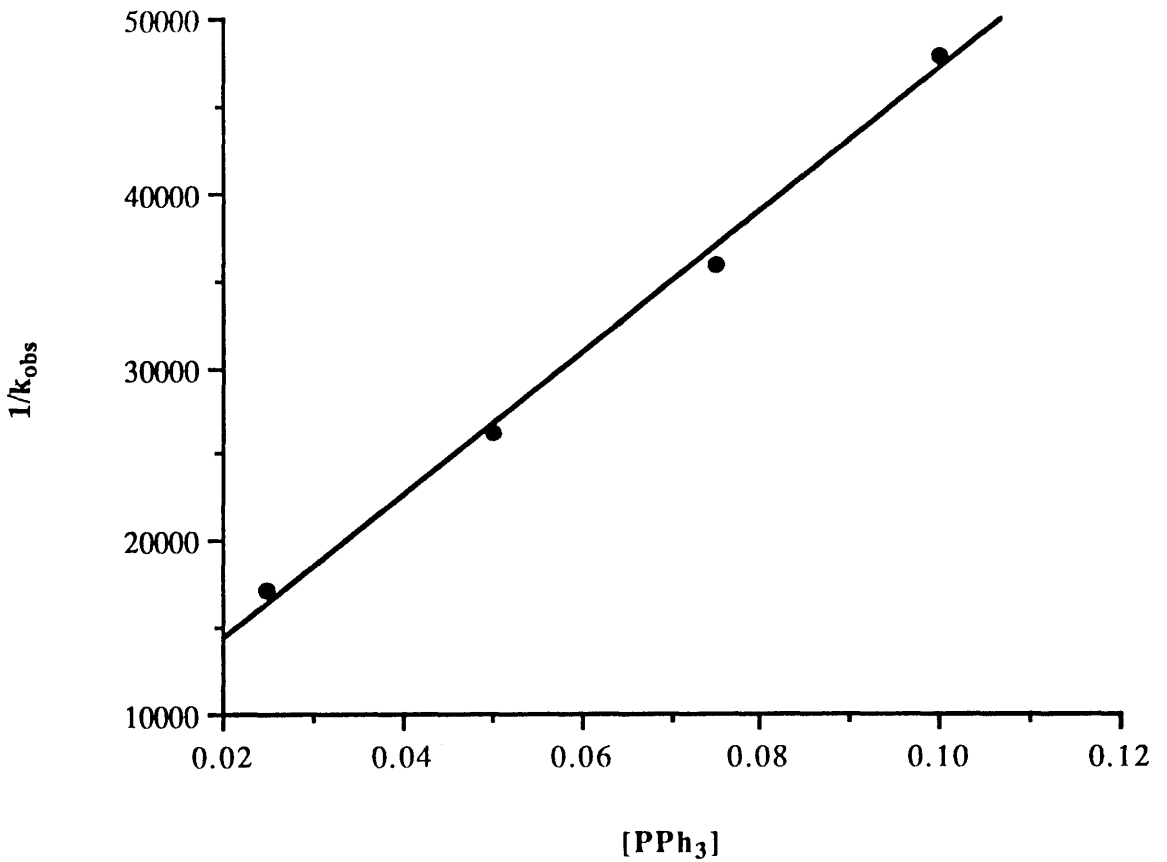


Fig. 5.10 : *Dependency of the Rate of Rearrangement of $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$ on Phosphine Concentration.*

is predicted, assuming steady state concentrations are applied for all intermediates, with an observed rate constant :-

$$k_{obs} = \frac{k_1 k_2 k_3}{k_2 k_3 + k_{-1}(k_{-2} + k_3)[L]}$$

At constant concentrations of phosphine, the rate equation takes the form :-

$$\frac{-d[L_2PtR_2]}{dt} = k_{obs}[L_2PtR_2]$$

Hence at constant temperature, k_{obs} is inversely proportional to the concentration of added phosphine :-

$$1/k_{obs} = \left\{ \frac{k_{-1}(k_{-2} + k_3)}{k_1 k_2 k_3} \right\} [L] + 1/k_1$$

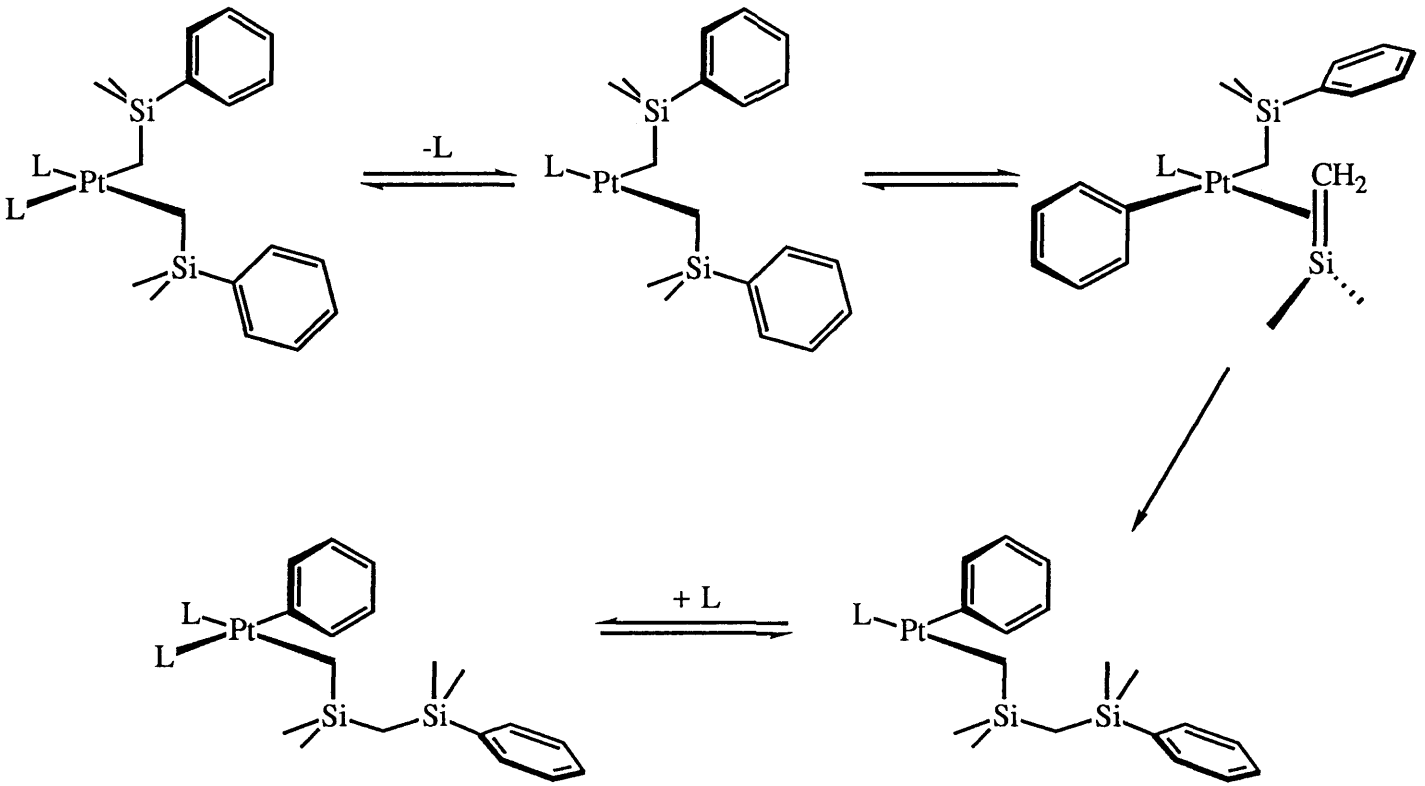
Thus, a plot of $1/k_{obs}$ against $[PPh_3]$ should be linear with an intercept of k_1, the rate of phosphine dissociation. An estimate of *ca.* $10^{-4} \leq k_1 \leq 10^{-3}$ can be made for k_1 for this process, significantly faster than the observed rates under these conditions. On this basis phosphine dissociation can be excluded as the rate limiting process.

A scheme consistent with the observations noted appears in Scheme. 5.3. Following dissociation of one phosphine, generating a tricoordinate intermediate, direct Si-C bond cleavage occurs, resulting in regiospecific phenyl transfer to platinum (*vide infra*) and formation, most plausibly, of an η^2-silene or sila-platinacyclopropane complex. Migratory "insertion" into the platinum-methylene bond of the remaining sila-neophyl group yields the observed asymmetric product.

The rate inhibition observed for $L_2Pt(CH_2SiMe_2Ph\text{-}d^5)_2$ is due to a secondary isotope effect on β-migration. Such deuterium isotope effects are observed in systems where the vibrational modes of the isotopically labelled site are perturbed during the transformation from reactant to product[99-102]. Secondary isotope effects are classified α, β, γ *etc.*, according to the position of the deuterium atom relative to the bond which is broken during the reaction; the carbon at which the reaction is taking place is designated α. Hence, the observed value of 1.2 is due to a β-secondary effect.

Secondary isotope effects are generally rationalised in terms of hybridisation effects, steric effects, inductive effects and hyperconjugative effects.

(i) The effect of change of hybridisation from sp^3 to sp^2 increases the s-character of the bonds and shortens them. As a result, an sp^3-carbon bearing hydrogen will have significantly higher bending vibrations associated with it than will an



L = PMe_3, PMe_2Ph, PPh_2Me, PPh_3, P-*p*-tol_3, $PPh_2C_6H_4$-2-CF_3

Scheme. 5.3 : *Proposed Mechanism for the Thermolytic Rearrangement of* $(PR_3)_2Pt(CH_2SiMe_2Ph)_2$.

sp^2-carbon bearing hydrogen.

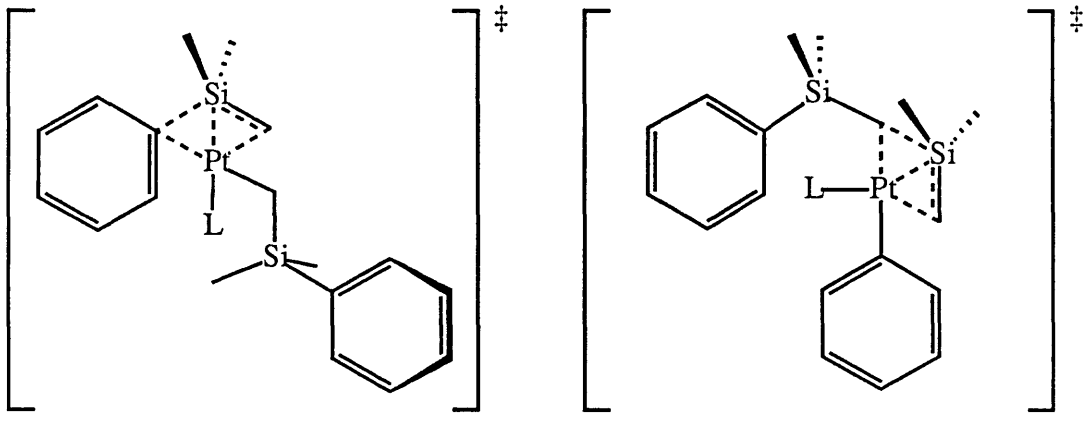
(ii) Steric effects originate as a direct result of an effectively shorter C-D bond relative to a C-H bond. Steric secondary isotope inhibitions usually exhibit inverse effects.

(iii) An inductive effect arises as a result of a shorter C-D bond having higher density and hence more effectively electron supplying than a C-H bond.

(iv) Hyperconjugation effects are observed with regard to β-substituted deuterium because CD_3 is effectively less delocalised than CH_3, as a result a cation or π-system is less stabilised by an adjacent CD_3 than by CH_3.

The magnitude of the observed β-effect is most likely to be a combination of an inductive effect and to a change in hybridisation at the silicon from sp^3 to sp^2.

Two possible transition states which are relatively high in energy can be envisaged in this mechanistic regime (Fig. 5.11). The fact that inhibition is observed on aryl transfer suggests that formation of the silene intermediate is, most plausibly, the most energetic step. If migratory insertion of silene into the Pt-CH_2 bond was controlling the rate of rearrangement, a zero isotope effect would be anticipated.



A B

Fig. 5.11 : *Possible Transition States for the Rearrangement of* $L_2Pt(CH_2SiMe_2Ph)_2$.

The isotope effect of 1.5 observed upon deuteration of triphenylphosphine is relatively large and generally larger than effects associated with secondary inhibition. Perhaps the best explanation is the development of an agostic interaction between platinum and a phosphine C-H bond as the other ligand dissociates. Numerous examples of isolated complexes, which demonstrate agostic interactions have been reported[103, 104]. Recently, the isotope effect observed during ligand substitution on $(PCy_3)_2W(CO)_3L$ [L = H_2, N_2, py, $POMe_3$] (k^H/k^D = 1.20) was attributed to an agostic interaction between a cyclohexyl C-H bond and tungsten as L dissociates[105].

It has been observed that ancillary ligands may influence ground and

transition-state energies through transmission of their stereo-electronic properties to the metal centre; often resulting in non-linear dependencies of log k_{obs} with steric bulk of phosphine[106].This analysis, termed QALE (quantitative analysis of ligand effects), predicts four steric profiles, which depend on the mechanism of the reaction. The QALE method assumes that $\Delta G^{\ddagger}$ consists of steric (k_{st}) and electronic (k_{el}) components such that :-

$$\log k_{obs} = \log k_{st} + \log k_{el}$$

and that there are different thresholds for the onset of steric effects in the ground and transition states. Electronic and steric profiles are generated; the electronic profile is a plot of $\log_{obs}$ for a series of isosteric ligands (most commonly various *para*-substituted triarylphosphines) against a measure of the σ-donicity (σ_d) of the phosphine ligand. Often pK_a values of HPR_3^+ have been employed as a measure of σ_d[107]. Steric components of the rate are obtained by determining the difference between data points for other ligands and the electronic profile (at the same pK_a). A steric profile is then constructed by plotting log k_{st} against the cone angle (θ)[91a] of the ligand.

For a dissociative mechanism, the departing ligand produces a transition state which is less congested and more flexible than the ground state. A more congested state has a lower steric threshold and the energy of the more flexible state rises less rapidly than that of a less flexible state after the onset of steric effects. Between the onset of steric effects in the ground and transition-states, the rate of reaction rises rapidly[106].

Although insufficient data precludes quantitative analysis, qualitatively, at small cone angles there is no steric effect. This region is followed by a threshold for the onset of steric effects ($\theta \approx 120°$) in a more congested transition state and the rate of reaction drops significantly. The transition state is more flexible than the ground state, so after the second steric threshold (θ *ca.* 140°), the transition state energy rises less rapidly than the ground state energy and an increase in the rate of reaction is observed. This analysis does not agree with a dissociative type mechanism; similarly QALE analysis of oxidative addition of methyl iodide to Vaska's compound yielded a complex steric profile and was attributed to the possibility of competing pathways involved in the mechanism of the reaction[91b].

The reactivity of PPh_2Me appears to deviate from that of the remainder of complexes studied and may be due to less bulky phosphines reacting by an energetically different pathway to their bulkier analogues. For bulky triarylphosphines dissociation of one ligand is rapid[91a], resulting in great steric relief in the tricoordinate intermediate. In such cases $k_{-1} >> k_2$, k_3 and the overall rate constant, k_{obs}, is dependent on the relative rates of subsequent steps. In contrast, dissociation of one phosphine with a small cone angle is slower. As a result, the reassociation of phosphine, k_{-1}, becomes increasingly important. If though, the reassociation of phosphine does not cause too much steric interference during aryl transfer, the reaction will remain relatively facile. In the limiting

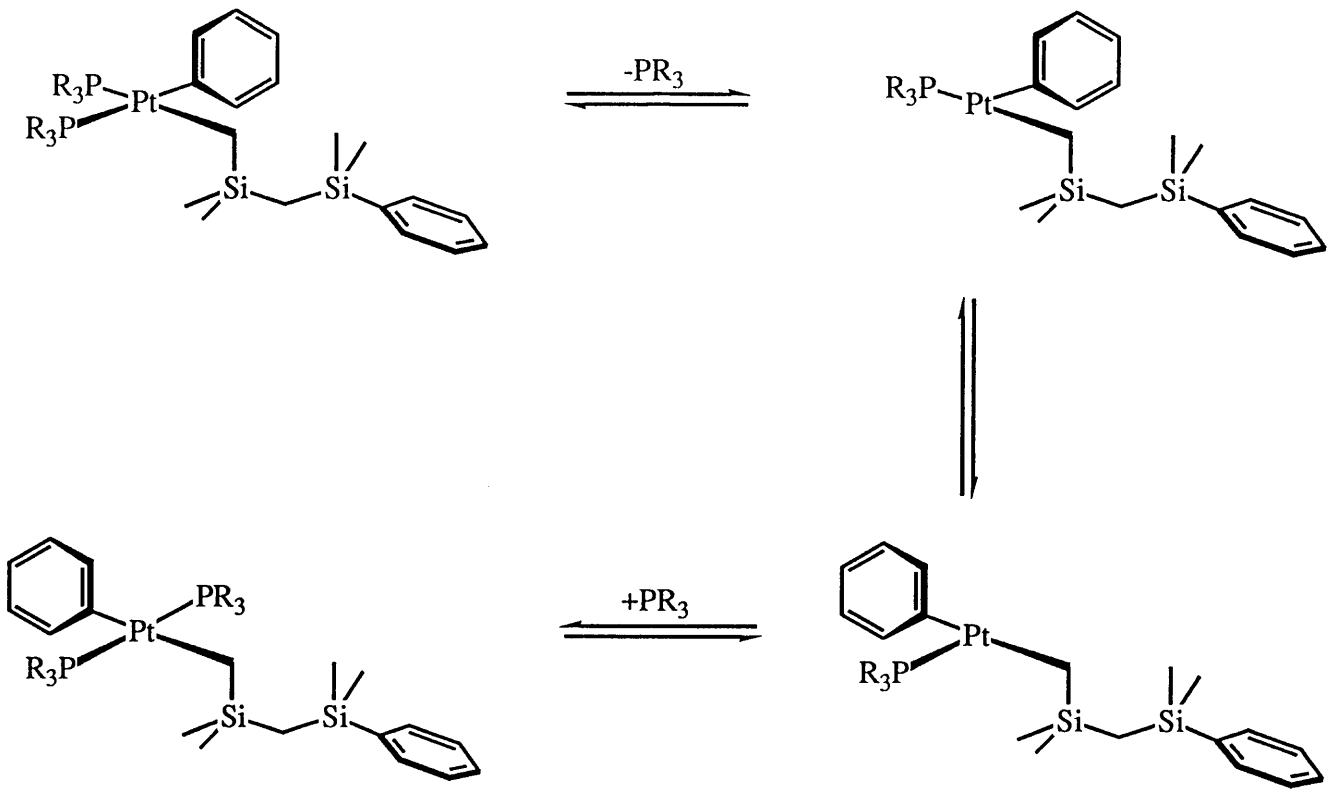
extreme, where steric bulk of the phosphine becomes important and dissociation of phosphine is relatively slow, the rate of reaction will decline and dissociation of phosphine will be truly rate-limiting. In order to determine the existence of such a regime, examination of the effect of added phosphine on the observed rate constant for each phosphine would be necessary. A value of k_1 of equal or lesser magnitude than k_{obs} would suggest that phosphine dissociation was relatively slow and high energy relative to the ground state.

Thermolysis of $(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$ does not always generate a product with *cis*-geometry. In the instances that it was observed, ^1H N.M.R. characteristics were inconsistent with *cis*-$(PEt_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)_2$ due to the absence of the Si-CH_2-Si group and the presence of only one Si-CH_3 resonance corresponding to only six hydrogens. The data suggest that the complex is $(PEt_3)_2Pt(Ph)(CH_2SiMe_2Ph)$, formed by loss of dimethylsilene, probably in an oligomeric form. Further characterisation of this compound by ^{13}C was prevented by the scarcity of the complex.

Often, though, a product with *trans*-geometry, namely *trans*-$(PEt_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$ is observed. ^{31}P N.M.R. consists of a 1:4:1 "triplet" with $^1J_{Pt\text{-}P} = 2800$ Hz, characteristic of *trans*-platinum(II) complexes. The signals due to hydrocarbyl fragments are very similar to those noted for *cis*-$L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$ by ^1H N.M.R. spectroscopy; excepting the Pt-CH_2 group, which appears as a triplet with satellites instead of an apparent quartet. Resonances assignable to triethylphosphine on the other hand, display a single phosphine environment, characteristic of a *trans*-configuration (Table 5.2).

Very few *trans*-platinum(II) complexes with alkyl groups are known. $(PEt_3)_2Pt(CH_2CMe_2Ph)(C_6H_4\text{-}2\text{-}CMe_3)$[31, 49] was found to isomerise to its *trans*-counterpart and *trans*-$(PR_3)_2Pt(CH_3)(Ar)$ [Ar = fluoroaryl group] have been characterised by ^{19}F N.M.R. spectroscopy[108]. Square planar platinum(II) complexes generally favour geometries in which ligands of strong *trans*-influence, such as R^- [R = alkyl or aryl] , are not mutually *trans* but are *trans* to groups of lower influence. *trans*-$(PEt_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$ is one of the few *trans*-(alkyl)(aryl)platinum(II) complexes to be characterised.

Prolonged thermolysis of $L_2Pt(CH_2SiMe_2Ph)_2$ [L = PMe_3, PMe_2Ph , PPh_2Me] also results in formation of the *trans*-isomer. The mechanism of this *cis-trans* isomerisation, in the absence of added phosphine is dissociative in nature[109]. Dissociation of one phosphine generates a tricoordinate T-shaped intermediate, which can readily transform to a second geometrically distinct 3-coordinate intermediate. Reassociation of the ligand produces the thermodynamically preferred *trans*-isomer (Scheme. 5.4). Presence of adventitious diethyl ether during thermolysis of $(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$ may have facilitated this reaction, since the amount of observed *cis*-isomer was negligible. Polar solvents are well known to aid isomerisations by coordinating weakly at the "vacant"



Scheme. 5.4 : *Proposed Mechanism for* cis-trans-*Isomerisation of* $(PPh_3)_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$.

site, stabilising the transition state[110].

5.2.2. *Mechanistic Studies of the Influence of Aromatic Substituent Effects on the Rearrangement of* cis-$(PPh_3)_2Pt(CH_2SiMe_2Ar)_2$.

5.2.2.1. Kinetic Studies.

cis-bis-(triphenylphosphine)-*bis*-[dimethyl(aryl)silylmethyl]platinum(II) [Ar = 2-Me, 3-Me, 4-Me, 4-OMe, 4-^{t}Bu, 4-F, 2-CF_3, 3-CF_3, 4-CF_3, 4-NMe_2] quantitatively rearrange to the corresponding *bis*-(phosphine)(aryl)({[dimethyl(aryl)-silylmethyl]dimethylsilyl}methyl)platinum(II) complexes, $(PPh_3)_2Pt(Ar)(CH_2SiMe_2CH_2SiMe_2Ar)$ between 60°C-90°C, with the exception of $(PPh_3)_2Pt(C_6F_5)(CH_2SiMe_2CH_2SiMe_2C_6F_5)$ where the dialkyl was only observed as a transient species. ^{31}P (Table 5.6) and ^1H (Table 5.7) N.M.R. characteristics are similar to

Table 5.6 : *^{31}P N.M.R. Characteristics of* cis-$(PPh_3)_2Pt(Ar)(CH_2SiMe_2CH_2SiMe_2Ar)$.

Ar	δ^a / ppm	J_{Pt-P} / Hz	J_{P-P} / Hz
C_6H_4-2-Me[b]	22.17, 25.17	1652.6, 2080.2	8.9
C_6H_4-3-Me[b]	23.95, 25.50	1660.4, 2085.7	8.9
C_6H_4-4-Me[b]	24.16, 24.80	1674.8, 2075.8	10.0
C_6H_4-4-OMe[b]	24.62, 25.14	1702.5, 2060.3	11.1
C_6H_4-4-^{t}Bu[b]	24.07, 25.29	1663.7, 2086.8	8.9
C_6H_4-4-F[b]	23.95, 24,89	1740.1, 2060.3	10.0
C_6H_4-2-CF_3[c]	22.27, 24.22	1889.7, 2042.6	13.3
C_6H_4-3-CF_3[b]	23.49, 24.95	1707.2, 2055.8	11.1
C_6H_4-4-CF_3[b]	23.55, 25.26	1743.5, 2073.5	13.3
C_6H_4-4-NMe_2[b]	24.52, 25.34	1710.2, 2113.4	11.1
C_6F_5[d]	21.93, 25.26	2040.3, 2545.6	13.3
C_6H_5[b]	23.95, 25.26	1670.4, 2082.4	11.1

a :- referenced to 85% H_3PO_4

b :- toluene-d^8

c :- benzene-d^6

d :- chloroform-d^1

Table 5.7 : *^1H N.M.R. Characteristics of $(PPh_3)_2Pt(Ar)(CH_2SiMe_2CH_2SiMe_2Ar)$.*

Aryl group	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*] (J_{P-H}) / Hz				δ ^{1}H ppm : Ancillary ligands [*Assignment*]
	Pt-CH_2	Si-CH_2	Si-CH_3	Aromatic	
C_6H_4-2-Me[a]	0.83	-0.64[b]	-0.39	2.28 [CH_3]; 2.78 [CH_3]; 6.50 m, [H_5];	6.70-6.80 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];
	(86.0)	-0.42	-0.18	6.63 dd, [H_3];	6.81-6.88 m, [H_3, H_4, H_5];
	0.93		0.23	6.90-7.12 m, [$H_{3'}$, H_4, $H_{4'}$, $H_{5'}$]; c [$H_{6'}$];	7.26-7.36 m, [$H_{2'}$, $H_{6'}$];
	(86.0)		0.26	7.51 t"t", (**51.3**) [H_6]	7.38-7.47 m, [H_2, H_6]
C_6H_4-2-CF_3[a]	0.70[d]	-0.71[e]	-0.52	6.45 m, [H_5]; 6.50 m, [H_3,];	6.70-6.80 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];
	(85.0)	-0.31	-0.18	6.92-7.07 m, [$H_{3'}$, H_4, $H_{4'}$, $H_{5'}$]; c [$H_{6'}$];	6.81-6.89 m, [H_3, H_4, H_5];
	1.08[f]		0.21	7.57 t"t", (**49.9**) [H_6];	7.29-7.36 [H_2 , H_6];
	(82.5)		0.27		7.42-7.49 [H_2, H_6]
C_6H_4-3-Me[a]	0.94	-0.54	-0.17	1.98 [CH_3], 2.18 [CH_3]; 6.49 m, [H_5];	6.72-6.81 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];
	(85.9)		0.22	6.87-7.15 m, [H_4, $H_{4'}$, $H_{5'}$, H_6, $H_{6'}$];	6.82-6.88 m, [H_3, H_4, H_5];
				c [H_2, $H_{2'}$]	7.27-7.50 m, [H_2, $H_{2'}$, H_6, $H_{6'}$]

Table 5.7 : (continued)

C_6H_4-3-CF_3[a]	0.79 (**83.6**)	-0.81	-0.26 0.07	c	6.53-6.84 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 6.91-7.07 m, [H_3, H_4, H_5]; 7.25-7.41 m, [$H_{2'}$, $H_{6'}$]; 7.56-7.77 m, [H_2, H_6]
C_6H_4-4-Me[a]	1.05 (**84.8**)	-0.47	-0.04 0.20	6.74 dd, [H_3, H_5]; c [$H_{3'}$, $H_{5'}$]; c [$H_{2'}$, $H_{6'}$]; 7.42 t"t", (**58.5**) [H_2, H_6]	6.87-6.97 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.03-7.15 m, [H_3, H_4, H_5]; 7.44-7.52 m, [$H_{2'}$, $H_{6'}$]; 7.55-7.60 m, [H_2, H_6]
C_6H_4-4-CF_3[a]	0.90 (**83.5**)	-0.70	-0.13 0.20	c [$H_{3'}$, $H_{5'}$]; 7.13 m, [H_3, H_5]; c [$H_{2'}$, $H_{6'}$]; 7.56 t"t", (**51.3**) [H_2, H_6]	6.92-6.97 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.01-7.09 m, [H_3, H_4, H_5]; 7.33-7.38 m, [$H_{2'}$, $H_{6'}$]; 7.55-7.60 m, [H_2, H_6]
C_6H_4-4-^{t}Bu[a]	0.96 (**85.7**)	-0.52	-0.20 0.22	1.21 [C-CH_3]; 6.73 m, [H_3, H_5]; 7.06 d, [$H_{3'}$, $H_{5'}$]; 7.22 d, [$H_{2'}$, $H_{6'}$]; 7.25 t"t", (**55.0**) [H_2, H_6]	6.76-6.81 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 6.83-6.89 m, [H_3, H_4, H_5]; 7.31-7.36 m, [$H_{2'}$, $H_{6'}$]; 7.37-7.44 m, [H_2, H_6]
C_6H_4-4-OMe[a]	0.94 (**82.5**)	-0.58	-0.14 0.22	3.33 [OCH_3]; 3.38 [O-CH_3]; 6.47 m, [H_3, H_5]; 6.90 d, [$H_{3'}$, $H_{5'}$]; 7.24 t"t", (**56.9**) [H_2, H_6]; 7.50 d, [$H_{2'}$, $H_{6'}$]	6.74-6.80 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 6.81-6.89 m, [H_3, H_4, H_5]; 7.33-7.42 m, [$H_{2'}$, $H_{6'}$]; 7.43-7.51 m, [H_2, H_6]

Table 5.7 : (continued)

C_6H_4-4-F[a]	0.82 (**84.4**) (***13.2***)	-0.73	-0.20 0.12	6.54 m, [H_3, H_5]; 6.73 m, [$H_{3'}$, $H_{5'}$] ($J_{H\text{-}F}$=16.6 Hz); 7.20 m, (**43.5**) [H_2, H_6]; 7.24 m, [$H_{2'}$, $H_{6'}$] ($J_{H_2\text{-}H_3}$=8.8 Hz) ($J_{H\text{-}F}$=11.0 Hz)	6.72-6.79 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 6.80-6.88 m, [H_3, H_4, H_5]; 7.25-7.36 m, [$H_{2'}$, $H_{6'}$]; 7.38-7.44 m, [H_2, H_6]
C_6H_4-4-NMe_2[a]	1.01 (**82.7**) (***13.3***)	-0.12	0.21 0.24	2.50 [*N-CH*$_3$]; 2.54 [*N-CH*$_3$]; 6.31 m, [H_3, H_5]; 6.54 d, [$H_{3'}$, $H_{5'}$]; ($J_{H_2\text{-}H_3}$=8.7 Hz); c [$H_{2'}$, $H_{6'}$]; 7.27 t"t", (**59.2**) [H_2, H_6]	6.84-6.87 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 6.93-6.99 m, [H_3, H_4, H_5]; 7.34-7.40 m, [$H_{2'}$, $H_{6'}$]; 7.42-7.48 m, [H_2, H_6]
C_6F_5[g]	0.85 (**81.2**) (***10.2***)	-0.53	-0.10 0.19[h]	-	6.91-7.05 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.07-7.16 m, [H_3, H_4, H_5]; 7.30-7.36 m, [$H_{2'}$, $H_{6'}$]; 7.39-7.46 m, [H_2, H_6]

a :- toluene-d^8

b :- $J_{H\text{-}H}$ = 14.2 Hz

c :- obscured by phosphine resonances

d :- $J_{H\text{-}F}$ = 28.2 Hz

e :- $J_{H\text{-}H}$ = 13.5 Hz

f :- $J_{H\text{-}F}$ = 6.0 Hz

g :-benzene-d^6

h :- $J_{H\text{-}F}$ = 3.4 Hz

Table 5.8 : *^{13}C N.M.R. Characteristics of* bis-*(triphenylphosphine)(aryl){([dimethyl(aryl)silylmethyl]dimethylsilyl}methyl)platinum(II) Complexes.*

Aryl group	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*]				δ ^{13}C ppm : Phosphine ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{P-C}) / Hz
	Pt-CH_2	Si-CH_2	Si-CH_3	Aromatic	
C_6H_4-2-Me[a]	9.45, 10.85 (**501.5**) ($J_{C-P_{Trans}}$=88.0 Hz) ($J_{C-P_{Cis}}$ = 4.5 Hz)	6.13 (**26.6**)	1.09 2.78 (**17.4**) 3.29 (**22.4**)	23.19 [CH_3]; 26.88 (**60.7**) [CH_3]; 121.05 [C_4]; 122.32 [C_2] (J_{C-P} = 69.3 Hz); 124.04 (**86.6**) [C_6]; (J_{C-P} = 6.2 Hz); 124.43 [$C_{5'}$]; 128.24 [$C_{3'}$]; 129.43 [$C_{4'}$]; 132.25 [$C_{6'}$]; 139.07 (**25.7**) [C_5]; 141.02 [$C_{2'}$]; 141.38 (**25.3**) [C_3]; 143.23 [$C_{1'}$]; 159.86 (**825.7**) [C_1] ($J_{C-P_{Trans}}$=113.2 Hz; $J_{C-P_{Cis}}$ = 10.0 Hz)	127.24 [$C_{3'}$, $C_{5'}$] (***9.4***); 127.62 [C_3, C_5] (***9.1***); 128.94 [C_4]; 129.18 [$C_{4'}$]; 133.65 (**17.5**) [$C_{1'}$] (***43.6***); 133.72 (**14.2**) [C_1] (***34.9***); 134.20 (**13.0**) [$C_{2'}$, $C_{6'}$] (***11.5***); 134.87 (**10.3**) [C_2, C_6] (**10.7**)
C_6F_5[a]	6.35, 7.81 (**538.3**) ($J_{C-P_{Trans}}$=89.7 Hz)	6.42 (**23.5**)	1.00 2.63 (**22.1**)	138.84 m, 139.26 m, 139.91 m, 143.58 m, 146.96 m, 147.35 m, 150.44 m, 151.60 m, [*Aromatic*]	127.63 [$C_{3'}$, $C_{5'}$]; (***8.7***); 127.80 [C_3, C_5]; (***3.7***); 129.64 [$C_{4'}$]; 129.77 [C_4];

Table 5.8 : (continued)

C_6F_5[a]	($J_{C\text{-}P_{Cis}}$ = 7.0 Hz)	131.14 (**17.0**) [$C_{1'}$] (***46.5***); b [C_1]; 133.94 (**18.8**) [$C_{2'}$, $C_{6'}$] (***17.9***); 134.92 (**17.4**) [C_2, C_6] (***15.6***);

a :- chloroform-d[1]

b :- obscured

those observed for $L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$. In addition, the aryl group was transferred regiospecifically (*vide infra*). For example, *para*-substituted sila-neophyl complexes exhibited two doublets attributable to protons of the alkyl bound aryl group and a further two multiplets; one coupled to both ^{195}Pt and ^{31}P is assigned to H_2, H_6 of the transferred aryl group.

There is evidence of restricted rotation about the platinum-aryl bond in the products where Ar = C_6H_4-2-CH_3 and C_6H_4-2-CF_3. Both these complexes have four silicon methyl groups, also both Pt-CH_2 and Si-CH_2 groups are diastereotopic hydrogen pairs. The Si-methylene hydrogens exhibit two doublets with $J_{H\text{-}H}$ = 14 Hz; the two distinct platinum-methylene signals are multiplets with platinum satellites. Additionally, for Ar = C_6H_4-2-CF_3 both protons experience through-space coupling to ^{19}F, one to a greater extent than the other, implying that it is more affected by the *ortho*-trifluoromethyl group.

Further proof of regiospecificity is demonstrated by ^{13}C N.M.R. spectroscopy (Table 5.8). $(PPh_3)_2Pt(C_6H_4\text{-}2\text{-}Me)(CH_2SiMe_2CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$ has two aryl-methyl resonances. The downfield signal, which has a spin-spin interaction with ^{195}Pt typical of $^3J_{Pt\text{-}C}$, is due to an *ortho*-substituted aryl group bound to platinum. *Meta*- or *para*-substitution would result in no observable coupling to platinum.

The kinetics of the rearrangement has been studied by ^1H or ^{19}F N.M.R. for $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}R)_2$ [R = ^{t}Bu, F] in some detail. For the remaining complexes, the rate of reaction was measured at a specific temperature. The reaction remained first order in substrate for at least two half-lives. Rate data is presented in Table 5.9 and graphically in Figs. 5.12 and 5.13. Investigation of the variation of k_{obs} with temperature corresponds linearly to the Arrhenius relationship (Figs. 5.14 and 5.15). Activation parameters obtained from these plots are presented in Table 5.10 and are very similar to those determined for thermolytic rearrangement of $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$, indicating that the mechanism of the reaction is independent of the nature of the substituent.

5.2.2.2. Mechanistic Implications.

The regiospecificity observed for β-aryl transfer, excludes any possibility of involvement of an aromatic C-H activation step. If C-H transfer were important, formation of a hydirdoalkylplatinum(IV) intermediate followed by cleavage of the Si-C_{Aryl} bond would lead to products, in which the position of the substituent of the transferred arene would differ from that in the β-sila-alkyl chain (Scheme. 5.5). It may be noted that $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$ can potentially form two isomeric species by this route, though it can be envisaged that cleavage of the metallacycle affording a *p*-tolyl group will be energetically preferred to its *o*-tolyl analogue.

The order of increasing reactivity for these substituted sila-neophyl groups is :-

$$4\text{-}NMe_2 < 4\text{-}OMe < 4\text{-}CH_3 \approx 3\text{-}CH_3 < 4\text{-}^t\!Bu < 4\text{-}F \approx H < 4\text{-}CF_3 \approx 3\text{-}CF_3 < 2\text{-}CH_3 < 2\text{-}CF_3 << C_6F_5$$

Table 5.9 : *Kinetic Data for Thermolysis of* cis-$(PPh_3)_2Pt(CH_2SiMe_2Ar)_2$.

Ar	T / °C	10^5 x k_{obs} / s^{-1}
C_6H_4-2-Me	65.0	3.13
C_6H_4-2-CF_3	65.0	20.42
Ph[a]	65.0	0.30
C_6H_4-3-Me	90.0	15.85
C_6H_4-3-CF_3	90.0	30.53
Ph[a]	90.0	18.16
C_6H_4-4-Me	85.0	7.18
C_6H_4-4-OMe	85.0	6.41
C_6H_4-4-^{t}Bu	75.0	1.26
C_6H_4-4-^{t}Bu	77.5	1.88
C_6H_4-4-^{t}Bu	80.0	3.20
C_6H_4-4-^{t}Bu	82.5	4.68
C_6H_4-4-^{t}Bu	85.0	7.49
C_6H_4-4-F	75.0	1.63
C_6H_4-4-F	77.5	2.32
C_6H_4-4-F	80.0	3.61
C_6H_4-4-F	82.5	5.26
C_6H_4-4-F	85.0	8.48
C_6H_4-4-CF_3	85.0	14.40
C_6H_4-4-NMe_2	85.0	4.12

a :- calulated from the Arrhenius plot

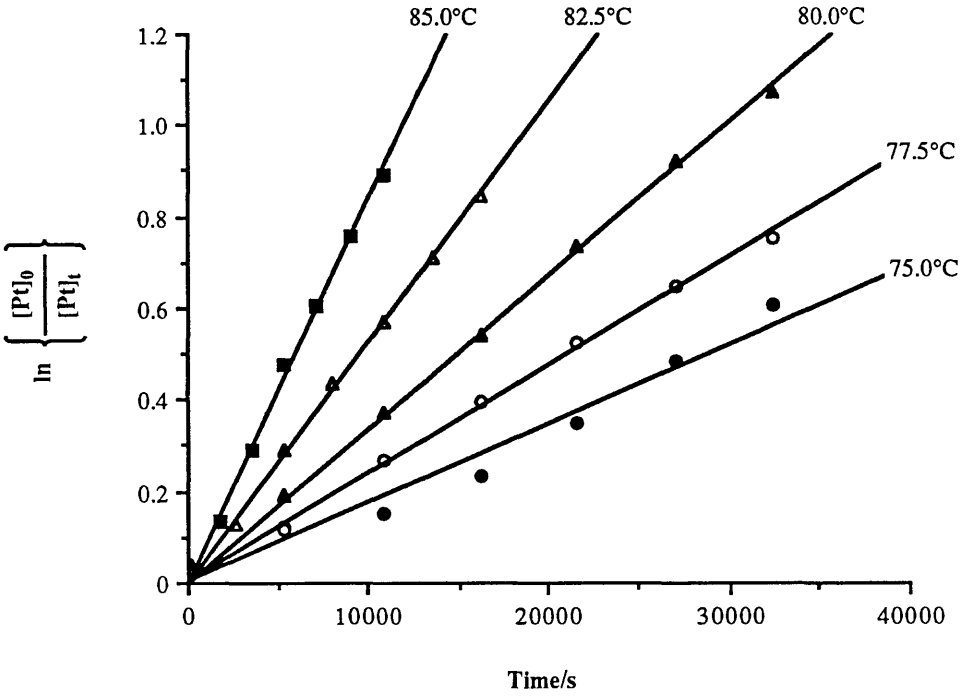


Fig. 5.12 : *Kinetic Data for the Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$.

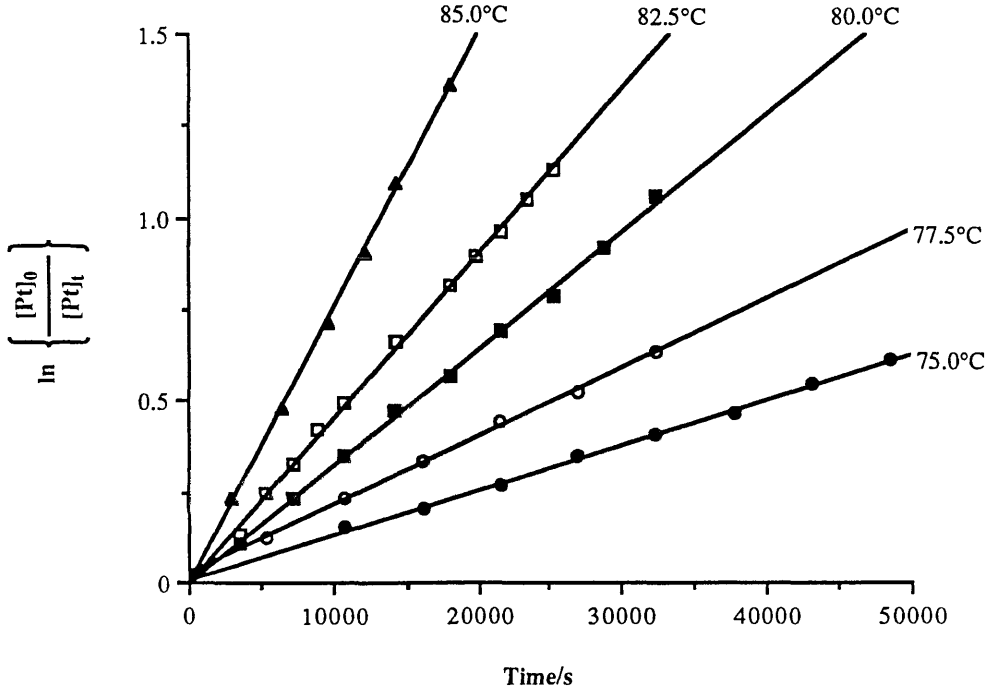


Fig. 5.13 : *Kinetic Data for the Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$.

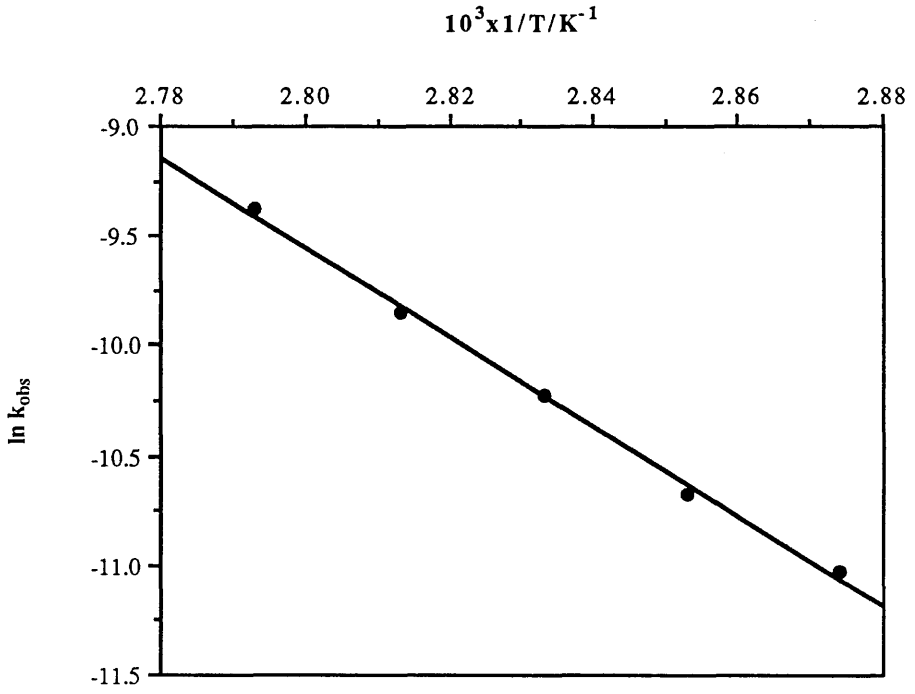


Fig. 5.14 : *Arrhenius Plot for the Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$.

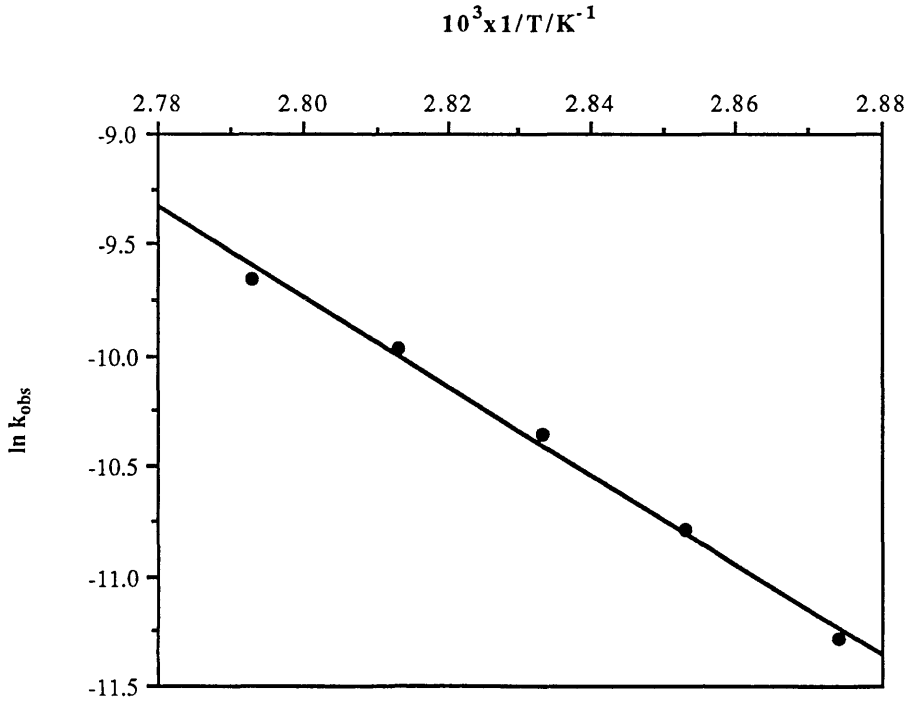
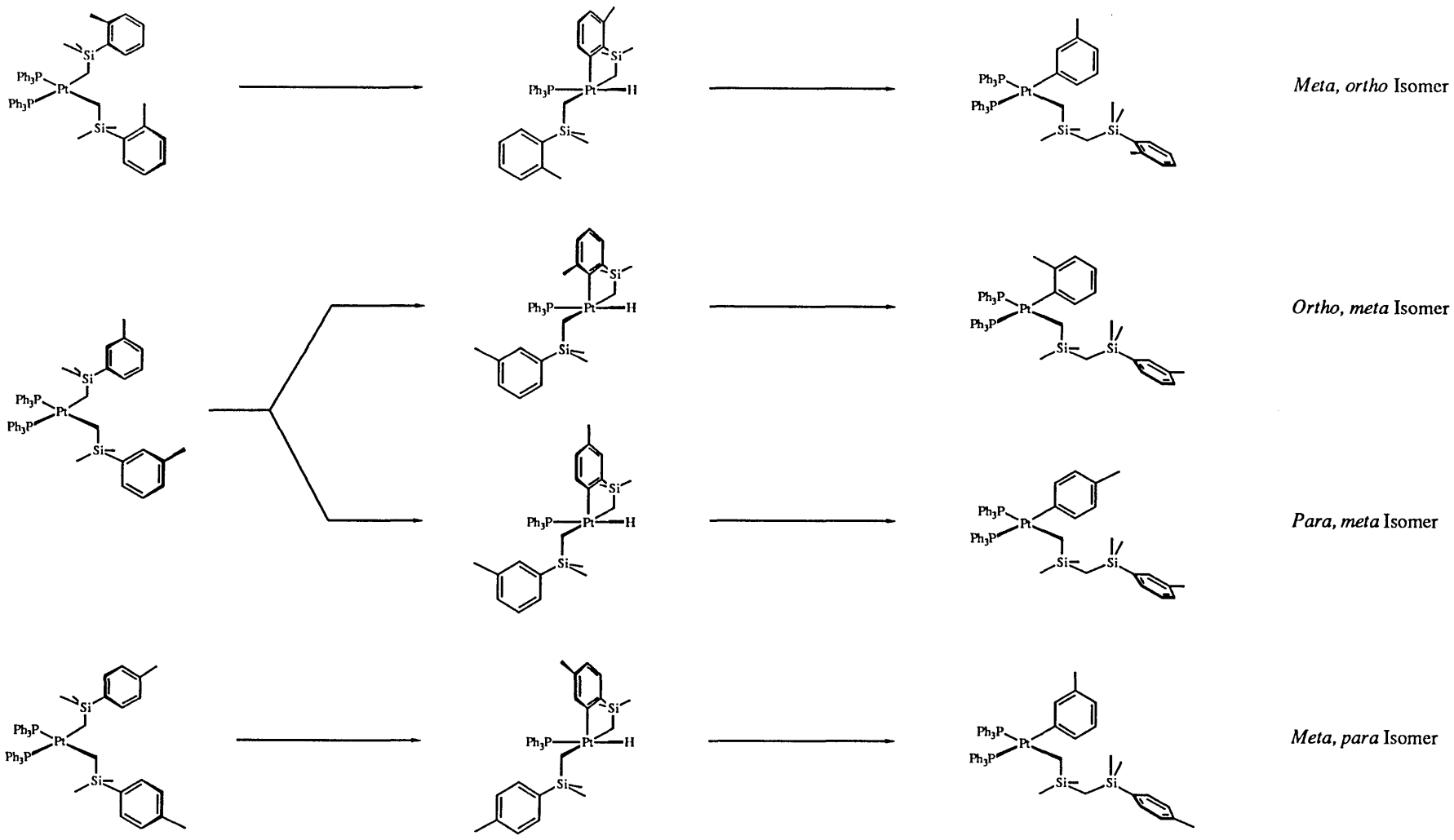


Fig. 5.15 : Arrhenius Plot for the Thermolysis of $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}^tBu)_2$.



