OXIDATIVE ADDITION REACTIONS OF IRIDIUM(I) 
AND IONIC PLATINUM(II) SPECIES

by

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To Dr Eric J. Wharton
- who fanned the flame
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ABSTRACT

This thesis describes some oxidative addition reactions of a platinum(II) cation, three platinum(II) anions and a 5-coordinate iridium(I) species. These reactions have all been studied by n.m.r. spectroscopy.

Chapter 3 describes the reactions of the cation [HPt(PEt₃)₃]⁺ with various silyl and germyl compounds and some other simple species. Six-coordinate intermediate species were observed for some of the reactions and a novel reductive elimination of the salt HPt⁺₃BPh₄⁻ was observed in some cases.

Chapter 4 describes the reactions of various anionic species [PtX₃(PEt₃)]⁻ with similar reagents and again some 6-coordinate intermediates were detected.

Chapter 5 describes the reactions of HIr(CO)(PPh₃)₃ with simple silyl and germyl compounds. The products were all 6-coordinate iridium(III) complexes containing two phosphine groups. Normally a mixture of products was obtained. With silyls, the prevalent isomer contained mutually cis-phosphines and in the case of germyls, trans-phosphines. High field ¹H n.m.r. spectroscopy was used to characterise these complexes and an ionic intermediate is postulated.

In none of the reactions was it possible to isolate the products but characterisation was carried out by various n.m.r. techniques.
1.1 General Background

The past decade or so has seen an upsurge of interest in transition metal complexes containing metal to silicon or germanium bonds\(^1,2,3\). This interest has, in part, been due to the importance of such species as intermediates in hydrosilation\(^4\) and hydrogermylation\(^5\) of alkenes. The majority of work on transition metal silicon or germanium compounds has involved organo silyl or germyl species which are more stable than the derivatives of the parent hydrides.

The first transition metal-silicon bond was reported in 1956\(^6\) by Wilkinson and co-workers by the reaction,

\[
\text{Na} [\text{Fe}(\eta^5-C_5\text{H}_5)(\text{CO})_2] + \text{Me}_3\text{SiCl} \rightarrow \text{Fe}(\eta^5-C_5\text{H}_5)\text{SiMe}_3(\text{CO})_2
\]

The product, an orange crystalline solid, was thermally stable to 200\(^\circ\)C but decomposed slowly on exposure to atmospheric oxygen.

Several other complexes were prepared by similar routes\(^7\). The first transition metal-germanium bond was also prepared by this route in 1962\(^8\).

The first transition-metal complex containing a silicon hydride was not reported until 1965\(^9\) when Aylett prepared silyl tetracarbonyl cobalt from iodosilane and the sodium salt of the tetracarbonyl cobalt anion. Using the di-iodo silane\(^10\) produced the silane bis(tetracarbonyl cobalt).

\[
\text{SiH}_4-n\text{I}_n + n \text{Na}^+[(\text{Co(CO)})_4]^- \xrightarrow{-20^\circ\text{C}} \text{SiH}_4-n[(\text{Co(CO)})_4]_n + n \text{NaI}
\]

(\(n = 1\) or 2)
These species were thermally unstable at room temperature and, typically of silyls, were air sensitive.

The first transition metal-germanium hydride complex was prepared by the reaction,

$$\text{GeH}_4 + \text{Mn(CO)}_5\text{H} \rightarrow \text{H}_2\text{Ge[Mn(CO)}_5\text{]}_2$$

The species was prepared by the reaction of GeH$_3$Br and Na$^+\text{[Mn(CO)}_5\text{]}^-$. Other similar species have also been prepared and found to be air stable unlike the silyl analogues. This probably reflects the greater resistance to oxidation of the Ge-H bond compared with the Si-H bond.