Scheme. 5.5 : *Possible Isomers Formed During the Rearrangement of* $(PPh_3)_2Pt(CH_2SiMe_2Ar)_2$.

The enhanced reactivity of *ortho*-substituted rings, most probably, derives principally from steric effects. Increased crowding in the transition state would lead to slow (rate-limiting) aryl transfer.

Table 5.10 : *Activation Parameters for the Rearrangement of* cis-$L_2Pt(CH_2SiMe_2C_6H_4R)_2$.

R	E_a kJ mol^{-1}	$\Delta H^{\ddagger}_{298}$ kJ mol^{-1}	Frequency factor, A	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$ kJ mol^{-1}
H	168.1 (±2)	165.6 (±2)	2.84×10^{20}	138.4 (±6)	124.4 (±2)
4-F	169.3 (±3)	166.9 (±3)	4.15×10^{20}	141.5 (±8)	124.7 (±4)
4-^{t}Bu	169.1 (±4)	166.5 (±4)	2.26×10^{20}	136.5 (±9)	124.9 (±6)

Linear free energy relationships have often been employed in correlations of reactivities with substituent effects. The rate constant, k_{obs} and free energy, $\Delta G^{\ddagger}$ are related by the Eyring equation :-

$$-RT \ln k = \Delta G^{\ddagger} - RT \frac{\kappa RT}{Nh}$$

At constant temperature, the proportionality constant relating the rate constant to the free energy is always the same, hence :-

$$\Delta G^{\ddagger}_A = m\Delta G^{\ddagger}_B + c$$

showing a linear dependence of the free energy of process B on that of A. Assessment of substituent effects on aromatic species are most commonly related by LFE relationships based on the Hammett equation[111] :-

$$\log k/k_0 = \rho\sigma$$

where :-

k_0 = rate of unsubstituted species
k = rate of substituted species
ρ = reaction constant at a given temperature

σ = substituent constant

The basic σ parameter is comprised of two components; an inductive contribution σ_I and a resonance (or mesomeric) component σ_R such that :-

$$\sigma = \sigma_I + \sigma_R$$

Not all reactions were found to correlate well with these parameters. For systems lacking direct resonance interactions with the functional group, *para*-substituents appear to have substituent constant values less negative or more positive than the Hammett σ-values suggest. A new series of constants for reactions deviating this way :-

$$\sigma^\circ = \sigma_I + \sigma_R^\circ$$

were proposed by Taft. Similarly systems with direct resonance interactions with strong +R subst withdrawing by a resonance effect) follow σ^- parameters and those with direct interactions with st R substituents (electron-releasing by direct resonance effects) correlate with σ^+ constants. On the other hand, *meta*-substituent constant values are essentially invariant because there is no direct resonance between
meta-substituents and functional groups[112].

The data best fit a correlation of log k/k_0 against σ_p, σ_m (Fig. 5.16), indicating that inductive effects are more important than resonance contributions. Greater scatter was observed when σ_p°, σ_p^+, σ_p^- parameters were employed. Although the error in determination of several rate constants is quite large, an estimate of the susceptibility of the reaction (ρ) was obtained. Generally, a positive value of ρ indicates the development of a negative charge (or disappearance of a positive charge) at the reaction centre during formation of the transition state; conversely a negative value implies the development of a positive charge (or disappearance of a negative charge at the centre). The magnitude of ρ indicates the charge density at the reaction centre during formation of the transition state. Values greater than unity indicate large charge density; less than one indicate relatively small effects.

The value of ρ of +0.9 is most consistent with a development of a cyclic transition state with little charge separation, though the positive charge suggests an increase in the natural partial positive charge at β-Si and a corresponding decrease in the negative charge at the *ipso*-carbon of the arene ring. Most plausibly, The action of platinum during aryl transfer is nucleophilic in nature.

For this system electron-withdrawing substituents on the aromatic ring accelerate the rate of aryl transfer by increasing δ^+ on silicon, whilst minimising δ^- on the migratory carbon relative to R = H. Thus, they lower the energy of the transition state and decrease the free energy difference between the dialkyl and the transition state. Electron-donating substituents push electron density into the aromatic ring and increase the negative charge at

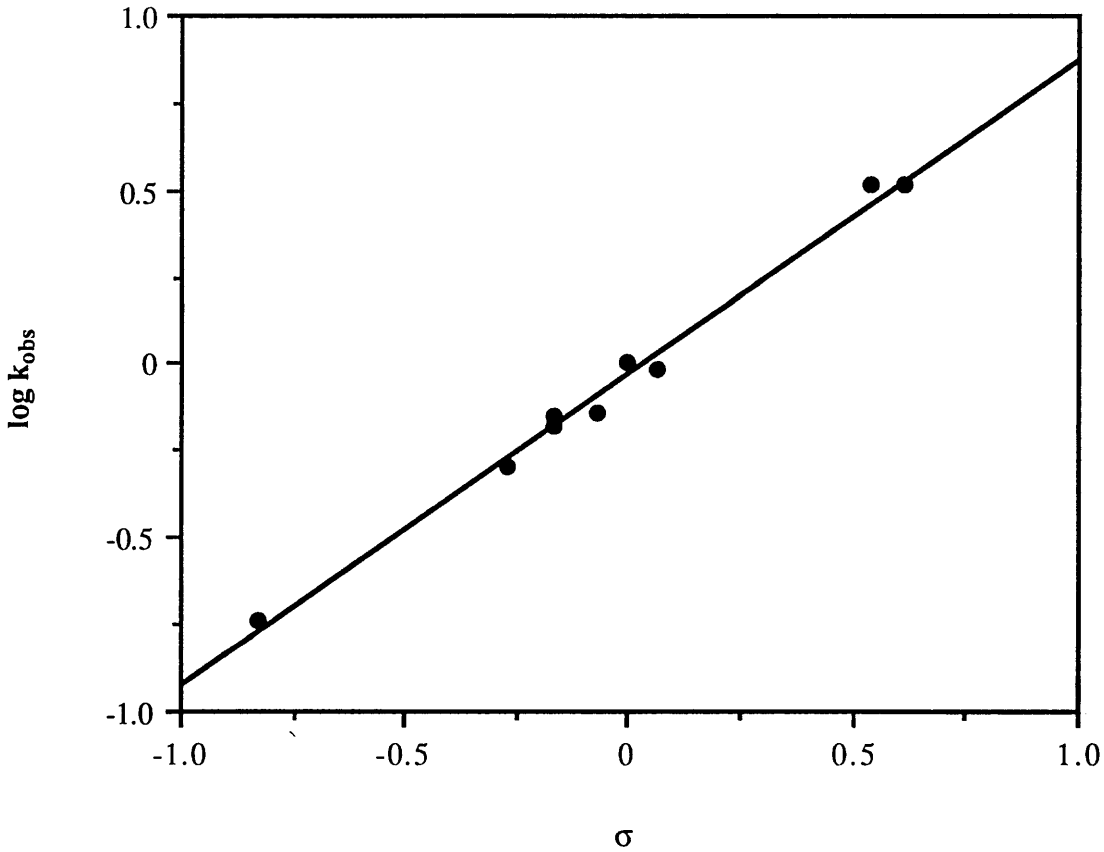


Fig. 5.16 : *Hammett Linear Free Energy Relationship.*

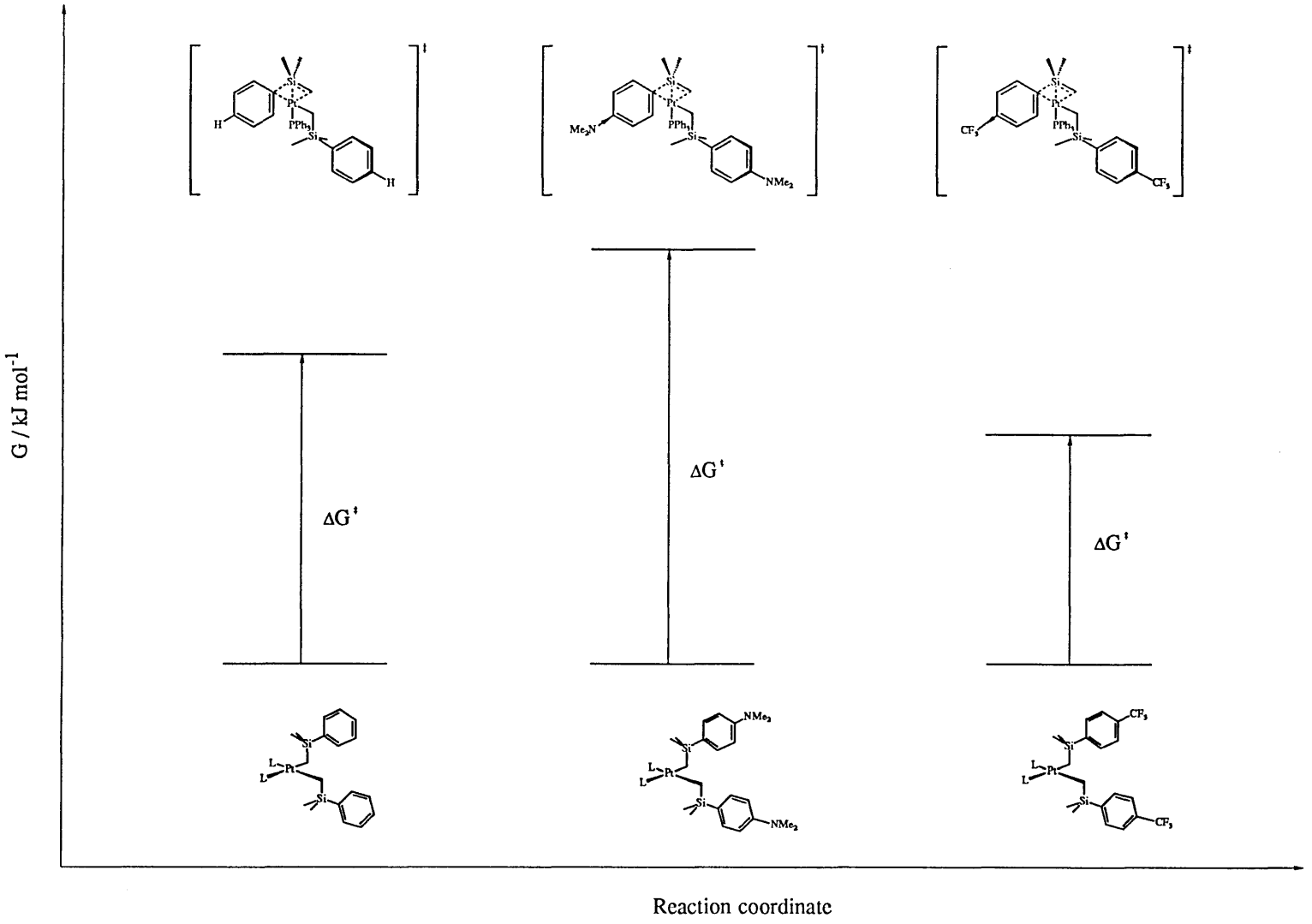


Fig. 5.17 : *Effect of Ring Substitution on the Free Energy of Activation.*

the *ipso*-carbon atom (simultaneously minimising δ^+ at Si) resulting in a rise in energy of the transition state and hence $\Delta G^{\ddagger}$ is raised (Fig. 5.17).

Despite a reasonable correlation of the rates of rearrangement with σ-constants, LFE relationships can only give an indication of possible charge distribution at the transition state.

5.2.3. Thermolysis of $(PPh_2$-o-tol$)_2Pt(CH_2SiMe_2Ph)_2$.

The ^{31}P N.M.R. spectrum of a thermolysed sample of $(PPh_2$-*o*-tol$)_2Pt(CH_2SiMe_2Ph)_2$ does not have the same N.M.R. characteristics as those obtained for derivatives from β-phenyl transfer. Two distinct phosphorus resonances, which are coupled to each other, suggesting they are mutually *cis*, are observed. Platinum-phosphorus coupling constants of 1890.5 Hz and 2169.9 Hz are indicative of an alkyl and a sila-alkyl fragment *trans* to phosphorus. In contrast to observations noted for $L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$, a difference in chemical shift between the two phosphorus nuclei of *ca.* 19 ppm and a ring contribution, Δ_R, of +19.3 imply the formation of a five-membered phosphorus containing metallacycle[82].

Characteristic ^1H N.M.R. features (Table 5.11) of this complex are a high field

Table 5.11 : *^1H N.M.R. Characteristics of $(PPh_2$-o-tol$)(2$-$\overbrace{CH_2C_6H_4Ph_2P)Pt}(CH_2SiMe_2Ph)$* .

δ^a ^1H ppm : Hydrocarbyl ligands ($J_{Pt\text{-}H}$) / Hz [*Assignment*] ($J_{P\text{-}H}$) / Hz				δ ^1H ppm : Phosphine [*Assignment*]
$Pt\text{-}CH_2$	$Si\text{-}CH_3$	$Ar\text{-}CH_3$	Aromatic	
1.25 (**83.6**) [CH_2-*Si*] (***11.4***) 4.01 (**76.0**) [CH_2-*P*] (***8.9***)	0.37	2.08	7.02 m, [H_3, H_5]; 7.06 m, [H_4]; 7.76 dd, [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.1 Hz)	6.75-6.90 m, [*Most* meta *and* para *phosphine signals*]; 7.20 dd, [H_3-*metallacycle*]; 7.24-7.41 m, [H_2, H_6 *and* H_6-*metallacycle*]; 7.44-7.48 m, [$H_{2'}$, $H_{6'}$]

a :- benzene-d^6

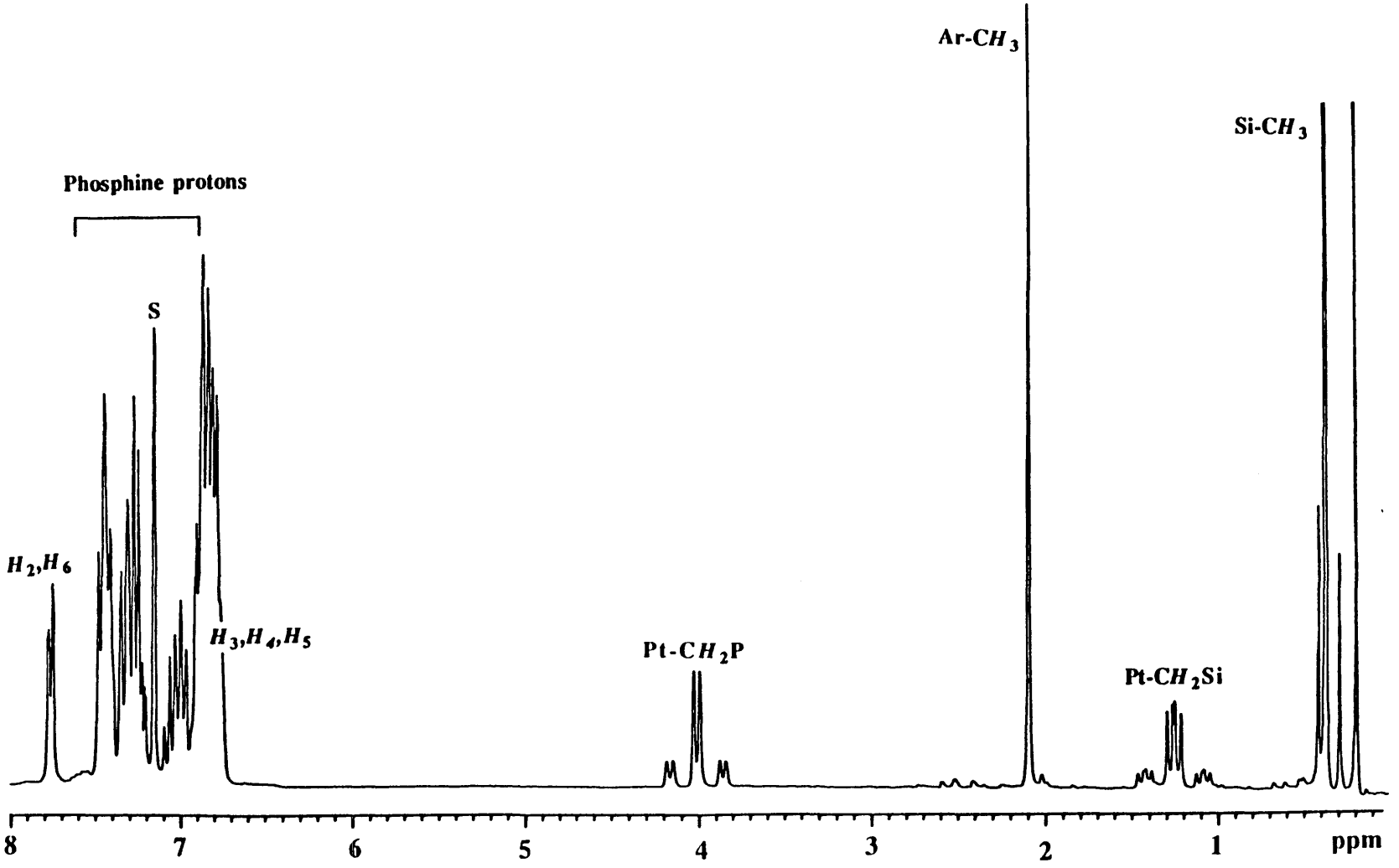


Fig. 5.18 : ^{1}H *N.M.R. of* $(PPh_2\text{-o-}tol)(2\text{-}\overline{CH_2C_6H_4Ph_2P)Pt}(CH_2SiMe_2Ph)$.

Table 5.12 : *^{13}C N.M.R. Characteristics of $(PPh_2\text{-}o\text{-}tol)(2\text{-}\overbrace{CH_2C_6H_4Ph_2P)Pt}(CH_2SiMe_2Ph)$* .

δ[a] ^1H ppm : Hyrdocarbyl ligands ($J_{Pt\text{-}C}$) / Hz [*Assignment*] ($J_{P\text{-}C}$) / Hz				δ ^1H ppm : Phosphine ligand ($J_{Pt\text{-}C}$) / Hz [*Assignment*] ($J_{P\text{-}C}$) / Hz
Pt-CH_2	Si-CH_3	Ar-CH_3	Aromatic	
4.35, 5.63 **(571.6)** ($J_{C\text{-}P_{Trans}}$=83.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.1 Hz) [CH_2-*Si*] 33.31, 34.82 **(596.1)** ($J_{C\text{-}P_{Trans}}$=96.9 Hz) [CH_2-*P*]	2.41 **(27.2)**	22.67 ***(8.8)***	126.93 [C_3, C_5]; 127.14 [C_4]; 133.91 [C_2, C_6]; 146.58 **(24.7)** [C_1]	124.51 [C_5-P_A] ***(5.7)***; 125.14 [C_5-P_B]; 127.59 [$C_{3'}$, $C_{5'}$-P_B] ***(9.5)***; 127.88 [C_3, C_5-P_A] ***(9.4)***; 129.16, 129.24 [C_4-P_A, $C_{4'}$-P_B]; 129.75 [C_4-P_B]; 130.18 [C_4-P_A]; 131.27 [C_3-P_A]; 131.46 [C_3-P_B] ***(9.7)***; 133.06 **(13.3)** [$C_{2'}$, $C_{6'}$-P_A] ***(11.8)***; 134.49 [C_6-P_B] ***(8.1)***; 134.58 [C_6-P_A]; 135.04 **(14.6)** [$C_{2'}$, $C_{6'}$-P_B] ***(12.0)***; 139.12 [C_1-P_B] ***(10.1)***; 140.02 **(124.9)** [C_1-P_A] ***(11.0)***; 142.38 [C_2-P_B] ***(10.3)***; 160.94 [C_2-P_A] ***(36.3)***

a :- chlorofrom-d^1

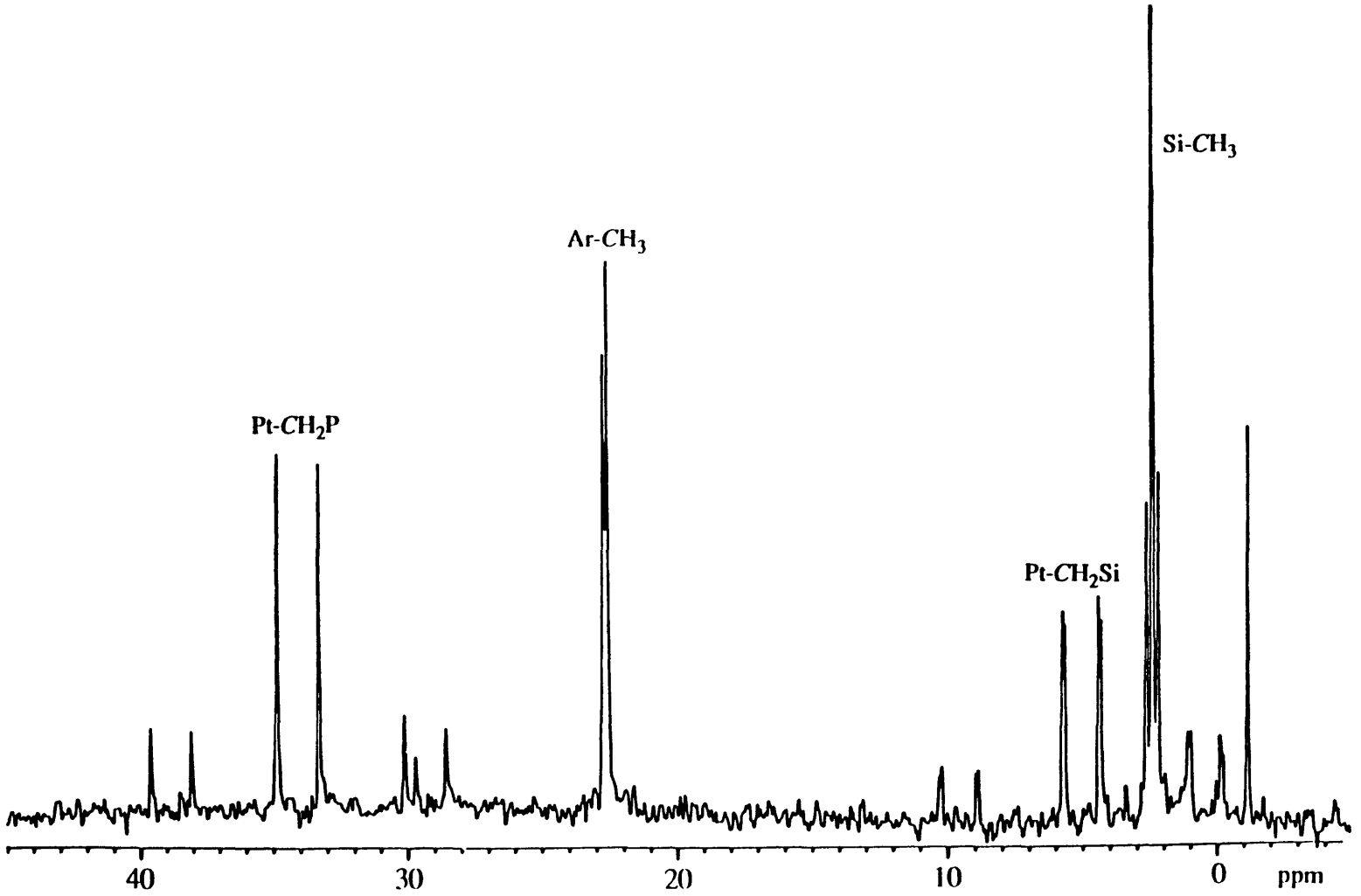


Fig. 5.19 a : *^{13}C N.M.R. of the Aliphatic Region of (PPh_2-o-tol)(2-$\overline{CH_2C_6H_4Ph_2P)Pt}$($CH_2SiMe_2Ph$)* .

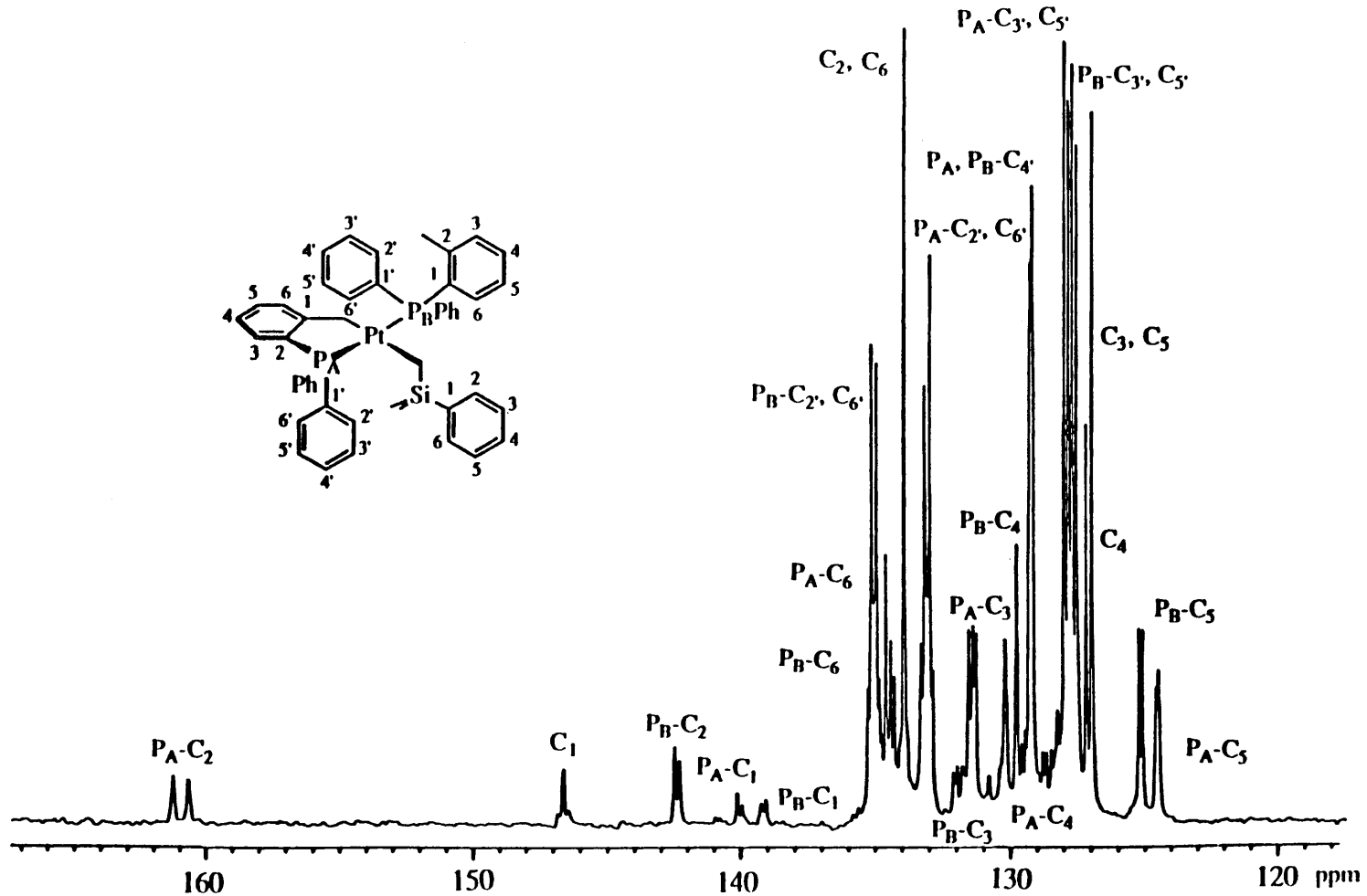


Fig. 5.19.b : *^{13}C N.M.R. of the Aromatic Region of (PPh_2-o-tol)(2-$\overline{CH_2C_6H_4Ph_2P)Pt}$($CH_2SiMe_2Ph$)* .

singlet due to Si-Me groups, an apparent quartet with ^{195}Pt satellites, typical for Pt-CH_2 protons and a low field singlet, which can be attributed to CH_3 hydrogens of an *o*-tolyl phosphine group. Additionally, a doublet with satellites at *ca.* 4.0 ppm, which corresponds to two hydrogens, strongly implies a second platinum bound methylene group (Fig. 5.18).

Further, the ^{13}C N.M.R. spectrum (Table 5.12) exhibits several interesting features, in addition to resonances typical of a coordinated sila-neophyl skeleton, notably the doublet centred at 39.0 ppm, which arises from a Pt-CH_2 group coupled to a *trans*-phosphorus nucleus (Fig. 5.19). The aromatic region is complicated but assignments due to aromatic ring carbons coupled to platinum and/or phosphorus can be made. A multiplet at *ca.* 140 ppm with $J_{Pt\text{-}C} = 124.9$ Hz and $J_{P\text{-}C} = 11.0$ Hz may be attributed to C_1 of the metallated ring; similarly the doublet at 161ppm with $J_{Pt\text{-}C} = 36.3$ Hz is due to C_2, bound to P_A of the metallacycle. C_3, C_5 and C_6 of this ring also appear as doublets coupled to ^{31}P.

On the basis of spectroscopic data, the proposed identity of the new complex is *cis*-(PPh_2-*o*-tol)(2-$\overline{CH_2C_6H_4Ph_2P}$)Pt($CH_2SiMe_2Ph$) (Fig. 5.20) a five membered metallacycle formed as a result of δ-aliphatic C-H activation of a PPh_2-*o*-tol phosphine CH_3 group, with concomitant loss of one equivalent of trimethylphenylsilane.

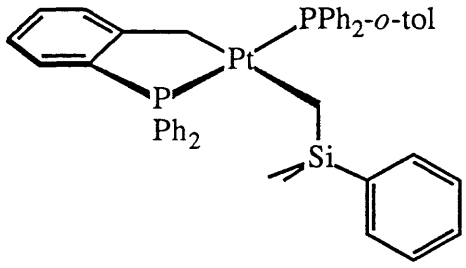


Fig. 5.20 : *Product formed During the Thermolysis of (PPh_2-o-tol)Pt(CH_2SiMe_2Ph)$_2$.*

Platinum(II) complexes of the type $(PBu^t_3)_2PtCl_2$ and $(PR_2R')_2PtCl_2$ [R = ^{t}Bu, R' = Ph, C_6H_4-4-Me, Pr; R = C_6H_4-4-Me, R' = ^{t}Bu, Ph; R = Ph, Pr, R' = ^{t}Bu; R = Me, R' = C_6H_4-2-Me] all generate phosphine metallated species[113]. Such reactivity has been attributed to bulky phosphines promoting intramolecular C-H transfer in response to relief of steric constraints in the parent complex[114].

Progress of the reaction between 32.5°C-45.0°C was monitored by ^{31}P N.M.R. in the probe of the N.M.R. spectrometer, preset at the required temperature. Appearance of trimethylphenylsilane could be quantified by ^1H N.M.R. or by HPLC. No product formed by β-aryl migration was observed under these conditions.

A first-order dependence of the rate of reaction on platinum substrate was observed for at least two half-lives. The data are presented in Table 5.13 and graphically in Fig. 5.21. Variation of temperature on the observed rate constant for cyclisation of

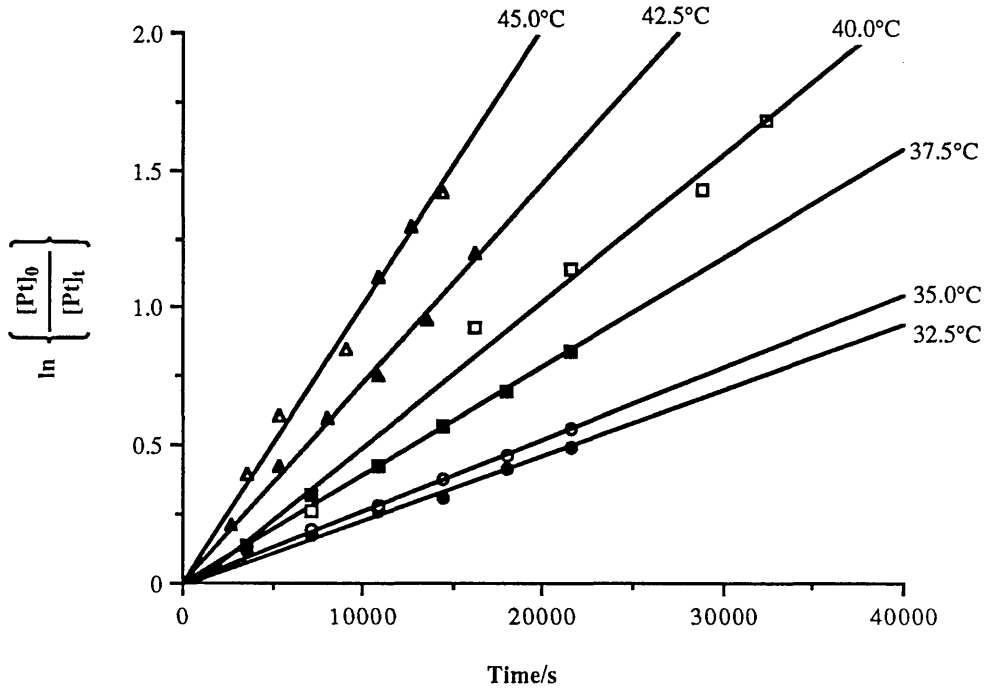


Fig. 5.21 : *Kinetic Data for the Metallacyclisation of* $(PPh_2\text{-o-}tol)Pt(CH_2SiMe_2Ph)_2$.

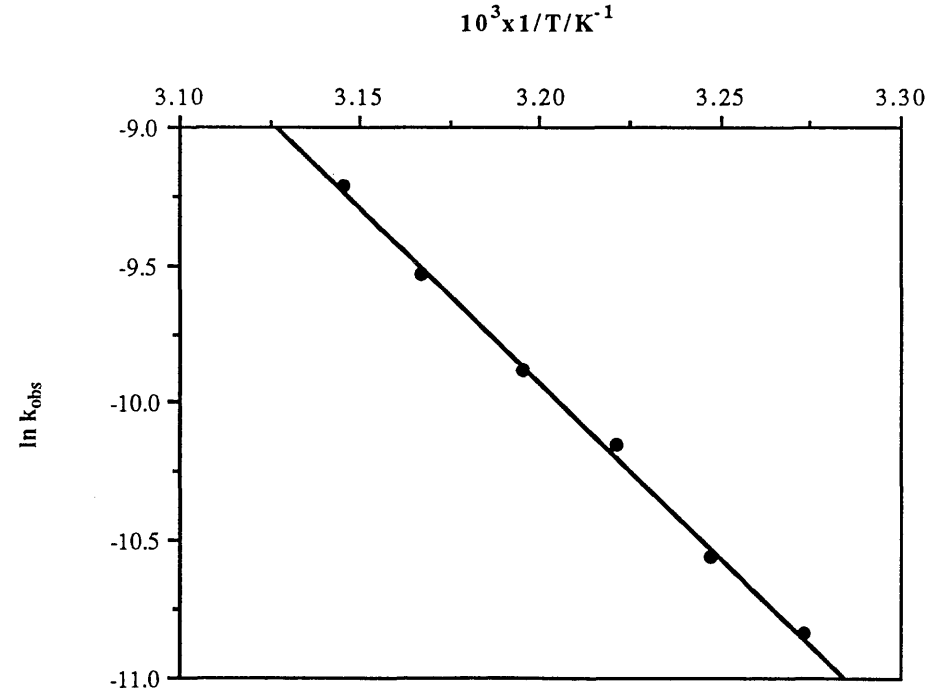


Fig. 5.22 : *Arrhenius Plot for the Cyclisation of* $(PPh_2\text{-o-}tol)Pt(CH_2SiMe_2Ph)_2$.

Table 5.13 : *Kinetic Data for the Thermolytic Rearrangement of* $(PPh_2\text{-o-}tol)_2Pt(CH_2SiMe_2Ph)_2$.

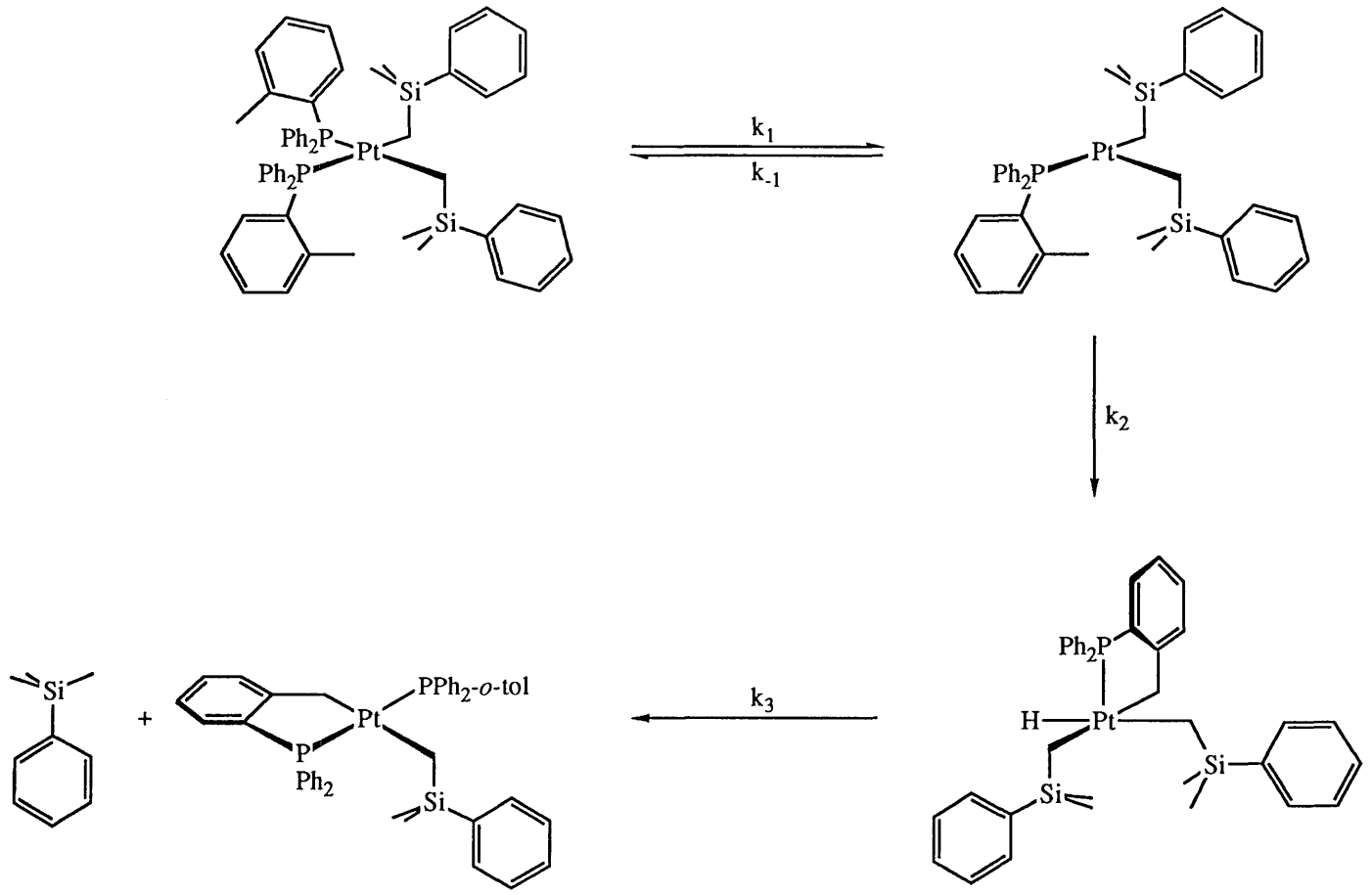
[L] / mol dm^{-3}	T / °C	$10^5 \times k_{obs}$ / s^{-1}
0.00	32.5	1.96
0.00	35.0	2.62
0.00	37.5	3.92
0.00	40.0	5.11
0.00	42.5	7.27
0.00	45.0	10.01
0.05	65.0	5.96

$(PPh_2\text{-}o\text{-tol})_2Pt(CH_2SiMe_2Ph)_2$, displays a linear Arrhenius correspondence (Fig. 5.22). Activation parameters derived from the Arrhenius plot are as follows :-

$$E_a = 105.2\ (\pm 2)\ kJ\ mol^{-1}$$
$$\Delta H^{\ddagger}_{298} = 102.7\ (\pm 2)\ kJ\ mol^{-1}$$
$$A = 1.91 \times 10^{13}$$
$$\Delta S^{\ddagger} = 1.0\ (\pm 6)\ J\ K^{-1}\ mol^{-1}$$
$$\Delta G^{\ddagger}_{298} = 102.4\ (\pm 3)\ kJ\ mol^{-1}$$

Addition of diphenyl-*o*-tolylphosphine retards C-H activation. Both dissociative and associative inhibition of the rate of cyclisation by phosphine is possible, however, in view of the steric bulk of the phosphine ($\theta = 161°$) a dissociative process is more likely. Dissociation of one ligand results in steric relief on formation of a tricoordinate intermediate; excess phosphine inhibits further reaction as phosphine reassociation becomes a significant factor.

Metallacyclisation of *cis*-$(PPh_2\text{-}o\text{-tol})_2Pt(CH_2SiMe_2Ph)_2$ displays a moderate enthalpy of activation and is entropically neutral, implying a more ordered transition state than that observed for metallacyclisation of $(PEt_3)_2Pt(CH_2CMe_2Ph)_2$. A net negative value of -13 JK^{-1} mol^{-1} of the entropy of activation was observed during thermolysis of $(dppe)Pt(CH_2CMe_2Ph)_2$. Also only a moderate isotopic inhibition on C-H transfer was noted, suggesting that oxidative addition of the neophyl C-H bond was the major energetic contributor to the reaction[50]. Though selective isotope effects for C-H transfer in $(PPh_2\text{-}o\text{-tol})_2Pt(CH_2SiMe_2Ph)_2$ have not been investigated, oxidative addition of a



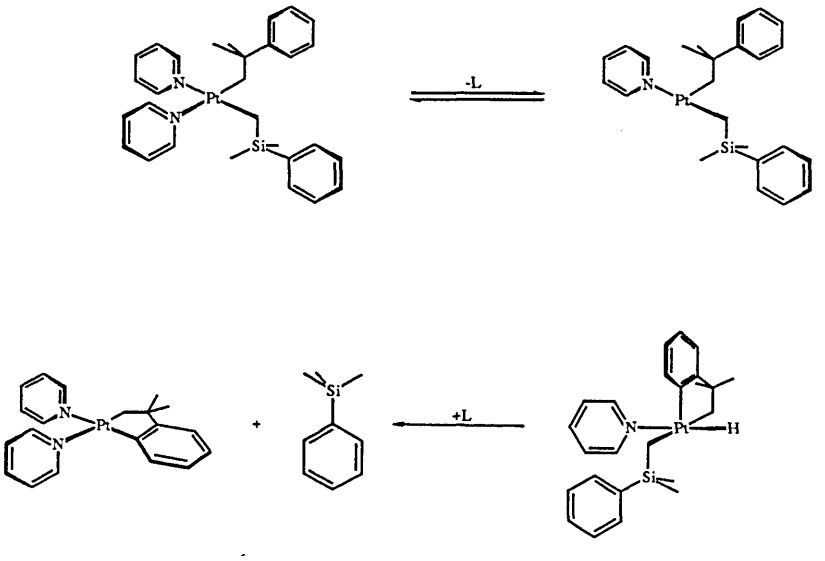
Scheme. 5.6 : *Proposed Mechanism for the Thermolytic Rearrangement of* $(PPh_2\text{-o-}tol)_2Pt(CH_2SiMe_2Ph)_2$.

phosphine C-H bond most probably makes a high contribution to k_{obs}. Reductive elimination can also proceed *via* an ordered transition state; formation of biaryl from $L_2Pt(C_6H_4R)_2$ [L = PPh_3, R = CH_3; L = py, R = CF_3] is characterised by a negative entropy of activation ($\Delta S^{\ddagger}$ = -100 J K^{-1} mol^{-1}).

Based on these observations, a mechanistic scheme can be postulated involving equilibrium phosphine dissociation (Scheme. 5.6). Even though an estimate of the rate of phosphine dissociation was not obtained, phosphine dissociation can be excluded, reasonably, as the rate-limiting step, since it has been well documented that dissociation of a bulky phosphine is generally rapid[91a]. Following formation of the T-shaped intermediate, slow irreversible oxidative addition of the *o*-tolyl CH_3 group occurs (k_2), generating a hydridoalkylplatinum(IV) intermediate. Subsequent rapid reductive elimination of trimethylphenylsilane (k_3) affords the 5-membered platinacycle.

5.2.4. *Reactivity of* cis-bis-*(pyridine)*-bis-*[dimethyl(aryl)silylmethyl] platinum(II).*

Toluene solutions of $(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}R)_2$ [R = H, OMe, ^{t}Bu, F, CF_3] at ambient temperature or above undergo metallacyclisation *via* δ-aromatic C-H activation to the corresponding platinasila-indan and liberate one equivalent of trimethylarylsilane (Scheme. 5.7). Qualitatively, replacing pyridine by its deuterated analogue results in a considerable retardation of the rate of rearrangement, suggesting that H-transfer from the ligand may be involved. With the exception of $(py)_2Pt(CH_2SiMe_2C_6H_4)$ and $(py)_2Pt(CH_2SiMe_2C_6H_3\text{-}4\text{-}CF_3)$ [the latter could not be isolated as the parent dialkyl],which were isolated as pale yellow and white crystalline solids respectively; the remainder were only observed in solution, characterised by ^{1}H N.M.R. spectroscopy (Table 5.14).



Scheme. 5.7 : *Aromatic C-H Transfer in* $(py)_2Pt(CH_2SiMe_2Ph)_2$.

Table 5.14 : *^1H N.M.R. Characteristics of* cis-bis-*(pyridine)-1-platina-3-sila-indans and Related Complexes.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]			δ ^{1}H ppm : Ancillary ligands (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Aromatic	
$(py)_2\overline{Pt(CH_2SiMe_2C_6H_4)}$[a]	0.86 (**100.4**)	0.07	7.01-7.19 m, [H_4, H_5]; 7.46 dd, [H_6] ($J_{H_5-H_6}$=7.5 Hz); 7.68 dd, (**67.0**) [H_3] ($J_{H_3-H_4}$=7.9 Hz)	6.20 m, [H_3, H_5] ($J_{H_3-H_4}$=6.4 Hz); 6.39 m, [$H_{3'}$, $H_{5'}$] ($J_{H_{3'}-H_{4'}}$=6.4 Hz); 6.65 m, [H_4] ($J_{H_2-H_4}$=1.6 Hz); 6.77 m, [$H_{4'}$] ($J_{H_{2'}-H_{4'}}$=1.4 Hz); 8.31 dd, (**25.7**)[H_2, H_6] ($J_{H_2-H_3}$=7.6 Hz); 8.47 dd, (**20.0**) [$H_{2'}$, $H_{6'}$] ($J_{H_{2'}-H_{3'}}$=7.6 Hz)
$(py\text{-}d^5)_2\overline{Pt(CH_2SiMe_2C_6H_4)}$[b]	0.97 (**98.4**)	0.31	7.36-7.43 m, [H_4, H_5, H_6]; 7.89 dd, (**62.4**) [H_3] ($J_{H_3-H_4}$=7.9 Hz)	-
$(py)_2\overline{Pt(CH_2SiMe_2C_6H_3\text{-}4\text{-}OMe)}$[a]	1.09 (**100.1**)	0.45	3.41 [$O\text{-}CH_3$]; 6.98 d, [H_5] ($J_{H_5-H_6}$=7.5 Hz); 7.56 dd [H_6];	6.28 m, [H_3, H_5] ($J_{H_3-H_4}$=7.2 Hz); 6.45 m, [$H_{3'}$, $H_{5'}$] ($J_{H_{3'}-H_{4'}}$=7.1 Hz);

Table 5.14 : (continued)

$(py)_2Pt(CH_2SiMe_2C_6H_3\text{-}4\text{-}OMe)$[a]			7.75 d, (**67.1**) [H_3] ($J_{H_2\text{-}H_3}$=7.9 Hz)	6.73 m, [H_4] ($J_{H_2\text{-}H_4}$=1.0 Hz); 6.82 m, [$H_{4'}$] ($J_{H_{2'}\text{-}H_{4'}}$=0.9 Hz); 8.45 dd, (**24.1**) [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.5 Hz); 8.62 dd, (**20.8**) [$H_{2'}$, $H_{6'}$] ($J_{H_{2'}\text{-}H_{3'}}$=7.4 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_3\text{-}4\text{-}^tBu)$[a]	1.11 (**100.3**)	0.44	1.38 [*C-CH*$_3$]; 7.28 dd, [H_5]; ($J_{H_5\text{-}H_6}$=7.6 Hz); 7.64 d, [H_6]; 7.83 d, (**63.2**) [H_3] ($J_{H_3\text{-}H_5}$=7.7 Hz)	6.19 m, [H_3, H_5] ($J_{H_3\text{-}H_4}$=7.9 Hz); 6.42 m, [$H_{3'}$, $H_{5'}$] ($J_{H_{3'}\text{-}H_{4'}}$=8.0 Hz); 6.67 m, [H_4] ($J_{H_2\text{-}H_4}$=2.0 Hz); 6.81 m, [$H_{4'}$] ($J_{H_{2'}\text{-}H_{4'}}$=1.4 Hz); 8.44 dd, (**22.1**) [$H_{2'}$, $H_{6'}$] ($J_{H_{2'}\text{-}H_{3'}}$=8.0 Hz); 8.59 dd, (**23.9**) [H_2, H_6] ($J_{H_2\text{-}H_3}$=8.0 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_3\text{-}4\text{-}F)$[a]	0.99 (**100.4**)	0.22	7.17 m, [H_5] ($J_{H_5\text{-}H_6}$=7.0 Hz) ($J_{H\text{-}F}$ =14.1 Hz); 7.40 m, [H_6] ($J_{H\text{-}F}$ =7.5 Hz); 7.71 m, (**64.8**) [H_3] ($J_{H_3\text{-}H_5}$=7.8 Hz) ($J_{H\text{-}F}$=14.9 Hz)	6.15 m, [H_3, H_5] ($J_{H_3\text{-}H_4}$=7.8 Hz); 6.24 m, [$H_{3'}$, $H_{5'}$] ($J_{H_{3'}\text{-}H_{4'}}$=7.7 Hz); 6.52 m, [H_4] ($J_{H_2\text{-}H_4}$=1.1 Hz); 6.69 m, [$H_{4'}$] ($J_{H_{2'}\text{-}H_{4'}}$=1.5 Hz); 8.29 dd, (**35.3**) [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.9 Hz); 8.62 dd, (**19.9**) [$H_{2'}$, $H_{6'}$] ($J_{H_{2'}\text{-}H_{3'}}$=7.7 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_3\text{-}4\text{-}CF_3)$[a]	1.00 (**100.0**)	0.24	7.31-7.37 m, [H_5, H_6]; 7.83 d, (**66.8**) [H_3] ($J_{H_3\text{-}H_5}$=7.8 Hz)	6.20 m, [H_3, H_5] ($J_{H_2\text{-}H_3}$=6.4 Hz); 6.42 m, [$H_{3'}$, $H_{5'}$]; 6.68 m, [H_4] ($J_{H_3\text{-}H_4}$=7.7 Hz); 6.78 m, [$H_{4'}$];

Table 5.14 : (continued)

$(py)_2Pt(\overline{CH_2SiMe_2C_6H_3}\text{-}4\text{-}CF_3)$[a]				8.18 m, (**30.0**) [H_2, H_6];
				8.53 dd, (**25.6**) [$H_{2'}$, $H_{6'}$]
$(py)_2Pt(C_6H_4\text{-}2\text{-}Me)$-	0.78	-0.10	2.36 [CH_3]; 2.79 [CH_3];	6.00 m, [H_3, H_5] ($J_{H_3\text{-}H_4}$=6.4 Hz);
$(CH_2SiMe_2CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$[a]	(**100.5**)	0.22	6.93-7.13 m,	6.27 m, [$H_{3'}$, $H_{5'}$] ($J_{H_{3'}\text{-}H_{4'}}$=6.4 Hz);
		0.36	[H_4, $H_{4'}$, H_5, $H_{5'}$];	6.50 m, [H_4] ($J_{H_2\text{-}H_4}$=1.2 Hz);
		[CH_3]	7.50 dd, [$H_{6'}$] ($J_{H_{5'}\text{-}H_{6'}}$=7.0 Hz);	6.65 m, [$H_{4'}$] ($J_{H_{2'}\text{-}H_{4'}}$=1.1 Hz);
		0.06	7.98 dd, (**67.0**) [H_6]	8.18 dd, (**26.6**) [H_2, H_6]($J_{H_2\text{-}H_3}$=7.5 Hz);
		[CH_2]	($J_{H_5\text{-}H_6}$=12.8 Hz)	8.38 dd, (**18.2**) [$H_{2'}$, $H_{6'}$] ($J_{H_{2'}\text{-}H_{3'}}$=7.5 Hz)

a :- toluene-d^8

b :- pyridine-d^5

These metallacycles have characteristic ^1H N.M.R. spectra. A numbering convention akin to that employed for platinaindans appears in Fig. 5.23. Hydrogen and carbon atoms *trans* to the aryl fragment are designated $H_{n'}$ and $C_{n'}$ respectively. Common to all these species is a singlet due to silicon-methyl groups, which occurs between 0.0-0.5 ppm and a "triplet" at *ca.* 1.0 ppm corresponding to Pt-CH_2 group. $^2J_{Pt-H}$ is usually of the order of 100 Hz. The most characteristic feature of the aromatic region is a doubled doublet at 7.7-7.9 ppm with platinum satellites. This resonance may be assigned to H_3 of the metallacyclic ring. $^3J_{Pt-H}$ is usually 62.0-67.0 Hz, similar to that observed for *cis*-$(py)_2PtAr_2$ [Ar = Ph, C_6H_4-4-^{t}Bu, C_6H_4-4-CF_3][85, 96].

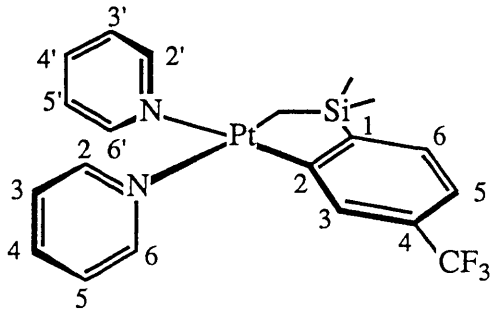


Fig. 5.23 : *N.M.R. Numbering Conventions for Platinasila-indans.*

The asymmetry of these complexes is clearly borne out by the signals due to the pyridine ligands. In total there are six pyridine environments, three in each pyridine ring. The furthest upfield is the multiplet due to H_3 and H_5 and the doubled doublet at lowest field is attributed to H_2 and H_6 of the ring, since it is coupled to platinum. The two values of $^3J_{Pt-H}$ are *ca.* 20 Hz and 25 Hz respectively; the larger of the two is assigned to the ligand *trans* to the alkyl moiety. Generally, the higher field multiplet of each set is associated with the pyridine *trans* to Pt-CH_2; the remaining signal is *trans* to an aryl fragment. An interesting feature observed in the aromatic region of $(py)_2Pt(CH_2SiMe_2C_6H_3$-4-$CF_3)$ is a further splitting of the resonances attributed to the pyridine ring *trans* to the Pt-methylene group by long-range coupling to ^{19}F (Fig. 5.24), allowing resonances due to pyridine to be assigned unequivocally.

^{13}C N.M.R. of $(py)_2Pt(CH_2SiMe_2C_6H_4)$ also demonstrates the inequivalence of the ligands (Table 5.15). Both C_2, C_6 and C_3, C_5 have observable interactions with ^{195}Pt; the larger coupling constant in each case due to pyridine *trans* to the alkyl group, which has a weaker *trans*-influence than an aryl group. With the exception of C_5 of the metallacyclic ring, each carbon atom exhibits platinum satellites. As with $L_2Pt(CH_2CMe_2Ph)_2$ [L = bidentate N-donor], the magnitude of $^2J_{Pt-C}$ is smaller than $^3J_{Pt-C}$ by 30 Hz. This effect has previously been observed in J_{P-C}[115] and $J_{^{13}C-^{13}C}$[116] and also in J_{Pt-C}[12a, 117] of related platinum(II) alkyl and metallacyclic species. Most probably it is due to anomalously low values of the two bond coupling, though theories governing

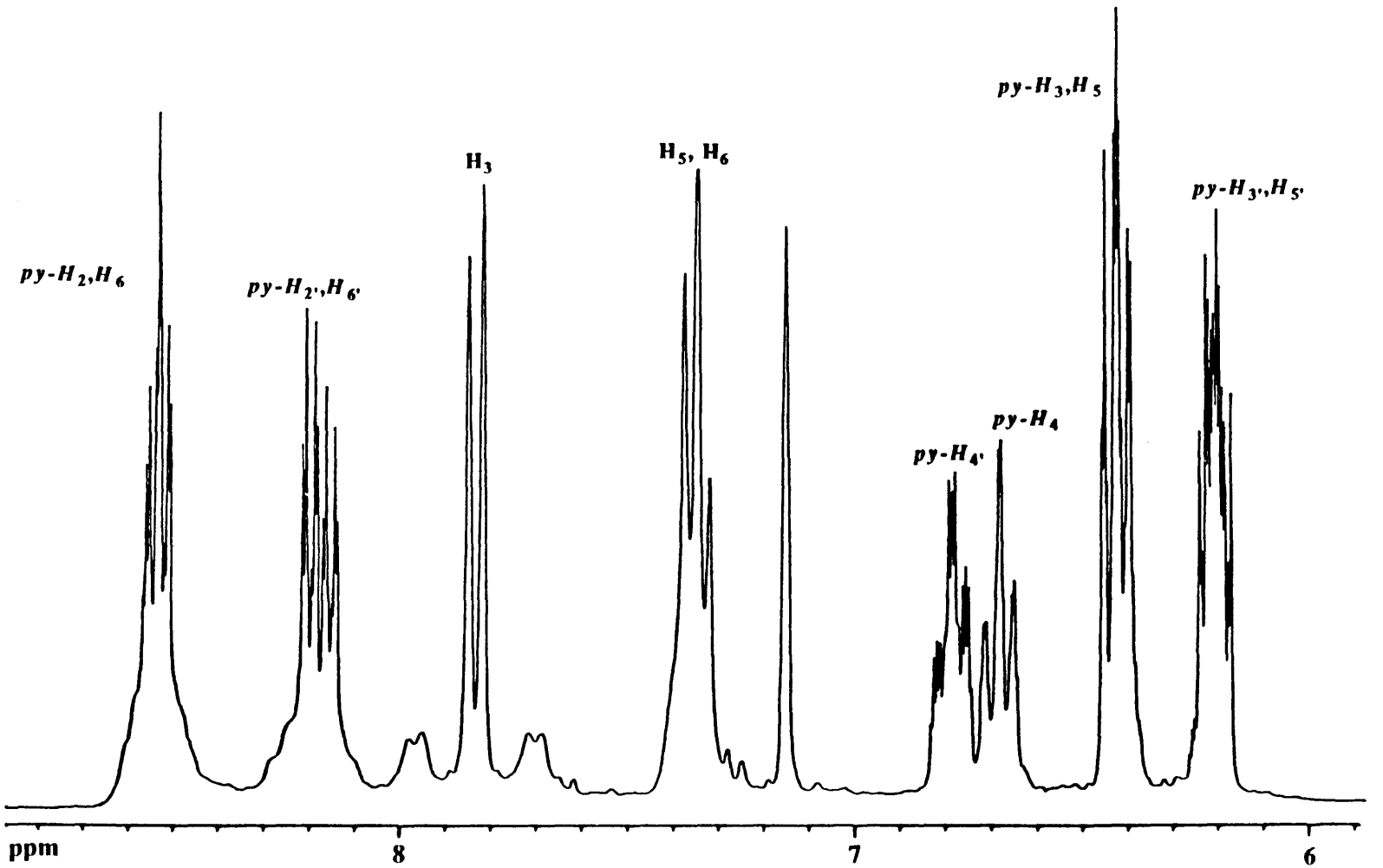


Fig. 5.24 : ^{1}H *N.M.R. of the Aromatic Region of* $(py)_2Pt(CH_2SiMe_2C_6H_3\text{-}CF_3)$.

Table 5.15 : *^{13}C N.M.R. Characteristics of $(py)_2Pt(\overline{CH_2SiMe_2C_6H_4})$ and $(py)_2Pt(C_6H_4\text{-}2\text{-}Me)(CH_2SiMe_2CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands ($J_{Pt\text{-}C}$) / Hz [*Assignment*]			δ ^{13}C ppm : Ancillary ligands ($J_{Pt\text{-}C}$) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_n	Aromatic	
$(py)_2Pt(\overline{CH_2SiMe_2C_6H_4})$[a]	- 8.56 (**771.0**)	4.29 (**33.3**) [CH_3]	121.92 (**12.9**) [C_6]; 126.80 (**77.8**) [C_4]; 133.94 [C_5]; 139.36 (**33.5**) [C_3]; 142.04 (**28.3**) [C_1]; 143.29 (**841.2**) [C_2]	124.75 (**20.6**) [C_3, C_5]; 124.91 (**14.5**) [$C_{3'}$, $C_{5'}$]; 135.20 [C_4]; 135.67 [$C_{4'}$]; 150.97 (**14.2**) [C_2, C_6]; 151.57 (**16.5**) [$C_{2'}$, $C_{6'}$]
$(py)_2Pt(C_6H_4\text{-}2\text{-}Me)$- $(CH_2SiMe_2CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$[a]	-11.68 (**772.0**)	1.52 3.56 (**27.0**) 4.30 (**23.9**) [CH_3]	14.09 [CH_3]; 22.68 (**31.3**) [CH_3]; 122.00 [C_4]; 124.30 [$C_{4'}$]; 125.03 (**31.5**) [C_5]; 127.22 [$C_{5'}$]; 128.74 [$C_{3'}$]; 130.17 [$C_{6'}$]; 134.89 (**32.4**) [C_3]; 139.29 (**33.4**) [C_6]; 143.51 (**19.6**) [C_2]; 143.68 [$C_{2'}$];	124.60 (**20.1**) [C_3, C_5]; 124.90 (**19.3**) [$C_{3'}$, $C_{5'}$]; 134.89 [C_4]; 134.97 [$C_{4'}$]; 150.56 (**17.2**) [C_2, C_6]; 151.58 (**15.0**) [$C_{2'}$, $C_{6'}$]

Tale 5.15 : (continued)

$(py)_2Pt(C_6H_4\text{-}2\text{-}Me)$- $(CH_2SiMe_2CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$[a]	6.30 (**45.2**) [CH_2]	143.82 (**831.9**) [C_1]; 150.29 [$C_{1'}$]

a :- benzene-d^6

coupling constants in these systems are not well developed.

In general *para*-substituted aromatic rings undergo facile aromatic C-H transfer forming a platinacycle. In marked contrast, $(py)_2Pt(C_6H_4\text{-}2\text{-}Me)(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$ is the only detectable product from the reaction of $(cod)Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$ with pyridine. Attempts to produce $(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CH_3)_2$, in which the phenyl group in sila-neophyl has been replaced by the bulkier *o*-tolyl ring, results in formation of a new complex, stoichiometrically identical to that of the expected dialkyl but with N.M.R. characteristics wholly inconsistent with such a proposition. ^1H N.M.R. reveals three distinct silicon-methyl environments in the ratio 2:1:1, implying four such groups (Fig. 5.25). Additionally at 0.06 ppm a less intense signal corresponding to two hydrogens may be attributed to a $Si\text{-}CH_2$ fragment, indicating that β-aryl transfer has occurred, in a similar fashion to $(PR_3)_2Pt(CH_2SiMe_2Ar)_2$, generating *cis*-$(py)_2Pt(C_6H_4\text{-}2\text{-}Me)(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$. Two singlets at 2.36 and 2.79 ppm respectively, due to arene methyl groups are also evident.

The aromatic region is complicated, the two most characteristic resonances of the arene groups are the doubled doublet of $H_{6'}$ and a lower field resonance with $^3J_{Pt\text{-}H} = 67.0$ Hz due to H_6. A variable temperature study of this derivative displayed broadening of two $Si\text{-}CH_3$ groups and one aryl-methyl group as the temperature was increased, indicative of restricted rotation about the platinum-aryl bond and consistent with observations noted for the analogous triphenylphosphine compound.

The most notable feature of the ^{13}C N.M.R. spectrum are four $Si\text{-}CH_n$ signals, three of which are coupled to ^{195}Pt (Table 5.15). The largest coupling is similar in value to that observed for $Si\text{-}CH_2\text{-}Si$ in the phosphine analogue. The other two with smaller $^3J_{Pt\text{-}C}$ are attributed to Si-Me groups nearest to platinum. A three bond coupling of 31.3 Hz to an aryl-methyl group, confirms the supposition that this derivative is obtained *via* β-aryl transfer followed by η^2-silene migratory insertion into a $Pt\text{-}CH_2$ bond.

Even though C-H activation for pyridine complexes is a relatively low energy process, the inherently large steric bulk of the *o*-tolyl group must increase the activation energy to such an extent that β-aryl transfer becomes lower in energy, consequently the favoured pathway.

5.2.5. *Investigations of the Thermolytic Behaviour of* bis-*[dimethyl(benzyl)silylmethyl]platinum(II) Complexes with N- and P-Donor ligands.*

Preliminary investigations of the thermolysis of $L_2Pt(CH_2SiMe_2CH_2Ar)_2$ [L = PPh_3, py; Ar = Ph, C_6H_4-4-Me] indicate that the reactivity of these complexes is more complicated than for analogous *bis*-sila-neophyl compounds. At 110°C, benzene or toluene solutions of $(PPh_3)_2Pt(CH_2SiMe_2CH_2Ph)_2$ generate three new species, which so far have only been characterised by ^{31}P N.M.R. spectroscopy (Table 5.16). Values of $^1J_{Pt\text{-}P}$ of 1945.1 Hz and 1960.9 Hz correspond closely to those obtained for

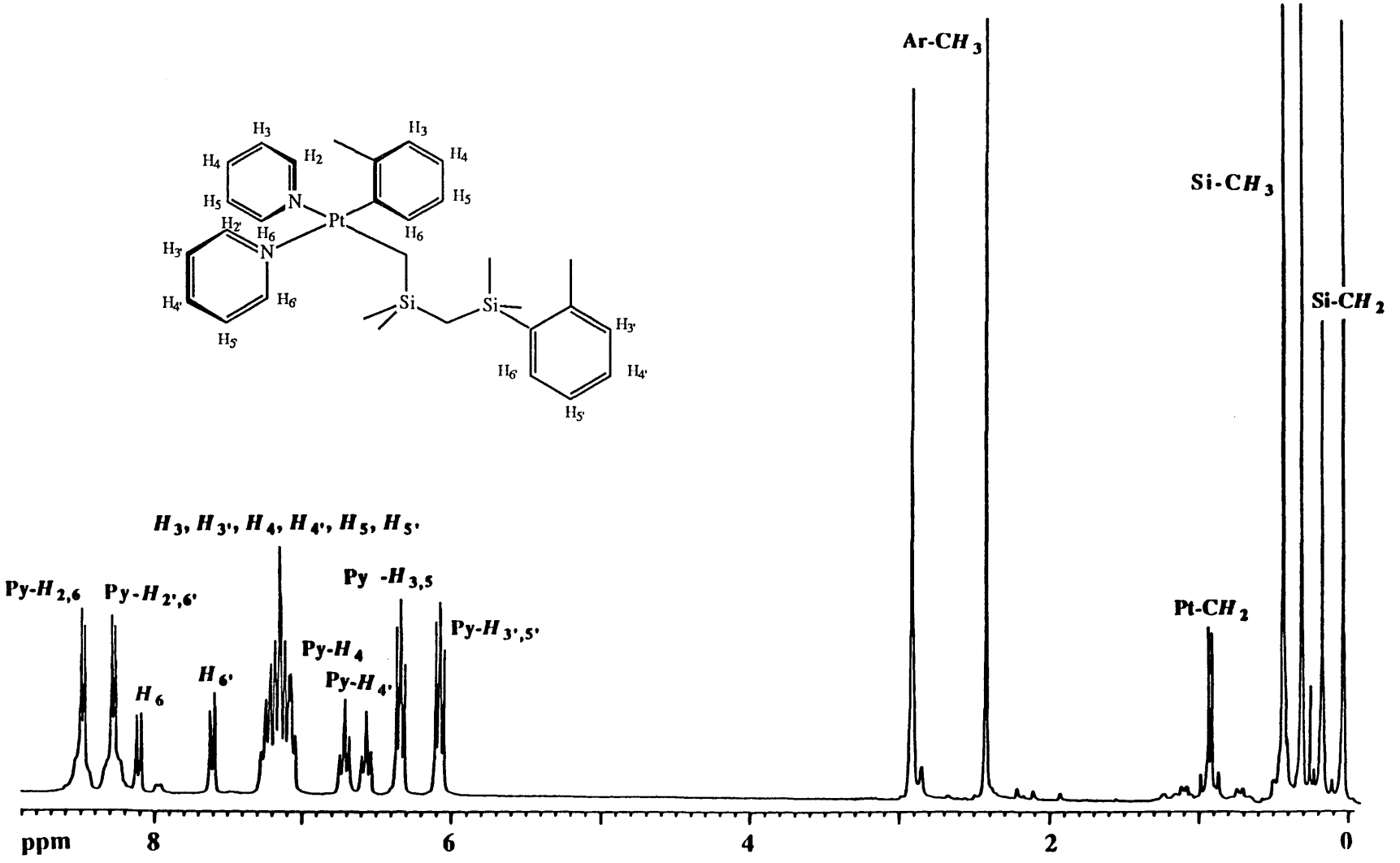


Fig. 5.25 : *^{1}H N.M.R of $(py)_2Pt(C_6H_4\text{-}2\text{-}Me)(CH_2SiMe_2CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)$.*

Table 5.16 : *^{31}P N.M.R. Characteristics of the Products from Thermolysis of $(PPh_3)_2Pt(CH_2SiMe_2CH_2Ar)$.*

Complex	δ^a / ppm	$J_{Pt\text{-}P}$ / Hz	$J_{P\text{-}P}$ / Hz
$(PPh_3)_2Pt(CH_3)(CH_2SiMeCH_2PhCH_2SiMe_2CH_2Ph)^b$	25.04, 27.73	1945.1, 1960.6	8.9
$(PPh_3)_2Pt(CH_2Ph)(CH_2SiMe_2CH_2SiMe_2CH_2Ph)^b$	22.78, 23.58	1832.1, 2090.9	7.8
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4)^b$	22.02, 24.19	1745.7, 2182.1	11.1
$(PPh_3)_2Pt(CH_3)(CH_2SiMeCH_2C_6H_4\text{-}4\text{-}MeCH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)^c$	25.28, 28.77	1941.7, 2018.2	8.9
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_3\text{-}4\text{-}Me)^c$	22.85, 25.97	1718.0, 2182.1	8.9
$(PPh_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMeCH_2C_6H_4\text{-}4\text{-}Me)(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)^c$	23.34, 24.62	1692.5, 4439.5	13.3

a :- referenced to 85% H_3PO_4 / D_2O

b :- benzene-d^6

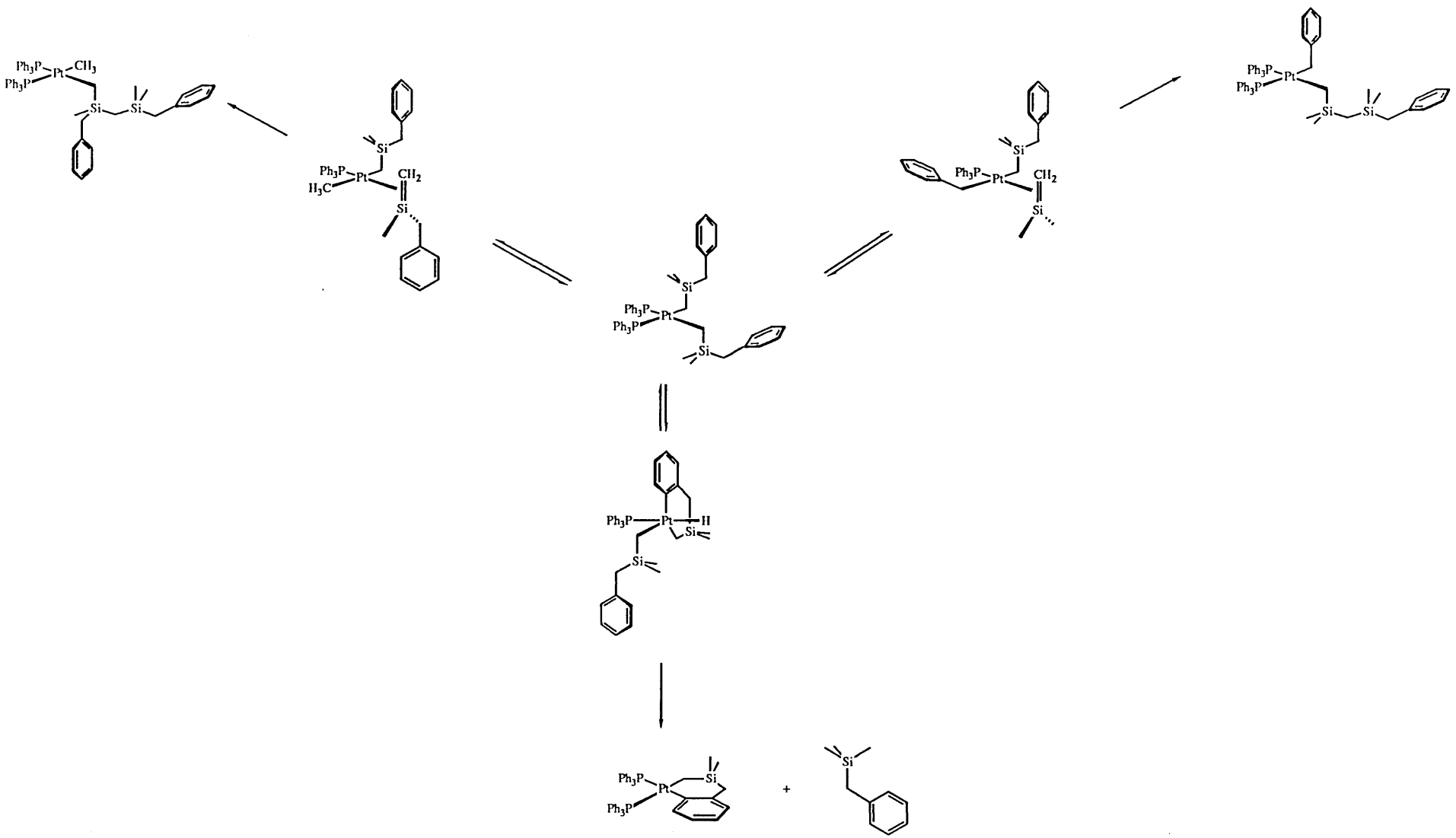
c :- toluene -d^8

$L_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$ and $L_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$ (*vide infra*), suggesting that this compound is $(PPh_3)_2Pt(CH_3)(CH_2SiMeCH_2PhCH_2SiMe_2Ph)$ arising from β-methyl migration. A second species with $^1J_{Pt\text{-}P}$ of 1832.1 Hz and 2090.9 Hz indicates an alkyl and a β-sila-alkyl fragment coordinated to platinum. The most likely explanation is transfer of a benzyl group from silicon to platinum forming a (benzyl)(sila-alkyl)derivative, $(PPh_3)_2Pt(CH_2Ph)(CH_2SiMe_2CH_2SiMe_2CH_2Ph)$. The remaining species has characteristics which are consistent with aryl and sila-alkyl groups bound to platinum. As aryl transfer can be deemed unlikely in this case, most plausibly, aromatic C-H activation results in formation of a six-membered platinacycle, $(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4)$ a platinasila-tetralin (Scheme. 5.8). The approximately statistical distribution of these derivatives implies that all three processes governing such behaviour are similar in energy.

$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$ is less reactive than the unsubstituted complex and gives rise to principally two species, though polymeric zerovalent platinum is also observed. ^{31}P N.M.R. characteristics are consistent with products obtained *via* β-methyl transfer and ε-aromatic C-H activation, forming $(PPh_3)_2Pt(CH_3)(CH_2SiMeCH_2C_6H_4\text{-}4\text{-}MeCH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)$ and $(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_3\text{-}4\text{-}Me)$ respectively. β-Benzyl transfer is not apparent, indicating that the electron-releasing effect of the methyl group raises the energy of benzyl transfer to the extent that methyl transfer occurs preferentially. A third species, with $^1J_{Pt\text{-}P}$ of 1692.5 Hz and 4439.5 Hz is similar to that observed during thermolysis of $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ (See 7.2.2) and may possibly be $(PPh_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMeCH_2C_6H_4\text{-}4\text{-}Me)(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)$.

Further characterisation of these complexes was precluded by ^1H and ^{13}C N.M.R. spectroscopy due to the complex nature of resonances associated with a mixture of species in solution and insufficient sample for informative data. In order to establish the identity of the compounds, chromatographic separation of the reaction mixture should lead to isolation of each species, which can then be fully characterised individually. In the event of non-resolution of the complexes, both J-correlated and shift-correlated 2D-N.M.R. experiments should help identify the species in solution.

Preliminary studies of the thermolysis of $(py)_2Pt(CH_2SiMe_2CH_2Ph)_2$ at 30°C generates two new compounds. The major product consists of two apparently equivalent pyridine groups, as only one environment for each hydrogen is observed by ^1H N.M.R. (Table 5.17). A further two multiplets in the aromatic region correspond to H_2, H_6 and H_3, H_4, H_5 of an arene ring. The aliphatic peaks are typical for benzylic-CH_2, Pt-CH_2 and Si-CH_3 groups. Though far from fully characterised, the proposed structure of this compound is $(py)_2Pt[CH_2SiMe(CH_2Ph)CH_2]$ derived by γ-C-H abstraction of a methyl group. The minor product has a more complex spectrum illustrated in Fig. 5.26. Of the several interesting features, there are no benzyl-CH_2 protons, although a new peak at 0.41 ppm may be assigned to a Si-CH_2 fragment. Si-CH_3 and Pt-CH_2 groups in the



Scheme. 5.8 : *Formation of Products from Thermolysis of* $(PPh_3)_2Pt(CH_2SiMe_2CH_2Ph)_2$.

Table 5.17 : *^1H N.M.R. Characteristics of the Products from Thermolysis of $(py)_2Pt(CH_2SiMe_2CH_2Ph)_2$.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]			δ ^{1}H ppm : Ancillary ligand (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	Si-CH_3	Aromatic	
$(py)_2\overline{Pt(CH_2SiMeCH_2PhCH_2)}$[a]	0.83 (**87.8**)	0.37	2.06 [*Ar-CH_2*]; 7.00-7.08 m, [*H_3, H_4, H_5*]; 7.62 dd, [*H_2, H_6*] ($J_{H_2-H_3}$=7.8 Hz)	6.24 m, [*H_3, H_5*] ($J_{H_3-H_4}$=6.3 Hz); 6.78 m, [*H_4*] ($J_{H_2-H_4}$=1.3 Hz); 8.08 dd, (**23.9**) [*H_2, H_6*] ($J_{H_2-H_3}$=7.7 Hz)
$(py)_2\overline{Pt(CH_2SiMe_2CH_2C_6H_4)}$[b]	1.16 (**102.7**)	0.33 [*CH_3*] 0.41 [*CH_2*]	7.10 m, [*H_6*] ($J_{H_5-H_6}$=8.0 Hz); 7.26 m, [H_4, H_5] ($J_{H_4-H_5}$=8.5 Hz); 7.91 dd, (**67.4**) [*H_3*] ($J_{H_3-H_4}$=7.6 Hz)	6.16 m, [*H_3, H_5*] ($J_{H_3-H_4}$=6.7 Hz); 6.35 m, [*$H_{3'}$, $H_{5'}$*] ($J_{H_{3'}-H_{4'}}$=6.5 Hz); 6.61 m, [*H_4*] ($J_{H_2-H_4}$=1.3 Hz); 6.70 m, [*$H_{4'}$*] ($J_{H_{2'}-H_{4'}}$=2.0 Hz); 8.30 dd, (**24.6**) [*H_2, H_6*] ($J_{H_2-H_3}$=7.8 Hz);

Table 5.17 : (continued)

$(py)_2\overline{Pt(CH_2SiMe_2CH_2C_6H_4)}$[b]				8.62 dd, (**18.1**) [$H_{2'}$, $H_{6'}$] ($J_{H_2\text{-}H_3}$=7.9 Hz)
$(py)_2\overline{Pt(CH_2SiMe_2CHPh)}$[a]	0.87 (**116.9**)	0.41	7.05-7.15 m, [H_3, H_4, H_5]; 7.66 dd, [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.5 Hz)	6.23 m, [H_3, H_5] ($J_{H_3\text{-}H_4}$=6.4 Hz); 6.78 m, [H_4] ($J_{H_2\text{-}H_4}$=1.3 Hz); 8.09 dd, (**22.3**) [H_2, H_6] ($J_{H_2\text{-}H_3}$=7.6 Hz)

a :- toluene-d^8

b :- benzene-d^6

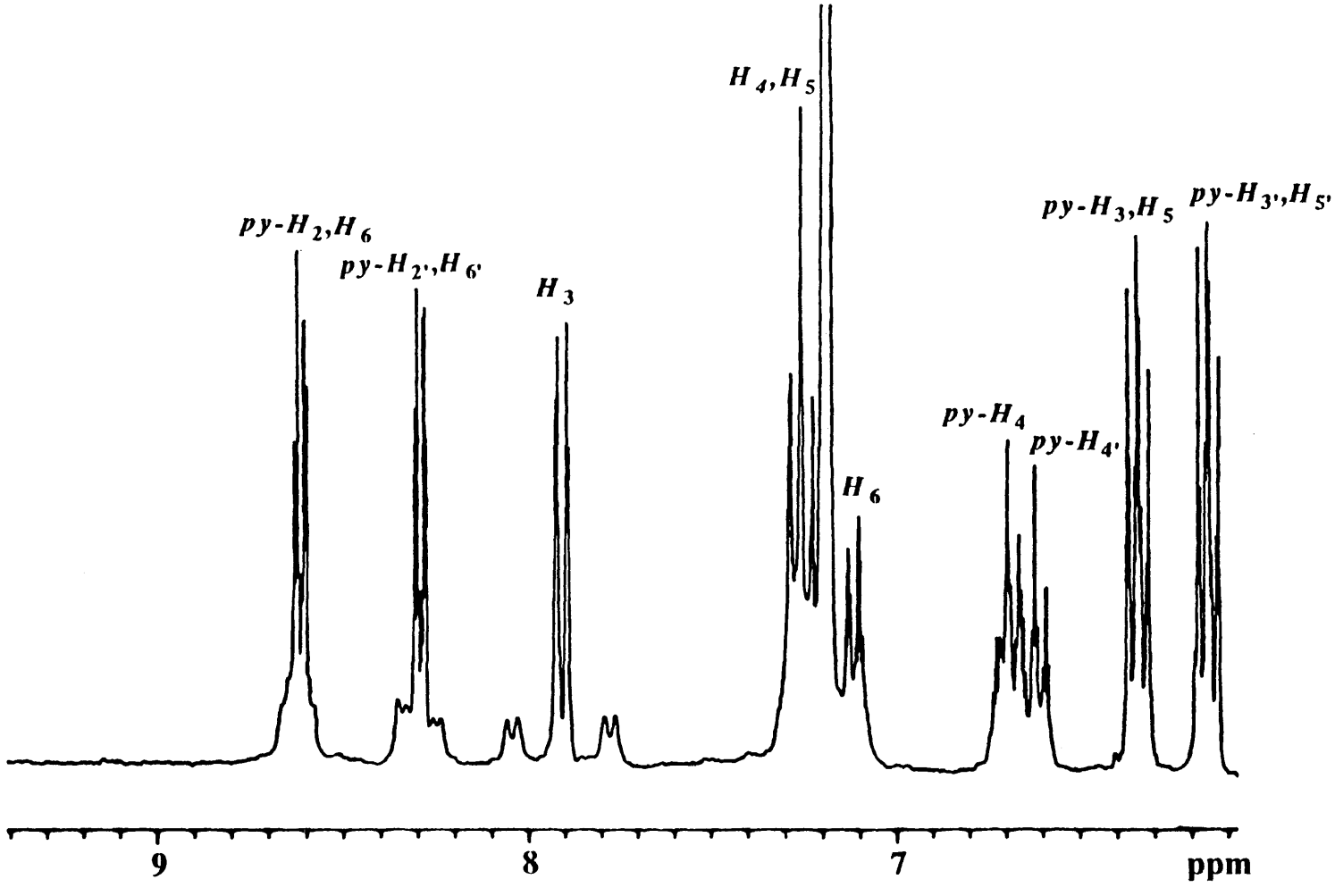
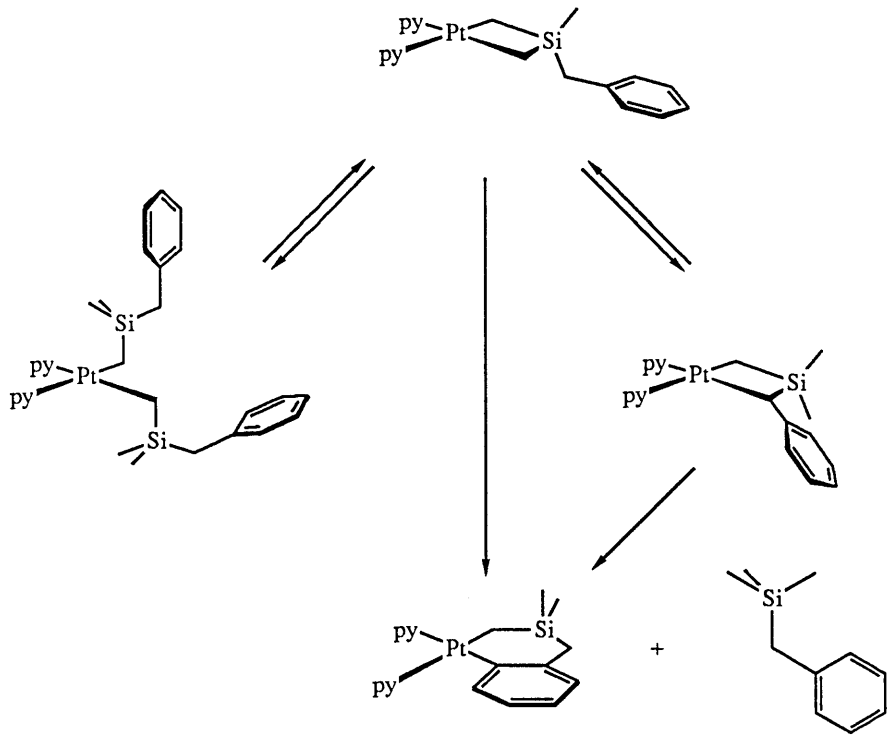


Fig. 5.26 : *^1H N.M.R. of the Aromatic Region of* $(py)_2Pt(CH_2SiMe_2CH_2C_6H_4)$.

ratio 2:1 are also evident. The aromatic region demonstrates the asymmetry of this compound, with $^3J_{Pt-H} = 24.6$ Hz and 18.1 Hz respectively for H_2, H_6 of each pyridine ring, consistent with platinum-bound aryl and sila-alkyl groups. The remaining aromatic resonances correspond to only 4-hydrogens. The furthest downfield with $^3J_{Pt-H} = 67.4$ Hz, further substantiates the conjecture of a Pt-aryl interaction. ε-Aromatic C-H activation forming a platinasila-tetralin, $(py)_2\overline{Pt(CH_2SiMe_2CH_2C_6H_4)}$ is consistent with data observed.

After several days, a 1:1 mixture of the 6-membered metallacycle and a new species is obtained. The latter has ^1H N.M.R. characteristics very similar to those of $(py)_2\overline{Pt(CH_2SiMeCH_2PhCH_2)}$ with the exception of no observable benzyl-methylene group. It is possible that this species is the other feasible 4-membered metallacycle, obtained by γ-C-H transfer of a benzyl-CH_2 group.

The 6-membered platinacycle is observed at all stages and appears to be the thermodynamically most stable product. Moreover, eventually it is the only visible species in solution. A possible mechanism explaining these observations occurs in Scheme. 5.9. The substrate undergoes C-H activation of a Si-Me group generating a 1-platina-3-methyl-3-benzylsila-cyclobutane, which can undergo reversible isomerisation forming its isomeric four-membered metallacycle by γ-C-H transfer of a benzyl-CH_2 hydrogen. Both these species, however, are metastable with respect to the larger platinacycle and undergo, essentially irreversible isomerisation to this derivative, the thermodynamically favoured product.



Scheme. 5.9 : *Formation of Products from the Thermolytic Rearrangement of* $(py)_2Pt(CH_2SiMe_2CH_2Ph)_2$.

5.2.6. Conclusions and Further Studies.

Several interesting points have been observed during thermolysis of β-sila-alkyl complexes. Steric and electronic properties of ancillary phosphines may affect the final outcome of the reaction. Investigation of the effect of phosphine dissociation on the rate of rearrangement should provide further understanding of these effects.

Substituents on the aryl ring of a sila-neophyl group alter the rate of reaction; electron-withdrawing groups accelerate the rate of aryl transfer and electron-releasing groups retard the rearrangement. A Hammett plot is only meaningful if either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ are essentially identical over the series of derivatives or if there is a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Rate structure profiles for as many complexes as possible should determine whether either of these criteria are satisfied, resulting in a more accurate LFE relationship, thus establishing a clearer picture of the transition state.

Transfer of a β-sila-alkyl group occurs regiospecifically, nevertheless, it is also important to determine the stereochemistry at silicon during migration. A possible solution may be achieved by use of a stereochemically active phosphine and a ligand CH_2SiR_2R', tailored so that migration of R is preferred to that of R'. Asymmetric induction in the product of migratory insertion will occur as a result of preference for one of the two possible η^2-binding configurations of the prochiral silene, CH_2=SiRR'.

Replacing pyridine by 4-*tert*-butylpyridine will result in thermolytically more robust complexes, $(^tBupy)_2Pt(CH_2SiMe_2Ar)_2$. Such complexes should be excellent candidates for determination of electronic effects on aromatic C-H activation with β-sila-alkyl ligands, allowing direct comparison with dineophyl analogues to be made.

5.3. Experimental.

5.3.1. General.

Elemental analyses and N.M.R. spectra were obtained as described previously (See 4.3).

All reactions were carried out under argon, unless otherwise noted, using standard Schlenk line techniques. Solvents were distilled under nitrogen prior to use (See 2.3).

Diphenyl-*ortho*-tolylphosphine, $BrMgC_6D_5$ and $ClMgCH_2SiMe_2Ph\text{-}d^5$ were prepared by previously described routes (See 2.3 and 3.3).

Bromine, phosphorus trichloride, triphenylphosphine, pyridine-d^5 and benzene-d^6 were all used as supplied by Aldrich Chem.Co.Ltd.. Pyridine, supplied by Rose Chemicals was dried over sodium hydroxide and distilled under argon prior to use. Chloromethyldimethylchlorosilane, supplied by Aldrich Chem.Co.Ltd. was stored under argon but used without further purification.

5.3.2. Syntheses.

Preparation of bromobenzene-d^5 [118].

Dry pyridine (0.2 cm^3, 2.5 mmol) was added to a stirred solution of benzene-d^6 (15.0g, 178 mmol). Bromine (34.8g, 218 mmol) was carefully poured down a condenser. A vigorous reaction ensued and HBr was evolved. After formation of HBr had ceased, the mixture was heated to 30°C for 3 hours and then 70°C for a further 2 hours. The cooled dark orange mixture was washed with dilute sodium metabisulphite solution (3 x 20 cm^3) until the washings were alkaline to litmus and the solution was straw yellow. The organic layer was then washed with water (1 x 20 cm^3), dried over $MgSO_4$, filtered and the residues washed with diethyl ether (2 x 15 cm^3). The solvent was removed *in vacuo* yielding a pale yellow liquid, which was distilled to afford BrC_6D_5 as a colourless liquid (bp. 155-158°C).
(Yield : 18.78g, 116 mmol, 65%)

[Mass. Spec. : $M^+ = 162$; >98% C_6D_5Br]

Preparation of chloromethyldimethylphenylsilane-d^5.

A solution of C_6D_5MgBr in diethyl ether (20 cm^3) was added slowly to a stirred solution of $ClCH_2SiMe_2Cl$ (8.1 cm^3, 61.8 mmol) in Et_2O (10 cm^3). Upon complete addition, the mixture was gently refluxed for 24 hours. After this time, a white precipitate of MgClBr and a pale yellow solution had formed, which was cooled to -78°C and quenched with degassed saturated ammonium chloride solution (60 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (3 x 20 cm^3). The ether extracts were combined, dried over $MgSO_4$, filtered and the inorganic residues washed with Et_2O (2 x 10 cm^3). Removal of the solvent *in vacuo* afforded a pale yellow

liquid. Distillation of this liquid gave $ClCH_2SiMe_2Ph\text{-}d^5$, a colourless liquid as the main fraction (bp. = 115-116°C, 10 mmHg).
(Yield : 7.9g, 41.6 mmol, 67%)

[Mass. Spec. : $M^+ = 190$; >97% $ClCH_2SiMe_2Ph\text{-}d^5$]

[^{1}H N.M.R. ($CDCl_3$) : $\delta \equiv 0.30$ ppm $-CH_3$, 2.91 ppm $-CH_2$]

Preparation of triphenylphosphine-d^{15} [83].