The first reported Pt-M (M = Si or Ge) bond was in 1964 when Glockling prepared trans-Pt(PEt$_3$)$_2$(GePh$_3$)$_2$ by the reaction,

$$\text{cis or trans Cl}_2\text{Pt(PEt}_3\text{)}_2 + 2\text{Ph}_3\text{GeLi} \rightarrow \text{Pt(PEt}_3\text{)}_2(\text{GePh}_3\text{)}_2 + 2\text{LiCl}$$

This species was found to be air and moisture stable. A variety of platinum compounds containing MR$_3$ (M = Si or Ge) groups has since been prepared by other routes, e.g.

$$\text{R}_3\text{MH} + \text{trans-PtClH(PEt}_3\text{)}_2 \rightarrow \text{trans-PtCl(MR}_3\text{)(PEt}_3\text{)}_2 + \text{H}_2$$

In 1971 Bentham prepared a series of silyl and germyl complexes of platinum and characterised them by $^1$H n.m.r. spectroscopy. Further characterisation was carried out by a number of double resonance experiments,

$$\text{MH}_3\text{X} + \text{trans-PtHY(PEt}_3\text{)}_2 \rightarrow \text{trans-Pt(MH}_2\text{X}Y(\text{PEt}_3\text{)}_2 + \text{H}_2$$

(M = Si or Ge; X,Y = halogen)
These reactions were postulated to proceed by a slow oxidative addition of M-H across the platinum to give a 6-coordinate Pt(IV) intermediate followed by a rapid reductive elimination of H₂ to give the 4-coordinate Pt(II) product, i.e.

However, in none of these reactions was the intermediate 6-coordinate Pt(IV) species detected. When SiH₃X (X = Cl or I) was reacted with trans-I₂Pt(PEt₃)₂ at -24°C, the species was isolated. Another 6-coordinate Pt(IV) species was detected by ¹H n.m.r. spectroscopy from the reaction,
Isolation of the product implied that the reaction proceeded via oxidative addition of the Hg-Si to the platinum. Many other reactions have been carried out producing labile 6-coordinate Pt(IV) intermediates and some have been shown to be capable of reductive elimination by more than one route, e.g. the product of the reaction between phenylacetylene and trans-ClPt(SiMe₃)(PET₃)₂.\(^{19}\)

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} \quad \text{C≡CPh} \quad \text{Me₃SiH} \\
\text{PET₃} & \quad \text{PET₃} \\
\text{C≡CPh} & \quad \text{H} \\
\text{Cl} & \quad \text{Pt} \quad \text{PET₃} \\
\text{Me₃Si} & \quad \text{PET₃} \\
\end{align*}
\]

Since PtHCl(PET₃)₂ was first prepared in 1957\(^{20}\) its reactions with various silyl and germyl species\(^{17,21}\) have been the subject of some interest. Various hydride species of platinum have been synthesised and found to be air stable, even the dihydride species PtH₂(PCy₃)₂\(^{20}\) (Cy = cyclohexyl). Various 6-coordinate mono- and dihydride species have been formed and studied mainly by \(^1\)H n.m.r. and some are fairly stable. PtHCl(PET₃)₂ reacts with HCl\(^{23}\) to produce cis-cis-trans-PtH₂Cl₂(PET₃)₂ which can be isolated at low temperatures. Reactions of Pt(o) complexes can also be used to produce platinum-hydride species\(^{24}\), e.g.
Although the cation \([\text{PtH(PPh}_3\text{)}_3]^{+}\) and anions \([\text{Pt(PEt}_3\text{)}X_3]^{-}\) (\(X = \text{halogen}\)) were prepared in 1966 and 1968 respectively, there has been no study of their reactions with silanes or germanes reported in the literature. Whereas the organosilyl or germyle derivatives of these species would probably be more stable, it is easier to obtain \(^1\text{H}\) n.m.r. parameters from the parent hydride derivatives, thus allowing more structural information to be obtained. These reactions will be described in Chapters 3 and 4 respectively.