A solution of $BrMgC_6D_5$ (60 mmol) in Et_2O (60 cm^3) was added slowly to a stirred solution of PCl_3 (2.1g, 15.0 mmol) in diethyl ether (20 cm^3) at 0°C. On warming to ambient temperature, the mixture was stirred for a further 16 hours, then cooled to -78°C and quenched with degassed saturated ammonium chloride solution (30 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (3 x 20 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with activated charcoal. After filtration and washing the residues with Et_2O (2 x 7 cm^3), evaporation to dryness yielded a pale yellow solid. This solid was dissolved in the minimum quantity of hot ethanol (20 cm^3) and cooled slowly to room temperature. The solid was filtered, washed with cold ethanol (2 x 5 cm^3), *n*-hexane (10 cm^3) and dried *in vacuo* to give a white crystalline solid.
(Yield : 2.99g, 10.8 mmol, 72%)

[Mass. Spec. : $M^+ = 277$; >96% $PPh_3\text{-}d^{15}$]

[^{31}P N.M.R. ($CDCl_3$) : $\delta \equiv -6.22$ ppm]

Preparation of bis-*(sila-neophyl)([2.2.1]bicyclohepta-2,5-diene)platinum(II).*

A solution of $ClMgCH_2SiMe_2Ph\text{-}d^5$ (8.4 mmol) in Et_2O (25 cm^3) was added dropwise to a stirred suspension of (nbd)$PtCl_2$ (1.00g, 2.8 mmol) in diethyl ether (10 cm^3) at -78°C. The mixture was gradually warmed to room temperature and then stirred for a further 16 hours. The dark coloured reaction mixture was cooled to -78°C and quenched with degassed saturated ammonium chloride solution (20 cm^3). The organic layer was separated and the aqueous phase washed with Et_2O (2 x 10 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with activated charcoal. After filtering and washing the residues with diethyl ether (2 x 8 cm^3), the solvent was removed *in vacuo* to yield a white oil, which was dissolved in the minimum amount of *n*-hexane (3 cm^3) and cooled to -20°C. The solid was filtered, washed with cold *n*-hexane (2 x 3 cm^3) and dried *in vacuo*, affording the product as a white crystalline solid.
(Yield : 1.48g, 2.5 mmol, 89%)

[*Analysis* : Found C=50.08%, H=5.76%; Calculated C=50.39%, H=5.75%]

Preparation of cis-bis-*(triphenylphosphine)*-bis-*(sila-neophyl-d^5)platinum(II).*

Triphenylphosphine (0.18g, 0.68 mmol) was added to (nbd)Pt(CH_2SiMe_2Ph-d^5)$_2$ (0.20g, 0.34 mmol) in diethyl ether (7 cm^3) and the mixture allowed to stand at ambient temperature for 7 days. Removal of the ether *in vacuo* afforded a pale yellow solid, which was dissolved in the minimum quantity of benzene (2 cm^3), *n*-hexane (2 cm^3) added and cooled to -20°C. The solid was filtered, washed with *n*-hexane (2 x 3 cm^3) and dried *in vacuo* giving the product as a white crystalline solid.
(Yield : 0.32g, 0.31 mmol, 92%)

[*Analysis* : Found C=62.93%, H=5.40%; Calculated C=63.38%, H=5.52%]

Prepared by an analogous method were :-

cis-bis-*(diphenylmethylphosphine)*-bis-*(sila-neophyl-d^5)platinum(II).*
Product : White solid from benzene and *n*-hexane.
(Yield : 0.27g, 0.30 mmol, 88%)

[*Analysis* : Found C=58.63%, H= 7.04%; Calculated C=58.46%, H=6.91%]

cis-bis-*(dimethylphenylphosphine)*-bis-*(sila-neophyl-d^5)platinum(II).*
Product : White crystalline plates from benzene and *n*-hexane.
(Yield : 0.26g, 0.33 mmol, 97%)

[*Analysis* : Found C= 52.68%, H=6.12%; Calculated C= 52.35%, H=6.20]

cis-bis-*(triphenylphosphine-d^{15})*-bis-*(sila-neophyl)platinum(II).*
Product : White crystalline solid from benzene and *n*-hexane.
(Yield : 0.33g, 0.31 mmol, 93%)

[*Analysis* : Found C=61.77%, H=5.54%; Calculated C=61.86%, H= 5.38%]

Preparation of cis-bis-*(triphenylphosphine)(phenyl)({[dimethyl(phenyl)silylmethyl] dimethylsilyl}methyl)platinum(II).*

(PPh_3)$_2$Pt(CH_2SiMe_2Ph)$_2$ (0.15g, 0.15 mmol) was dissolved in toluene (6 cm^3) and freeze-thaw degassed through three cycles. The colourless solution was heated to 100°C for 24 hours, cooled and the resultant yellow solution filtered through a plug of fluorosil and activated charcoal. The solvent was evaporated to dryness and the solid

recrystallised from the minimum amount of benzene (1 cm^3) and *n*-hexane (1 cm^3) yielding a white crystalline solid of the product.
(Yield : 0.14g, 0.14 mmol, 92 %)

[*Analysis* : Found C=63.68%, H=5.61%; Calculated C=63.70%, H= 5.54%]

Preparation of cis-bis-*(diphenylmethylphosphine)(phenyl)({[dimethyl(phenyl)silylmethyl] dimethylsilyl}methyl)platinum(II).*

This complex was obtained as a white solid from *n*-hexane by heating a toluene solution of $(PPh_2Me)_2Pt(CH_2SiMe_2Ph)_2$ to 135°C for 24 hours by a procedure similar to that described above.
(Yield : 0.13g, 0.14 mmol, 87%)

Preparation of cis-bis-*(triphenylphosphine)(2-methylphenyl)({[dimethyl(2-methylphenyl) silylmethyl]dimethylsilyl}methyl)platinum(II).*

The title compound was synthesised as a white crystalline solid by heating a toluene solution to 70°C for 16 hours by essentially an identical procedure to that described above.
(Yield : 0.14g, 0.15 mmol, 95%)

Preparation of cis-bis-*(triphenylphosphine)(pentafluorophenyl)({[dimethyl (pentafluorophenyl)silylmethyl]dimethylsilyl}methyl)platinum(II).*

Triphenylphosphine (0.14g, 0.52 mmol) was added to a solution of $(cod)Pt(CH_2SiMe_2C_6F_5)_2$ (0.20g, 0.24 mmol) in Et_2O (5 cm^3) and heated to 60°C for 35 days. Removal of the solvent *in vacuo* afforded the product as a white solid.
(Yield : 0.24g, 0.20 mmol, 77%)

Preparation of cis-*(diphenyl-*o*-tolylphosphine)(sila-neophyl)-1,1-diphenylphosphino-2-platinaindan.*

$(PPh_2\text{-}o\text{-}tol)_2Pt(CH_2SiMe_2Ph)_2$ (0.09g, 0.09 mmol) was dissolved in toluene (3 cm^3) and freeze-thaw degassed through three cycles. The solution was heated to 40°C for 16 hours. Removal of the solvent *in vacuo* yielded the product as a white analytically pure solid.
(Yield : 0.06g, 0.08 mmol, 89%)

[*Analysis* : Found C=63.52%, H=5.14%; Calculated C=63.35%, H=5.32%]

Preparation of cis-bis-*(pyridine)-platina-3-sila-indan.*

$(py)_2Pt(CH_2SiMe_2Ph)_2$ (0.10g, 0.20 mmol) was dissolved in toluene (8 cm^3) and left at ambient temperature for 4 days. Removal of toluene *in vacuo* afforded a

yellow-brown oily residue, which was recrystallised from diethyl ether (1 cm^3) and *n*-hexane (0.5 cm^3) to give the product as pale yellow crystalline solid.
(Yield : 0.07g, 0.18 mmol, 91%)

[*Analysis* : Found C=45.11%, H=4.63%, N=5.74%; Calculated C=45.50%, H=4.42%, N=5.59%]

Preparation of cis-bis-*(pyridine)-1-platina-3-sila-7-trifluoromethylindan.*

(cod)Pt($CH_2SiMe_2C_6H_4$-4-CF_3)$_2$ (0.20g, 0.24 mmol) was dissolved in excess pyridine (10 cm^3) and heated to 60°C for 24 hours. Excess pyridine was removed *in vacuo* to give an off white oil, which was recrystallised from diethyl ether (1 cm^3) and *n*-hexane (0.3 cm^3) to afford the product as colourless plates.
(Yield : 0.12g, 0.21 mmol, 88%)

[*Analysis* : Found C=41.87%, H=3.54%, N=5.19%; Calculated C=42.18%, H=3.72%, N=5.19%]

Preparation of cis-bis-*(pyridine)(2-methylphenyl)({[dimethyl(2-methylphenyl)silylmethyl] dimethylsilyl}methyl)platinum(II).*

(cod)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2$ (0.20g, 0.32 mmol) was dissolved in excess pyridine (15 cm^3) and heated to 60°C for 24 hours. Excess pyridine was removed *in vacuo* yielding a pale yellow oily residue, which was dissolved in Et_2O (1 cm^3), *n*-hexane (0.2 cm^3) added and cooled to -20°C. The solid was filtered, washed with cold *n*-hexane (2 x 2 cm^3) and dried *in vacuo*, to give a pale yellow crystalline solid of the product.
(Yield : 0.17g, 0.27 mmol, 85%)

[*Analysis* : Found C=52.71%, H=5.84%, H=4.10%; Calculated C=52.99%, H=5.93%, N=4.12%]

5.3.3. Kinetic Measurements.

Toluene-d^8 and benzene-d^6, supplied by MSD isotopes, were distilled from sodium and Na/K alloy respectively and were stored under argon prior to use. Measurements were performed in 5mm-diameter, medium-walled N.M.R. tubes equipped with sealable Teflon valves (J. Young Scientific Ltd.).

Samples were prepared by freeze-thaw degassing toluene-d^8 or benzene-d^6 solutions (either prepared on the day or from a stock solution stored under argon) through five deoxygenating cycles and then sealed under argon. For reactions monitored by ^{31}P N.M.R., solutions whose concentrations were 0.02 M with respect to platinum were prepared. Only 0.01 M solutions were required for reactions followed by ^1H or ^{19}F N.M.R. spectroscopy.

The tube was either maintained at the required temperature (±0.1°C) with a variable temperature probe heater in the Jeol FX90Q spectrometer or by immersion in a Haake W13 thermoregulated silicone oil bath (±0.1°C). Progress of the rearrangements was monitored by either ^{1}H, ^{19}F or ^{31}P N.M.R. spectroscopy periodically.

No internal standards were used; the initial concentration of organoplatinum(II) complex, $[Pt]_0$ was determined by summation of the amount of this complex at any time t, $[Pt]_t$ and the amount of rearranged product present at that time, since only one product is formed during the reaction.

Hence :-

$$\ln \left\{ \frac{[L_2PtR_2]_0}{[L_2PtR_2]_t} \right\} = \ln \left\{ \frac{[L_2PtR_2]_t + [L_2PtRR']_t}{[L_2PtR_2]_t} \right\}$$

Thus, a plot of $\ln\{[Pt]_0/[Pt]_t\}$ against reaction time, t, gives straight lines, allowing calculation of the first order rate constant, k_{obs} from the gradient of these lines.

Chapter Six :

MECHANISTIC STUDIES OF THERMOLYTIC REARRANGEMENTS OF *CIS-BIS*-(PHOSPHINE)(NEOPHYL)(SILA-NEOPHYL) PLATINUM(II) COMPLEXES.

6.1. Introduction.

Dineophylplatinum(II) complexes; $L_2Pt(CH_2CMe_2Ph)_2$ with bidentate N-donor ligands (L = bipy, bipym, phen, Ph_2phen, Me_4phen) and with P-donor ligands (L = PPh_3, PEt_3; L_2 = dppe) undergo thermolytic metallacyclisation *via* aromatic δ-hydrogen transfer, generating *tert*-butylbenzene and 3,3-dimethylplatinaindan. The facility of reaction is dependent on the ancillary ligand, L (L_2)[30, 32, 49, 50].

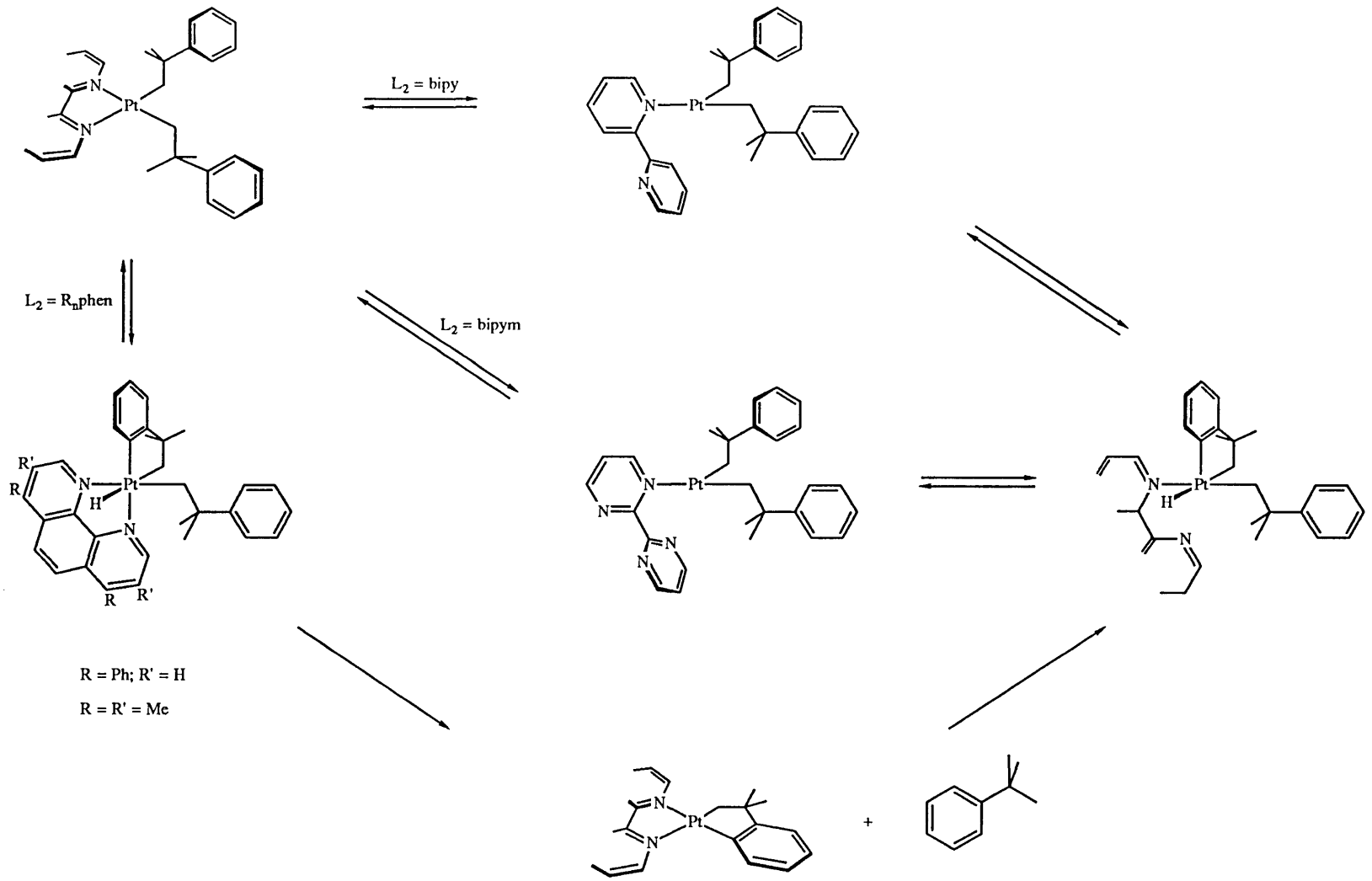
When L_2 is bipy or bipym, scission of one Pt-N is proposedly rate-limiting on the basis of a small deuterium isotope effect. Bipy and bipym have the capacity to rotate the dissociating ring out of coplanarity with its coordinated neighbour about the C_2-$C_{2'}$ bond (Scheme. 6.1). As a result recoordination of this ring is less rapid, allowing oxidative addition of the aromatic C-H bond and reductive elimination of *tert*-butylbenzene to occur *via* relatively less energetic steps along the reaction pathway.

The mechanism is altered, however, for the phenanthroline family of ligands, which are conformationally rigid about their C_2-$C_{2'}$ bond. Consequently, the tricoordinate intermediate has a shorter lifetime, should a Pt-N bond dissociate, and the energetic contribution of an H-transfer step in the mechanism is greater. The observation of a significant isotope effect and a large positive entropy of activation, suggests that C-H reductive elimination is, most plausibly, controlling the rate of reaction.

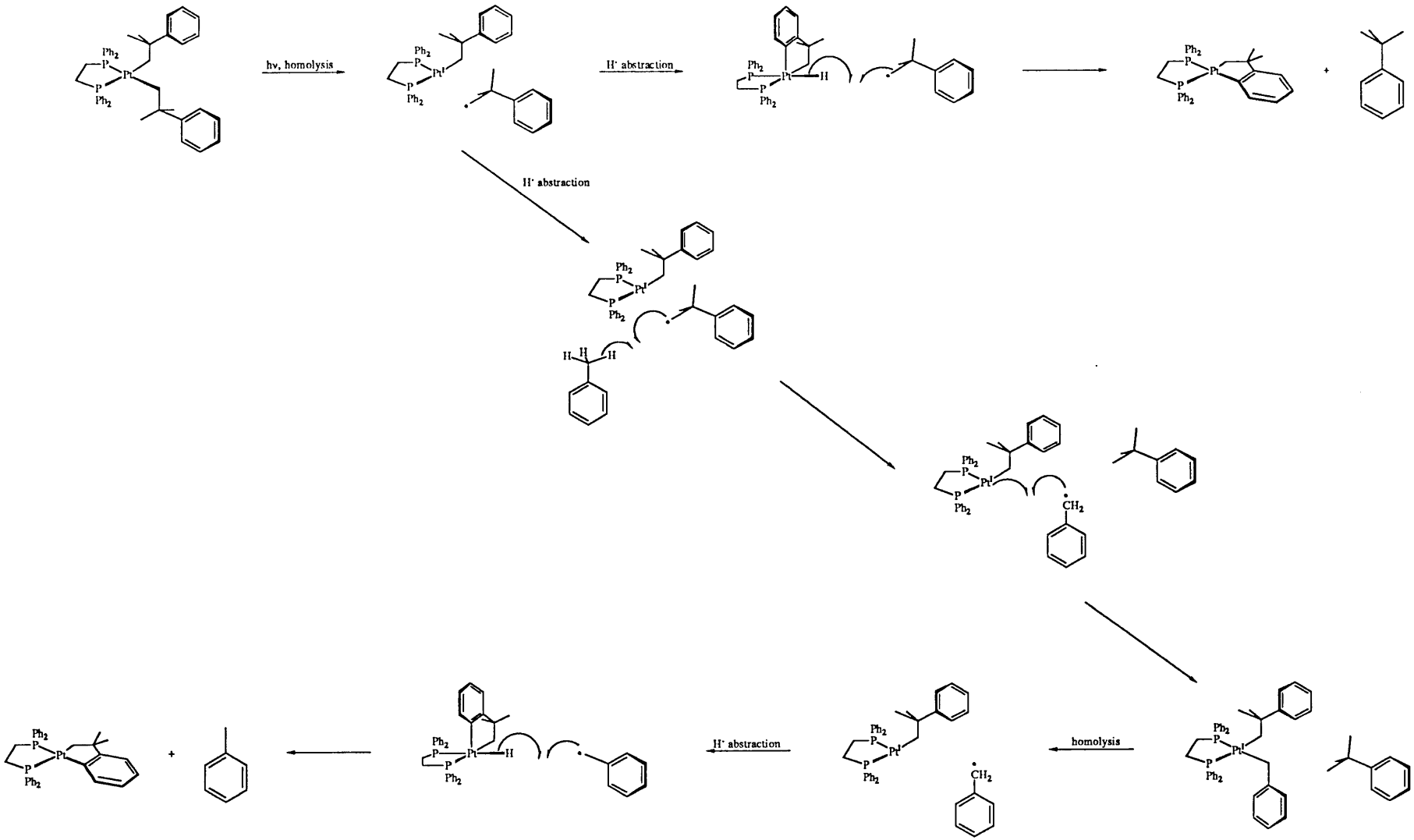
Among the P-donors, the chelating ligand, dppe, is found to have an isotope effect intermediate between that of bipy and Ph_2phen; indicating that neither Pt-P or C-H transfer is truly rate-limiting, but rather, both are excersising considerable effect on the overall rate. The observation of a small negative entropy of activation - suggesting overall loss of molecular freedom on approach to the most energetic transition state - leads to the proposition of oxidative addition of a neophyl C-H bond as the most energetic step in the reaction pathway.

Photolysis of (dppe)$Pt(CH_2CMe_2Ph)_2$ also produced the metallacycle, although this was not the only species observed. It emerges that photoinduced Pt-C bond homolysis occurs initially yielding (dppe)$Pt^{I}(CH_2CMe_2Ph)$ and a neophyl radical. This species rapidly abstracts an aliphatic hydrogen from toluene, generating a benzyl radical. Recombination of the platinum(I) species with this new radical results in the (observed) benzyl derivative, (dppe)$Pt(CH_2CMe_2Ph)(CH_2Ph)$. This complex is also photolabile, forming 3,3-dimethylplatinaindan as the major product (Scheme. 6.2).

The triphenylphosphine derivative was found to be so labile, that only the metallacycle was isolated. The parent dialkyl complex could only be observed as a transient intermediate in the presence of a large excess of triphenylphosphine. With triethylphosphine, mechanistic observations were very similar to those of the neopentyl analogue. Phosphine dissociation was found to be a prerequisite, although not the rate-limiting step. Reductive elimination of *tert*-butylbenzene was again deduced to be the most energetic step in the reaction pathway, based on a very large positive entropy of activation and a large isotope effect on the observed rate.



Scheme. 6.1 : *Proposed Mechanism for the Thermolytic Rearrangement of $L_2Pt(CH_2CMe_2Ph)_2$ with N-Donor Ligands.*



Scheme. 6.2 : *Proposed Scheme for the Photolysis of (dppe)Pt(CH_2CMe_2Ph)$_2$.*

In view of the thermolytic behavour of *bis*-(sila-neophyl) complexes, which do not undergo metallacyclisation in most cases (*vide supra*) it seemed appropriate to investigate systems in which one neophyl and one sila-neophyl group were attached simultaneously to platinum. It was recognised that derivatives of this type could, plausibly, undergo several types of rearrangement; either metallacyclisation by δ-H abstraction of the aromatic ring an either C or β-Si alkyl group - though the latter is judged unlikely - or competing β-aryl migration, analogous to that observed for *cis-bis*-(sila-neophyl)platinum(II). PPh_3 and PEt_3 were the ligands chosen for study, since direct comparisons with the reactivity of disila-neophyl and dineophyl as well as the related dineopentyl complexes could be made.

6.2. Results and Discussion.

6.2.1. Spectroscopic Characteristics of mixed (neophyl)(sila-neophyl) platinum(II) Complexes.

The numbering convention employed is shown in Fig. 6.1 and is similar to that employed for neophyl and platinaindan analogues. The phenyl carbon atoms of the aromatic ring of sila-neophyl are designated $C_{n'}$, as are ligand carbon atoms *trans* to sila-neophyl.

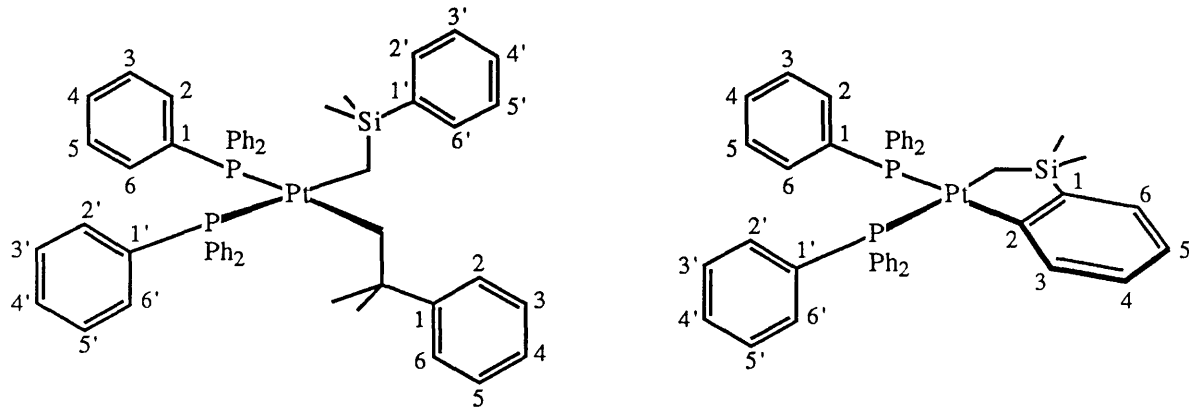


Fig. 6.1 : *N.M.R. Numbering Conventions for* $L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ *and* $L_2Pt\widehat{(CH_2CMe_2C_6H_4)}$.

^{1}H N.M.R. spectra of these mixed (neophyl)(sila-neophyl) complexes (Table 6.1) show several characteristic resonaces. The singlet close to 0.0 ppm is due to the silicon methyl groups, while the resonance *ca.* 1.30 ppm is attributable to neophyl methyl groups. Diagnostic of both co-ordinated neophyl and sila-neophyl skeletons is the low field doubled doublet, due to the *ortho*-phenyl hydrogens. Selective deuteration of the rings enable resonances due to each alkyl group to be assigned unequivocally (Fig. 6.2). Generally the doubled doublet of sila-neophyl occurs at lower field than the corresponding resonance of the neophyl group. The platinum bound methylene hydrogens generate 1:4:1 "triplets" with diene ligands; the value of $^2J_{Pt\text{-}H}$ is in the range 84.0-103.0 Hz, depending on the alkyl group. Similarly the usual apparent quartets with satellites are observed for the methylene protons in $(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$. The magnitude of these couplings is 70.4 and 84.0 Hz for neophyl and sila-neophyl respectively.

Table 6.1 : *^1H N.M.R. Characteristics of (neophyl)(sila-neophyl)platinum(II) and Related Complexes with Diene and Phosphorus Donor Ligands.*

Complex	δ ^1H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*] ($J_{H_2-H_3}$) / Hz			δ ^1H ppm : Ancillary ligands (J_{Pt-H}) / Hz [*Assignment*] (J_{P-H}) / Hz
	$Pt-CH_2$	$E-CH_3$	Aromatic	
$(nbd)Pt(CH_2CMe_2Ph)_2$[a]	2.09	1.30	7.07 m, [H_4]; 7.21 m, [H_3, H_5];	1.09 t, [H_B] ($J_{H_B-H_C}$=2.9 Hz);
	(**91.5**)	(**8.0**)	7.41 dd, [H_2, H_6] (**8.3**)	3.34 m, [H_C]; 4.20 t"t", (**39.4**) [H_A]
$(nbd)Pt(CH_2CMe_2Ph)Cl$[b]	2.04	1.33	7.13 m, [H_4]; 7.25 m, [H_3, H_5];	1.42-1.53 m, [H_B]; 3.64 m, [H_C];
	(**96.0**)		7.42 dd, [H_2, H_6] (**7.9**)	3.75 t"t", (**79.0**) [$H_{A'}$];
				5.46 t"t", (**30.1**) [H_A]
$(nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[a]	1.03	0.24	7.09 m, [H_4]; 7.22 m, [H_3, H_5];	1.16 m, [H_B]; 3.43 m, [H_C];
	(**102.2**)	[*Si-CH_3*]	7.27-7.35 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	4.04 t"t", (**42.0**) [$H_{A'}$];
	[*CH_2-Si*]	1.30	7.41 dd, [H_2, H_6] (**8.3**);	4.55 t"t", (**37.6**) [H_A]
	2.19	(**7.5**)	7.62 dd, [$H_{2'}$, $H_{6'}$] (**8.1**)	
	(**91.7**)	[*C-CH_3*]		
	[*CH_2-C*]			

Table 6.1 : (continued)

(cod)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)[a]	1.17	0.28	7.11 m, [H_4]; 7.18 m, [H_3, H_5];	1.39-1.47 m, [CH_2];
	(**101.7**)	[*Si-CH*$_3$]	7.24-7.31 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	3.88 t"t", (**45.8**) [*CH'*];
	[CH_2-*Si*]	1.33	7.45 dd, [H_2, H_6] (**7.8**);	4.55 t"t", (**38.1**) [*CH*]
	1.98	(**7.2**)	7.52 dd, [$H_{2'}$, $H_{6'}$] (**7.9**)	
	(**83.9**)	[*C-CH*$_3$]		
	[CH_2-*C*]			
(nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph-d^5)[a]	0.87	0.16	6.98 m, [H_4]; 7.10 m, [H_3, H_5];	1.08 s, [H_B]; 3.35 s, [H_C];
	(**101.9**)	[*Si-CH*$_3$]	7.28 dd, [H_2, H_6] (**8.0**)	3.93 t"t", (**43.2**) [$H_{A'}$];
	[CH_2-*Si*]	1.16		4.45 t"t", (**37.4**) [H_A]
	2.04	(**7.3**)		
	(**91.8**)	[*C-CH*$_3$]		
	[CH_2-*C*]			
(nbd)Pt(CH_2CMe_2Ph-d^5)$_2$[a]	2.10	1.31	-	1.15 m, [H_B]; 3.35 m, [H_C];
	(**91.2**)	(**8.0**)		4.22 t"t", (**38.5**) [H_A]
(nbd)Pt(CH_2CMe_2Ph-d^5)Cl[a]	2.02	1.16	-	1.21-1.36 m, [H_B]; 3.46 m, [H_C];
	(**94.2**)			3.58 "t", (**81.0**) [$H_{A'}$];
				5.28 t"t", (**30.7**) [H_A]
(nbd)Pt(CH_2CMe_2Ph-d^5)(CH_2SiMe_2Ph)[a]	1.11	0.39	7.35-7.41 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	1.39 m, [H_B]; 3.53 m, [H_C];
	(**102.3**)	[*Si-CH*$_3$]	7.70 dd, [$H_{2'}$,$H_{6'}$] (**7.2**)	4.13 t"t", (**43.2**) [$H_{A'}$];

Table 6.1 : (continued)

(nbd)Pt(CH_2CMe_2Ph-d^5)(CH_2SiMe_2Ph)[a]	[CH_2-Si]	1.39		4.64 t"t", (**37.5**) [H_A]
	2.27	[C-CH_3]		
	(**91.8**)			
	[CH_2-C]			
(PPh_3)$_2$Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)[b]	0.91[c]	0.44	7.07 m, [H_4]; 7.18 m, [H_3, H_5];	6.87 m, [H_3, H_4, H_5];
	[CH_2-Si]	[Si-CH_3]	7.18 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	6.91 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];
	2.42[c]	1.61[c]	7.31 dd, [H_2, H_6] (**9.1**);	7.36 m, [H_2, H_6]; 7.62 m, [$H_{2'}$, $H_{6'}$]
	(**68.2**)	[C-CH_3]	7.80 dd, [$H_{2'}$, $H_{6'}$] (**7.6**)	
	[CH_2-C]			
(PPh_3)$_2$Pt(CH_2CMe_2Ph-d^5)(CH_2SiMe_2Ph)[b]	0.86	0.43	7.28-7.33 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$];	6.88 m, [H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$];
	(**88.8**)	[Si-CH_3]	7.79 dd, [$H_{2'}$, $H_{6'}$] (**7.2**)	7.38 m, [H_2, H_6]; 7.65 m, [$H_{2'}$, $H_{6'}$]
	[CH_2-Si]	1.67[c]		
	2.41	[C-CH_3]		
	(**71.5**)			
	[CH_2-C]			
(PPh_3)$_2$Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph-d^5)[a]	0.77[c]	-0.03[c]	6.84 m, [H_4]; 7.17 m, [H_3, H_5];	6.91 m, [H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$];
	[CH_2-Si]	[Si-CH_3]	7.34 dd, [H_2, H_6] (**7.7**)	7.38 m, [H_2, H_6]; 7.65 m, [$H_{2'}$, $H_{6'}$]
	1.71	1.28		
	(**69.2**)	[C-CH_3]		
	[CH_2-C]			

Table 6.1 : (continued)

$(PPh_3\text{-}d^{15})_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[b]	0.87[c] [CH_2-Si] 2.38 **(69.6)** [CH_2-C]	0.41 [Si-CH_3] 1.63[c] [C-CH_3]	6.89 m, [H_4]; 7.13-7.31 m, [H_3, H_5] and [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.37 dd, [H_2, H_6] (**7.9**); 7.54 dd, [$H_{2'}$, $H_{6'}$] (**7.6**)	-
$(PPh_3)_2Pt(CH_2CMe_2C_6H_4)$[b]	2.40 **(64.2)**	1.74	6.67 m, [H_4]; [H_5][d]; 7.06 m, **(63.7)** [H_3]; 7.16 m, [H_6]	6.77-6.92 m, [H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$]; 7.57-7.67 m, [H_2, $H_{2'}$, H_6, $H_{6'}$]
$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[b]	1.04[c] **(84.0)** [CH_2-Si] 2.09 **(70.4)** [CH_2-C]	0.53 [Si-CH_3] 1.70 [C-CH_3]	7.08 m, [H_4]; 7.21-7.36 m, [H_3, H_5] and [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.61 dd, [H_2, H_6] (**8.0**); 7.83 dd, [$H_{2'}$, $H_{6'}$] (**7.5**)	0.77 m, **(15.0)** [P-CH_2CH_3] (***14.3***); 0.80 m, **(15.4)** [P-CH_2CH_3'] (***14.3***); 1.42 m, **(14.8)** [P-CH_2], [P-CH_2'] (***14.4***)
$(PEt_3)_2Pt(CH_2CMe_2Ph\text{-}d^5)(CH_2SiMe_2Ph)$[b]	1.09 **(83.6)** [CH_2-Si] 2.10 **(70.6)** [CH_2-C]	0.58 [Si-CH_3] 1.71 [C-CH_3]	7.18-7.39 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 7.85 dd, [$H_{2'}$, $H_{6'}$] (**7.8**)	0.79 m, **(15.5)** [P-CH_2CH_3'] (***14.4***); 0.81 m, **(15.3)** [P-CH_2-CH_3] (***14.3***); 1.44 m, **(14.9)** [P-CH_2], [P-CH_2'] (***15.0***)

Table 6.1 : (continued)

$(PEt_3)_2Pt(CH_2CMe_2C_6H_4)$[b]	2.03 (**57.6**)	1.62	6.92-7.11 m, [H_4, H_5, H_6]; 7.65 "t"d, (**54.7**) [H_3]	0.73-0.89 m, [$P\text{-}CH_2CH_3$]; 1.50 m, (**15.0**) [$P\text{-}CH_2'$] (***15.1***); 1.56 m, (**14.7**) [$P\text{-}CH_2$] (***15.0***)

a :- chloroform-d^1

b :- benzene-d^6

c :- broad resonance

d :- obscured

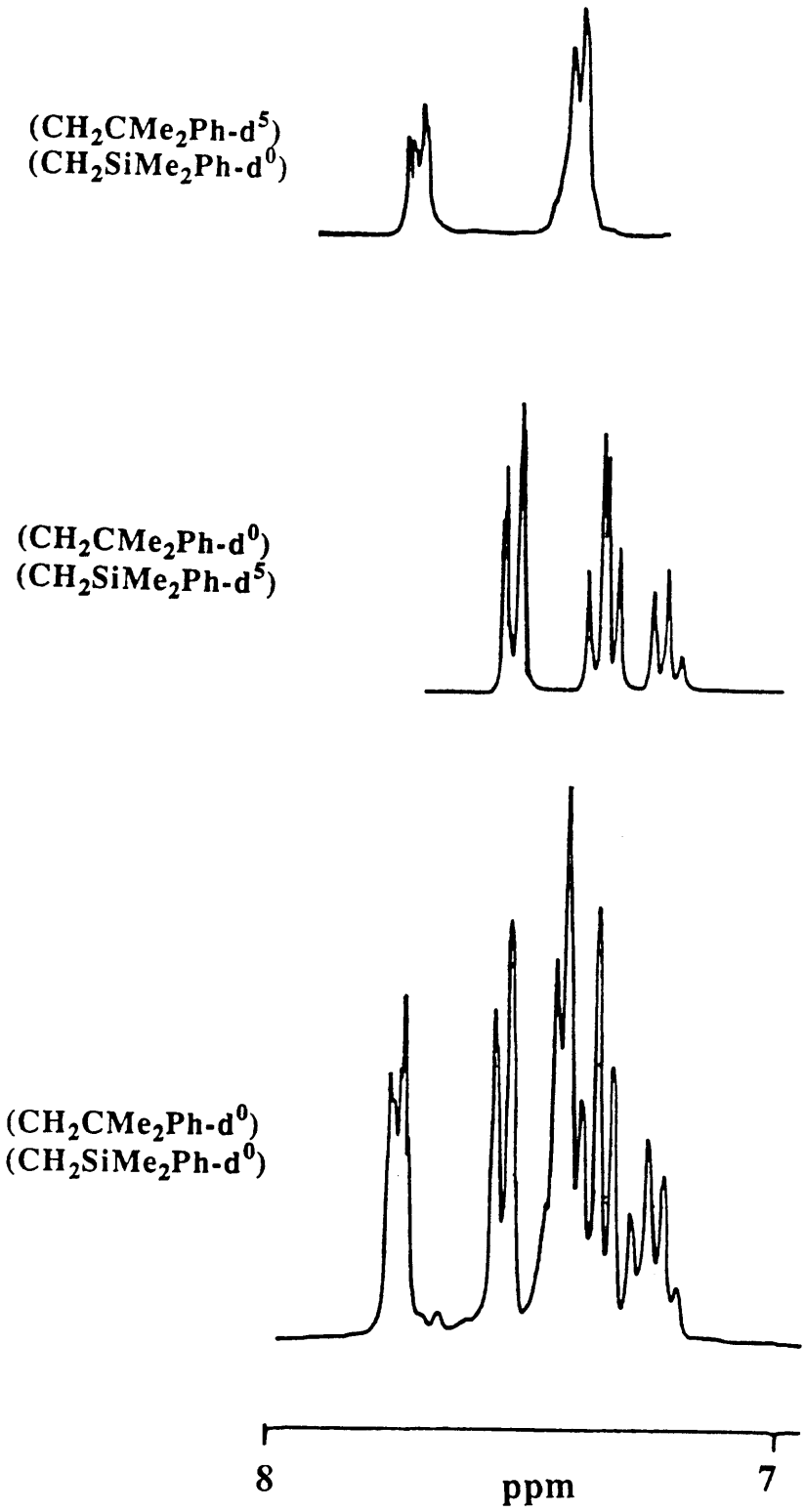


Fig. 6.2 : *^1H N.M.R. of the Aromatic Region of (nbd)PtRR'.*

Replacing triethylphosphine by triphenylphosphine results in broadened methylene signals, presumably because the coupling between the diastereotopic methylene protons and between the phosphourus nuclei remain unresolved. Moreover, the neophyl-methyl signal is considerably broadened - the resonance due to Si-CH_3 groups also displays broadening, possibly due to restricted rotation about the Pt-C bond in both neophyl and sila-neophyl groups. Variable temperature measurements were precluded at temperatures above 20°C, however, due to the rapid thermolytic rearrangement of this complex.

^{13}C N.M.R. characteristics (Table 6.2) of most of the complexes described in this section have been recorded and generally show resonances expected for a coordinated neophyl and sila-neophyl skeleton. $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ at -20°C, exhibits two distinct broadened resonances for the silicon-bound methyl groups and a further two broad signals for the neophyl methyl carbon atoms, again suggestive of restricted motion around the Pt-C bonds (Fig. 6.3).

Both $(PPh_3)_2PtRR'$ and $(PEt_3)_2PtRR'$ exhibit typical ^{31}P N.M.R. spectra observed for superimposed AB (66%) and ABM (34%) [A, B = ^{31}P; M = ^{195}Pt] systems (Table 6.3). The magnitude of $^1J_{Pt\text{-}P}$ *trans* to sila-neophyl is *ca.* 200 Hz larger than in the parent dialkyl. Corresponding $^1J_{Pt\text{-}P}$ *trans* to neophyl has a value *ca.* 200 Hz smaller than the dialkyl analogue. The origin of these effects has been discussed elsewhere (See 2.2.3).

6.2.2. Mechanistic Studies of Thermolytic Rearrangements of cis-bis-*(phosphine)(neophyl)(sila-neophyl)platinum(II).*

6.2.2.1. Kinetic Studies.

Benzene or toluene solutions of *cis*-$L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ [L = PEt_3, PPh_3] at >20°C undergo quantitative metallacyclisation *via* aromatic δ-C-H activation at an *ortho* site of the neophyl group, affording a platinaindan, $L_2Pt(CH_2CMe_2C_6H_4)$ and one equivalent of trimethylphenylsilane. The metallacycles have very characteristic ^{13}C N.M.R. spectra, which clearly show a platinum bound methylene group and phenyl carbon atoms. Most of the signals are coupled to ^{195}Pt as well as two different phosphorus nuclei (Fig. 6.4 and Table 6.2). Assignment of the methyl, methylene and methyne carbons is straightforward. C_1 and C_2 of the metallacycle are characterised by their low field shifts and reduced intensity; C_2 by its large coupling to platinum. The peak at *ca.* 140 ppm, assigned to C_3, at lower field than the remaining aromatic carbons by analogy with corresponding ^1H-chemical shifts. H_3 (attached to C_3) appears as a multiplet with platinum "satellites" (Table 6.1). The singlet at 123 ppm is ascribed to C_5 as it is the most distant from platinum.

Progress of the rearrangement was conveniently monitored by ^{31}P N.M.R., since resonances due to product and substrate were clearly separated. In fact, the ^{31}P resonances of the platinacycle generates a second order spectrum; an apparent singlet, with two sets of

Table 6.2 : *^{13}C N.M.R. Characteristics of (neophyl)(sila-neophyl)platinum(II) and Related Complexes with Diene and Phosphorus Donnor Ligands.*

Complex	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{P-C}) / Hz			δ ^{13}H ppm : Ancillary ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{P-C}) / Hz
	Pt-CH_2	E-CH_3	Aromatic	
(nbd)Pt(CH_2CMe_2Ph)$_2$[a,b]	42.98 (**928.2**)	34.39 (**67.3**) [*C-CH$_3$*] 42.00 (**23.2**) [*C-CH$_3$*]	125.22 [C_4]; 125.90 [C_3, C_5]; 127.62 [C_2, C_6]; 153.22 (**17.9**) [C_1]	48.79 (**36.3**) [C_B]; 74.16 (**46.6**) [C_C]; 91.23 (**41.6**) [C_A]
(nbd)Pt(CH_2CMe_2Ph)Cl[a,b]	40.15 (**769.3**)	32.18 (**45.9**) [*C-CH$_3$*] 41.68 (**16.7**) [*C-CH$_3$*]	125.43 [C_4]; 125.76 [C_3, C_5]; 127.93 [C_2, C_6]; 152.54 (**16.8**) [C_1]	48.48 (**51.4**) [C_B]; 70.28 (**101.5**)[C_C]; 70.28 (**212.5**) [$C_{A'}$]; 107.56 (**17.6**) [C_A]
(nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)[a,b]	17.77 (**785.9**) [*CH_2-Si*] 39.45	1.66 (**33.4**) [*Si-CH$_3$*] 34.31 (**65.7**) [*C-CH$_3$*]	124.88 [C_4]; 125.96 [C_3, C_5]; 127.40 [$C_{3'}$, $C_{5'}$]; 127.64 [C_2, C_6];	48.80 (**38.8**) [C_B]; 75.35 (**51.0**) [C_C]; 85.74 (**60.6**) [$C_{A'}$]; 90.94 (**38.0**) [C_A]

Table 6.2 : (continued)

(nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)[a,b]	(**889.1**) [CH_2-C]	41.68 (**25.1**) [C-CH_3]	128.02 [$C_{4'}$]; 133.60 [$C_{2'}$, $C_{6'}$]; 144.55 (**24.1**) [$C_{1'}$]; 153.22 (**19.9**) [C_1]	
(cod)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)[a]	12.93 (**745.5**) [CH_2-Si] 38.58 (**854.9**) [CH_2-C]	1.74 (**31.8**) [Si-CH_3] 33.98 (**58.9**) [C-CH_3] 42.44 (**13.2**) [C-CH_3]	124.78 [C_4]; 126.14 [C_3, C_5]; 127.36 [$C_{3'}$, $C_{5'}$]; 127.61 [C_2, C_6]; 127.73 [$C_{4'}$]; 133.87 [$C_{2'}$, $C_{6'}$]; 144.69 (**27.2**) [$C_{1'}$]; 154.16 (**20.0**) [C_1]	29.04 [CH_2']; 30.13 [CH]; 96.31 (**69.8**) [CH']; 101.64 (**42.4**) [CH]
(cod)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph-d^5)[a,c]	17.94 (**782.4**) [CH_2-Si] 39.26 (**885.2**) [CH_2-C]	1.59 (**33.9**) [Si-CH_3] 34.35 (**66.8**) [C-CH_3] 41.45 (**25.4**) [C-CH_3]	124.90 [C_4]; 125.90 [C_3, C_5]; 126.21 [$C_{3'}$, $C_{5'}$] ($J_{C\text{-}D}$=24.9 Hz); 127.24 [$C_{4'}$] ($J_{C\text{-}D}$=24.1 Hz); 127.63 [C_2, C_6]; 133.08 [$C_{2'}$, $C_{6'}$]	48.74 (**38.1**) [C_B]; 72.98 (**50.7**) [C_C]; 85.77 (**60.0**) [$C_{A'}$]; 90.86 (**38.1**) [C_A]

Table 6.2 : (continued)

(nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph-d^5)[a,c]			(J_{C-D}=23.6 Hz); 144.16 (**20.0**) [$C_{1'}$]; 152.90 (**17.9**) [C_1]	
(nbd)Pt(CH_2CMe_2Ph-d^5)(CH_2SiMe_2Ph)[a,c]	18.04 (**779.8**) [CH_2-Si] 39.05 (**880.2**) [CH_2-C]	1.49 (**33.4**) [Si-CH_3] 34.35 (**67.6**) [C-CH_3] 41.16 (**24.4**) [C-CH_3]	128.84 [C_4] (J_{C-D}=21.7 Hz); 125.69 [C_3, C_5] (J_{C-D}=21.7 Hz); 127.35 [$C_{3'}$, $C_{5'}$]; 127.59 [C_2, C_6] (J_{C-D}=22.8 Hz); 128.06 [$C_{4'}$]; 133.44 [$C_{2'}$, $C_{6'}$]; 144.27 (**25.5**) [$C_{1'}$]; 152.42 (**15.6**) [C_1]	48.66 (**38.3**) [C_B]; 73.39 (**49.4**) [C_C]; 85.81 (**60.5**) [$C_{A'}$]; 90.79 (**37.8**) [C_A]
$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[a,d]	5.98, 7.47 (**585.2**) ($J_{C-P_{Trans}}$=79.9 Hz) ($J_{C-P_{Cis}}$ = 5.3 Hz) [CH_2-Si] 35.80, 37.44	2.06[b], 3.67[b] [Si-CH_3] 31.74[b], 33.61[b] [C-CH_3] 42.52 [C-CH_3]	123.69 [H_4]; 125.59 [C_3, C_5]; 126.94 [$C_{4'}$]; 127.08 [$C_{3'}$, $C_{5'}$]; 128.96 [C_2, C_6]; 134.39 [$C_{2'}$, $C_{6'}$];	127.32 (**7.3**) [C_3, $C_{3'}$, C_5, $C_{5'}$] (***14.7***); 129.25 [C_4, $C_{4'}$]; 132.64 (**16.2**) [C_1] (***41.7***); 133.67 (**17.0**) [$C_{1'}$] (***39.6***); 134.67 (**21.3**) [C_2, $C_{2'}$, $C_6C_{6'}$] (***24.7***)

Table 6.2 : (continued)

$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[a,d]	(**702.1**) ($J_{C\text{-}P_{Trans}}$=100.0 Hz) ($J_{C\text{-}P_{Cis}}$ = 4.8 Hz) [CH_2-C]		146.23 (**19.6**) [C_1]; 155.19 (**46.4**) [$C_{1'}$] (***7.7***)	
$(PPh_3)_2Pt(\overline{CH_2CMe_2C_6H_4})$[a]	52.33, 53.66 (**616.8**) ($J_{C\text{-}P_{Trans}}$=83.7 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.6 Hz)	34.63 (**48.2**) [C-CH_3] (***4.7***) 50.20 (**34.8**) [C-CH_3]	121.54 (**61.0**) [C_6] (***2.9***); 122.65 [C_5]; 123.51 (**60.0**) [C_4] (***7.3***); 140.25 (**41.8**) [C_3] ($J_{C\text{-}P_{Trans}}$=8.2 Hz) ($J_{C\text{-}P_{Cis}}$ = 4.5 Hz); 160.32 (**951.4**) [C_2] ($J_{C\text{-}P_{Trans}}$=11.8 Hz) ($J_{C\text{-}P_{Cis}}$ = 8.6 Hz) 166.92 (**85.9**) [C_1] (***4.2***)	127.53 m, [C_3, $C_{3'}$, C_5, $C_{5'}$]; 129.16, 129.26 [C_4, $C_{4'}$]; 133.83 (**19.8**) [C_1, $C_{1'}$] (***46.4***); 134.28 (**18.6**) [C_2, C_6] (***11.4***); 135.00 (**18.8**) [$C_{2'}$, $C_{6'}$] (***10.6***);
$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[a]	5.21, 6.64 (**547.2**) ($J_{C\text{-}P_{Trans}}$=89.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.1 Hz)	35.14 (**47.1**) [Si-CH_3] 33.66 (**37.7**) [C-CH_3]	123.97 [C_4]; 125.81 [C_3, C_5]; 127.17 [$C_{3'}$, $C_{5'}$]; 127.37 [C_2, C_6], [C_4];	8.26 (**12.7**) [P-$CH_2C'H_3$]; 8.67 (**18.9**) [P-CH_2CH_3]; 16.01 (**19.3**) [P-CH_2CH_3]; 17.86 (**23.6**) [P-$C'H_2CH_3$]

Table 6.2 : (continued)