Whereas the literature contains a large number of studies of reactions of platinum compounds, the studies involving iridium species are much less frequent. The reactions of Co and Rh are the most extensively studied within the triad. Probably the most studied iridium complex is the so-called Vaska's compound, \(\text{Ir(CO)Cl(PPh}_3\text{)}_2\). This compound was not originally prepared by Vaska but by Anoletta in 1959\(^{26}\). Two years later, Vaska and DiLuzio\(^{27}\) described a novel synthesis of the compound and due to the large amount of interest shown in the compound, especially by Vaska, it became generally known as Vaska's compound\(^{28}\):

\[
\text{IrCl}_3 + \text{PPh}_3 \overset{\text{D.M.F.}}{\rightarrow} \text{Ir(CO)Cl(PPh}_3\text{)}_2
\]

In the same paper Vaska described how the compound underwent an oxidative addition with HCl to give a stable 6-coordinate \(\text{Ir(III)}\) species. This was in marked contrast to platinum chemistry where the
lower oxidation state 4-coordinate species are the more stable. Vaska later showed that oxidative addition also occurred between his compound and $\text{H}_2$ or $\text{Cl}_2$ and there are many other reports of reactions with other small molecules\textsuperscript{29}. The mechanism of oxidation addition to Vaska's compound have been studied by various workers\textsuperscript{30,31,32} who showed the addition to be cis with the phosphines mutually trans. Trans addition was postulated for oxidative reactions to $\text{Ir(CO)Cl(Me}_2\text{PhP)}_2$\textsuperscript{33,34} but it was not established whether the initial addition was cis followed by a rearrangement process. This has been supported by addition of $\text{HX}$ to Vaska's compound where, in the absence of solvent, cis addition was observed but in certain solvents apparent trans addition occurred. Addition of $\text{R}_3\text{SiH}$ gave a structure

![Structure 1](image1.png)

Analogous reactions were observed with $\text{R}_3\text{GeH}$\textsuperscript{37,38} which produced a similar species but ruled out the structure:

![Structure 2](image2.png)
due to failure to observe the trans coupling $^4J_{HIrGeCH}$. Results
detailed in Chapter 5 of this work suggest that this coupling may
not be observed and as such, this structure could still be
considered. While the silyl species were insoluble, the germyl
adducts were soluble for about 30 minutes before precipitating and
it has been suggested that this could be due to rearrangement to a
different isomer resulting in the final isomer being insoluble. If
this was the case, it would be another example of secondary
rearrangement of the initial addition product.

In 1963 Vaska prepared $\text{HIr(CO)(PPh}_3\text{)}_3$ from Vaska's compound$^{39}$
but little mechanistic work on oxidative addition was carried out
using this species until the late '60s. In part this was due to
Vaska's discovery, in the same year, of the ability of Vaska's
compound to combine reversibly with molecular oxygen$^{40}$. Due to the
parallel with the uptake of oxygen by haemoglobin in the bloodstream,
a great deal of interest was shown in this property. Even an X-ray
structure$^{41}$ has failed to clarify the bonding within this molecule.
Harrod$^4$ and co-workers$^{36}$ studied the reactions between $\text{HIr(CO)(PPh}_3\text{)}_3$
and $\text{R}_3\text{SiH}$ and assigned the products as having the structures

\[
\begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{SiR}_3 \\
\text{Ph}_3\text{P} \quad \text{CO}
\end{array}
\]

The reaction was suggested to be stereospecific with the hydride
trans to the phosphine arising from $\text{R}_3\text{SiH}$. In 1970 Harrod$^{42}$
reported that the mechanism of these reactions proceeded via
elimination of \( \text{PPh}_3 \) and subsequent addition of \( \text{R}_3\text{SiH} \). A subsequent study\(^{43}\) of the oxidative addition reactions of \( \text{MH}_3\text{X} \) (\( \text{M} = \text{Si} \) or \( \text{Ge} \); \( \text{X} = \text{H}, \text{Cl}, \text{Br}, \text{I} \)) with both Vaska's compound and \( \text{H}i\text{r}(\text{CO})(\text{PPh}_3)_3 \) was hampered by the complexity of the n.m.r. spectra obtained by continuous wave spectra recorded at 100 MHz. The reactions of Vaska's compound with \( \text{MH}_3\text{X} \) (\( \text{M} = \text{Si} \) or \( \text{Ge} \); \( \text{X} = \text{H}, \text{Cl}, \text{Br}, \text{I} \)) was further studied in 1979\(^{44}\) and showed the products to contain trans phosphines. This study of the reactions between \( \text{H}i\text{r}(\text{CO})(\text{PPh}_3)_3 \) and \( \text{MH}_3\text{X} \) (\( \text{M} = \text{Si} \) or \( \text{Ge} \); \( \text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I} \)) by n.m.r. spectroscopy at high field (360 MHz) was hoped would clarify the results.