$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$[a]	[CH_2-Si] 33.03, 34.58 (**673.2**) ($J_{C\text{-}P_{Trans}}$=98.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.6 Hz) [CH_2-C]	42.62 [C-CH_3]	133.68 [$C_{2'}$, $C_{6'}$]; 147.00 (**25.9**) [$C_{1'}$] (***3.8***) 156.63 (**40.6**) [C_1] (***5.2***)	
$(PEt_3)_2Pt(CH_2CMe_2C_6H_4)$[a]	47.67, 49.06 (**609.0**) ($J_{C\text{-}P_{Trans}}$=87.1 Hz) ($J_{C\text{-}P_{Cis}}$ = 7.1 Hz)	35.14 (**47.1**) [C-CH_3] (***6.5***) 50.07 (**25.8**) [C-CH_3] (***7.7***[e], ***4.5***[f])	122.02 (**54.8**) [C_6] (***2.7***); 122.98 [C_5]; 123.87 (**60.8**) [C_4] (***9.7***); 137.15 (**51.6**) [C_3] ($J_{C\text{-}P_{Trans}}$=7.0 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.4 Hz) 162.96 (**917.2**) [C_2] ($J_{C\text{-}P_{Trans}}$=114.0 Hz) ($J_{C\text{-}P_{Cis}}$ = 9.1 Hz) 167.16 (**74.2**) [C_1] (***5.4***)	8.55 (**23.2**) [P-CH_2CH_3] (***13.5***); 17.33 (**18.7**) [P-CH_2CH_3] (***26.5***); 18.51 (**20.6**) [P-$C'H_2CH_3$] (***24.5***)

a :- chloroform-d^1 b :- run at 288K c :- run at 273K d :- run at 253K e :- $J_{C\text{-}P_{Trans}}$ f :- $J_{C\text{-}P_{Cis}}$

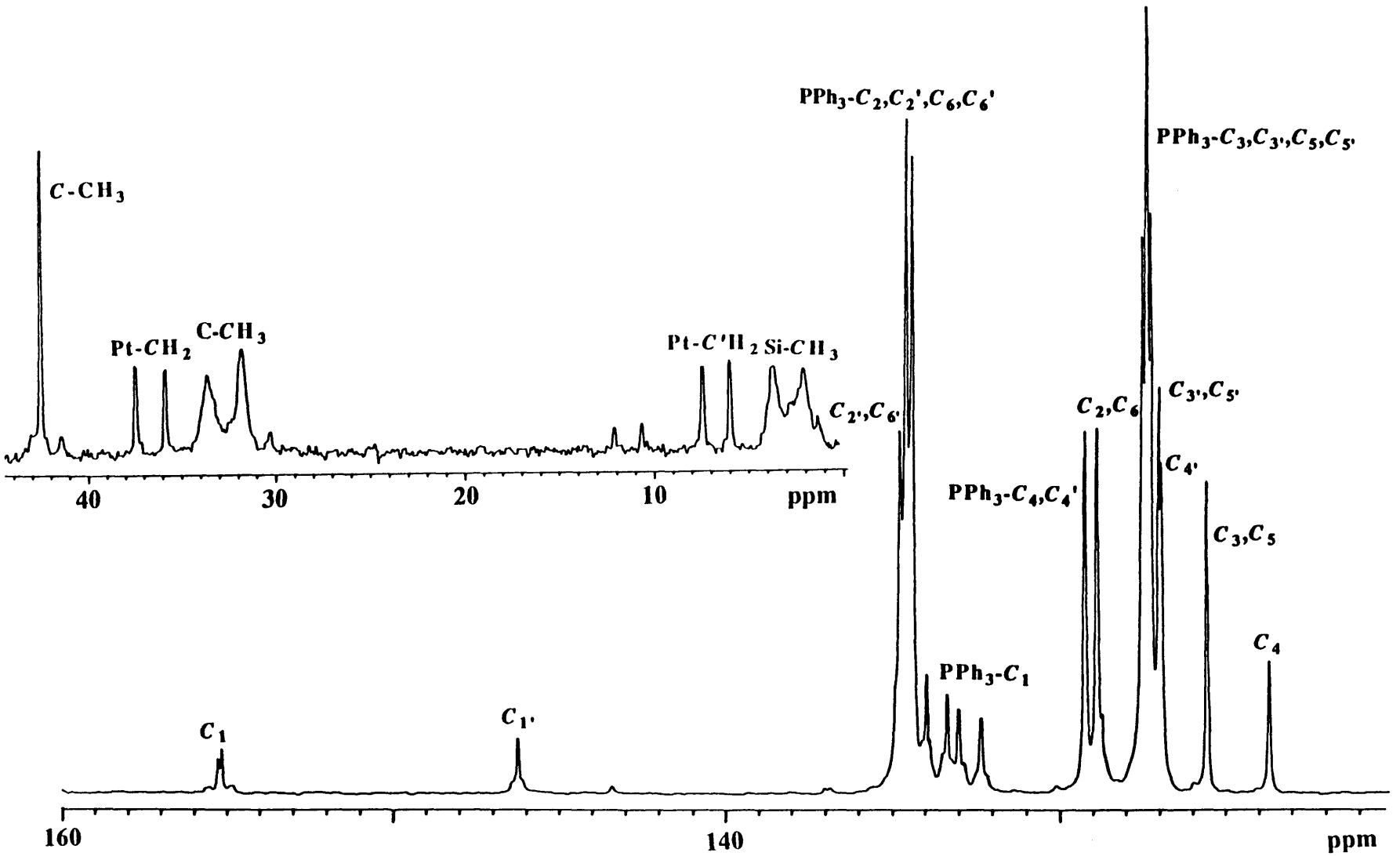


Fig. 6.3 : *^{13}C N.M.R. of $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.*

Table 6.3 : *^{31}P N.M.R. Characteristics of $L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ and $L_2Pt(\overbrace{CH_2CMe_2C_6H_4})$.*

Complex	δ^a / ppm	$J_{Pt\text{-}P}$ / Hz	$J_{P\text{-}P}$ / Hz
$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)^b$	22.02	2204.2	8.9
	25.59	1530.8	
$(PPh_3)_2Pt(CH_2CMe_2Ph\text{-}d^5)(CH_2SiMe_2Ph)^c$	22.05	2202.0	8.9
	25.53	1529.7	
$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph\text{-}d^5)^c$	22.05	2202.0	8.9
	25.53	1531.9	
$(PPh_3\text{-}d^{15})_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)^c$	21.59	2202.0	8.9
	25.04	1531.9	
$(PPh_3)_2Pt(\overbrace{CH_2CMe_2C_6H_4})^b$	29.32	1958.4	8.9
		1821.0	
$(PPh_3)_2Pt(\overbrace{CH_2CMe_2C_6D_4})^c$	29.16	1962.8	8.9
		1821.0	
$(PPh_3\text{-}d^{15})_2Pt(\overbrace{CH_2CMe_2C_6H_4})^c$	28.59	1960.6	8.9
		1822.1	
$(PEt_3)_2(CH_2CMe_2Ph)(CH_2SiMe_2Ph)^c$	0.33	2124.5	11.1
	2.01	1603.9	
$(PEt_3)_2(CH_2CMe_2Ph\text{-}d^5)(CH_2SiMe_2Ph)^c$	2.11	2127.8	11.1
	3.88	1605.0	
$(PEt_3)_2Pt(\overbrace{CH_2CMe_2C_6H_4})^d$	9.90	1896.3	13.3
	12.34	1816.6	
$(PEt_3)_2Pt(\overbrace{CH_2CMe_2C_6D_4})^c$	6.84	1869.7	13.3
	9.53	1834.3	
$(PEt_3)_2Pt(\text{-}2\text{-}CMe_3C_6H_4)(CH_2CMe_2Ph)^c$	-3.51	2086.8	11.1
	0.58	1739.0	

a :- referenced to 85% H_3PO_4 / D_2O

b :- toluene-d^8

c :- benzene-d^6

d :- chlorofom-d^1

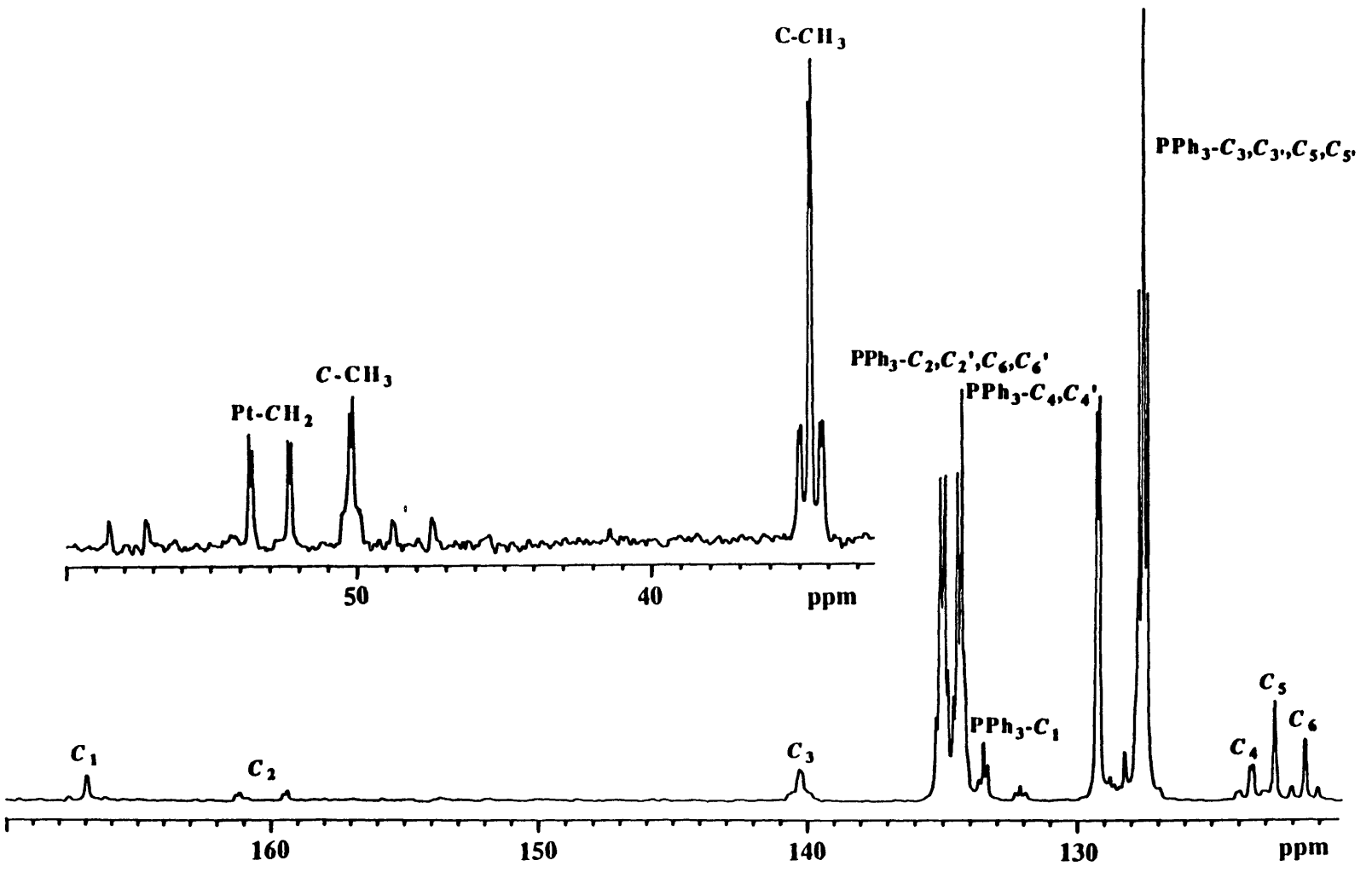


Fig. 6.4 : ^{13}C *N.M.R. of* $(PPh_3)_2Pt(\overbrace{CH_2SiMe_2C_6H_4})$.

^{195}Pt "satellites" is observed (Fig. 6.5). The appearance of the organic product could be quantified by ^{1}H N.M.R. (the signal due to the methyl groups occurs at 0.19 ppm) or by HPLC. Products arising from aromatic C-H transfer of the sila-alkyl group or from β-aryl migration were not detected under any of the conditions employed.

The kinetic data show the reaction to be first order with respect to platinum for at least two half-lives. These data appear in Table 6.4 and are represented graphically in Figs. 6.6 and 6.7. In the absence of added PPh_3, the reaction generally conformed to first order kinetics, although poor reproducibility and occasionally curved plots were observed. Similar inconsistencies have emerged from studies of *cis*-$(PEt_3)_2Pt(CH_2CMe_3)_2$ and *cis*-$(PEt_3)_2Pt(CH_2SiMe_2Ph)_2$ and were attributed to the presence of traces of oxygen[7b, 30b]. However, the poor reproducibility and curvature of the plots may be due to the reaction exhibiting half-order kinetics with respect to platinum (*vide infra*). The majority of kinetic experiments of $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ were thus carried out in the presence of PPh_3.

The temperature dependence of the observed first order rate constant, k_{obs}, conforms linearly to the Arrhenius relationship for the rearrangement of L_2PtRR' [L = PEt_3, PPh_3] in both the presence and absence of PPh_3 and is presented in Figs. 6.8 and 6.9.

The values of the Arrhenius activation energy, E^a, derived from these plots are 192 kJ mol^{-1} for $(PEt_3)_2PtRR'$ in the absence of PEt_3, 188 kJ mol^{-1} for $(PPh_3)_2PtRR'$ in the presence of 0.05M PPh_3 and 135 kJ mol^{-1} in the absence of PPh_3. Rearrangement of $(PEt_3)_2PtRR'$ and $(PPh_3)_2PtRR'$ in the presence of PPh_3 afford similar activation parameters (Table 6.5) suggesting that the two decompose by similar pathways. The difference in $\Delta S^{\ddagger}$ for $(PPh_3)_2PtRR'$ in the presence and absence of PPh_3 may possibly be attributable to half-order kinetic behaviour of the decomposition of the complex in the absence of phosphine. This type of behaviour has been observed in the thermal decomposition of *trans*-chloro(neopentyl)-*bis*-(tricyclopentylphosphine)platinum(II), where the reaction was deduced to be kinetically first order in the presence of tricyclopentylphosphine and half-order in its absence[119]. The difference between half-order and first-order behaviour is difficult to detect experimentally and the quality of the data in this case are insufficient to permit this distinction.

Upon deuteration of the aromatic sites on the neophyl ligand, cyclisation is markedly inhibited, both when L = PEt_3 and PPh_3 (Figs. 6.10 and 6.11). Analysis of the ^{1}H N.M.R. spectrum of thermolytic products from *cis*-$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ confirms the presence of $PhSiMe_2CH_2D$. The d^1-methyl group appears as a 1:1:1 triplet, slightly upfield of the signal due to the protiated groups. Use of triphenylphosphine-d^{15} resulted in a small but significant isotope effect; $k^H/k^D = 1.6$, whereas isotopic replacement of the phenyl hydrogens of sila-neophyl produced essentially no rate effect (Fig. 6.10).

The dependence of k_{obs} on the concentration of added phosphine, was determined

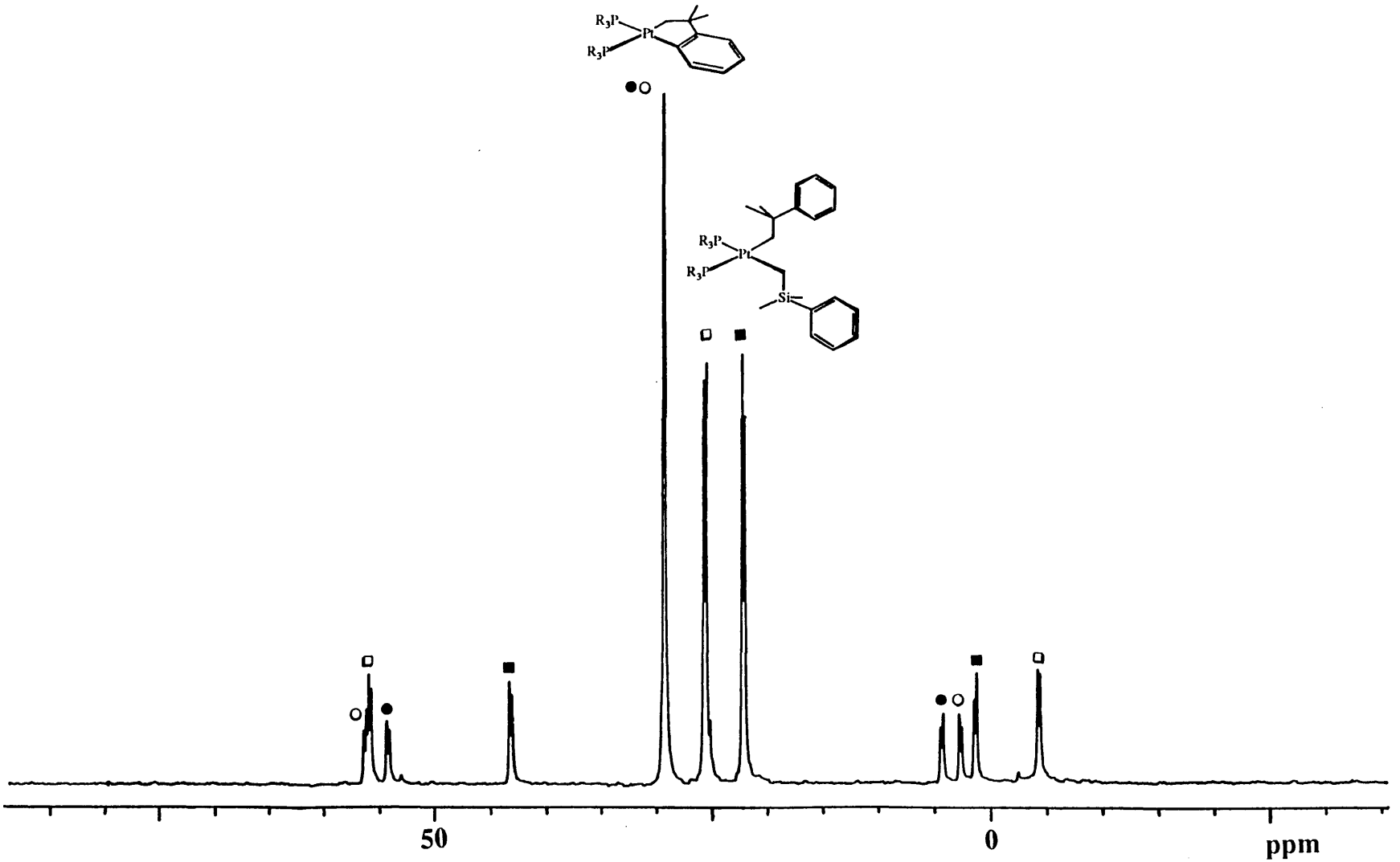


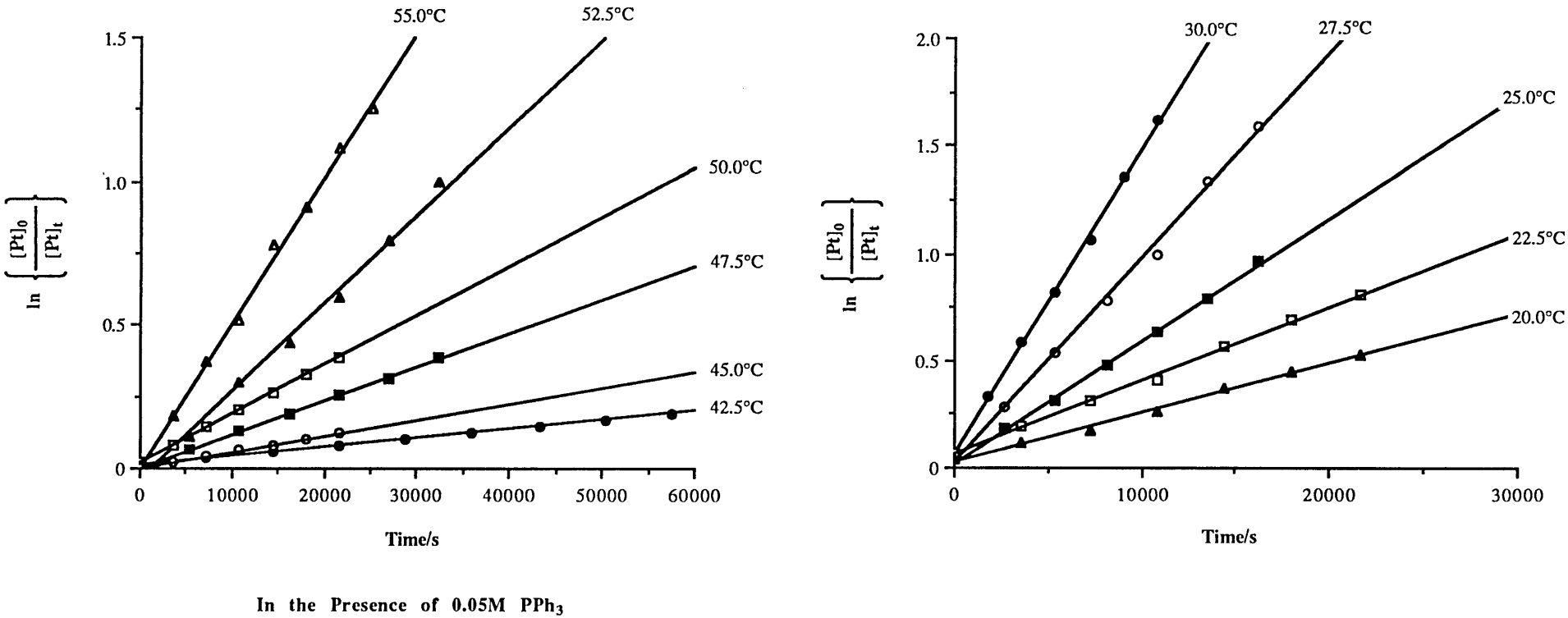
Fig. 6.5 : *^{31}P N.M.R. of a Typical Mixture of Products During Thermolysis of $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.*

Table 6.4 : *Variation of the Rate Constant with Temperature for the Metallacyclisation of* $L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

R	R'	L	[L] /M	T/°C	$10^5 \times k_{obs} / s^{-1}$
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0	20.0	2.30
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0	22.5	3.55
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0	25.0	5.73
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0	27.5	9.62
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0	30.0	14.50
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.05	42.5	0.32
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.05	45.0	0.56
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.05	47.5	1.12
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.05	50.0	1.71
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.05	52.5	3.17
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.05	55.0	4.77
$CH_2CMe_2Ph\text{-}d^5$	CH_2SiMe_2Ph	PPh_3	0.05	55.0	1.50
CH_2CMe_2Ph	$CH_2SiMe_2Ph\text{-}d^5$	PPh_3	0.05	55.0	4.39
CH_2CMe_2Ph	CH_2SiMe_2Ph	$PPh_3\text{-}d^{15}$	0.05	55.0	3.08
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.025	55.0	7.38
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.075	55.0	3.19

Table 6.4 : (continued)

CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.10	55.0	2.63
CH_2CMe_2Ph	CH_2SiMe_2Ph	PPh_3	0.15	55.0	1.89
CH_2CMe_2Ph	CH_2SiMe_2Ph	PEt_3	0	65.0	1.96
CH_2CMe_2Ph	CH_2SiMe_2Ph	PEt_3	0	67.5	3.09
CH_2CMe_2Ph	CH_2SiMe_2Ph	PEt_3	0	70.0	5.05
CH_2CMe_2Ph	CH_2SiMe_2Ph	PEt_3	0	72.5	8.56
CH_2CMe_2Ph	CH_2SiMe_2Ph	PEt_3	0	75.0	13.77
CH_2CMe_2Ph-d^5	CH_2SiMe_2Ph	PEt_3	0	75.0	3.94



In the Presence of 0.05M PPh_3

Fig. 6.6 : *Kinetic Data for the Thermolysis of $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ in Both the Presence and Absence of Phosphine.*

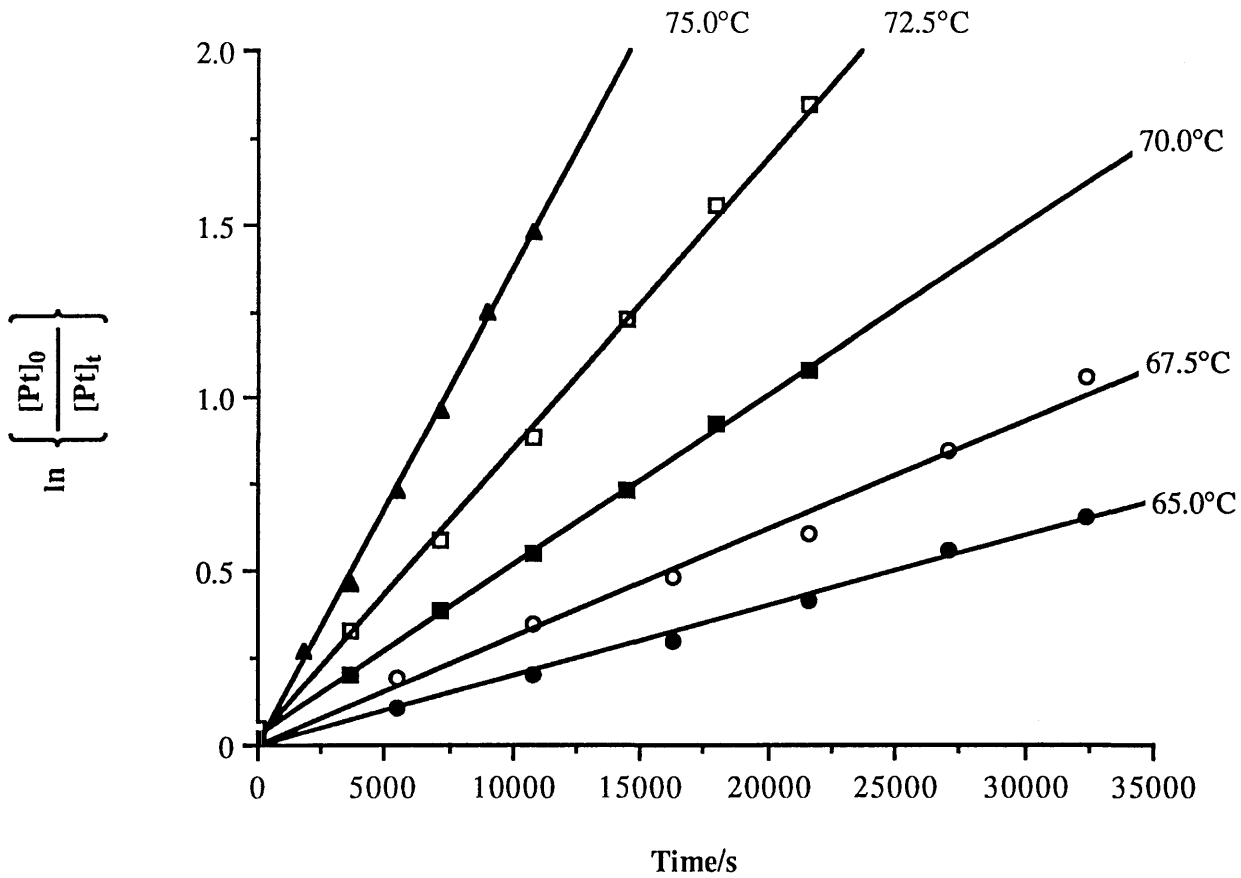
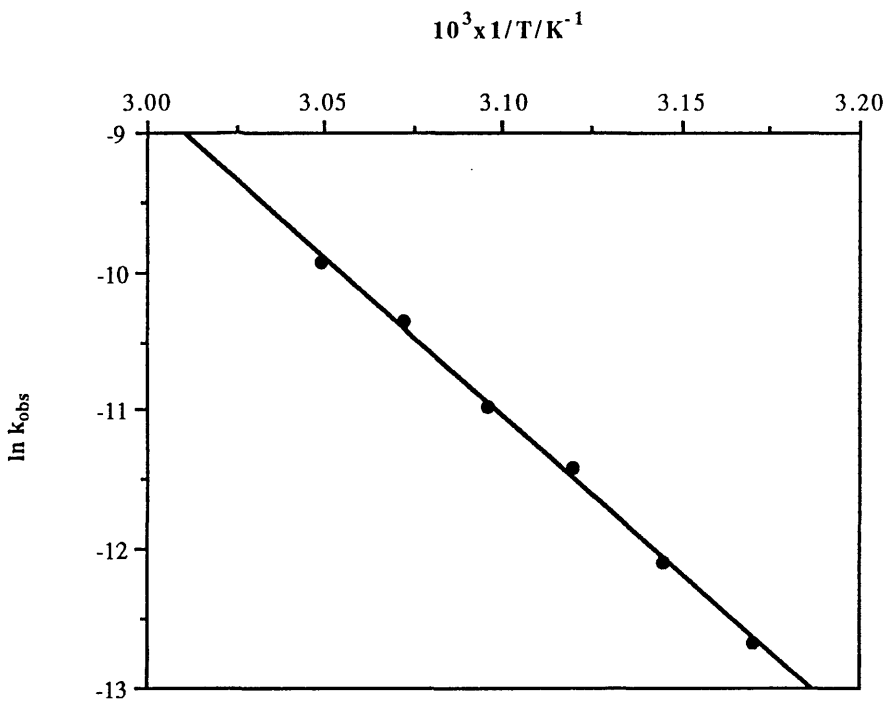
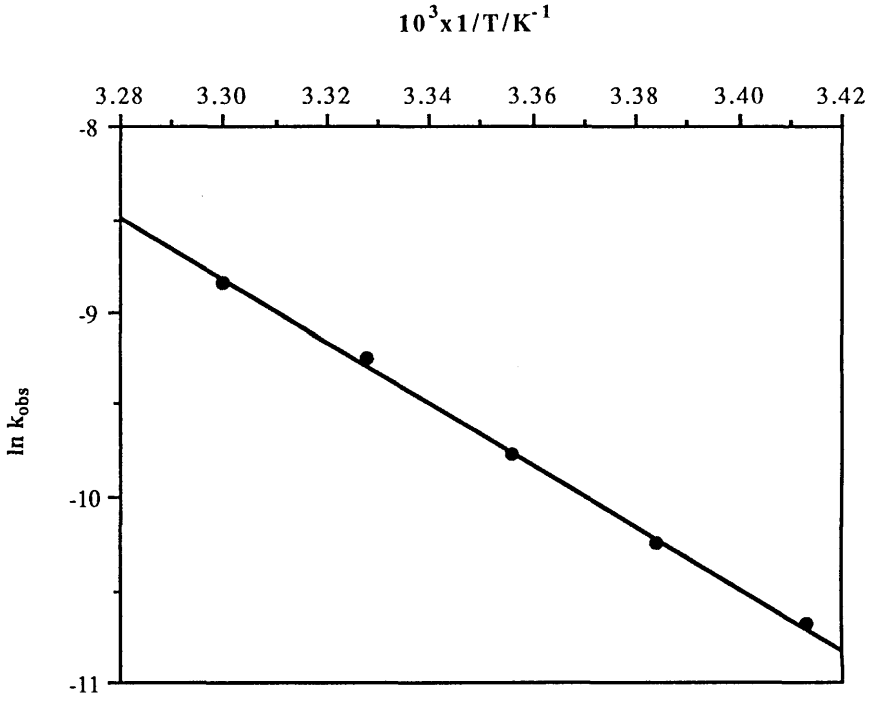


Fig. 6.7 : *Kinetic Data for the Thermolysis of* $(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

Table 6.5 : *Selected Activation Parameters for the Thermolytic Rearrangement of* cis-bis-$L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

Complex	[L] /M	E_a / kJ mol^{-1}	$\Delta H^{\ddagger}_{298}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$ / kJ mol^{-1}
$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$	-	137.9 (±5)	135.4 (±5)	128.5 (±16)	97.1 (±9)
$(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$	0.05	189.2 (±2)	186.7 (±2)	241.5 (±7)	114.7 (±4)
$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$	-	191.7 (±3)	189.2 (±3)	223.7 (±9)	122.5 (±6)





In the Presence of 0.05M PPh_3

Fig. 6.8 : *Arrhenius Plot for the Thermolysis of $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ in Both the Presence and Absence of Phosphine.*

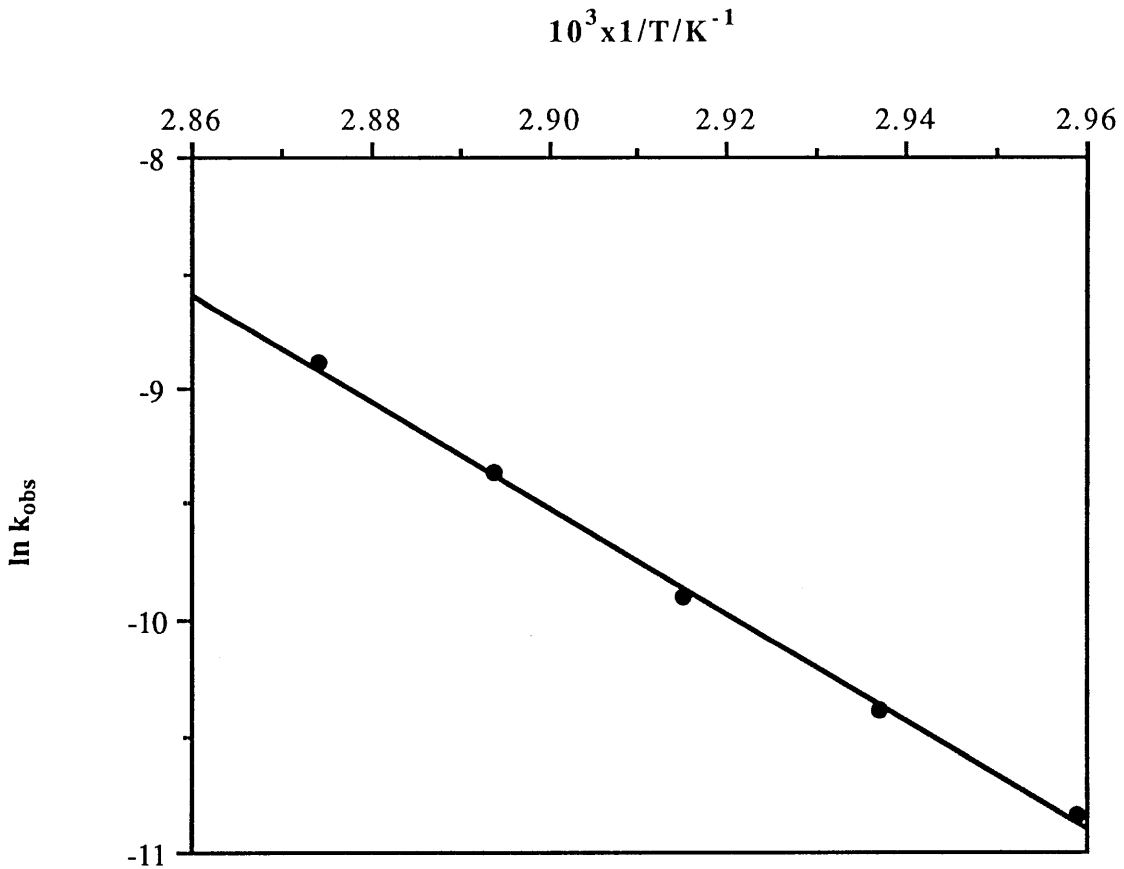


Fig. 6.9 : *Arrhenius Plot for the Thermolysis of* $(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

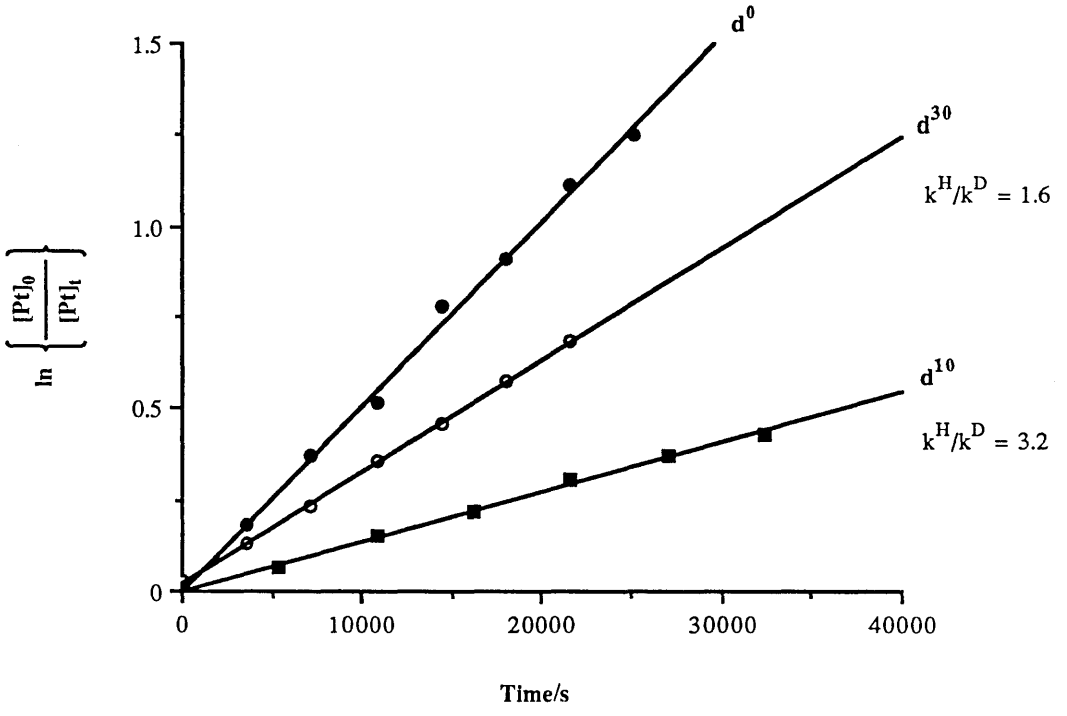


Fig. 6.10 : *Deuterium Isotope Studies for the Thermolysis of* $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

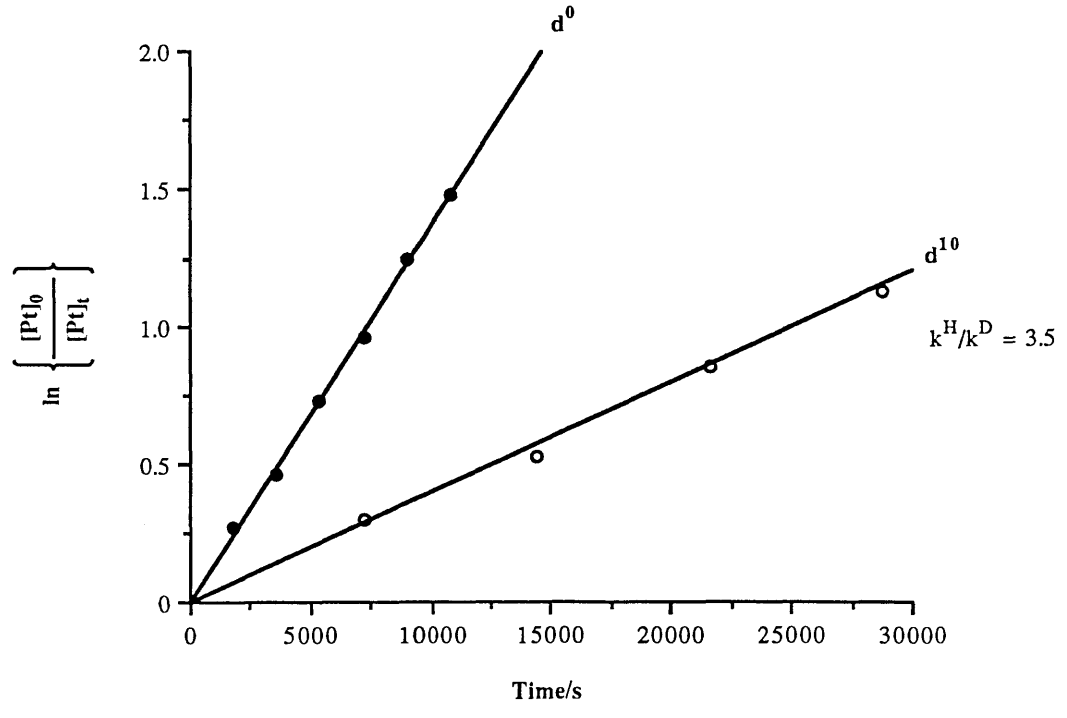


Fig. 6.11 : Deuterium Isotope Studies for the Thermolysis of $(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

for $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ by plotting the reciprocal of the rate constant ($1/k_{obs}$) against the phosphine concentration ($[PPh_3]$). A straight-line was obtained with a non-zero intercept (Fig. 6.12).

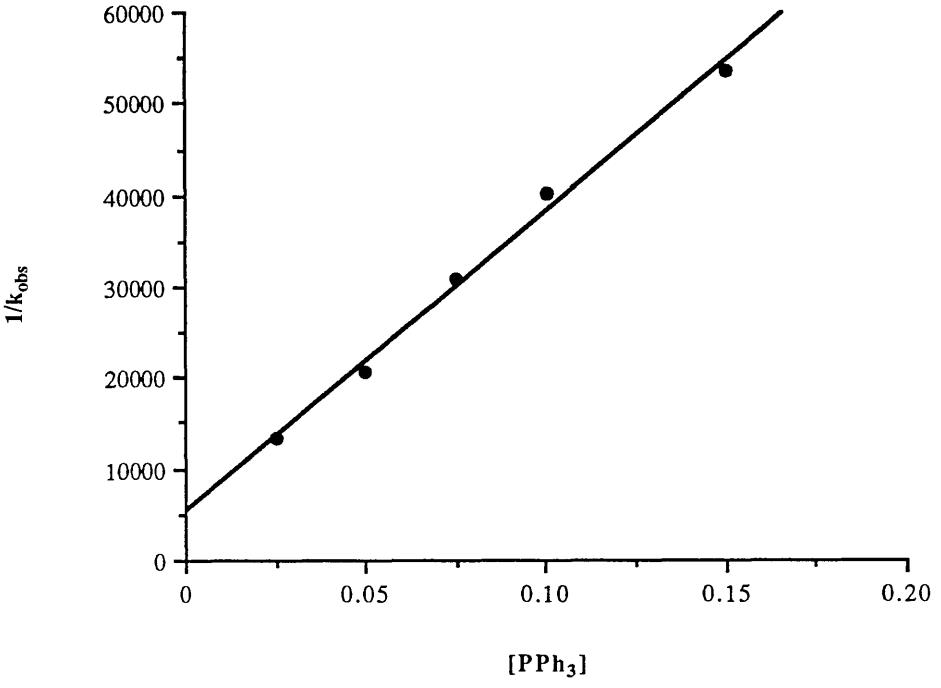


Fig. 6.12 : *Dependency of the Rate of Cyclisation of $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ on Phosphine Concentration.*

6.2.2.2. Mechanistic Implications.

The importance of steps in the reaction pathway involving C-H scission or formation can be deduced by replacement of the migrating hydrogen with deuterium. Primary isotope effects (under these conditions) arise from differences in total zero point energies between corresponding species - *ie.* reactants, intermediates and transition states - along heavy and light isotope paths, which can give rise to a significant difference in $\Delta G^{\ddagger}$ [99]. In a transition state where Pt-L is broken or formed, then the Pt-L vibration is the relaxation mode for the transition state and the zero point energy contains contributions from all C-H or C-D bonds. The energy difference is essentially the same as in the reactant and intermediate, hence activation energies for either direction are independent of the isotope ($k^H/k^D = 1$).

If though, a C-H bond is broken or formed, a C-H vibration becomes the relaxation mode for the transition state and does not contribute to the zero point energy.

The magnitude of the energy required to reach this transition state will be smaller for a C-H compared to a C-D bond and thus C-D transfer becomes relatively less favoured (Fig. 6.13).

The observations here are consistent with the loss of a phosphine prior to the most energetic step of the reaction pathway; such a step is likely to be reversible. Assuming that this precedes H-transfer a simple scheme can be envisaged :-

$$L_2PtRR' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LPtRR' \xrightarrow[\text{H-transfer}]{k_2} \text{Products}$$

Assuming steady state concentration of tricoordinate intermediate, then a first order rate law is predicted where :-

$$k_{obs} = \frac{k_1 k_2}{(k_2 + k_{-1})}$$

Hence the isotope effect on k_{obs} is :-

$$\frac{k^H_{obs}}{k^D_{obs}} = \frac{k^H_1 k^H_2 (k^D_2 + k^D_{-1})}{k^D_1 k^D_2 (k^H_2 + k^H_{-1})}$$

Since k_1 and k_{-1} do not involve C-H(D) scission or formation, the isotope effects on these steps will differ little from zero, *ie.*

$$\frac{k^H_1}{k^D_1} = \frac{k^H_{-1}}{k^D_{-1}} = 1$$

This simplifies the above expression to :-

$$\frac{k^H_{obs}}{k^D_{obs}} = \frac{k^H_2}{k^D_2}\left[\frac{1 + k^D_2/k^D_{-1}}{1 + k^H_2/k^H_{-1}}\right]$$

The observed isotope efect will depend not only on the ratio of k^H_2 and k^D_2 (H-transfer step) but also on the relative magnitudes of the rate of H-transfer and recoordination of ligand *ie.* k_2 and k_{-1}. The total zero point energy differences for light and heavy transition states are shown in Fig. 6.13.

There are two limiting extremes :-

(i) When $k_{-1} >> k_2$ (6.13 a), then

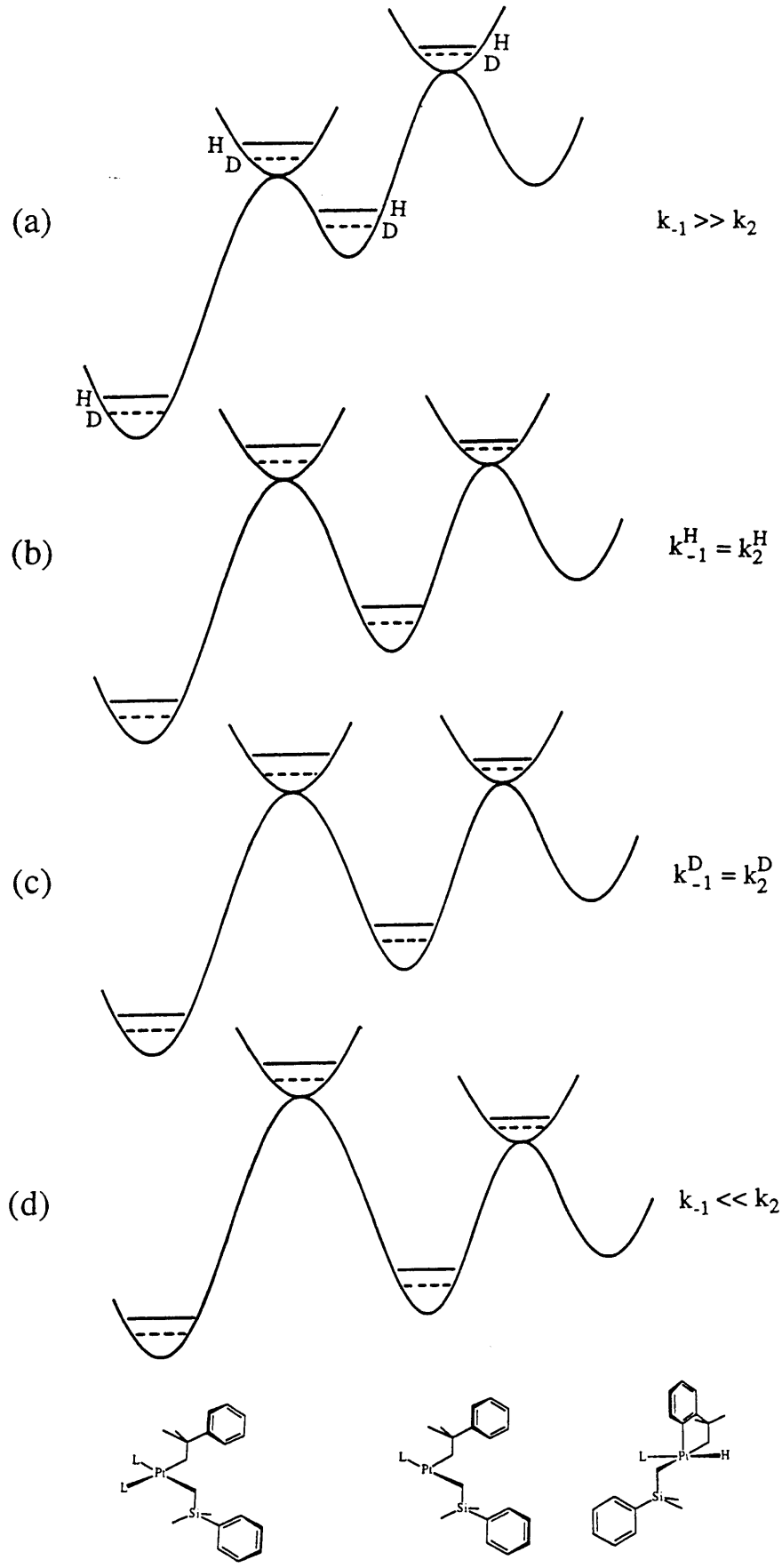


Fig. 6.13 : *Isotopic Transition States.*

$$\frac{k^H_{obs}}{k^D_{obs}} = \frac{k^H_2}{k^D_2}$$

Even with preliminary Pt-P scission, a full isotope effect is expected.

(ii) If $k_{-1} << k_2$ (6.13 d), it follows that

$$\frac{k^H_{obs}}{k^D_{obs}} = \frac{k^H_1}{k^D_1} = 1$$

and a zero isotope effect emerges. In this case Pt-P scission would be rate-limiting. Between these extremes, the isotope effect actually observed will be in the range

$$\frac{k^H_2}{k^D_2} \geq \frac{k^H_{obs}}{k^D_{obs}} \geq 1$$

Intermediate, although unlikely cases are depicted in :-

(iii) $k^H_2 = k^H_{-1}$ ($k^D_2 = k^D_{-1}$) (6.13 b) where the rate ratio becomes :-

$$\frac{k^H_{obs}}{k^D_{obs}} = \frac{k^H_2}{k^D_2}\left[\frac{1 + k^D_2/k^D_{-1}}{2}\right] = \frac{1}{2}\left[\frac{k^H_2}{k^D_2} + 1\right]$$

Assuming $k^H_2/k^D_2 = 3.0$, based on previous observations, the corresponding lower limit for the primary isotope effect k^H_{obs}/k^D_{obs} is 2.0. This hypothetical case represents the condition at which H-migration ceases to be "rate-limiting"; the transition state is no longer the most energetic along the reaction coordinate.

(iv) Similarly if $k^D_2 = k^D_{-1}$ ($k^D_2 = k^H_{-1}$) (6.13 c), then the lower limit becomes 1.5.

Rearrangement of the phosphine complexes with their significant primary isotope effect, clearly resemble (i) most closely. The most energetic transition state involves hydrogen transfer. The fact that a zero isotope effect is observed by deuterating the sila-neophyl phenyl ring, further indicates that this group does not transfer hydrogen to form a platinacycle.

The isotope effect of 1.6 observed on deuterating the phosphine might be due to the development of an agostic interaction between one of its ring C-H bonds and the metal as the other ligand dissociates. Even though attainment of this transition state involves a considerable amount of energy, it is not the most energetic along the reaction pathway. The energy profile for this reaction is illustrated in Fig. 6.14. A smaller isotope effect of 1.2 has been observed for ligand substitution of the complex $W(CO)_3(PCy_3)_2L$, which was attributed to the presence of a W····H-C "agostic" interaction[105].

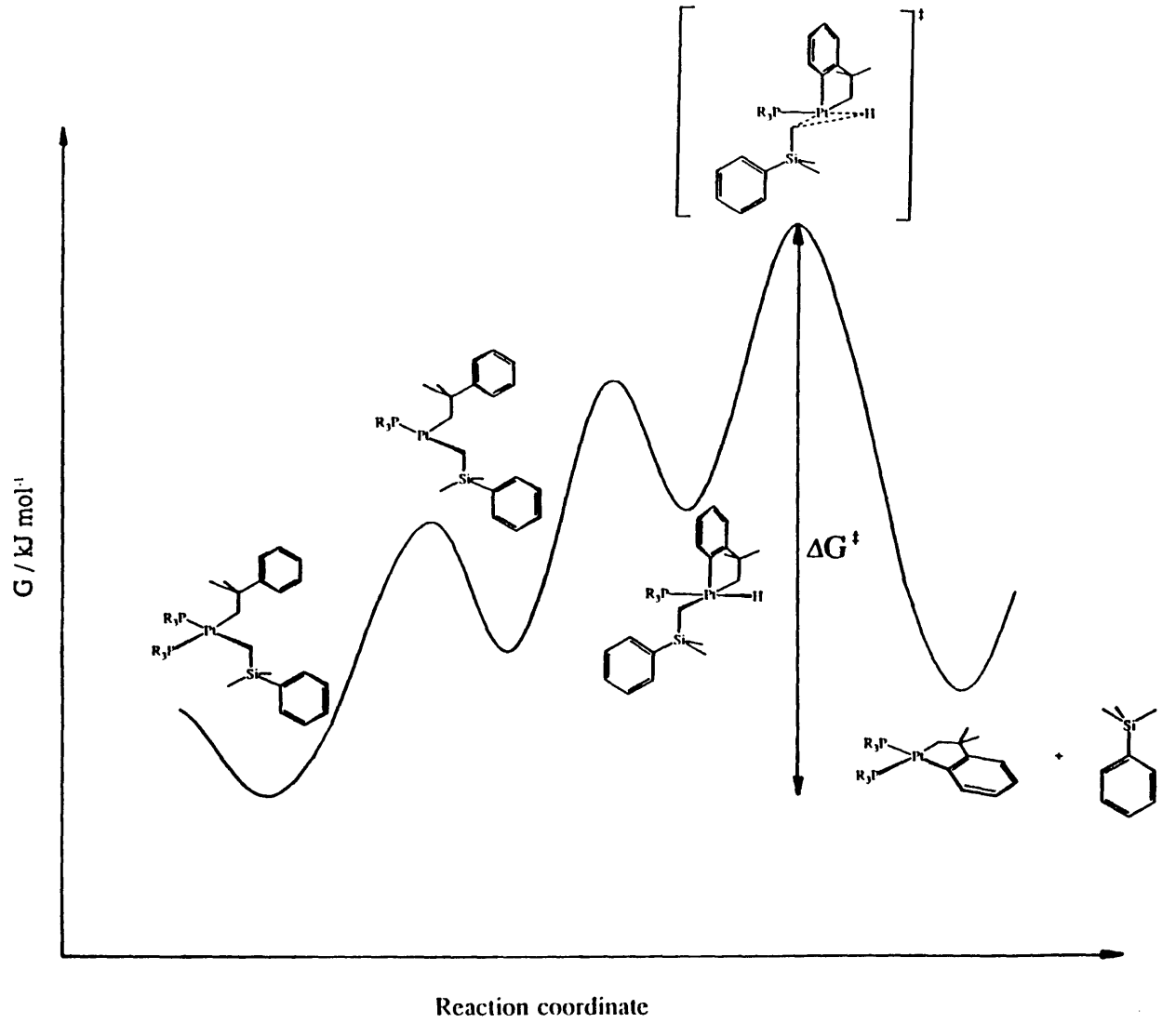
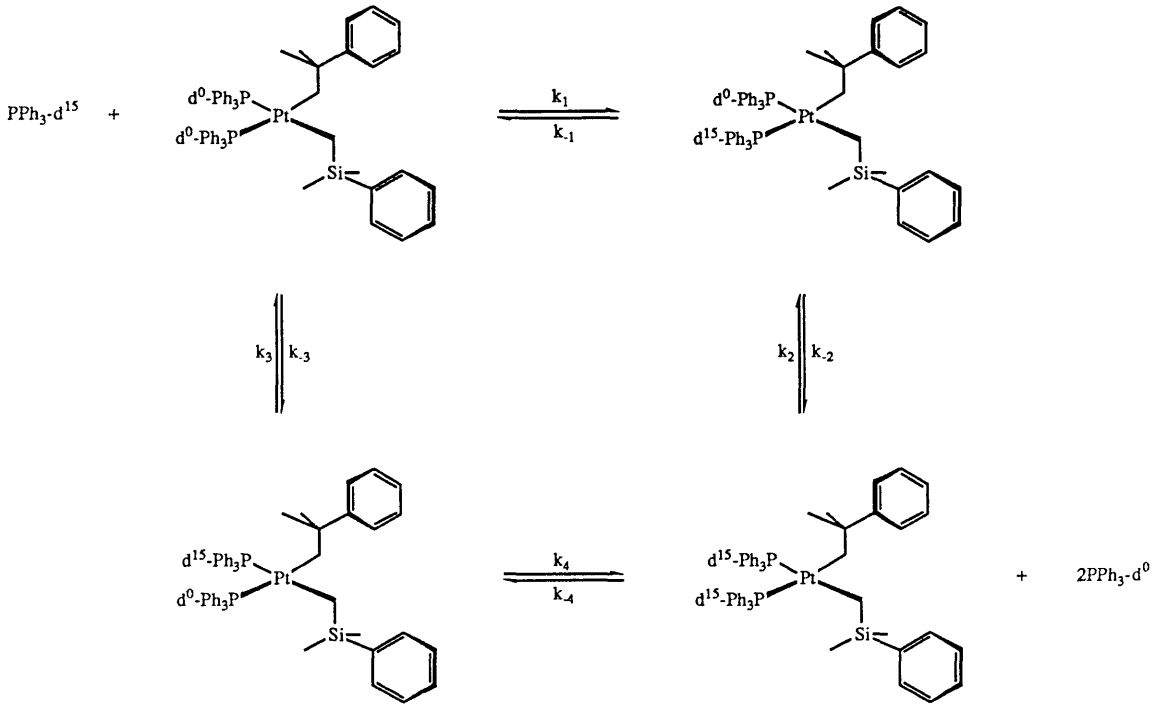


Fig 6.14 : *Reaction Profile for δ-Aromatic C-H Transfer.*

The inhibiting effect of added phosphine on the rate of rearrangement could be rationalised on the basis of either dissociative or associative equilibria involving L_2PtRR'. Association of phosphine could afford a species L_3PtRR', which is inert compared to L_2PtRR'. Alternatively, ligand dissociation forming $LPtRR'$, which would be retarded by excess L, may be a prerequisite to C-H activation. The exchange of triphenylphosphine by its fully deuterated analogue in $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ was examined in an attempt to quantify more accurately the rate of dissociation of phosphine (k_1).
A simple scheme (Scheme. 6.3) for ligand transfer can be envisaged :-



Scheme. 6.3 : *Phosphine Substitution in $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.*

The equilibrium constant for each step is given by :-

$$K_n = \frac{k_n}{k_{-n}}$$

Hence, the overall equilibrium constant can be defined as :-

$$K_{eq} = \frac{K_1K_2}{K_3K_4}$$

Consequently in the presence of two equivalents of PPh_3-d^{15}, a statistical distribution,

comprising of a 1:1:1:1 mixture of the four $(PR_3)_2Pt(CH_2SiMe_2Ph)_2$ isotopomers and a 1:1 ratio of dueterated and undeuterated phosphine would be expected. If, however, x is the isotope effect on replacement of L *cis* to PPh_3-d^0 *versus* PPh_3-d^{15} where $[k^H/k^D > 1]$ then :-

$$x = \frac{k_1}{k_4} = \frac{k_{-1}}{k_{-4}} = \frac{k_2}{k_3} = \frac{k_{-2}}{k_{-3}}$$

and represents the thermodynamic isotope effect on phosphine substitution. Thus, a deviation from unity for the value of the equilibrium constant allows an estimate of this isotope effect to be determined.

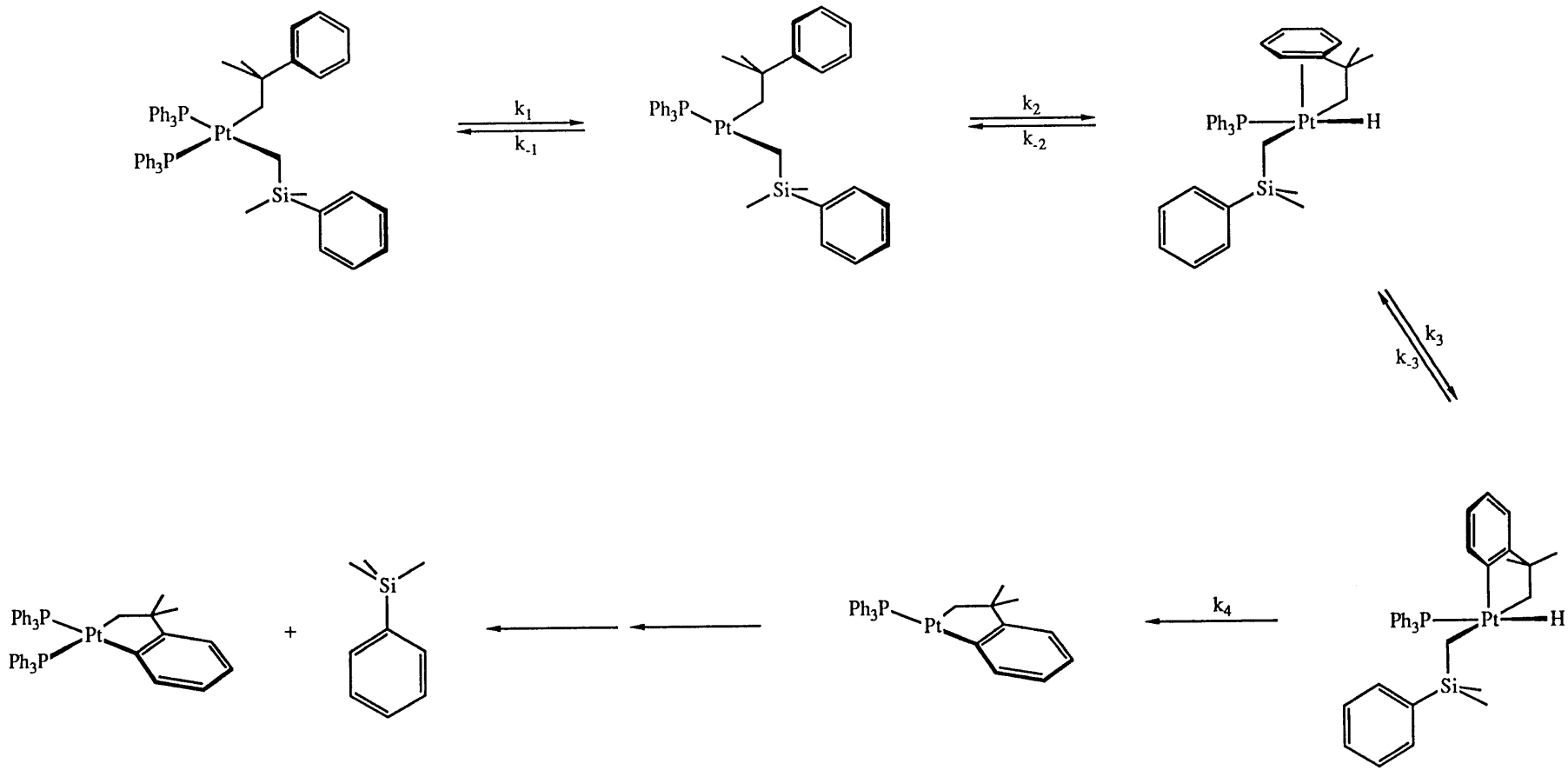
Although $(PPh_3\text{-}d^{15})_2PtRR'$ showed distinct resonances from $(PPh_3)_2PtRR'$, the signals due to the two mixed triphenylphosphine complexes, $(PPh_3)(PPh_3\text{-}d^{15})PtRR'$, were partially obscured by the signals of the parent complex. In addition because of the short pulse delay, spin-saturation of the free phosphine signal resulted in considerable imprecision in determining the concentrations of PPh_3-d^0 and PPh_3-d^{15} and hence the equilibrium constant could not be measured with certainty. Similarly, determination of the rate of dissociation of phosphine was precluded, since equilibrium was achieved within two hours even at 10°C in benzene-d^6; too quick for accurate measurement by N.M.R.

Previous studies of phosphine exchange in $(PEt_3)_2Pt(CH_2CMe_3)_2$ indicated that the interchange of phosphines occurs by a stoichiometrically dissociative or D-mechanism, based on the empirical rate law for the reaction, which was found to be independent of phosphine concentration within experimental error. Rate-limiting dissociation of phosphine from $(PEt_3)_2Pt(CH_2CMe_3)_2$ is followed by recombination of a new phosphine with the resulting $(PEt_3)Pt(CH_2CMe_3)_2$ intermediate.

Even though the rate of phosphine exchange could not be determined for $(PPh_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$, the observation that initial dissociation of a phosphine occurred selectively *trans* to the neophyl group, suggests that neophyl exerts a stronger *trans*-labilising effect than does sila-neophyl, in parallel with its apparently stronger *trans*-influence (See 2.2.3).

A mechanistic scheme consistent with the observations noted and based on equilibrium dissociation of L appears in Scheme. 6.4. A first order rate law is predicted, assuming that steady state concentrations develop for all the intermediates and is of the form :-

$$\frac{-d[L_2PtRR']}{dt} = \left\{ \frac{k_1k_2k_3k_4}{k_{-1}[k_4(k_{-2}+k_3)+k_{-2}k_{-3}][L] + k_2k_3k_4} \right\} [L_2PtRR']$$



Scheme. 6.4 : *Proposed Mechanism for the Thermolytic Cyclisation of* $L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

with an observed rate constant, k_{obs},

$$k_{obs} = \frac{k_1k_2k_3k_4}{k_{-1}[k_4(k_{-2}+k_3)+k_{-2}k_{-3}][L] + k_2k_3k_4}$$

Hence at constant concentrations of phosphine the rate equation can be written as :-

$$\frac{-d[L_2PtRR']}{dt} = k_{obs}\,[L_2PtRR']$$

At constant temperature k_{obs} is inversely proportional to the phosphine concentration :-

$$\frac{1}{k_{obs}} = \left\{\frac{k_{-1}[k_4(k_{-2}+k_3)+k_{-2}k_{-3}]}{k_1k_2k_3k_4}\right\}[L] + \frac{1}{k_1}$$

A plot of $1/k_{obs}$ against phosphine concentration should generate a straight line, with the intercept yielding a value of the phosphine dissociation constant k_1. The experimental uncertainty in determining the intercept allows an estimate of k_1 within broad limits: $10^{-2}\ s^{-1} > k_1 \geq 10^{-4}\ s^{-1}$. Nevertheless, the presence of phosphine, is further proof that phosphine dissociation is not rate-limiting, since k_1 is more than an order of magnitude greater than any rate observed under these conditions (Table 6.4). This contention is supported by the inability to determine k_1 for phosphine interchange, even at sub-ambient temperature; also by the considerable deuterium isotope effect ($k^H/k^D > 3.0$), which would not be expected if preliminary ligand loss was rate-determining (*vide supra*).

The large positive entropy of activation observed for cyclisation of L_2PtRR' is comparable to that for the dineophyl analogues and may be attributed to a product-like transition state. It may be best explained if reductive elimination of phenyltrimethylsilane from the hydridoplatinum(IV) intermediate (k_4) makes a high contribution to k_{obs}. Similar gains of molecular freedom (on approach to a dissociative transition state) have been correlated with the formation of two translationally independent particles from one[120].

The (neophyl)(sila-neophyl) derivatives are considerably more labile than their *bis*-(sila-neophyl) and dineopentyl analogues but less labile than their dineophyl counterparts. Thus *cis*-$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ cyclises in the absence of PEt_3 with $k_{obs} = 2.0\times10^{-5}\ s^{-1}$ at 65°C, while *cis*-$(PEt_3)_2Pt(CH_2CMe_3)_2$ reacts at a comparable rate, $k_{obs} = 1.5\times10^{-5}\ s^{-1}$ at 118°C and *cis*-$(PEt_3)_2Pt(CH_2CMe_2Ph)_2$ has a value of $k_{obs} = 1.8\times10^{-5}\ s^{-1}$ at 25°C. Clearly, given the choice, δ-aromatic C-H activation on a hydrocarbyl group is favoured in preference to β-phenyl migration from silicon to platinum.

Activation of aromatic C-H bonds is often more facile than the corresponding aliphatic reaction[22, 23]. This may be due to the accessibility of an η^2-arene intermediate prior to C-H transfer, which gives aromatic sites an activation enthalpy advantage over aliphatic competitors. Spectroscopic evidence for the formation of an intramolecular η^2-arene cationic complex by treating (dppe)Pt(CH_2CMe_2Ph)I with $AgBF_4$ in $CDCl_3$ has been observed[49]. Though, an η^2-arene complex may occur, it was not observed during cyclisation of $L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$.

The reason for the difference in δ-aromatic C-H activation in these complexes compared to γ-aliphatic C-H transfer in $L_2Pt(CH_2CMe_3)_2$ appears to be entropic in origin. The neophyl group may be sufficiently bulky that the relaxation of steric congestion assiociated with both k_1 and k_4 is proportionally greater than for the neopentyl system. The same argument can be extended to explain the retarded activity of $L_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ compared to dineophyl derivatives. Modification of the steric demands of neophyl by sila-neophyl have been previously discussed (See 2.2.3.). If it is reasonable to assume that the mixed (neophyl)(sila-neophyl) complexes are less sterically demanding than dineophyl analogues, it can be envisaged that there would be less steric relief associated with both k_1 and k_4 and hence the complexes are inherently less labile. There may also be electronic modifications at the metal, associated with the different alkyl ligand (*vide supra*).

The enhanced reactivity of the triphenylphosphine complex may be attributed to the effect of increased bulk of the phosphine ligand. The mechanism of the reaction is affected in two ways:

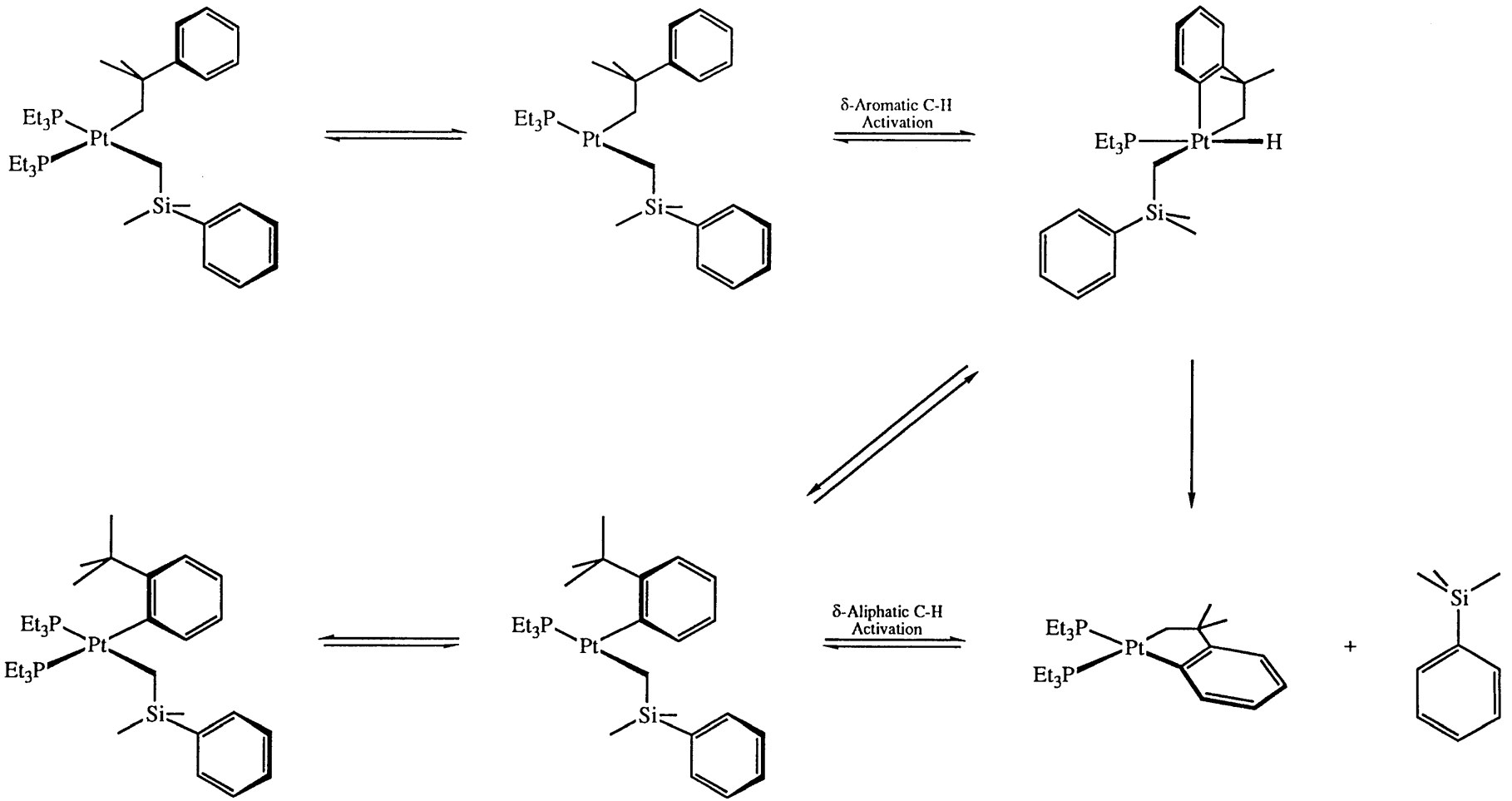
(i) Ligand dissociation forming the three coordinate intermediate LPtRR' will be favoured.

(ii) Greater steric crowding of the transition state should promote reductive elimination of phenyltrimethylsilane.

Even though phosphine dissociation is not the "rate-limiting" process, acceleration of the reaction may be achieved by effectively increasing the concentration of the precursor to the most energetic step in the pathway.

6.2.3. Thermolytic Rearrangement of cis-$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ *at Higher Temperatures.*

Benzene-d^6 solutions of $(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ heated to >80°C exhibit the formation of a significant amount (15-25%) of a new species, as well as the metallacycle and parent mixed-dialkyl. The ^{31}P N.M.R. of this species appears as an AB quartet, δ = -3.51, 0.58 ppm, with $^1J_{Pt-P}$ values of 1739.0 Hz and 2086.8 Hz. These characteristics are most consistent with an aryl group *trans* to phosphine and a β-sila-alkyl group *trans* to phosphine. Moreover, the new derivative also undergoes metallacyclisation affording a platinacycle. In fact the same platinaindan is obtained as in aromatic C-H activation, though formation of the metallacycle is slower in this case.



Scheme. 6.5 : *Proposed Mechanism of Formation of* $(PEt_3)_2Pt(CH_2SiMe_2Ph)(C_6H_4\text{-}2\text{-}^tBu)$.

These observations can be most readily rationalised if the new species is *cis-bis*-$(PEt_3)_2Pt(CH_2SiMe_2Ph)(C_6H_4\text{-}2\text{-}CMe_3)$, where the neophyl group has undergone an isomerisation reaction affording a (*tert*-butylphenyl)(sila-neophyl) complex. Similar observations have been noted for $(PEt_3)_2Pt(CH_2CMe_2Ph)_2$, notably in polar solvents, in which isomerisation to $(PEt_3)_2Pt(CH_2CMe_2Ph)(C_6H_4\text{-}2\text{-}CMe_3)$ occurs to a small extent[31, 49]. This complex , though, was excluded as an intermediate in the metallacyclisation of *cis*-$(PEt_3)_2Pt(CH_2CMe_2Ph)_2$; an authentic sample was found to cyclise at a rate approximately half that observed for the decomposition observed of the parent complex. In addition, deuterium labelling studies were able to show that aromatic C-H activation was favoured energetically over aliphatic C-H transfer.

The formation of *cis*-$(PEt_3)_2Pt(CH_2SiMe_2Ph)(C_6H_4\text{-}2\text{-}CMe_3)$ from *cis*-$(PEt_3)_2Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph)$ must involve initial activation of the neophyl aromatic C-H bond. Reductive elimination of the hydride with the $-CH_2$ bond of the metallacycle, instead of trimethylphenylsilane follows, affording the isomeric complex. This can undergo δ-aliphatic C-H activation forming the hydridoalkylplatinum(IV) intermediate, which reductively eliminates trimethylphenylsilane to yield the metallacycle (Scheme. 6.5). So, clearly *aliphatic* δ-C-H transfer is also preferred to β-C migration between Si and Pt.

6.3. Experimental.

6.3.1. General.

Elemental analyses and N.M.R. spectra were obtained as described previously (See 4.3).

All reactions were carried out under nitrogen or argon unless otherwise noted, using standard anaerobic techniques. Solvents were distilled under nitrogen prior to use (See 2.3).

Triphenylphosphine-d^{15}, sila-neophyl chloride-d^0 and sila-neophyl chloride-d^5 were prepared as before (*vide supra*). Neophyl chloride-d^5 [121], (cod)Pt(CH_2CMe_2Ph)$_2$ and (cod)Pt(CH_2CMe_2Ph)Cl[50] were prepared by established routes.

Methallyl chloride (3-chloro-2-methyl-1-propene) was used as supplied by BDH Ltd.. Benzene-d^6 supplied by Aldrich Chem. Co. was dried over sodium prior to use, triphenylphosphine (Aldrich Chem. Co.) was used as supplied. Triethylphosphine, supplied by Strem Chemicals, was stored under argon but used without further purification.

6.3.2. Syntheses.

Preparation of bis-*(neophyl)([2.2.1]bicyclohepta-2,5-diene)platinum(II).*

A solution of $PhMe_2CCH_2MgCl$ (6.0 mmol) in diethyl ether (30 cm^3) was added dropwise at -78°C to a stirred suspension of (nbd)$PtCl_2$ (0.72g, 2.0 mmol) in diethyl ether (20 cm^3). The mixture was gradually warmed to room temperature and then stirred for a further 7 hours. The stirred suspension was then cooled to -25°C and hydrolysed with saturated ammonium chloride solution (20 cm^3). The ethereal layer was separated and the aqueous phase washed with diethyl ether (2 x 20 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with activated charcoal. Filtration, washing the $MgSO_4$ with diethyl ether (2 x 10 cm^3) and removal of the solvent *in vacuo* gave a lemon-yellow oil, which was recrystallised from the minimum amount of *n*-hexane (2 cm^3) to give lemon-yellow needles of the product.
(Yield : 1.01g, 1.82 mmol, 91%).

[*Analysis* : Found C=58.28%, H=6.11%; Calculated C=58.57%, H=6.19%]

Prepared analogously was:-

Bis-*(neophyl-d^5)([2.2.1]bicyclohepta-2,5-diene)platinum(II).*
Product : Pale yellow solid.
(Yield : 0.75g, 1.19 mmol, 77%).

Preparation of chloro(neophyl)([2.2.1]bicyclohepta-2,5-diene)platinum(II).

To a solution of (nbd)Pt(CH_2CMe_2Ph)$_2$ (1.60g, 2.81 mmol) in diethyl ether (15 cm^3) cooled to -78°C was added dropwise dry HCl (3.6 mmol) in Et_2O (10 cm^3). The stirred mixture was gradually warmed to ambient temperature and stirred for a further 16 hours. The solvent was removed *in vacuo* affording a pale yellow oily residue, which was dissolved in CH_2Cl_2 (2 cm^3), methanol (1 cm^3) added, then cooled to -20°C. Filtration, washing the solid with *n*-hexane (2 x 3 cm^3) and drying *in vacuo* yielded the product as a white crystalline solid.
(Yield : 1.21g, 2.63 mmol, 94%).

[*Analysis* : Found C=44.76%, H=4.63%; Calculated C=44.79%, H=4.64%].

Prepared analogously was:-

Chloro(neophyl-d^5)([2.2.1]bicyclohepta-2,5-diene)platinum(II).
Product : White crystalline solid.
(Yield : 0.55g, 1.18 mmol, 99%).

[*Analysis* : Found C=44.76%, H=4.36%; Calculated C=44.30%, H=4.59%].

Preparation of (neophyl)(sila-neophyl)([2.2.1]bicyclohepta-2,5-diene)platinum(II).

A solution of $PhMe_2SiCH_2MgCl$ (4.0 mmol) in diethyl ether (20 cm^3) was added dropwise to a stirred suspension of (nbd)Pt(CH_2CMe_2Ph)Cl (0.62g, 1.36 mmol) in Et_2O (10 cm^3) at -78°C. With continued stirring, the reaction mixture was gradually warmed to room temperature and stirred for a further 6 hours. After this time, the suspension was cooled to -25°C and hydrolysed with saturated aqueous ammonium chloride solution (20 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (2 x 10 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with activated charcoal. Filtration, evaporation of the solvent *in vacuo* and recrystallisation in the minimum amount of *n*-hexane (2 cm^3) afforded the product as a pale yellow crystalline solid.
(Yield : 0.75g, 1.32 mmol, 97%).

[*Analysis* : Found C=54.87%, H=6.01%; Calculated C=54.81%, H=6.02%].

Prepared analogously were:-

(neophyl)(sila-neophyl-d^5)([2.2.1]bicyclohepta-2,5-diene)platinum(II).
Product : Citron needles.
(Yield : 1.26g, 2.19 mmol, 95%).

[*Analysis* : Found C=54.08%, H=5.79%; Calculated C=54.33%, H=5.96%].

(neophyl-d^5)(sila-neophyl)([2.2.1]bicyclohepta-2,5-diene)platinum(II).
Product : Citron crystalline solid.
(Yield : 0.60g, 1.04 mmol, 88%).

[*Analysis* : Found C=54.22%, H=5.96%; Calculated C=54.33%, H=5.96%].

Preparation of (neophyl)(sila-neophyl)(cycloocta-1,5-diene)platinum(II).

This compound was prepared by a similar procedure described for (nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph) from (cod)Pt(CH_2CMe_2Ph)Cl and $PhMe_2SiCH_2MgCl$.
Product : White crystalline solid.
(Yield : 0.70g, 1.23 mmol, 84%).

[*Analysis* : Found C=55.16%, H=6.71%; Calculated C=55.36%, H=6.54%].

Preparation of cis-bis-*(triphenylphosphine)(neophyl)(sila-neophyl)platinum(II).*

To a solution of (nbd)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph) (0.20g, 0.35 mmol) in diethyl ether (6 cm^3) was added triphenylphosphine (0.185g, 0.70 mmol) and the solution maintained at 4°C for 24 hours. The colourless crystalline solid was filtered, washed with *n*-hexane (2 x 3 cm^3) and dried *in vacuo* , affording analytically pure product.
(Yield : 0.34g, 0.34 mmol, 97%).

[*Analysis* : Found C=65.74%, H=5.57%; Calculated C=65.92%, H=5.63%].

Prepared in an analogous fashion were:-

cis-bis-*(triphenylphosphine)(neophyl)(sila-neophyl-d^5)platinum(II).*
Product : Colourless crystalline rods.
(Yield : 0.29g, 0.29 mmol, 83%).

[*Analysis* : Found C=65.53%, H=5.78%; Calculated C=65.72%, H=5.57%].

cis-bis-*(triphenylphosphine)(neophyl-d^5)(sila-neophyl)platinum(II).*
Product : Colourless crystalline blocks.
(Yield : 0.30g, 0.30 mmol, 86%).
[*Analysis* : Found C=65.57%, H=5.63%; Calculated C=65.72%, H=5.57%].

cis-bis-*(triphenylphosphine-d^{15})(neophyl)(sila-neophyl)platinum(II).*
Product : Colourless crystalline solid.
(Yield : 0.31g, 0.31 mmol, 89%).

[*Analysis* : Found C=63.77%, H=5.42%; Calculated C=63.99%, H=5.47%].

Preparation of cis-bis-*(triethylphosphine)(neophyl)(sila-neophyl)platinum(II).*

To a solution of (cod)Pt(CH_2CMe_2Ph)(CH_2SiMe_2Ph) (0.25g, 0.43 mmol) in diethyl ether (6 cm^3) was added triethylphosphine (115 µl, 8.6 mmol) and the reaction mixture left standing at ambient temperature for 3 days. Removal of the solvent *in vacuo* afforded a crystalline mass. The product could be obtained as a colourless crystalline solid by extraction into *n*-hexane (2 cm^3) and prolonged cooloing at -20°C.
(Yield : 0.28g, 0.39 mmol, 91%).

Prepared by a similar procedure was:-

cis-bis-*(triethylphosphine)(neophyl-d^5)(sila-neophyl)platinum(II).*
Product : Colourless oil.
(Yield : 0.37g, 0.52 mmol, 100%).

6.3.3. Kinetic Measurements.

Benzene-d^6, supplied by MSD Isotopes, was distilled from Na/K alloy and stored under argon prior to use. Measurements were performed in 5mm-diameter medium-walled N.M.R. tubes equipped with sealable Teflon valves. The samples were prepared by the following methods:-

(i) A stock solution of L_2PtRR', whose concentration was 0.02M with respect to platinum, was prepared in bezene-d^6 and stored at -20°C. An aliquot was transferred anaerobically to the N.M.R. tube and subjected to five freeze-thaw-pump degassing cycles, before being sealed under argon.

(ii) Benzene-d^6 solutions of L_2PtRR' were prepared, which were 0.02M with respect to platinum, freeze-thaw deoxygenated through five cycles and sealed under argon.

(iii) Where thermolyses were conducted in the presence of triphenylphosphine, benzene-d^6 solutions of known concentrations of PPh_3 were prepared, then transferred to the reaction tubes containing the appropriate amount of L_2PtRR'.

The tube was maintained at the required temperature with a variable temperature probe heater in the Jeol FX90Q spectrometer. Sub-ambient runs used liquid nitrogen to cool the probe. The probe was maintained at the desired temperature (±0.1°C) throughout the run. The progress of the rearrangement was monitored periodically by ^{31}P N.M.R.

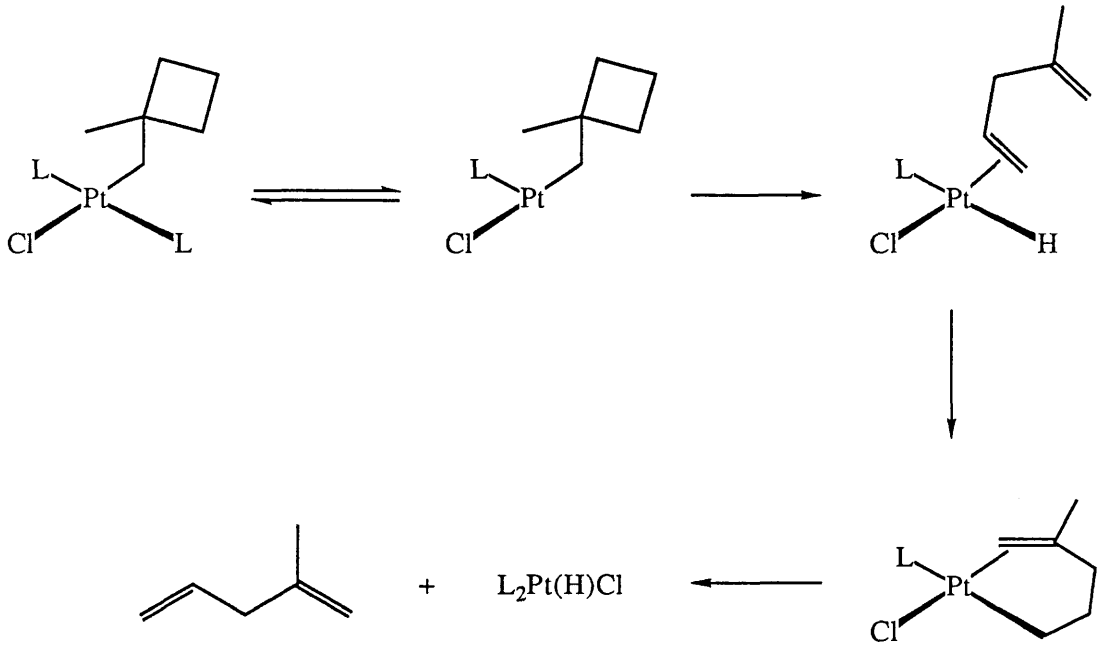
spectroscopy.

Chapter Seven :

THERMOLYTIC REARRANGEMENT OF *CIS-BIS*-(TRIPHENYLPHOSPHINE)-*BIS*-(SILA-NEOPENTYL)PLATINUM(II) AND RELATED COMPLEXES.

7.1. Introduction.

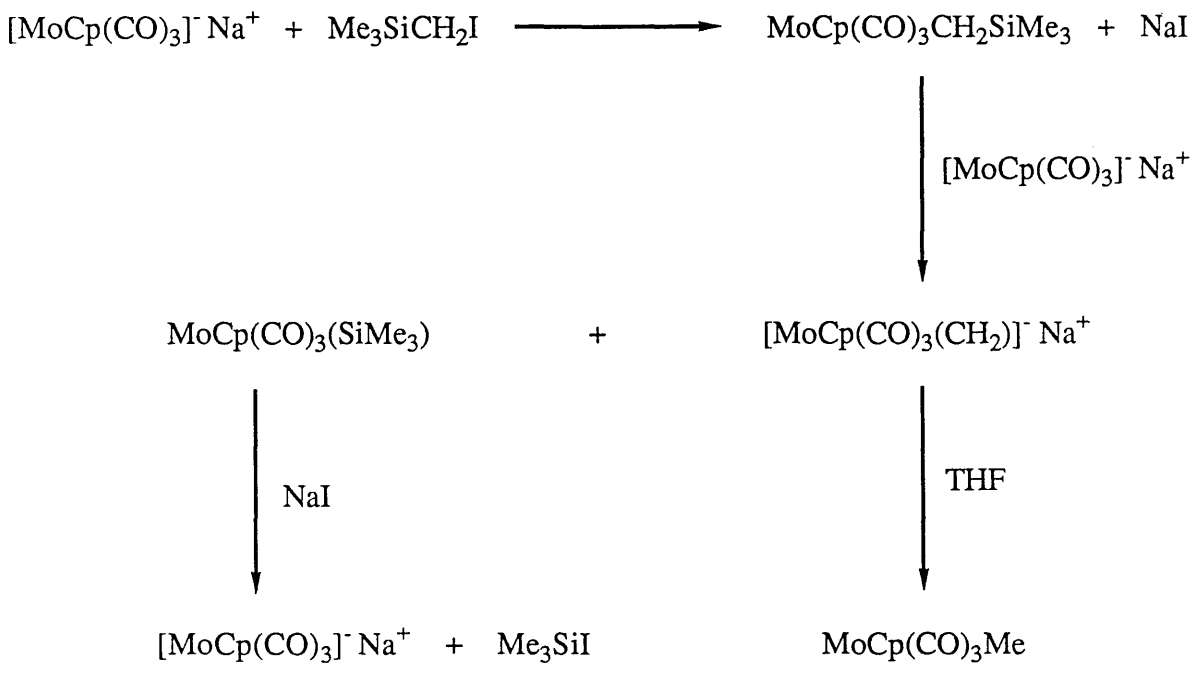
In contrast to their neopentylplatinum analogues, thermolysis of *bis*-(trimethyl)silylmethylplatinum(II) complexes does not yield 1-platina-3-silacyclobutanes. Instead quantitative rearrangement to ({[(trimethyl)silylmethyl]dimethylsilyl}methyl)platinum(II) complexes; *cis*-$L_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$ is observed. Thermolysis of the selectively deuterated derivatives *cis*-$L_2Pt[CH_2Si(CD_3)_3]_2$ reveals the presence of only Pt-CD_3 and Pt-CH_2-Si groups, suggesting that the rearrangement features an effective β-methyl migration from silicon to platinum, most plausibly *via* an η^2-silene intermediate[16, 50]. Although β-alkyl transfers are rare for d-block metals, examples of such reactivity have been observed in organoplatinum(II) systems, which not only lack a transferable hydrogen but also have a strained alicyclic ring incorporating the β-carbon atom[122] (Scheme. 7.1).



Scheme. 7.1 : *Proposed Thermolytic Rearrangement of trans-$L_2Pt(CH_2CMeR)Cl$ [R = cyclobutyl] by β-alkyl transfer.*

There is no literature precedent for the observed rearrangement of $L_2Pt(CH_2SiMe_3)_2$. Recently, an apparent β-methyl migration has been induced in the reaction of $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ with silver fluoride or silver tetrafluoroborate to yield $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_2F)Me$[123]. The mechanism of this rearrangement is not clear, but the process is assisted by hard nuleophilic reagents with strong affinities for sila-alkyl groups. Generation of $MCp(CO)_3CH_3$ (M = Mo or W) from the interaction of $[MoCp(CO)_3]^-\ Na^+$ with Me_3SiCH_2I in THF was shown not to have resulted from methyl migration: use of selectively deuterated $Me_3SiCHDI$ afforded

$MCp(CO)_3(CH_2D)$[124]. Instead the observed product, proposedly, arises from reaction of the initial product, $MoCp(CO)_3(CH_2SiMe_3)$, with its precursor, $[MoCp(CO)_3]^- Na^+$ (Scheme. 7.2).



Scheme. 7.2 : *Proposed Mechanism for Formation of $Mo(Cp)(CO)_3Me$.*

As part of a study to explore further the scope of this type of reaction and evaluate its mechanistic controls, the thermolytic behaviour of monodentate phosphine complexes, $L_2Pt(CH_2SiMe_3)R$ [R = CH_2SiMe_3, CH_2CMe_3, C_6H_4-4-Me; L = PPh_3, PEt_3] has been investigated.

7.2. Results and Discussion.

7.2.1. Thermolytic Rearrangement of cis-bis-*triphenylphosphine*-bis-*(trimethylsilylmethyl)platinum(II).*

7.2.1.1. Kinetic Studies.

The thermolysis of $(PPh_3)_2Pt(CH_2SiMe_3)_2$ was conveniently monitored by ^{31}P N.M.R. at regular intervals. At temperatures >100°C this results in isomerisation to a methyl({[(trimethylsilyl)methyl]dimethylsilyl}methyl)platinum(II) species. This derivative has very distinctive N.M.R. characteristics. ^{31}P N.M.R. clearly indicates the inequivalence of the two ^{31}P nuclei coupled to ^{195}Pt (Table 7.1). The similar magnitudes of $^1J_{Pt\text{-}P}$ suggest, though, that both alkyl groups exert similar *trans*-influences.

Table 7.1 : *^{31}P N.M.R. Characteristics of* cis-*$(PPh_3)_2Pt(CH_2SiMe_3)_2$ and* cis-*$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$.*

Complex	δ^a / ppm	$J_{Pt\text{-}P}$ / Hz	$J_{P\text{-}P}$ / Hz
$(PPh_3)_2Pt(CH_2SiMe_3)_2$[b]	24.61	2002.6	-
$(PPh_3\text{-}d^{15})_2Pt(CH_2SiMe_3)_2$[c]	24.56	2007.1	-
$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$[b]	25.09	1920.7	8.9
	28.98	1955.0	
$(PPh_3\text{-}d^{15})_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$[b]	25.07	1921.1	8.9
	28.03	1957.2	

a :- referenced to 85% H_3PO_4 / D_2O

b :- toluene-d^8

c :- chloroform-d^1

^1H N.M.R. (Table 7.2) show some interesting features, notably two distinct resonances for Si-Me protons in the integral ratio 2:3 and a characteristic high field singlet (*ca.* -0.5 ppm) attributable to the methylene group bound to two silicon atoms. The aromatic region confirms the inequivalence of the phosphine ligands.

The ^{13}C N.M.R. spectrum (Table 7.3) displays resonances due to two Si-$(CH_3)_n$ carbons, one with a $^3J_{Pt\text{-}C}$ coupling of 20.0 Hz, the second, more intense, with no

Table 7.2 : *^1H N.M.R. Characteristics of* cis-bis-*$(PPh_3)_2Pt(CH_2SiMe_3)_2$ and Related Complexes.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]			δ ^{1}H ppm : Ancillary ligand [*Assignment*]
	Pt-CH_2	Si-CH_3	Si-CH_2	
$(PPh_3)_2Pt(CH_2SiMe_3)_2$[a]	1.14 b	0.38	-	6.94 m, [H_3, H_4, H_5]; 7.66 m, [H_2, H_6]
$(PPh_3\text{-}d^{15})_2Pt(CH_2SiMe_3)_2$[a]	1.18 b	0.43	-	-
$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$[c]	0.99 (**68.2**)	0.11 [*Si-Me_3*] 0.29 [*Si-Me_2*]	-0.22	6.78-6.83 m, [$H_{3'}$, $H_{4'}$, $H_{5'}$]; 6.84-6.90 m, [H_3, H_4, H_5]; 7.39 m, [$H_{2'}$, $H_{6'}$]; 7.52 m, [H_2, H_6]

a :- benzene-d^6

b :- broad resonance

c :- toluene-d^8

Table 7.3 : *^{13}C N.M.R. Characteristics of* cis-*$(PPh_3)_2Pt(CH_2SiMe_3)_2$ and* cis-*$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$.*

	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*]			δ ^{13}C ppm : Ancillary ligands (J_{Pt-C}) / Hz [*Assignment*]
	Pt-CH_n	Si-CH_3	Si-CH_2	
$(PPh_3)_2Pt(CH_2SiMe_3)_2$[a]	7.80, 9.26 (**586.3**) [CH_2] ($J_{C\text{-}P_{Trans}}$=91.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 6.7 Hz)	4.04	-	127.39 [C_3, C_5] ($J_{C\text{-}P}$ = 8.7 Hz); 129.16 [C_4]; 133.90 (**18.5**) [C_1] ($J_{C\text{-}P}$ = 43.9 Hz); 134.57 (**10.8**) [C_2, C_6] ($J_{C\text{-}P}$ = 10.9 Hz)
$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$[a,b]	6.93, 7.52 (**608.8**) [CH_3] ($J_{C\text{-}P_{Trans}}$=98.6 Hz) ($J_{C\text{-}P_{Cis}}$ = 9.5 Hz) 13.65, 14.78 (**651.1**) [CH_2] ($J_{C\text{-}P_{Trans}}$=92.2 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.7 Hz)	1.99 [*Si-Me*$_3$] 6.28 (**20.8**) [*Si-Me*$_2$]	8.80 (**33.8**)	127.57 [C_3, $C_{3'}$, C_5 $C_{5'}$] ($J_{C\text{-}P}$ = 12.6 Hz); 129.1 [C_4]; 129.48 [$C_{4'}$]; 134.07 (**21.5**) [C_1] ($J_{C\text{-}P}$ = 40.1 Hz); 134.31 (**18.3**) [$C_{1'}$] ($J_{C\text{-}P}$ = 40.8 Hz); 134.95 (**15.7**) [C_2, $C_{2'}$, C_6, $C_{6'}$] ($J_{C\text{-}P}$ = 21.6 Hz)

a :- chloroform-d[1] b :- from Ref. 50

observed coupling. The additional "triplet" at 8.80 ppm, with a $^3J_{Pt-C}$ of 35 Hz, is due to the methylene group bound to two silicon atoms. Further distinctive features are the Pt-CH_n resonances, which were unequivocally assigned by an ADEPT experiment. This technique produces positive signals for CH_3 and CH carbon atoms and negative signals for CH_2 and quarternary carbons. The higher field signal corresponds to the Pt-CH_3 group, the lower field resonance to a Pt-CH_2 fragment. In addition, the structure of $(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$ has been confirmed by an X-ray diffractometric study[50].