1.2 N.m.r. spectroscopy

No attempt will be made in this section to produce a comprehensive treatise on n.m.r. spectroscopy as this has already been carried out by numerous authors. Instead it is intended to concentrate on specific aspects relevant to this work.

Platinum possesses 33.7% of \( ^{195}\text{Pt} \) with \( I = \frac{7}{2} \). This means that when platinum couples to another spinning nucleus, the spectrum of the other nucleus shows a 1:4:1 pseudo triplet. In the case of platinum species containing tertiary phosphines and hydrides a great deal of information can be gained from the chemical shift and coupling constants in both the \( ^{31}\text{P} \) and \( ^{1}\text{H} \) n.m.r. spectra. The \( ^{1}\text{H} \) n.m.r. spectrum always shows the hydride resonance to low frequency of TMS. This effect has in part been responsible for the rapid growth in metal-hydride chemistry. The large shifts of hydride
protons are ascribed to a shielding of the proton by the nonbonding electrons of the metal\(^{45}\). In the case of platinum(II)hydrides the shielding by the 5d electrons of platinum is thought to be the dominant term in determining the chemical shift of theproton\(^{46}\). The platinum-hydrogen coupling constants in complexes of the type PtHX(PEt\(_3\))\(_2\) are strongly dependant on the nature of the trans ligand (Table 1.1).

**TABLE 1.1** \(^1J_{\text{PtH}}\) for trans PtHX(PEt\(_3\))\(_2\)

<table>
<thead>
<tr>
<th>X</th>
<th>I</th>
<th>Br</th>
<th>NO(_3)</th>
<th>Cl</th>
<th>SCN</th>
<th>CNO</th>
<th>NO(_2)</th>
<th>CN</th>
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<td>(^1J_{\text{PtH}}) Hz</td>
<td>1369</td>
<td>1346</td>
<td>1322</td>
<td>1275</td>
<td>1233</td>
<td>1080</td>
<td>1003</td>
<td>778</td>
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The dominant term in determining this variation is the Fermi contact interaction\(^{47}\), which in turn depends on the degree of s-character at each nucleus, upon the degree of s-character in the Pt-H bond and the mean excitation energy. The last term is dependant on the ligand field splitting parameter. In practise it is found that when trans ligands are sufficiently different to give substantial differences in the mean excitation energy term, then this term dominates the observed platinum hydrogen coupling constants. However, when these differences are small, then differences in the s-characters of the platinum-hydrogen bonds determine the magnitude of the coupling constant.

In spite of the large amount of \(^{31}\)P chemical shift data available for coordination compounds\(^{48}\), the interpretation of this data is still very uncertain, because although the main factors that contribute to the chemical shifts have been described\(^{49}\), there are
uncertainties in the magnitudes and even occasionally in the signs of some of these factors. The chemical shifts of tertiary phosphines move to high frequency on coordination, indicating that the phosphorus atom is less shielded from the magnetic field in the complex than in the free ligand\textsuperscript{50}. In cases where halide ligands are also present the \textsuperscript{31}P chemical shift moves to lower frequency as the atomic number of the halogen increases\textsuperscript{50}. This can be accounted for by either a decrease in the $\sigma$ component or an increase in the $\pi$ component of the platinum(II)-phosphorus bond as a result of an increase in the covalency of the platinum(II)-halogen bond as the halogen increases in atomic number\textsuperscript{51}.