The reaction was found to be first-order in platinum substrate for at least two half-lives; rate data appear in Table 7.4. The rearrangement of $(PPh_3)_2Pt(CH_2SiMe_3)_2$ was studied over the temperature range 102.5-112.5°C and the observed rate constants are represented graphically in Fig. 7.1. The temperature variation of the observed rate constant shows a linear correspondence with the Arrhenius relationship (Fig. 7.2). From this plot, activation parameters were calculated [for methodology see 5.2.1.2] (Table 7.5). Data obtained for triethylphosphine and diphenylmethylphosphine[50] display similar values for the activation parameters, implying a common mechanism for the rearrangement.

Table 7.4 : *Kinetic Data for the Rearrangement of* cis-bis-*$(PPh_3)_2Pt(CH_2SiMe_3)_2$*.

L	R	T / °C	$10^5 \times k_{obs}$ / s^{-1}
PPh_3	CH_2SiMe_3	102.5	2.49
PPh_3	CH_2SiMe_3	105.0	3.35
PPh_3	CH_2SiMe_3	107.5	4.45
PPh_3	CH_2SiMe_3	110.0	6.68
PPh_3	CH_2SiMe_3	112.5	9.91
PPh_3[a]	$CH_2Si(CD_3)_3$	105.0	1.95
PPh_3-d^{15}	CH_2SiMe_3	112.5	4.77

a :- from Ref. 50

Rearrangement of *cis*-$(PPh_3)_2Pt[CH_2Si(CD_3)_3]_2$ is slower than the undeuterated analogue; $k^H/k^D = 1.7$. Similar values were obtained for PEt_3 and PPh_2Me, indicating that the small but significant isotope effect is essentially independent of the nature of L. Deuteration of triphenylphosphine results in a larger isotope effect; $k^H/k^D = 2.1$. These results are depicted in Fig. 7.3. Importantly, $(PEt_3\text{-}d^{15})_2Pt(CH_2SiMe_3)_2$ was shown to

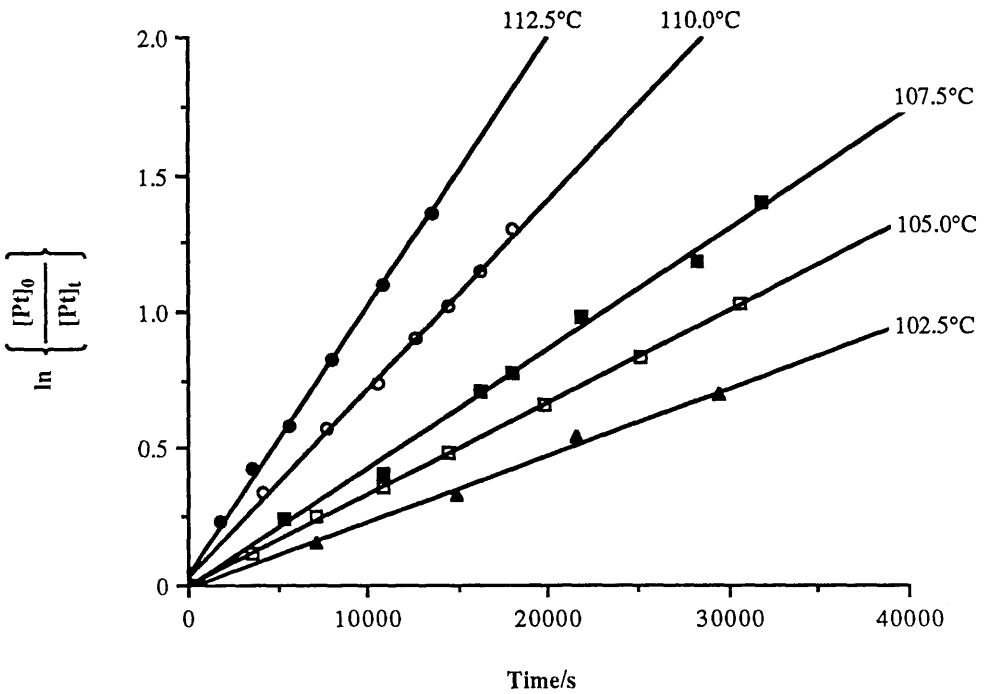


Fig. 7.1 : *Kinetic Data for the Thermolysis of* $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

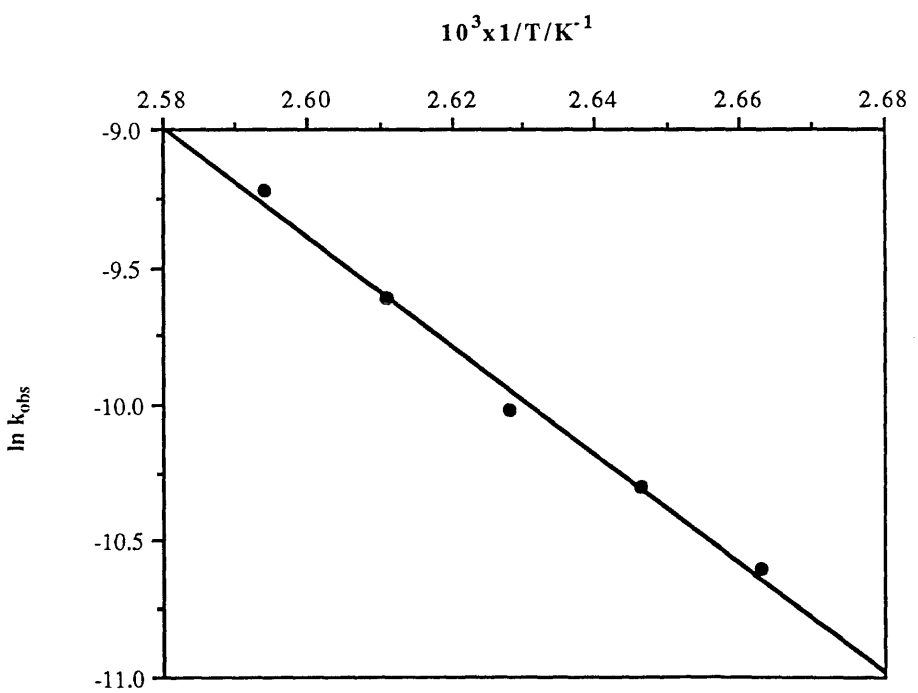


Fig. 7.2 : *Arrhenius Plot for the Thermolysis of* $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

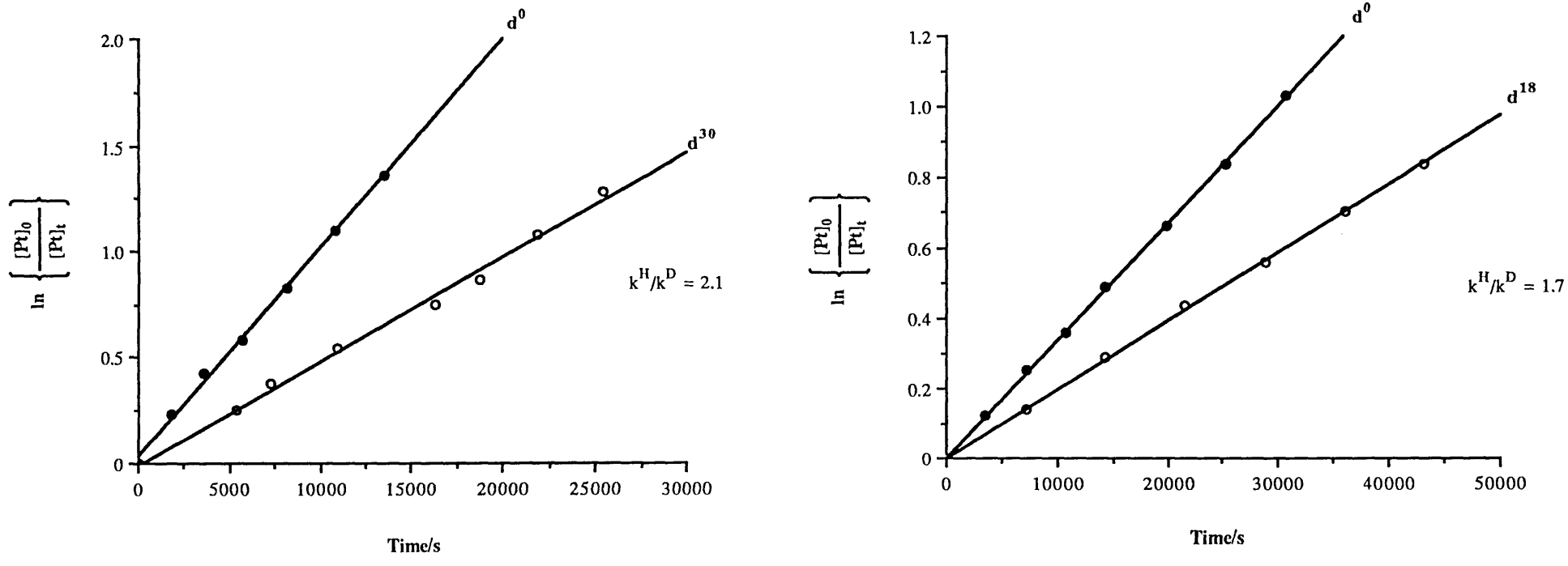


Fig. 7.3 : *Deuterium Isotope Studies for the Thermolysis of* $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

Table 7.5 : *Activation Parameters for the Rearrangement of* cis-$L_2Pt(CH_2SiMe_3)_2$.

L	E_a kJ mol^{-1}	$\Delta H^{\ddagger}_{298}$ kJ mol^{-1}	Frequency factor, A	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$ kJ mol^{-1}
PPh_3	166 (±2)	163 (±2)	2.75×10^{18}	100 (±10)	134 (±2)
PPh_2Me[a]	157 (±9)	155 (±9)	5.85×10^{16}	68 (±27)	135 (±2)
PEt_3[a]	143 (±2)	141 (±2)	5.58×10^{14}	29 (± 4)	132 (±1)

a :- from Ref. 50

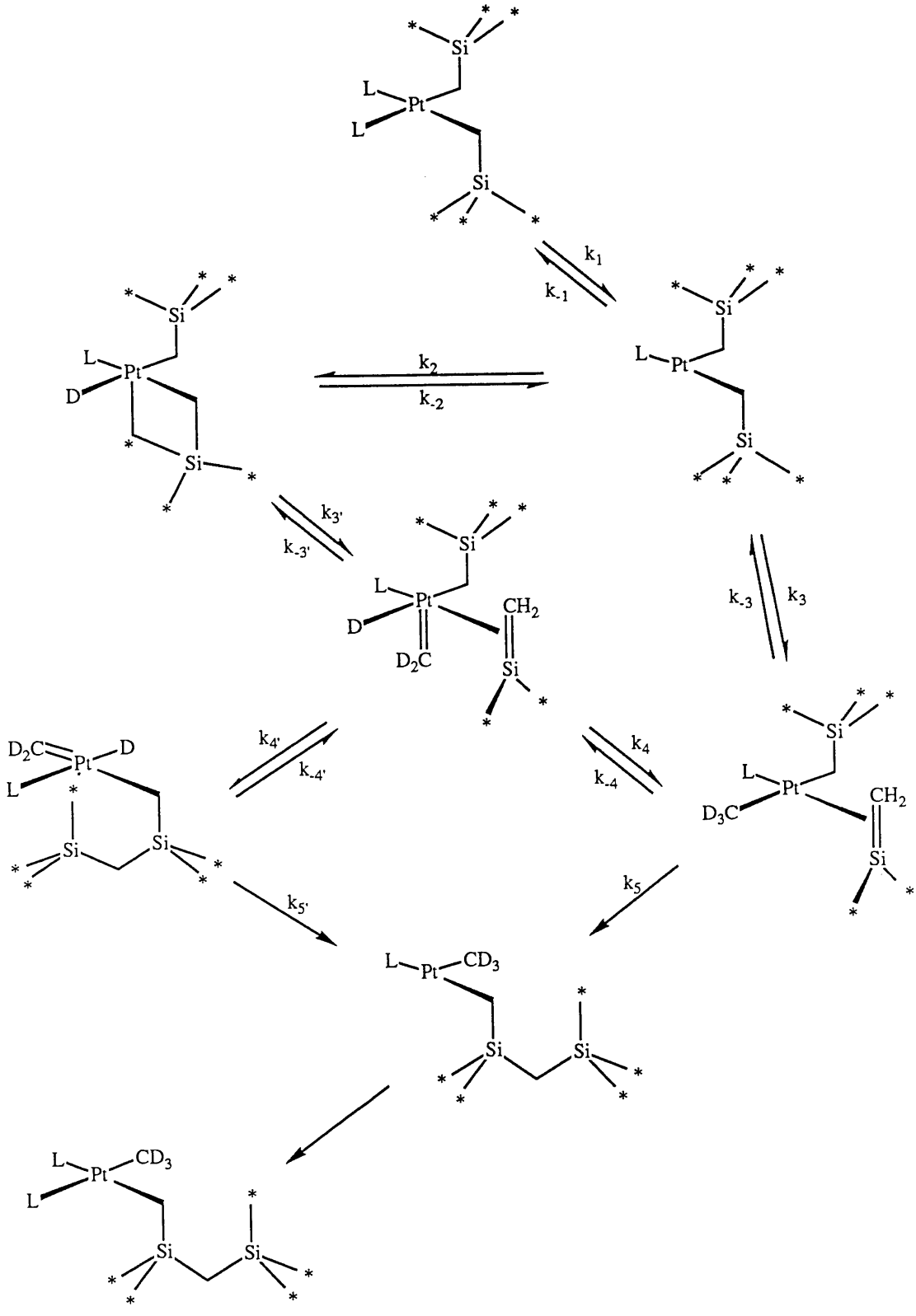
have a large isotope effect ($k^H/k^D = 6.0$), with a substantial effect ($k^H/k^D = 13.9$) observed for $(PEt_3\text{-}d^{15})_2Pt[CH_2Si(CD_3)_3]_2$[50].

Addition of triphenylphosphine to a solution of $(PPh_3)_2Pt(CH_2SiMe_3)_2$ inhibits the reaction, just as the presence of triethylphosphine during thermolysis of $(PEt_3)_2Pt(CH_2SiMe_3)_2$ retarded isomerisation[50]. The value for k_1 of 10^{-3}-10^{-4}, estimated from a plot of $1/k_{obs}$, suggests that this step is not rate-limiting.

During the reaction, only $(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)_2$ is formed. No evidence, based on ^{31}P N.M.R., of either a sila-cyclobutane (from γ-C-H activation of a trimethylsilylmethyl-CH_3), for which there are several precedents, or phosphine metallation at an *ortho*-phenyl carbon, forming a four-membered metallacycle was observed. The former would be expected to generate just a 1:4:1 "triplet" and the latter should display a marked upfield ^{31}P shift [$\Delta_R \approx$ 40-50 ppm] for the phosphorus in the metallacyclic ring.

7.2.1.2. Mechanistic Implications.

Preliminary dissociation of one phosphine is strongly implied by the retardation of the rate of reaction in the presence of excess triphenylphosphine. Following this step, two plausible mechanisms for this rearrangement can be envisaged (Scheme. 7.3). The first involves γ-C-H activation of a Si-CH_3 group, generating a platinum(IV)hydridoalkyl intermediate (k_2). Increased ring strain may account for the instability of the sila-cyclobutane formed, preventing reductive elimination of tetramethylsilane. Instead, cycloreversion, of the type established for metallacyclobutane derivatives, affording both an alkylidene and an η^2-silene ligand may be favoured ($k_{3'}$). This species could in turn undergo migratory insertion forming either a methylidene ($k_{4'}$) or an η^2-silene complex (k_4), which rearranges to the product (k_5, $k_{5'}$).

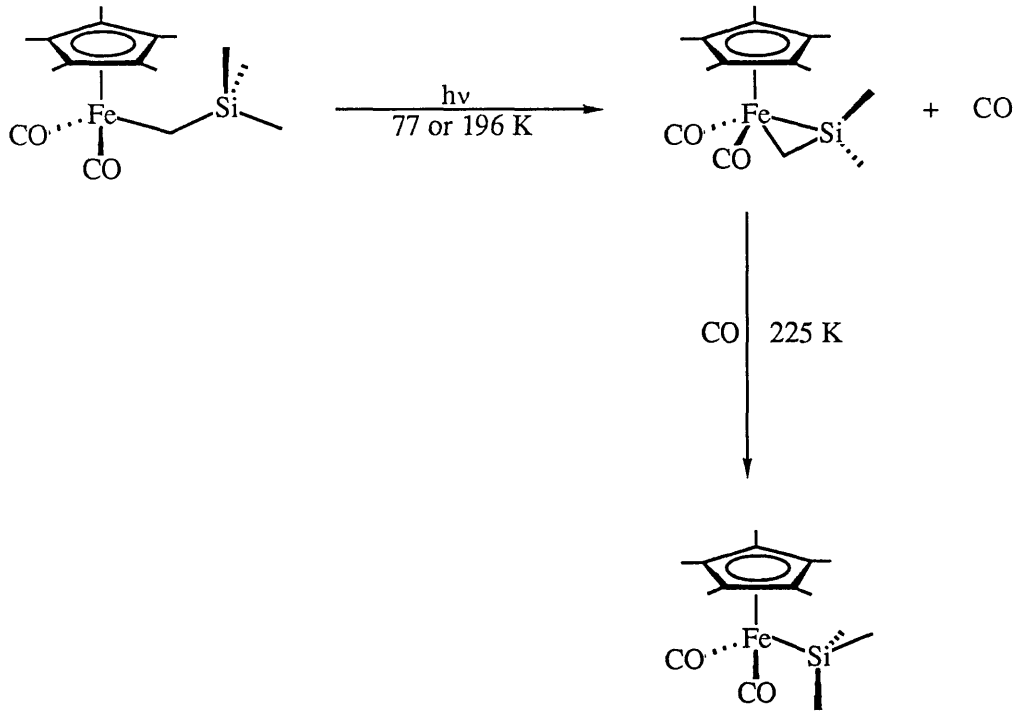


Scheme. 7.3 : *Proposed Mechanism for the Thermolytic Rearrangement of* $(PPh_3)_2Pt(CH_2SiMe_3)_2$.

The second involves direct migration of a methyl group from silicon to platinum (k_3), followed by regiospecific insertion of the silene into the platinum-carbon bond of the remaining trimethylsilylmethyl group (k_5), generating the asymmetric product.

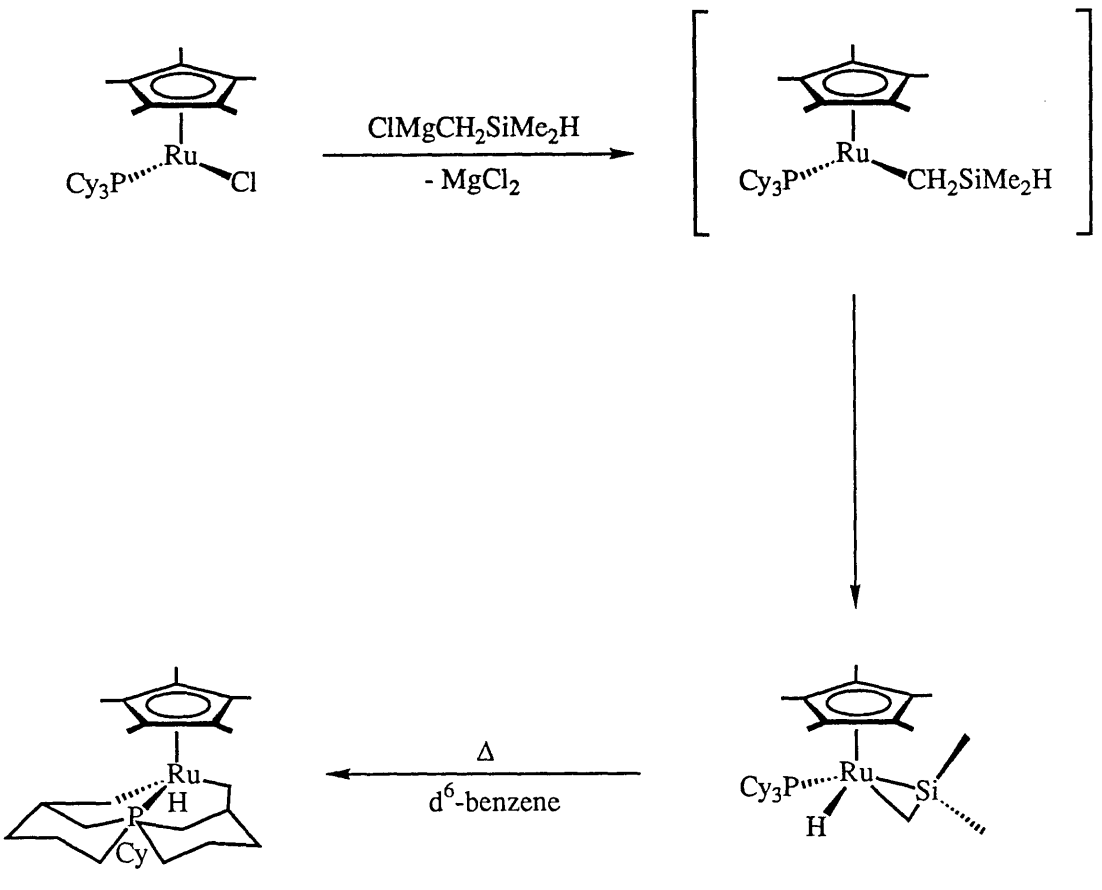
Thermolysis of the selectively deuterated complex, $(PPh_3)_2Pt[CH_2Si(CD_3)_3]_2$, reveals the origin of the methyl group ultimately bound to platinum. The $^{13}C-\{^1H\}$ N.M.R. spectrum of the product shows the presence of only Pt-CD_3 and Pt-CH_2-Si groups. Additionally, the Si-CH_2-Si group is completely protiated; there is *no* H-incorporation into the methyl groups. Hence the platinum-methyl group of $(PPh_3)_2Pt[CD_3)(CH_2Si(CD_3)_2CH_2Si(CD_3)_3]$ has been transferred intact from silicon to platinum. Alkyl migration provides the simplest explanation for the specificity demonstrated by the labelling experiment. Regiospecific migration of the remaining trimethylsilylmethyl group to silicon in an η^2-silene intermediate would be in accord with the relative electrophilicity of the silicon-site.

Silenes are inherently unstable, transient species[125]; unless they are stabilised by bulky substituents[126]. Such complexes have been proposed as intermediates in a number of metal-mediated rearrangements of organo-silicon ligands[127]. Intermediates generated by β-hydrogen transfer from silicon to a metal were originally proposed by Pannell[128] and have been observed spectroscopically at low temperature by Wrighton[129]. Photolysis of $Cp^*(CO)_2FeCH_2SiMe_2H$ in the presence of CO or PPh_3 was shown to result in formation of $Cp^*(CO)Fe(L)SiMe_3$ *via* the intermediate, $Cp^*(CO)Fe(H)(\eta^2\text{-}CH_2SiMe_2)$ (Scheme. 7.4).



Scheme. 7.4 : *Generation of an η^2-silene Intermediate Photochemically.*

Recently η^2-silene complexes of ruthenium, $Cp^*(PR_3)Ru(H)(\eta^2\text{-}CH_2SiPh_2)$ ($PR_3 = PCy_3$, PPr^i_3), have been isolated and structurally characterised[130]. Reaction of $Cp^*(PR_3)RuCl$ with $ClMgCH_2SiPh_2H$ proposedly generates an intermediate alkyl species, $Cp^*(PR_3)Ru(CH_2SiPh_2H)$, which undergoes β-Si-H transfer affording the observed η^2-silene complex (Scheme.7.5). The general reactivity of such species has yet to emerge, however.

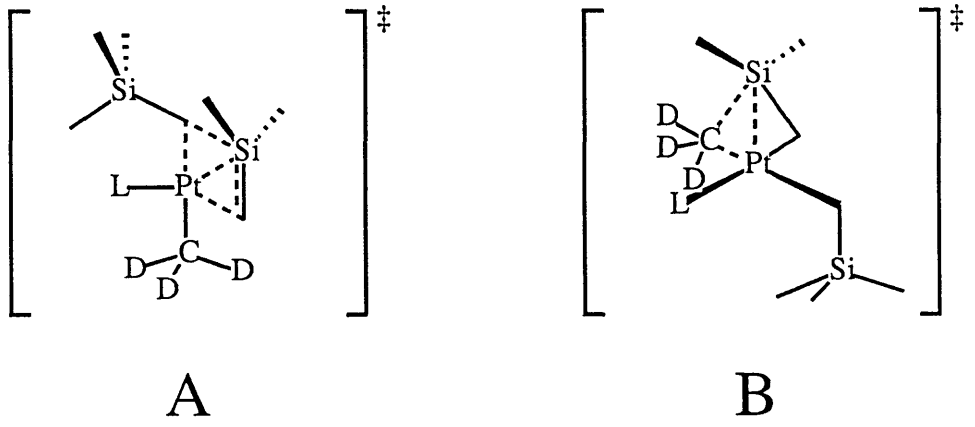


Scheme. 7.5 : *Formation of an Isolable η^2-silene Complex.*

The relatively small isotope effect observed on deuteration of the methyl groups may be a primary effect on γ-hydrogen transfer, partly diluted as a result of phosphine reassociation rate (k_{-1}), which is significant compared with that of successive steps (k_2 *etc.*). More plausibly, however, it is a secondary effect on direct β-methyl migration (k_3). Secondary isotope effects arise when there is a change in a stretching or bending vibration between the reactant and the transition state involving the isotopically substituted position[99].

The major factor influencing secondary α-isotope effects has been suggested to involve a hybridisation change at the α-carbon from sp^3-in the reactant to sp^2-in the transition state (Fig. 7.4a). The values of k^H/k^D of 1.7, 1.5 and 1.35 for L = PPh_3, PPh_2Me and PEt_3 respectively are slightly larger than those expected for secondary

isotope effects of this type. A contribution to this secondary inhibition can also be anticipated to arise from insertion of the η^2-silene into the remaining sila-neopentyl group (Fig. 7.4b). Aryl transfer has been suggested as the most energetic step along the reaction pathway during isomerisation of $L_2Pt(CH_2SiMe_2Ph)_2$ to $L_2Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)$ (See 5.2.1.2). Also, β-aryl transfer is apparently more facile, in general, than β-methyl transfer (*vide infra*). Hence, by inference, methyl transfer is also likely to proceed *via* the most energetic transition state. Even though considerable energy is required to attain the transition state, migratory insertion of the silene into a Pt-CH_2 bond is unlikely to be controlling the rate of reaction.



A B

Fig. 7.4 : *Possible Transition States for the Rearrangement of* $L_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

For L = PPh_3, the isotopic inhibition observed upon deuteration of the phosphine, may again be attributed to the development of an agostic interaction between platinum and a C-H bond of a phosphine-phenyl ring, as the other ligand dissociates (*vide supra*). The magnitude of the isotope effect ($k^H/k^D = 2.1$), suggests quite a strong interaction between platinum and the C-H bond. Thermolysis of $(PEt_3\text{-}d^{15})_2Pt(CH_2SiMe_3)_2$, however, generates an isotope effect of 6.0 for the isomerisation reaction[50]. It is difficult to envisage how an effect of this size arises, although it is indicative of C-H activation of a phosphine methyl group prior to methyl transfer from a trimethylsilylmethyl group. Phosphine metallation has been observed as a minor component during the thermal rearrangement of *cis*-$(PEt_3)_2Pt(CH_2CMe_3)_2$[7b] but it can effectively be ruled out during isomerisation of $(PEt_3)_2Pt(CH_2SiMe_3)_2$.

Thermolysis of $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$ clearly requires less energy than that of the corresponding trimethylsilylmethyl complex (Fig. 7.5). Comparison of the activation parameters of this pair of compounds (Table 7.6) suggests that the difference in reactivity is entropic in origin. (Aryl transfer proceeds with an overall greater increase in degrees of freedom than methyl transfer). Calculation of the energetic preference for β-aryl transfer over β-methyl transfer ($\Delta\Delta G^{\ddagger}$) may be obtained from the following equation :-

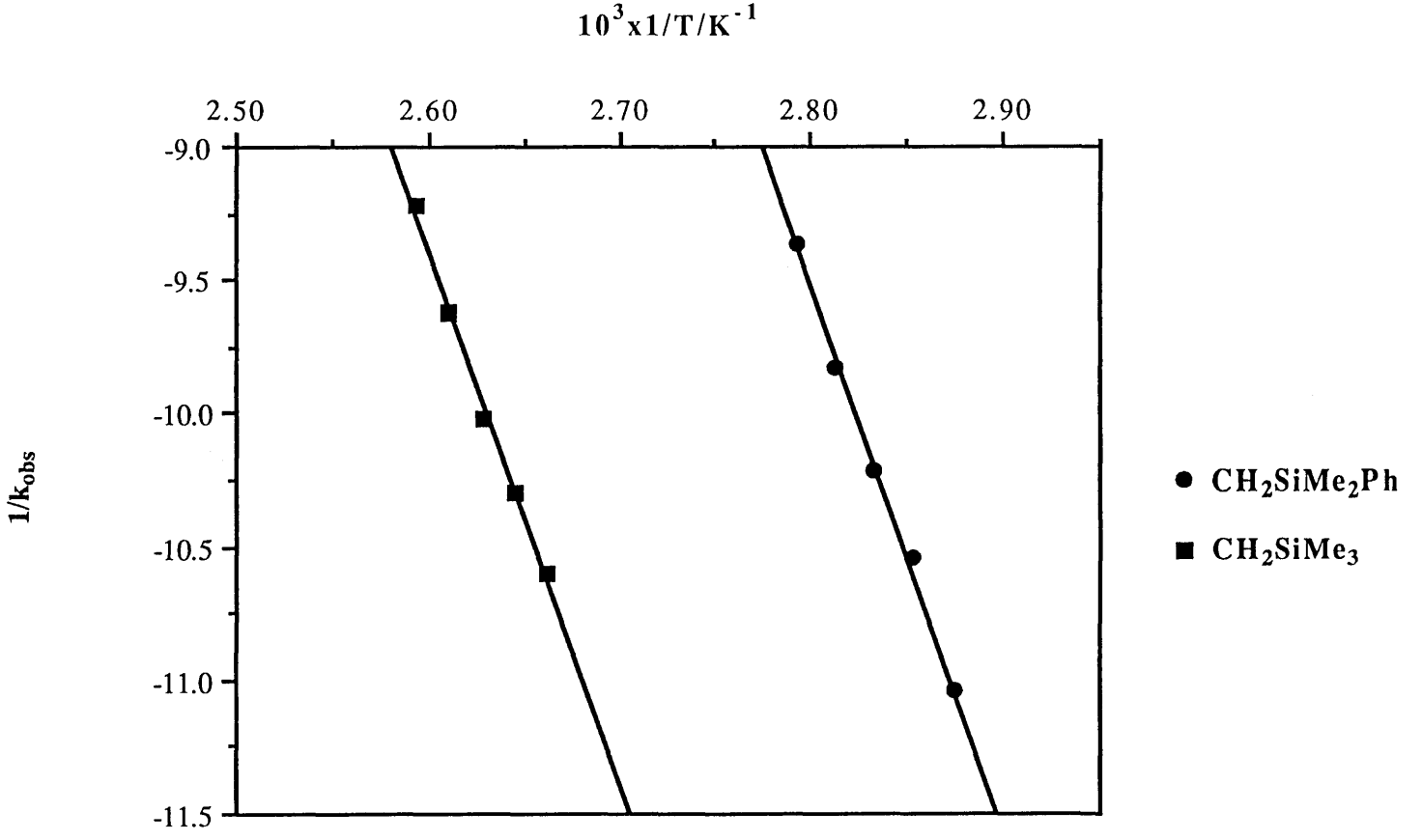


Fig. 7.5 : *Comparative Arrhenius Data for* $(PPh_3)_2PtR_2$ *[R =* CH_2SiMe_3, CH_2SiMe_2Ph*].*

$$\Delta\Delta G^{\ddagger} = RT \ln \left\{ \frac{k_{Aryl\ transfer}}{k_{Methyl\ transfer}} \right\}$$

Assuming that transfer of either a phenyl or methyl group is reversible, then the ratio of the products reflects the kinetic selectivity of the intermediate and is equal to the ratio of the rate constants for the two processes. Also, as a result, a statistical correction factor must be applied since there are three transferrable methyl groups in CH_2SiMe_3 but only one phenyl group in sila-neophyl. Thus,

$$\Delta\Delta G^{\ddagger} = RT \ln \left\{ \frac{3}{1} \cdot \frac{1.656 \times 10^{-3}}{3.351 \times 10^{-5}} \right\}$$

$$\Delta\Delta G^{\ddagger} = 15.7 \text{ kJ mol}^{-1} \text{ at } 378 \text{ K } (105°C)$$

Given the choice, β-aryl migration is preferred to β-CH_3 transfer by 15.7 kJ mol^{-1} at 378 K. If the transfer step is irreversible, there is no need for a statistical correction factor to be applied. In such an extreme case, $\Delta\Delta G^{\ddagger}$ = 12.3 kJ mol^{-1} (378 K).

Table 7.6 : *Comparison of Activation Parameters for the Rearrangement of* cis-L_2PtR_2.

L	R	$\Delta H^{\ddagger}_{298}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$ kJ mol^{-1}
PPh_3	CH_2SiMe_2Ph	138.4	165.6	124.4
PPh_3	CH_2SiMe_3	99.8	163.3	138.6
PPh_2Me	CH_2SiMe_2Ph	68.0	161.4	141.1
PPh_2Me[a]	CH_2SiMe_3	68.0	155.2	135.4

a :- from Ref. 50

The observed value of $\Delta\Delta G^{\ddagger}$ of 15.7 kJ mol^{-1} in favour of β-aryl migration is much greater than that found for the kinetic preference of δ-aromatic *versus* aliphatic C-H transfer in $(PEt_3)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)$, where $\Delta\Delta G^{\ddagger}$ was 4.4 kJ mol^{-1} at

327 K[49]. A much smaller effect of 3.3 kJ mol^{-1} was also observed for the preference of intermolecular aromatic aryl transfer over aliphatic cycloalkyl activation by $[(Cp^*)Rh(PMe_3)]$[23].

Obtaining the temperature dependence of $\Delta\Delta G^{\ddagger}$ for the difference in transfer of aryl and methyl groups permits calculation of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ (Table 7.7). A plot of $\Delta\Delta G^{\ddagger}$ against T should give rise to a linear plot of gradient $\Delta\Delta S^{\ddagger}$ and a non-zero intercept coresponding to $\Delta\Delta H^{\ddagger}$ (Fig. 7.6). Values of 1.2 kJ mol^{-1} and 44.6 J K^{-1} mol^{-1} were obtained for $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ respectively. As the temperature is increased, β-aryl transfer becomes correspondingly more favourable, again confirming that this process has a more favourable entropy of activation than does β-methyl transfer.

Table 7.7 : *Temperature Dependency of* $\Delta\Delta G^{\ddagger}$.

T / K	$\Delta\Delta G^{\ddagger}$ / kJ mol^{-1}
358	14.8
363	15.0
368	15.2
373	15.4
378	15.7
383	15.9

On the other hand, comparison of activation parameters for these processes when L = PPh_2Me (Table 7.6; Fig.7.7) indicates that the converse is true, $\Delta\Delta G^{\ddagger}$ = 5.7 kJ mol^{-1} in favour of methyl transfer. Since $\Delta S^{\ddagger}$ does not vary between the two processes, the difference in reactivity must be enthalpic in origin. This result is anomalous for two reasons :-

(i) A phenyl group is known to be a better migrating species than a methyl group; this point is exemplified by the difference in reactivity between $(PPh_3)_2Pt(CH_2SiMe_2Ph)_2$ and $(PPh_3)_2Pt(CH_2SiMe_3)_2$.

(ii) If in this case alkyl migration is favoured over aryl transfer, why does aryl transfer occur selectively for $(PPh_2Me)_2Pt(CH_2SiMe_2Ph)_2$, when even statistically methyl migration would be favourable?

For greater clarification of the discrimination of aryl and alkyl transfer, it would be necessary to study mixed complexes of the type *cis*-$(PR_3)_2Pt(CH_2SiMe_2Ph)(CH_2SiMe_3)$. In such compounds direct comparison between methyl and phenyl migration may be determined.

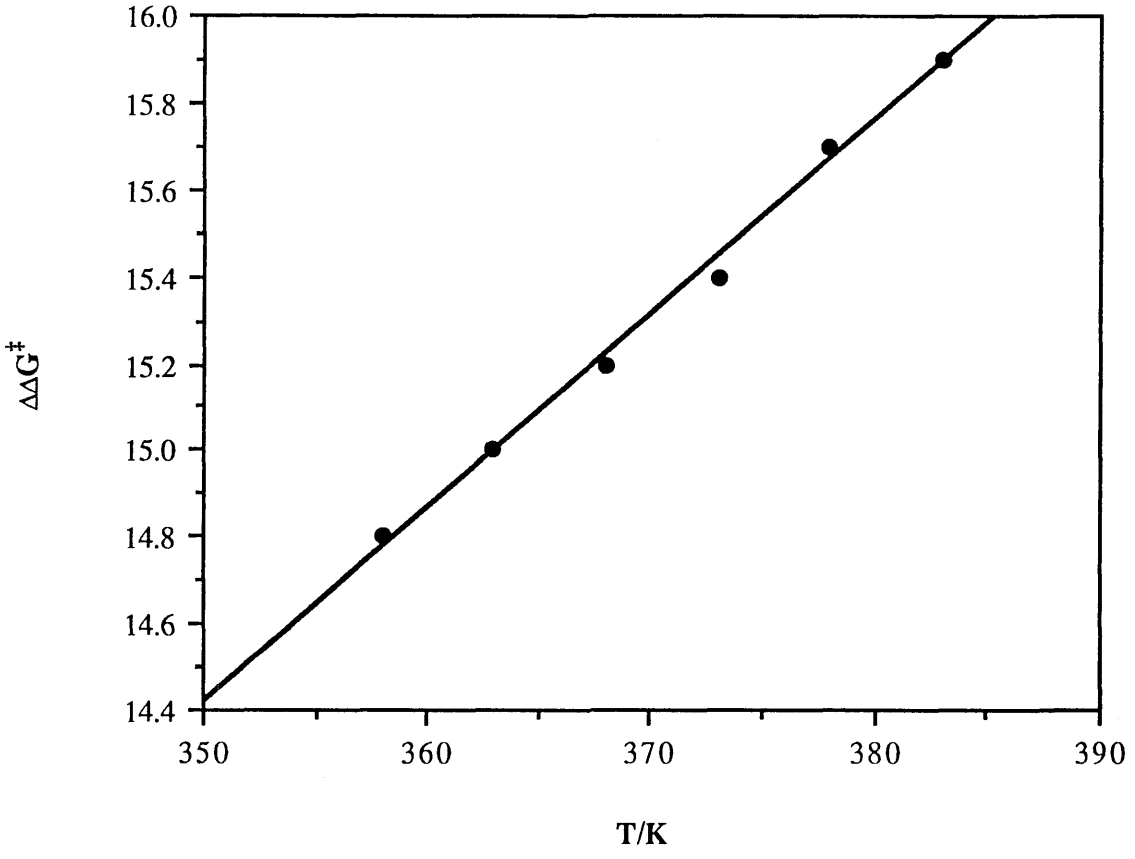


Fig. 7.6 : *Temperature Variation of* $\Delta\Delta G^{\ddagger}$.

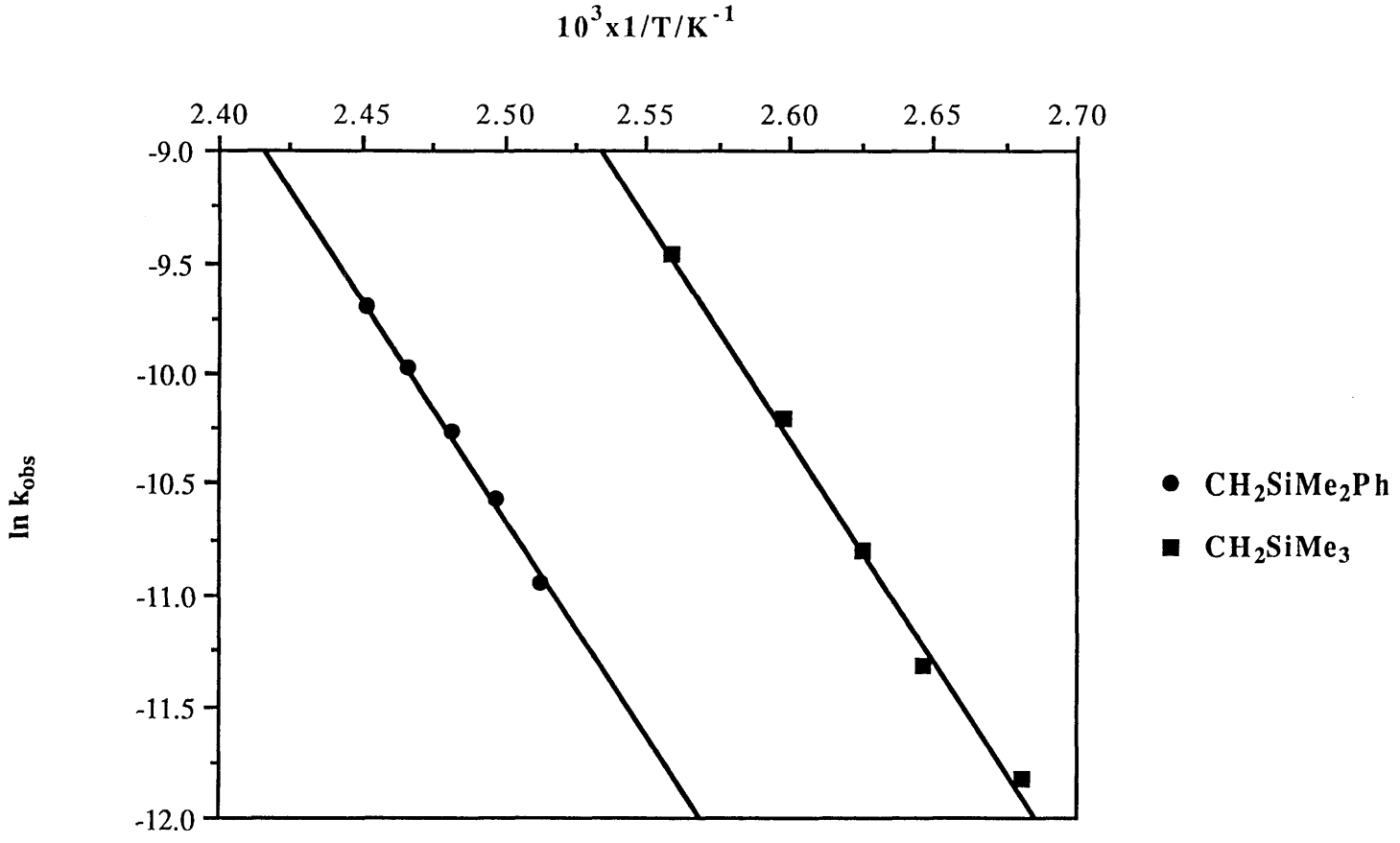


Fig. 7.7 : *Comparative Arrhenius Data for* $(PPh_2Me)_2PtR_2$ *[R =* CH_2SiMe_3, CH_2SiMe_2Ph*].*

7.2.2. *Thermolytic Rearrangement of* cis-bis-*(phosphine)(neopentyl)-(trimethylsilylmethyl)platinum(II).*

7.2.2.1. Introduction.

Thermal isomerisation of $(PEt_3)_2Pt(CH_2SiMe_3)_2$ by β-methyl transfer occurs more readily than metallacyclisation of the neopentyl analogue. Comparison of the reactivity of *bis*-(sila-neophyl) complexes with their dineophyl counterparts, however, clearly indicates that δ-C-H activation is less energetic than transfer of an aryl group. Further evidence is presented from the study of mixed (neophyl)(sila-neophyl)platinum(II) complexes, where only metallacyclisation is observed.

As an additional probe of the generality of alkyl or aryl migration from silicon to platinum and also in an effort to understand the differences in reactivity between alkyl and β-sila-alkyl fragments, complexes containing one trimethylsilylmethyl and one neopentyl ligand were prepared and thermolysed.

7.2.2.2. Spectroscopic Characteristics of Mixed (neopentyl)(trimethylsilylmethyl)platinum(II) complexes.

A numbering convention, similar to that for the mixed (neophyl)(sila-neophyl) complexes is employed (Fig. 7.8). Ligand hydrogen and carbon atoms *trans* to the neopentyl group are designated $H_{n'}$ and $C_{n'}$ respectively.