The \textsuperscript{31}P chemical shifts of the cis isomers of tertiary phosphine complexes are to low frequency of those of the trans isomers\textsuperscript{52}. This is consistent with the simple idea that strong $\sigma$ donation by the phosphorus atom gives rise to a large shift to high frequency whereas platinum(II)-phosphorus $\pi$-back donation gives a shift to low frequency\textsuperscript{53}, since the opportunities for $\pi$ bonding are greater in the cis- than in the trans-isomers\textsuperscript{54}.

Probably the most useful aspect of \textsuperscript{31}P n.m.r. spectroscopy of platinum complexes is the simplicity with which it is possible to distinguish between 4- and 6-coordinate species. The value of $^1J_{\text{PtP}}$ in a 6-coordinate Pt(IV) species is approximately two thirds the value for a comparable 4-coordinate Pt(II) species. This can be explained on the basis of the degree of $s$ orbital character in the overall hybridisation. In an octahedral species, the hybridisation is $d^2sp^3$ and in a square planar complex, $dsp^2$. 

As has been previously mentioned, all other factors being equal, the degree of s-character in the bond affects the coupling constant. As the s-character of a bond can be regarded as the component which transmits coupling, then the greater the s-character, the greater the value of the coupling constant. Thus in an octahedron, one s orbital is shared between 6 ligands but in square planar it is only shared between 4 ligands. Thus:

\[
\frac{J_{\text{Pt(IV)-P}}}{J_{\text{Pt(II)-P}}} = 0.667
\]

While this is a fairly simple treatment, it does work for the majority of cases.

One of the problems which arises in n.m.r. spectroscopy is 2nd order effects. These arise when the effective chemical shifts of the nuclei involved are no longer large compared with the coupling constants between them. This effect is reduced by increasing the magnetic field at which the sample is observed and problems which appeared 2nd order at 100 MHz are often simpler at 360 MHz.

One technique which is fairly extensively used in Chapter 5 of this work is "Line Narrowing". This is an optimum resolution enhancement function which basically looks at the latter part of the Free Induction Decay (F.I.D.) with a greater weighting than it does the early part; the net result of which is an enhancement of resolution.
REFERENCES (CHAPTER 1)

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CHAPTER 2: EXPERIMENTAL TECHNIQUES AND PREPARATION OF STARTING MATERIALS

2.1 Experimental Techniques

2.1.1 Apparatus for preparation

All manipulations of volatile compounds were carried out in a conventional design of pyrex vacuum system. High vacuum was obtained by a glass, three stage mercury diffusion pump backed by a rotary oil pump. The degree of vacuum was monitored by a Pirani-type vacuum gauge. Pressures of volatile materials within the line were measured by a spiral gauge with mirror operating as a null zero device with lamp and scale.

The line was constructed of detachable pyrex glass sections joined by ground glass joints to facilitate cleaning. Apiezon L & N greases were used on ground glass joints and stopcocks respectively. N.m.r. tubes used were of conventional 5 mm or 10 mm design and attached to the vacuum line via a ground glass joint and sealed once filled. Reaction ampules were all fitted with 'Soveril' greaseless taps and attached to the line via a ground glass joint. The volume of each section of the line was determined using a molecular weight bulb, enabling the rapid quantitative measurement of volatile reagents.

2.1.2 Criteria of purity

The purity of reagents was checked by several methods. Infra-red spectroscopy was the main tool used to identify products and impurities. The impurities were generally removed by trap to trap
distillation through traps held at reduced temperature by slush baths of standard temperatures.

Vapour phase molecular weights were determined by standard methods and vapour pressures at standard temperatures were used as purity criteria.

$^{31}$P and $^1$H n.m.r. spectroscopy and C & H elemental analysis were used to establish the purity of the platinum species.