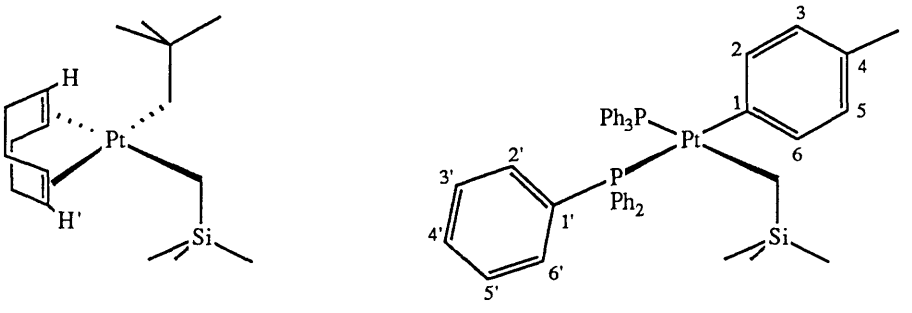


Fig. 7.8 : *N.M.R. Numbering Conventions for* $L_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

Common ^1H N.M.R. features of these mixed (neopentyl)(trimethylsilylmethyl) derivatives (Table 7.8) are the characteristic singlet near 0.0 ppm, generally slightly upfield of TMS, for the methyl hydrogens of the trimethylsilylmethyl group and a singlet resonance at *ca.* 1.0 ppm corresponding to the methyl groups of the neopentyl fragment Also distinctive are the two resonances associated with the methylene protons. In the diene complex these appear as 1:4:1 "triplets", as a result of coupling to ^{195}Pt. For L = PEt_3, the

Table 7.8 : *^1H N.M.R. Characteristics of (neopentyl)(trimethylsilylmethyl)platinum(II) and Related Complexes with Diene and P-Donor Ligands.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]			δ ^{1}H ppm : Ancillary ligands (J_{Pt-H}) / Hz [*Assignment*]
	Pt-CH_2	E-CH_3	Aromatic	
(cod)Pt(CH_2CMe_3)(CH_2SiMe_3)[a]	1.06 (**95.9**) [*CH_2-Si*] 1.66 (**90.1**) [*CH_2-C*]	0.16 [*Si-CH_3*] 1.01 (**3.8**) [*C-CH_3*]	-	2.10-2.30 m, [*CH_2, CH_2'*]; 4.69 "t", (**42.1**) [*CH*]; 4.82 "t", (**40.4**) [*CH'*]
(PEt_3)$_2$Pt(CH_2CMe_3)(CH_2SiMe_3)[a]	0.53 (**77.7**) [*CH_2-Si*] 1.41 (**67.5**) [*CH_2-C*]	-0.04 [*Si-CH_3*] 0.99 [*C-CH_3*]	-	0.97-1.09 m, [*P-CH_2CH_3*]; 1.68-1.85 m, [*P-CH_2CH_3*]
(PPh_3)$_2$Pt(CH_2CMe_3)(CH_2SiMe_3)[a]	0.78 b [*CH_2-Si*] 1.51 b [*CH_2-C*]	-0.15 [*Si-CH_3*] 0.81 [*C-CH_3*]	-	7.04 m, [*H_2, H_6*]; 7.17-7.24 m, [*H_3, $H_{3'}$, H_4,$H_{4'}$, H_5, $H_{5'}$*]; 7.59 m, [*$H_{2'}$, $H_{6'}$*]

Table 7.8 : (continued)

$(cod)Pt(CH_2SiMe_3)(C_6H_4\text{-}4\text{-}Me)$[c]	0.81 (**97.8**)	-0.30 [*Si-CH*$_3$]	2.19 [*Ar-CH*$_3$]; 6.86 d, [*H*$_3$, *H*$_5$] ($J_{H_2\text{-}H_3}$=7.4 Hz); 7.10 d, (**60.2**) [*H*$_2$, *H*$_6$]	2.12-2.46 m, [*CH*$_2$]; 4.61 "t", (**41.7**) [*CH*]; 5.04 "t", (**38.8**) [*CH'*]
$(PPh_3)_2Pt(CH_2SiMe_3)(C_6H_4\text{-}4\text{-}Me)$[a]	0.46 (**85.6**) ($J_{H\text{-}P_{Trans}}$=13.2 Hz) ($J_{H\text{-}P_{Cis}}$ = 7.8 Hz)	-0.68 [*Si-CH*$_3$]	2.02 [*Ar-CH*$_3$]; 6.38 d, [*H*$_3$, *H*$_5$] ($J_{H_2\text{-}H_3}$=6.6 Hz); 6.93 t"t", (**58.1**) [*H*$_2$, *H*$_6$]	6.99 m, [*H*$_2$, *H*$_{2'}$, *H*$_6$, *H*$_{6'}$]; 7.12 m, [*H*$_3$, *H*$_4$, *H*$_5$]; 7.21 m, [*H*$_{3'}$, *H*$_{4'}$, *H*$_{5'}$];

a :- chloroform-d[1]

b :- broad resonance

c :- benzene-d[6]

Table 7.9 : *^{13}C N.M.R. Characteristics of (neopentyl)(trimethylsilylmethyl)platinum(II) and Related Complexes with Diene and P-Donor Ligands.*

Complexes	δ ^{13}C ppm : Hydrocarbyl ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{P-C}) / Hz			δ ^{13}C ppm : Ancillary ligands (J_{Pt-C}) / Hz [*Assignment*] (J_{P-C}) / Hz
	Pt-CH_2	E-CH_3	Other	
$(cod)Pt(CH_2CMe_3)(CH_2SiMe_3)$ $[CDCl_3]$	14.12 (**745.4**) [CH_2-*Si*] 36.57 (**843.3**) [CH_2-*C*]	3.40 (**32.8**) [*Si*-CH_3] 35.19 (**47.9**) [*C*-CH_3]	36.19 (**10.6**) [***C***-CH_3]	29.42 [CH_2]; 30.25 [CH_2']; 96.11 (**69.6**) [*CH*]; 101.62 (**39.9**) [*CH'*]
$(PEt_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ $[CDCl_3]$	7.21, 8.08 (**602.3**) ($J_{C-P_{Trans}}$=89.3 Hz) ($J_{C-P_{Cis}}$ = 6.3 Hz) [CH_2-*Si*] 31.61, 33.21 (**682.6**) ($J_{C-P_{Trans}}$=100.5 Hz) ($J_{C-P_{Cis}}$ = 7.3 Hz) [CH_2-*C*]	4.29 (**29.3**) [*Si*-CH_3] 35.68 (**41.9**) [*C*-CH_3]	36.22 [***C***-CH_3] (***2.5***)	8.39 (**19.6**) [*P*-CH_2CH_3] (***18.0***); 16.40 (**18.0**) [*P*-***C'***H_2CH_3] (***22.7***); 18.32 (**24.1**) [*P*-CH_2CH_3] ($J_{C-P_{Trans}}$=24.0 Hz; $J_{C-P_{Cis}}$ =2.5 Hz)

Table 7.9 : (continued)

$(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ [$CDCl_3$]	8.30, 9.62 (**602.3**) ($J_{C\text{-}P_{Trans}}$=92.2 Hz) ($J_{C\text{-}P_{Cis}}$ = 4.8 Hz) [CH_2-*Si*] 34.19, 35.69 (**698.3**) ($J_{C\text{-}P_{Trans}}$=98.1 Hz) ($J_{C\text{-}P_{Cis}}$ = 5.3 Hz) [CH_2-*C*]	4.50 (**30.5**) [*Si*-CH_3] 35.00 (**42.3**) [*C*-CH_3] (***4.1***)	36.03 [*C*-CH_3]	127.27 [C_3, C_5]; 127.41 [$C_{3'}$, $C_{5'}$]; 128.89 [C_4]; 129.20 [$C_{4'}$]; 133.56 (**19.4**) [C_1] (***41.1***); 134.19 (**16.7**) [$C_{1'}$] (***33.9***); 134.86 (**18.7**) [C_2, $C_{2'}$, C_6, $C_{6'}$] (***18.5***)
(cod)Pt(CH_2SiMe_3)(C_6H_4-4-Me) [$CDCl_3$]	18.01 (**712.2**)	2.48 (**30.2**) [*Si*-CH_3]	20.83 [*Ar*-CH_3]; 128.31 (**75.9**) [C_3, C_5]; 131.72 (**10.9**) [C_4]; 135.05 (**35.8**) [C_2, C_6]; 151.90 (**1083.6**) [C_1]	29.59 [CH_2]; 30.29 [CH_2']; 99.35 (**60.8**) [*CH*]; 102.59 (**48.4**) [*CH'*]
$(PPh_3)_2Pt(CH_2SiMe_3)(C_6H_4$-4-Me) [$CDCl_3$]	11.84, 13.69 (**599.3**) ($J_{C\text{-}P_{Trans}}$=84.1 Hz) ($J_{C\text{-}P_{Cis}}$ = 4.2 Hz)	2.54 (**26.0**) [*Si*-CH_3]	20.69 [*Ar*-CH_3]; 127.04 (**78.5**) [C_3, C_5]; 137.70 (**35.2**)[C_2, C_6] (***2.5***); 133.88 [C_4]; 154.78 (**988.8**) [C_1] ($J_{C\text{-}P_{Trans}}$=105.6 Hz)	127.10 [C_3, C_5] (***8.0***); 127.50 [$C_{3'}$, $C_{5'}$] (***10.0***); 128.78 [C_4]; 129.04 [$C_{4'}$]; 131.16 (**16.1**) [$C_{1'}$] (***6.5***); 131.42 (**24.1**) [C_1] (***9.6***); 134.02 (**17.6**) [C_2, C_6] (***11.6***); 134.74 (**15.6**) [$C_{2'}$, $C_{6'}$] (***12.6***);

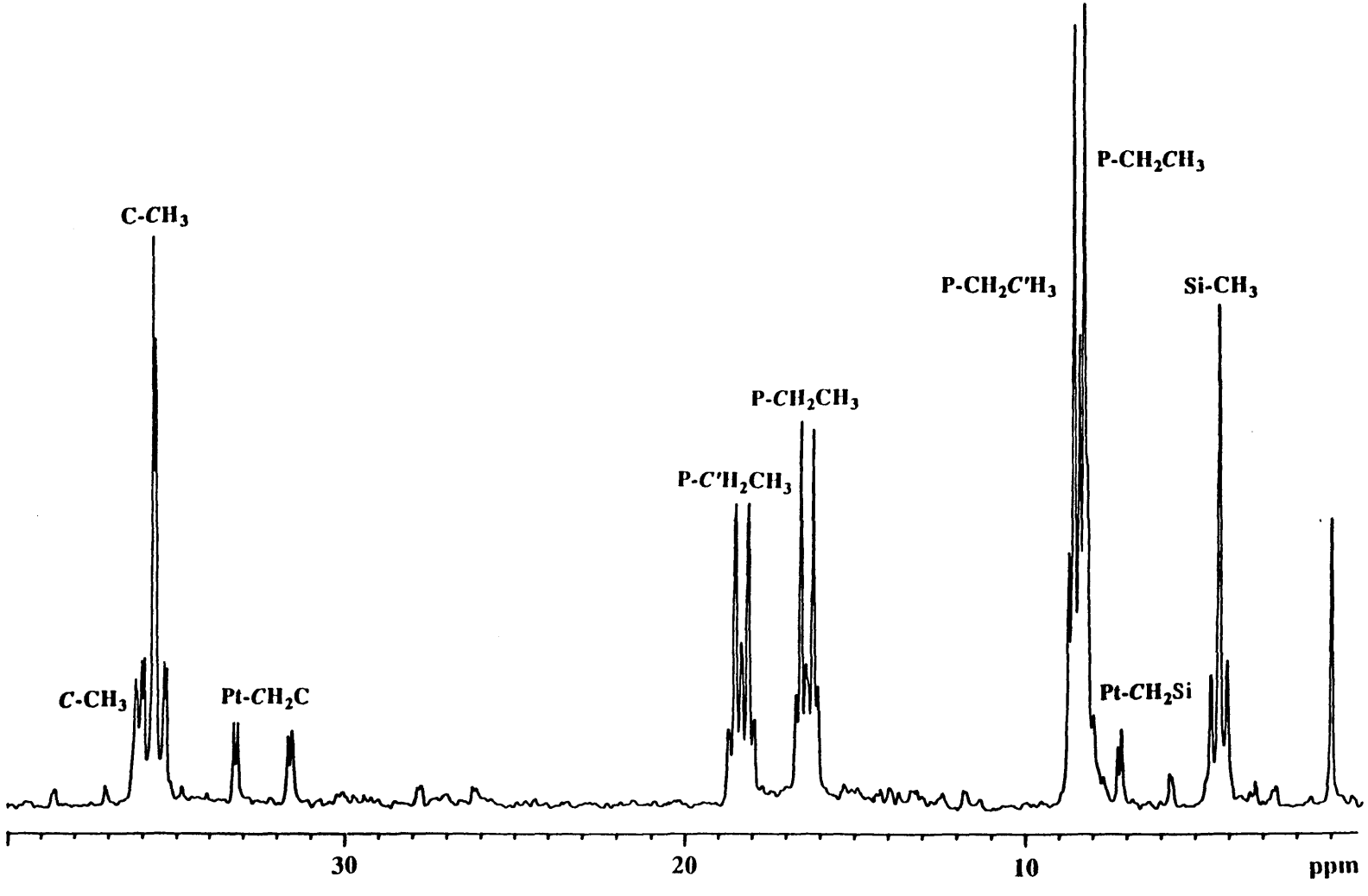


Fig. 7.9 : *^{13}C N.M.R. of $(PEt_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.*

Table 7.10 : *^{31}P N.M.R. Characteristics of* cis-$L_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ *and Related Complexes.*

Complex	δ^a / ppm	J_{Pt-P} / Hz	J_{P-P} / Hz
$(PPh_3)_2Pt(CH_2CMe_3)_2$[b]	21.62	1641.6	-
$(PPh_3)_2Pt(CH_2CMe_2CH_2)$[b]	26.91	1846.3	-
$(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$[c]	22.63	2177.6 (*trans* to β-Si)	8.9
	25.90	1502.0 (*trans* to β-C)	
$(PEt_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$[d]	1.93	2109.0 (*trans* to β-Si)	11.1
	4.37	1561.8 (*trans* to β-C)	
$(PPh_3)_2Pt(CH_2SiMe_3)(C_6H_4\text{-}Me)$[d]	23.67	2096.8 (*trans* to β-Si)	11.1
	24.34	1679.2 (*trans* to aryl)	

a :- referenced to 85% H_3PO_4 / D_2O

b :- benzene-d^6

c :- toluene-d^8

d :- chloroform-d^1

usual "triplet" of quartets is observed for each CH_2 group. $^2J_{Pt-H}$ is 77.7 Hz and 67.5 Hz for trimethylsilylmethyl and neopentyl respectively. Broad resonances were again obtained for L = PPh_3, demonstrating unresolved coupling between phosphorus and hydrogen nuclei (*vide supra*).

The $^{13}C-\{^1H\}$ N.M.R. characteristics (Table 7.9) of (neopentyl)(trimethylsilylmethyl) complexes are in accord with those expected for a coordinated neopentyl and trimethylsilylmethyl group (Fig. 7.9). The magnitude of $^1J_{Pt-C}$ for the methylene carbon is less than that observed in the parent dialkyl, whereas for the corresponding CH_2 group of trimethylsilylmethyl an increase in $^1J_{Pt-C}$ is observed. This effect, attributed to the modification of steric requirements of neopentyl by its silylmethyl neighbour, closely parallels the trend observed for neophyl and sila-neophyl (See 2.2.3).

^{31}P N.M.R. characteristics (Table 7.10) are consistent with two inequivalent phosphorus nuclei. One phosphorus is *trans* to a group with a relatively high *trans*-influence (CH_2CMe_3) and the other *trans* to a group exerting a weaker *trans*-influence (CH_2SiMe_3).

7.2.2.3. Thermolysis of $L_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

Analysis by ^{31}P N.M.R. spectroscopy of thermochemically degraded toluene-d^8 solutions of $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ at 125°C reveals formation of three new species. After 30 minutes, the parent dialkyl and a new species **A** are the only platinum-containing compounds present. **A** has ^{31}P N.M.R. characteristics (Table 7.11) consistent with two inequivalent phosphorus nuclei. The size of the coupling constants, nevertheless are unusual. A value of $^1J_{Pt-P}$ of 1433 Hz suggests phosphorus ligated *trans* to an alkyl group with a very strong *trans*-influence. The second phosphorus is *trans* to a fragment exerting a very weak *trans*-influence ($^1J_{Pt-P}$ = 3850.2 Hz). The magnitude of this coupling constant is similar to that observed in $(PPh_3)_2Pt(\eta^2-C_2H_4)$, perhaps implying phosphorus *trans* to a π-bound fragment. After 60 minutes, in addition to the mixed (neopentyl)(trimethylsilylmethyl) complex and **A**, a new compound **B** emerges. The ^{31}P N.M.R. characteristics of **B** are consistent with an asymmetric platinum(II) derivative. Further heating generates a small amount of product **C**, which has only one environment (Fig. 7.10). Thermolysis of a genuine sample of $(PPh_3)_2Pt(CH_2CMe_3)_2$ afforded the metallacyclobutane with ^{31}P N.M.R. characteristics identical to those of **C**. On this basis, **C** was established as the metallacycle, produced *via* γ-C-H abstraction of the neopentyl group.

A kinetic analysis on the products of thermolysis of $(PPh_3)_2(CH_2CMe_3)(CH_2SiMe_3)$ (Fig. 7.11) indicates that the parent dialkyl initially rearranges to unknown **A**. As the reaction proceeds, the concentration of the parent complex diminishes and that of **A** and **B** increase. A small amount of $(PPh_3)_2\overline{Pt(CH_2CMe_2CH_2)}$ is also formed at the expense of **A**, although the amount of

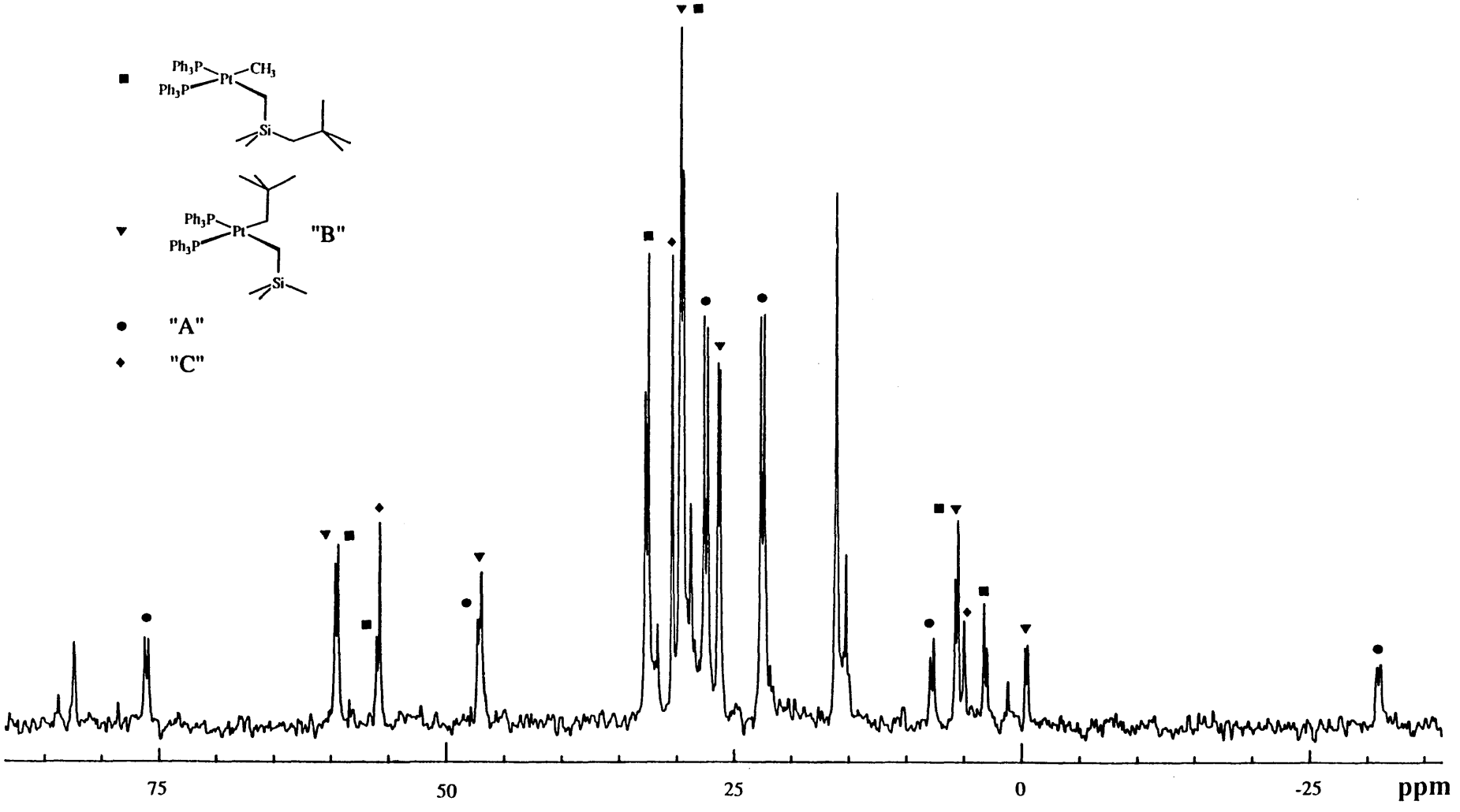


Fig. 7.10 : *^{31}P N.M.R. of the Products formed During Thermolysis of $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.*

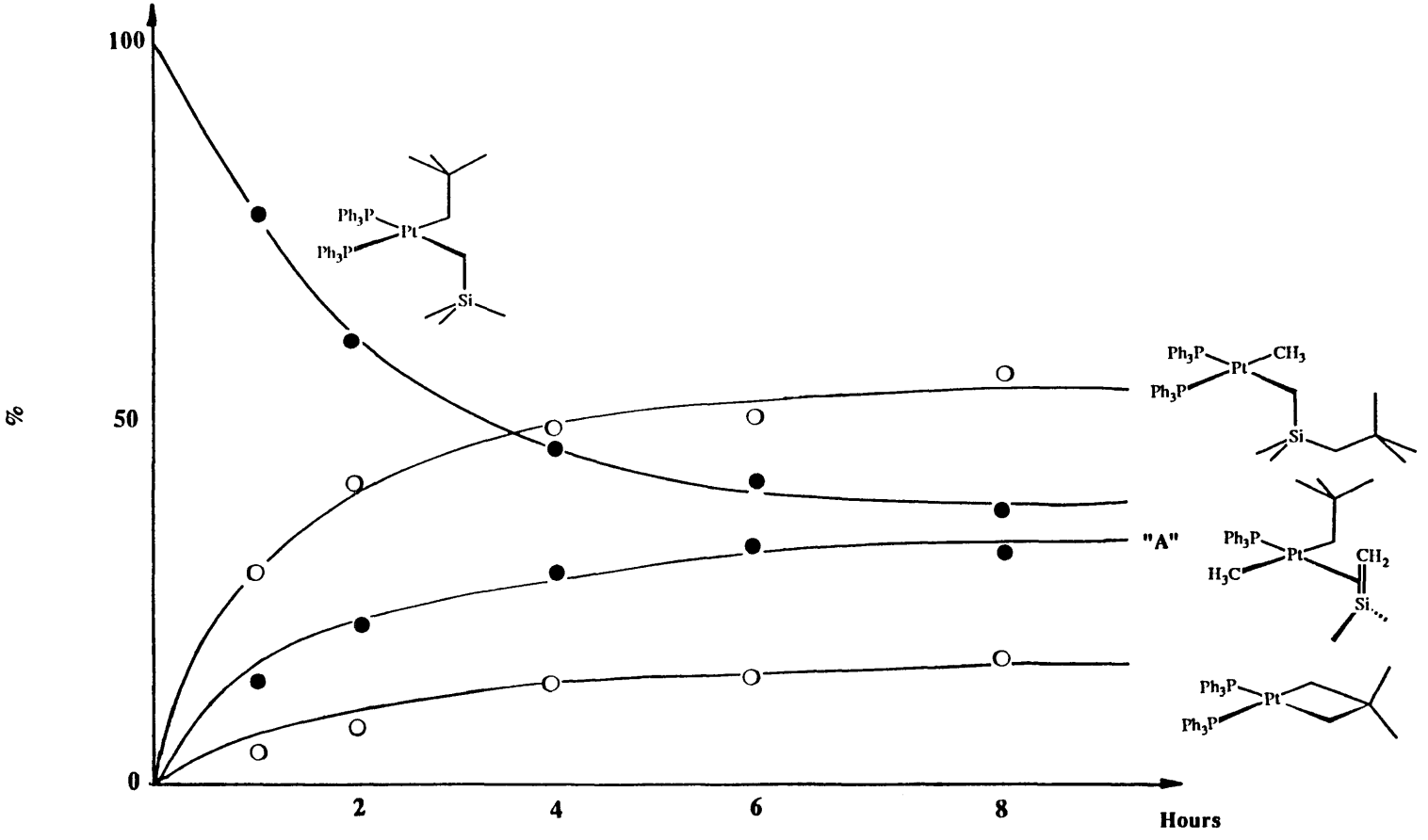


Fig. 7.11 : *Kinetic Analysis of the Products formed During Thermolysis of* $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

Table 7.11 : *^{31}P N.M.R. Characteristics of the Products from Thermolysis of $L_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.*

Complex	δ^a / ppm	J_{Pt-P} / Hz	J_{P-P} / Hz
A	19.15	3850.2	11.1
$(PPh_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMe_2)(CH_2SiMe_3)^b$	23.79	1433.3	
B	25.99	1957.2	8.9
cis-$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)^b$	29.01	1916.3	
C	26.82	1843.2	-
$(PPh_3)_2Pt(CH_2CMe_2CH_2)^b$			
D	-1.10	3659.7	13.3
$(PEt_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMe_2)(CH_2CMe_3)^b$	14.20	1523.8	
E	12.04	3015.1	-
trans-$(PEt_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)^b$			

a :- referenced to 85% H_3PO_4 / D_2O

b :- toluene-d^8

metallacycle never exceeds 13% of the total amount of platinum containing species in solution. Further thermolysis results in the decay of **A** and to a large increase in **B**. Upon complete thermolysis, the only species present are **B**, metallacycle and a small amount of zerovalent $(PPh_3)_nPt$ [n = 3 or 4], presumably generated by the decomposition of the metallacyclobutane, for which there is precedent[7b].

^1H N.M.R. characteristics (Table 7.12) of **B** show some interesting features, notably two multiplets, which exhibit coupling to both ^{31}P and ^{195}Pt nuclei. The resonance at higher field, an apparent triplet corresponding to two hydrogens, is attributed to the methylene group of a β-sila-alkyl fragment. The apparent quartet further downfield, assigned as a platinum-bound methyl group, corresponds to three protons. Also evident are two distinct methyl resonances; a singlet at $\delta = 0.47$ ppm due to Si-CH_3 protons and a signal at 1.12 ppm ascribed as neopentyl methyl hydrogens. In addition at $\delta = 1.10$ ppm a less intense resonance, which has an integral ratio of two protons corresponds to a CH_2 group. The aromatic region confirms the inequivalence of the phosphine ligands. Both

Table 7.12 : *^1H N.M.R. Characteristics of the Products from Thermolysis of* cis-*$(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.*

Complex	δ ^{1}H ppm : Hydrocarbyl ligands (J_{Pt-H}) / Hz [*Assignment*]	δ ^{1}H ppm : Ancillary ligands [*Assignment*]
A	0.20 s, [*Si-CH_3*];	6.92-7.02 m, [*H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$*];
$(PPh_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMe_2)(CH_2CMe_3)$[a]	0.99 m[b], [*Pt-CH_3*];	7.43-7.48 m, [*H_2, H_6*];
	1.26 s, [*C-CH_3*];	7.57-7.65 m, [*$H_{2'}$, $H_{6'}$*]
	1.74 m, (**75.3**) [*Pt-CH_2CMe_3*]	
B	0.47 s, [*Si-CH_3*];	6.77-6.95 m, [*H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$*];
cis-$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$[a]	0.66 m, (**82.9**) [*Pt-CH_2*];	7.33-7.41 m, [*$H_{2'}$, $H_{6'}$*];
	1.04 m, (**63.6**) [*Pt-CH_3*];	7.50-7.58 m, [*H_2, H_6*]
	1.10 s, [*Si-CH_2-C*];	
	1.12 s, [*C-CH_3*]	
C	1.23 s, [*C-CH_3*];	6.18-6.76 m, [*H_3, H_4, H_5*];
$(PPh_3)_2Pt(CH_2CMe_2CH_2)$[a]	2.44 m, (**86.0**) [*Pt-CH_2*]	7.80-7.86 m, [*H_2, H_6*]

Table 7.12 : (continued)

E *trans*-$(PEt_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$[a]	0.13 s, [*Si-CH*$_3$]; c [*Pt-CH*$_3$]; c [*Pt-CH*$_2$]; 1.15 s, [*C-CH*$_3$]; 1.23 s, [*Si-CH*$_2$*-C*]	0.92-0.99 m, [*P-CH*$_2$***CH***$_3$]; 1.75-1.82 m, [*P-CH*$_2$***CH***$_3$]

a :- toluene-d^8

b :- satellites obscured

c :- obscured by parent complex

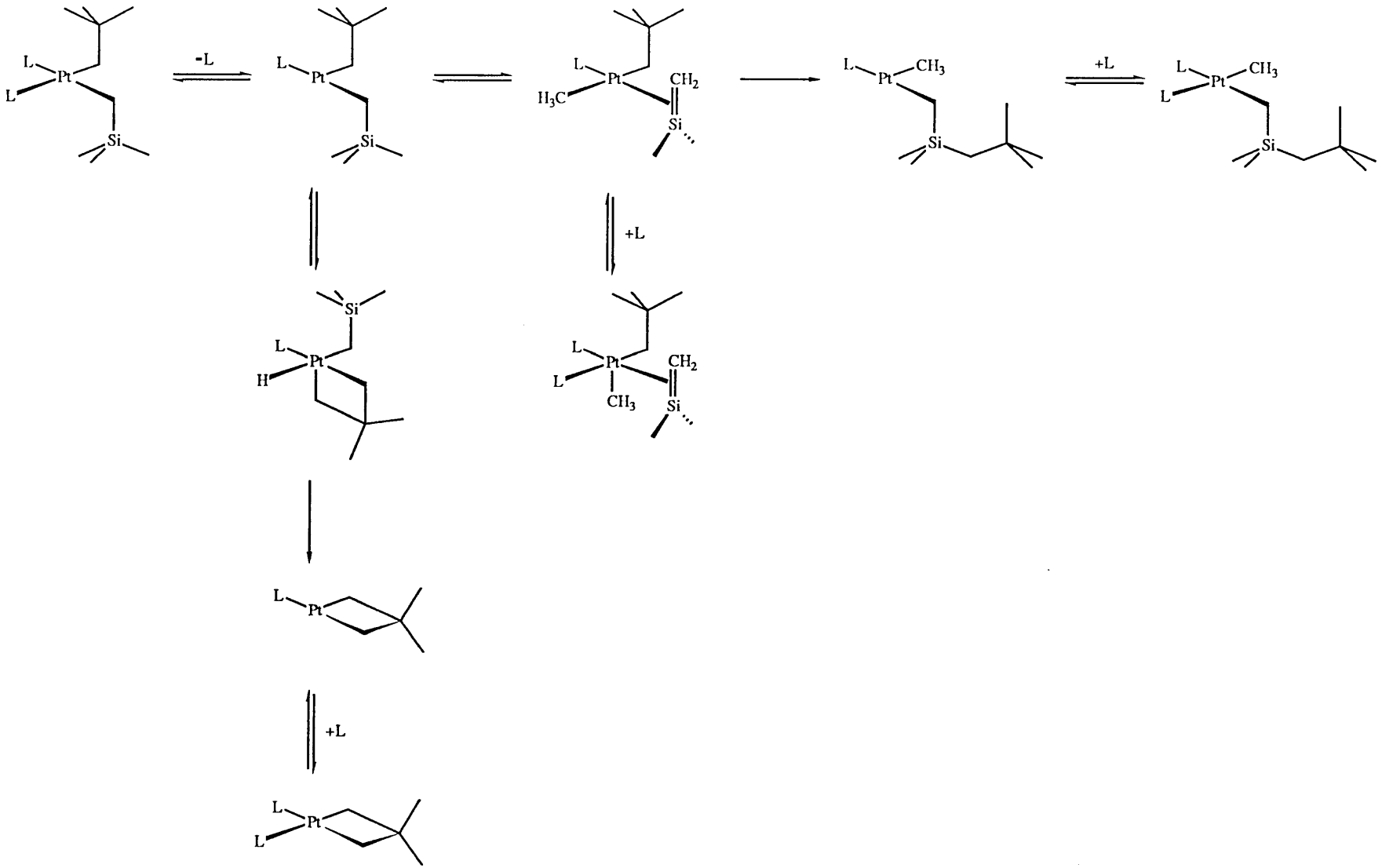
^{31}P and ^{1}H N.M.R. characteristics of **B** are similar to those observed for *cis*-$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)$, suggesting that **B** is *cis*-$(PPh_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$, derived by β-$CH_3$ transfer from silicon to platinum.

A also displays notable ^{1}H N.M.R features (Table 7.12). The singlet at 1.26 ppm and the multiplet with platinum satellites centred at 1.74 ppm are characteristic of a neopentyl group. In addition, a further multiplet at higher field, assignable to a bound methyl group is also observed, though the satellites are obscured by other species. A new signal due to silicon-methyl groups is also evident. The spectroscopic characteristics of **A** are consistent with a pentacoordinate platinum(II) species. Although unequivocal proof is not yet complete, on the basis of the foregoing spectroscopic evidence, **A** is tentatively assigned as an η^2-silene complex, $(PPh_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMe_2)(CH_2CMe_3)$. Pentacoordinate platinum(II) compounds bearing a coordinated ethylene and with nitrogen donor ligands have been reported[131]; phosphine analogues remain unobserved to date.

A mechanistic scheme, consistent with the observations appears in Scheme. 7.6. Initial dissociation of one triphenylphosphine is likely to be a prerequisite, as is often the case for square-planar platinum(II). The resultant tricoordinate species undergoes methyl migration forming the η^2-silene intermediate, which may recoordinate phosphine giving rise to $(PPh_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMe_2)(CH_2CMe_3)$. (It is also possible that **A** is formed directly from the 4-coordinate parent complex). Alternatively, it may undergo essentially irreversible insertion into the CH_2 group of neopentyl, generating the (methyl)(sila-alkyl) complex **B**. A further option for the 3-coordinate intermediate is oxidative addition of a neopentyl γ-C-H bond forming a hydridoplatinum(IV) intermediate, which reductively eliminates neopentane and generates the metallacyclobutane. Metallacyclisation, in this case, evidently competes with β-methyl transfer, although it is energetically less favoured.

In contrast to $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$, toluene-$d^8$ solutions of $(PEt_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ at 120 °C do not give rise to *cis*-$(PEt_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$ as major product. A complex, **D**, with ^{31}P N.M.R. characteristics similar to **A** [L = PPh_3] is observed, suggesting that $(PEt_3)_2Pt(CH_3)(\eta^2\text{-}CH_2SiMe_2)(CH_2CMe_3)$ is formed, although it is only present in small quantities (<18%). The major product of the reaction is **E**, whose ^{31}P N.M.R. characteristics consist of a 1:4:1 "triplet" with $^{1}J_{Pt\text{-}P} = 3015.1$ Hz, strongly implying *trans* geometry; *cf.* *trans*-$(PEt_3)_2PtPh_2$, $^{1}J_{Pt\text{-}P} = 2824$ Hz; *trans*-$(PEt_3)_2Pt(2\text{-}C_6H_4CMe_3)_2$, $^{1}J_{Pt\text{-}P} = 3075$ Hz and *trans*-$(PEt_3)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)$, $^{1}J_{Pt\text{-}P} = 3148$ Hz.

Analysis of the ^{1}H N.M.R. spectrum of a solution containing this new species and comparison with the spectrum of the starting material enables peaks due to **E** to be assigned. Particularly characteristic of this derivative are the multiplets due to phosphine methyl and methylene groups, which are much less complicated than those observed for the parent complex; a singlet at $\delta = 0.13$ ppm corresponding to silicon-methyl groups and



Scheme. 7.6 : *Proposed Mechanism for the Formation of the Observed Products During Thermolysis of* $(PPh_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$.

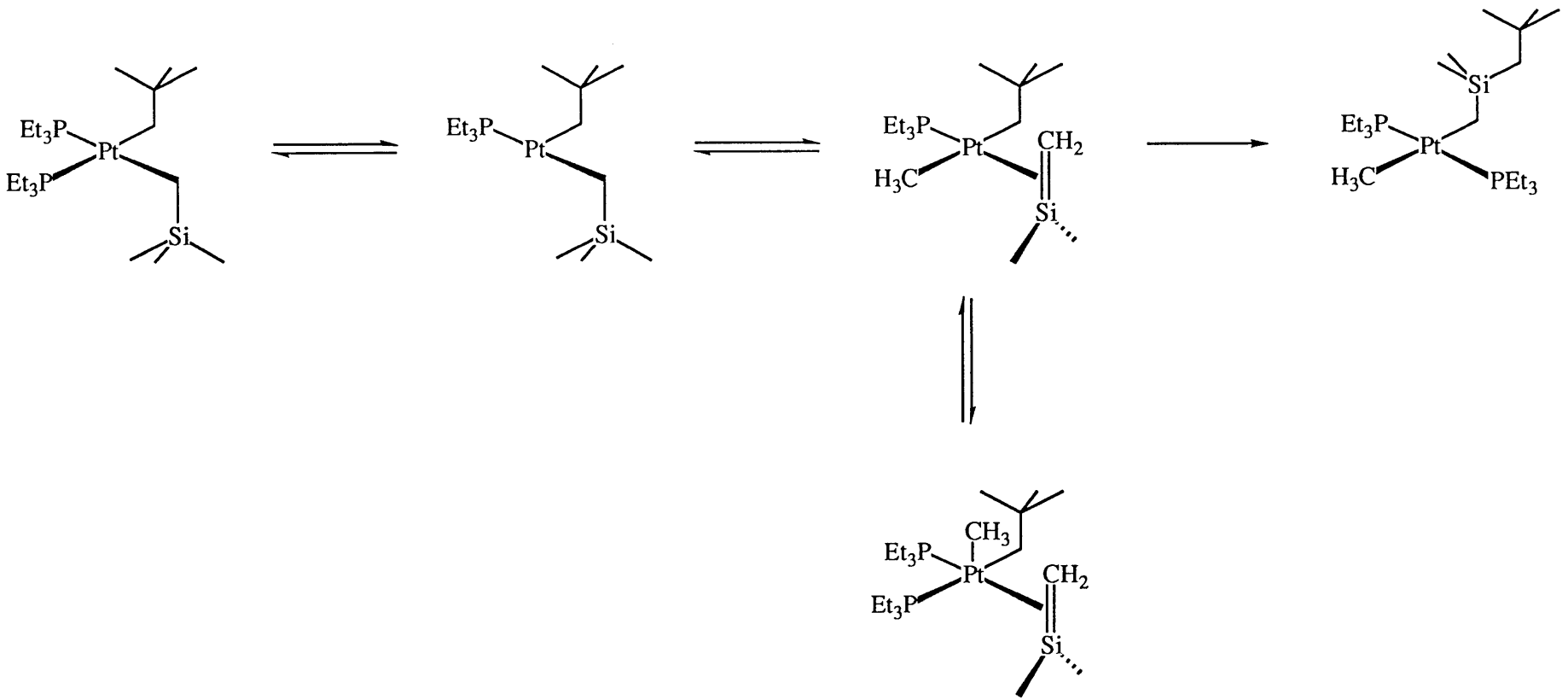
two further singlets at $\delta = 1.15$ and 1.23 ppm, ascribable to neopentyl CH_3 and CH_2 groups respectively, are also evident. Unfortunately any platinum bound CH_2 or CH_3 groups were obscured by resonances due to starting material. The ratio of Si-CH_3 to P-$CH_2\boldsymbol{CH_3}$ groups is 1:3, confirming the presence of two triethylphosphine groups. On the basis of this ^1H and ^{31}P N.M.R. evidence, **E** is proposed to be *trans*-$(PEt_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$. There are no well characterised examples of *trans-bis*-(phosphine)-*bis*-(alkyl)platinum(II), although a few examples of *trans*-$(PR_3)_2Pt$(alkyl)(hydrocarbyl) complexes do exist (*vide supra*).

Displayed in Scheme. 7.7 is the proposed mechanism for formation of *trans*-$(PEt_3)_2Pt(CH_3)$ $(CH_2SiMe_2CH_2CMe_3)$. The loss of one phosphine ligand to form a tricoordinate T-shaped intermediate is followed by methyl transfer from silicon to platinum, resulting in an η^2-silene intermediate. As for L = PPh_3, recoordination of PEt_3 results in formation of **D**. On the other hand, insertion of the η^2-silene intermediate into the neopentyl Pt-CH_2 bond generates the thermodynamically favoured *trans* product. Significantly, no detectable amount of $(PEt_3)_2\overline{Pt(CH_2CMe_2CH_2)}$ is observed. In contrast to the corresponding mixed (neophyl)(sila-neophyl) complex, $(PEt_3)_2Pt(CH_2CMe_3)(CH_2SiMe_3)$ preferentially undergoes β-carbon transfer in favour of γ-C-H activation.

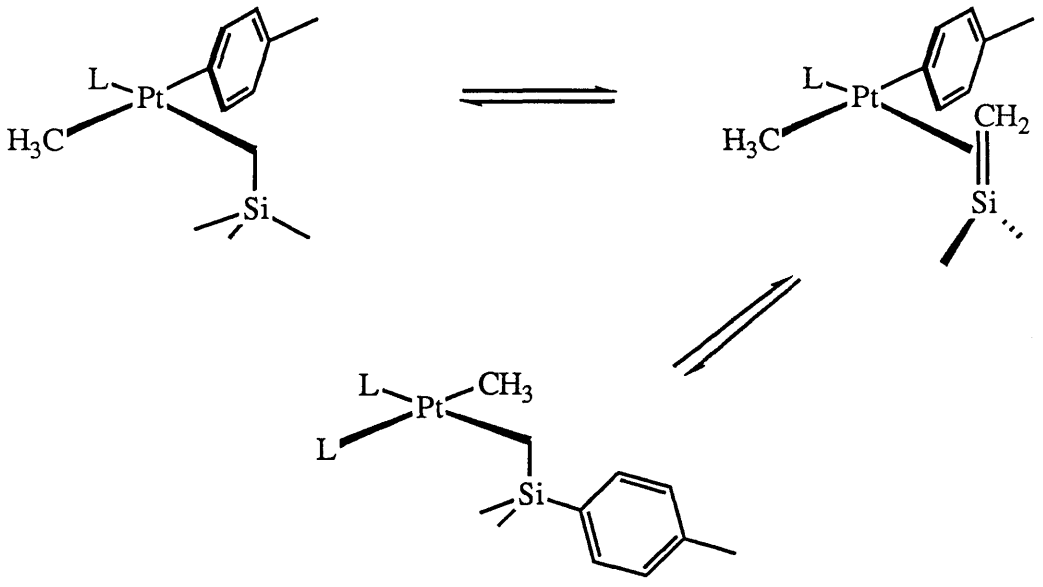
7.2.3. Thermolytic Rearrangement of cis-bis-*(triphenylphosphine)(p-tolyl)(trimethylsilylmethyl)platinum(II).*

Preliminary investigations indicate that thermolysis of $(PPh_3)_2Pt(C_6H_4$-4-Me$)(CH_2SiMe_3)$ induces isomerisation yielding the (methyl)[dimethyl(4-methylphenyl)silylmethyl]platinum(II) complex, $(PPh_3)_2Pt(CH_3)(CH_2SiMe_2C_6H_4$-4-Me). The ^{31}P N.M.R. consists of an ABM quartet with satellites; $\delta = 25.99$, 28.77 ppm; $^1J_{Pt\text{-}P} = 1939.5$ Hz; 1971.7 Hz, $^2J_{P\text{-}P} = 10.0$ Hz and is consistent with expected values for complexes of this type. Only small amounts of the (methyl)(4-methylsila-neophyl) complex are observed, due to the insolubility of this species in toluene-d^8, hence ^1H N.M.R. characteristics have been unobtainable so far. This reaction proceeds at temperatures in excess of 125°C, implying that methyl transfer is a relatively high energy process.

The data obtained indicate that an equilibrium between the (*p*-tolyl)(sila-neopentyl) and (methyl)(4-methylsila-neophyl) complexes, by way of an η^2-silene intermediate, is in operation, with the equilibrium strongly in favour of the former complex (Scheme. 7.8). An estimate of the equilibrium constant for this reaction could not be determined, since the amount of $(PPh_3)_2Pt(CH_3)(CH_2SiMe_2C_6H_4$-4-Me) formed could not be quantified accurately. As a direct consequence of precipitation of this product, β-methyl transfer was further induced. Formation of a significant amount of zerovalent platinum species, however, clearly indicates requirement of considerable energy for transfer to occur.



Scheme. 7.7 : *Proposed Mechanism for* cis-trans-*Isomerisation of* $(PEt_3)_2Pt(CH_3)(CH_2SiMe_2CH_2CMe_3)$.



Scheme. 7.8 : *Proposed Scheme for Formation of* $(PPh_3)_2Pt(CH_3)(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)$.

7.2.4. Further Studies.

This work has demonstrated how variation of the ancillary ligand and/or the migrating group, R, can appreciably alter the intimate mechanism of β-methyl transfer by platinum(II). Further studies involving variation of the migrating group, to establish a pattern of migratory aptitude, should lead to useful information about both electronic and steric controls on R transfer, which are as yet poorly understood.

7.3. Experimental.

7.3.1. General.

Elemental analyses and N.M.R. spectra were obtained as described previously (*vide supra*). All reactions were carried out under nitrogen or argon unless otherwise noted using standard anaerobic techniques. Solvents were distilled under nitrogen prior to use (See 2.3).

(cod)Pt(CH_2CMe_3)$_2$[7b], (cod)Pt(CH_2SiMe_3)$_2$[41], (nbd)Pt(CH_2SiMe_3)$_2$[41], (cod)Pt(CH_2SiMe_3)Cl[41] and (cod)Pt(CH_2SiMe_3)(C_6H_4-4-CH_3)[50] were all prepared by previously established routes.

7.3.2. Syntheses.

Preparation of cis-bis-*(triphenylphosphine)*-bis-*(trimethylsilylmethyl)platinum(II).*

To a solution of (nbd)Pt(CH_2SiMe_3)$_2$ (0.20g, 0.43 mmol) in diethyl ether (8 cm^3) was added triphenylphosphine (0.23g, 0.87 mmol) and the mixture allowed to stand at ambient temperature for 7 days. Removal of the solvent *in vacuo* left a pale yellow solid. The product was obtained as a colourless crystalline solid by recrystallisation from toluene (2 cm^3) and *n*-hexane (1 cm^3).
(Yield : 0.34g, 0.38 mmol, 90%)

[*Analysis* : Found C=59.58%, H=5.87%; Calculated C=59.71%, H=5.86%].

Preparation of cis-bis-*(triphenylphosphine-d^{15})*-bis-*(trimethylsilylmethyl)platinum(II).*

The product was synthesised by the procedure described above, affording colourless blocks from toluene (2 cm^3) and *n*-hexane (1 cm^3).
(Yield : 0.36g, 0.40 mmol, 95%).

[*Analysis* : Found C=56.94%, H=5.57%; Calculated C=57.17%, H=5.67%].

Preparation of cis-bis-*(triphenylphosphine)*-bis-*(neopentyl)platinum(II).*

To a solution of (cod)Pt(CH_2CMe_3)$_2$ (0.12g, 0.28 mmol) in Et_2O (5 cm^3) was added triphenylphosphine (0.15g, 0.56 mmol). After 48 hours stirring at ambient temperature, the solvent was removed *in vacuo* leaving a white microcrystalline solid, which could be recrystallised from toluene (3 cm^3).
(Yield : 0.22g, 0.26 mmol, 93%)

[*Analysis* : Found C=63.85%, H=6.14%; Calculated C=64.10%, H=6.08%].

Preparation of (cycloocta-1,5-diene)(neopentyl)(trimethylsilylmethyl)platinum(II).

To a stirred suspension of (cod)Pt(CH_2SiMe_3)Cl (0.88g, 2.06 mmol) in diethyl

ether (10 cm^3) at -78°C was added dropwise a solution of $BrMgCH_2CMe_3$ (3.10 mmol) in Et_2O (20 cm^3). The reaction mixture was gradually allowed to warm to room temperature, then stirred for a further 12 hours. The resulting suspension was cooled to -78°C and hydrolysed with saturated ammonium chloride solution (10 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (2 x 10 cm^3). The ether extracts were combined, dried over $MgSO_4$ and decolourised with activated charcoal. The mixture was filtered and removal of the ether *in vacuo* afforded a white solid. An analytically pure sample was obtained by recrystallisation from diethyl ether (2 cm^3) and *n*-hexane (2 cm^3).
(Yield : 0.71g, 1.54 mmol, 75%)

[*Analysis* : Found C=43.92%, H=7.54%; Calculated C=44.23%, H=7.42%].

Preparation of cis-bis-*(triphenylphosphine)(neopentyl)(trimethylsilylmethyl)platinum(II).*

Triphenylphosphine (0.22g, 0.84 mmol) was added to a solution of (cod)Pt(CH_2CMe_3)(CH_2SiMe_3) (0.20g, 0.42 mmol) in diethyl ether (8 cm^3) and allowed to stand at ambient temperature for 10 days. The solvent was removed *in vacuo* to give a pale yellow solid, which was dissolved in the minimum amount of toluene (2 cm^3), *n*-hexane (1 cm^3) added and cooled to -20°C. Filtration, washing the solid with *n*-hexane (2 x 3cm^3) and drying *in vacuo* yielded the product as large colourless plates.
(Yield : 0.31g, 0.32 mmol, 76%)

[*Analysis* : Found C=61.44%, H=5.97%; Calculated C=61.56%, H=5.97%].

Preparation of cis-bis-*(triethylphosphine)(neopentyl)(trimethylsilylmethyl)platinum(II).*

This derivative was prepared from (cod)Pt(CH_2CMe_3)(CH_2SiMe_3) and PEt_3, as colourless prisms, by a similar method to the one described above, except the reaction mixture was allowed to stand at ambient temperature for 5 days.
(Yield : 0.20g, 0.33 mmol, 92%)

[*Analysis* : Found C=42.81%, H=8.91%; Calculated C=42.77%, H=8.89%].

Preparation of cis-bis-*(triphenylphosphine)(4-methylphenyl)(sila-neopentyl)platinum(II).*

Triphenylphosphine (0.165g, 0.62 mmol) was added to a solution of (cod)Pt(CH_2SiMe_3)(C_6H_4-4-CH_3) (0.15g, 0.31 mmol) in diethyl ether (6 cm^3). After 7 days at ambient temperature, the solvent was removed *in vacuo* affording analytically pure product as a white microcrystalline solid.
(Yield : 0.28g, 0.31 mmol, 99%).

[*Analysis* : Found C=62.64%, H=5.40%; Calculated C=62.86%, H=5.39%].

7.3.3. Kinetic Measurements.

Toluene-d^8, supplied by MSD-isotopes, was distilled from sodium and stored under argon prior to use. Thermolyses were carried out in 5mm-diameter medium-walled N.M.R. tubes equipped with sealable Teflon valves. Solutions of the complex to be studied, which were 0.02M with respect to platinum, were prepared and freeze-thaw deoxygenated through five cycles prior to sealing under argon. The tubes were maintained at the desired temperature by immersion in a Haake W13 thermoregulated silicone oil bath; progress of the rearrangement was monitored at regular intervals by ^{31}P N.M.R. spectroscopy.

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