2.1.3 Instrumentation

Infra-red spectra were recorded on a Perkin Elmer 557 grating spectrophotometer. The vapour cell had a path length of 10 cm and was fitted with KBr end-plates attached with Apiezon W cement. Mull spectra of solids were recorded using KBr or CsI plates. Nujol or hexachlorobutadiene, dried over molecular sieve, were used as mulling agents.

Nuclear magnetic resonance spectra were recorded on a variety of instruments, as detailed below.

Varian Associates HA100 - continuous wave $^1$H spectrometer fitted with double resonance and variable temperature facilities.

Jeol FX60 Q - fourier transform $^{31}$P and $^1$H spectrometer fitted with variable temperature facility and both broad band and selective $^1$H decoupling facilities.

Varian Associates XL100 - fourier transform multinuclear spectrometer with variable temperature facility used to observe $^1$H, $^{31}$P and $^{19}$F. Homo- and heteronuclear
decoupling, both broad band and selective, was available for most nuclei with the exception of $^{19}\text{F}$ which could not be $^1\text{H}$ decoupled.

Bruker WH360 - fourier transform multinuclear high field spectrometer with variable temperature facility used to observe $^1\text{H}$, $^{77}\text{Se}$ and $^{195}\text{Pt}$. $^1\text{H}$ decoupling, broad and selective, facilities were available.

### 2.2 Preparation of Volatile Reagents

Procedures for the preparation and purification of the volatile compounds used during the course of this work are listed below. Appropriate references and any modifications to the standard technique are detailed. Purity checks were applied to commercial starting materials as appropriate.

#### 2.2.1 Silane

Silane was prepared by the standard method on a 20 m mole scale. The reduction was carried out in di-iso-pentyl ether under 10 cm nitrogen pressure.

$$\text{SiCl}_4 + \text{LiAlH}_4 \rightarrow \text{SiH}_4 + \text{LiCl} + \text{AlCl}_3$$

#### 2.2.2 Phenylsilane and Silyl bromide

Phenylsilane and silyl bromide were prepared by a variation on the method of Kummer and Fritz on a 50 mM scale. 50 m moles of phenylsilane and 100 m moles of HBr were cocondensed in a 250 ml ampule fitted with a Soveril tap. The ampule was immersed in a $-78^\circ\text{C}$ bath overnight. Fractionation was achieved as normal.

$$4\text{PhSiCl}_3 + 3\text{LiAlH}_4 \rightarrow 4\text{PhSiH}_3 + 3\text{LiCl} + 3\text{AlCl}_3$$
$$\text{PhSiH}_3 + \text{HBr} \stackrel{-78^\circ\text{C}}{\rightarrow} \text{SiH}_3\text{Br} + \text{PhH}$$
2.2.3 Silyl fluoride was prepared by streaming silyl chloride through an excess of antimony(III)fluoride\(^3\) diluted with powdered glass.

\[
\text{SiH}_3\text{Cl} + \text{SbF}_3 \rightarrow \text{SiH}_3\text{F} + \text{SbF}_{3-x}\text{Cl}_x
\]

2.2.4 Silyl chloride was prepared by streaming silyl bromide through an excess of mercury(II)chloride\(^4\).

\[
2\text{SiH}_3\text{Br} + \text{HgCl}_2 \rightarrow 2\text{SiH}_3\text{Cl} + \text{HgBr}_2
\]

2.2.5 Silyl iodide was prepared by the gas phase reaction of hydrogen iodide with trisilylamine\(^5\).

2.2.6 Germane was prepared by the reduction of a basic solution of germanium dioxide in acetic acid\(^6\) with KBH\(_4\).

\[
\text{GeO}_2 + \text{KOH} + \text{KBH}_4 \xrightarrow{\text{glacial acetic acid}} \text{GeH}_4 \text{ etc.}
\]

2.2.7 Germym chloride was prepared by the chlorination of germane using stannic chloride\(^7\).

\[
\text{GeH}_4 + \text{SnCl}_4 \rightarrow \text{GeH}_3\text{Cl} + \text{HCl} + \text{SnCl}_2
\]

2.2.8 Germym bromide was prepared by reacting germym chloride with hydrogen bromide\(^8\).

\[
\text{GeH}_3\text{Cl} + \text{HBr} \rightarrow \text{GeH}_3\text{Br} + \text{HCl}
\]

If hydrogen iodide is used instead of hydrogen bromide then germym iodide is produced\(^9\).

2.2.9 Germym fluoride was prepared by streaming germym bromide through an excess of freshly prepared lead(II)fluoride\(^10\).
2.2.10 **Hydrogen chloride** and **iodide** were prepared by dehydrating the aqueous acids using concentrated sulphuric acid\(^{11}\) and phosphorus pentoxide\(^{12}\) respectively.

2.2.11 **Hydrogen sulphide** was prepared by reacting iron(II)sulphide with 2M sulphuric acid\(^{11}\).

2.2.12 **Hydrogen selenide** was prepared by reacting aluminium selenide with 2M sulphuric acid\(^{11}\).

2.2.13 **Chlorine** was obtained from a commercial cylinder and fractionated through \(-120^\circ C\) to trap water and \(-140^\circ C\) to pass hydrogen chloride.

2.2.14 **Deuterium chloride** - a sample was kindly donated by Dr F. Reed.

### 2.3 Preparation of Platinum and Iridium Compounds

2.3.1 **cis-Cl\(_2\)Pt(PEt\(_3\))\(_2\)** can be prepared from K\(_2\)PtCl\(_4\) and triethyl phosphine in water\(^{13}\). This produces a mixture of the cis and trans isomers. The trans isomer can be isomerised to the cis isomer by stirring in n-pentane containing two drops of triethyl phosphine. Alternatively, stirring PtCl\(_2\) in acetone with triethyl phosphine also gives the mixture of isomers\(^{14}\).

2.3.2 **trans-(PEt\(_3\))\(_2\)PtCl** was prepared by reacting **cis-Cl\(_2\)Pt(PEt\(_3\))\(_2\)** with hydrazine hydrate in water\(^{15}\) at \(100^\circ C\) then recrystallising from methylene chloride.
2.3.3 $\text{HgPt(PEt}_3\text{)}_2^+\text{B(OH)}_4^-$ was prepared by stirring trans $\text{HgPtCl(PEt}_3\text{)}_2$ with NaB(OH)$_4$ and PEt$_3$ in methanol$^{14}$. The product so obtained required no further purification before use.

2.3.4 $\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2$ was prepared by stirring a slurry of cis $\text{Cl}_2\text{Pt(PEt}_3\text{)}_2$ and PtCl$_2$ in 2-dichlorobenzene at its boiling point under nitrogen. Crude product was precipitated with ether and recrystallised from CH$_2$Cl$_2$.

2.3.5 $\text{Pr}_4\text{N}^+\text{[Cl}_3\text{Pt(PEt}_3\text{)]}^-$ was prepared by stirring Pt$_2$Cl$_4$(PEt$_3$)$_2$ with either $\text{Pr}_4\text{N}^+\text{Cl}^-$ or Me$_4\text{N}^+\text{Cl}^-$ to give the desired counter cation$^{18}$. Both products are recrystallised from CH$_2$Cl$_2$.

2.3.6 $\text{Pr}_4\text{N}^+\text{[I}_3\text{Pt(PEt}_3\text{)]}^-$ was prepared by stirring $\text{Pr}_4\text{N}^+\text{[Cl}_3\text{Pt(PEt}_3\text{)]}^-$ with excess NaI in acetone$^{19}$. The product was recrystallised from CH$_3$OH.

2.3.7 $\text{ClIr(CO)(PPh}_3\text{)}_2$ was prepared by reacting IrCl$_3$·3H$_2$O with PPh$_3$ in formdimethylamide overnight under nitrogen$^{20}$. The product was precipitated by addition of methanol.

2.3.8 $\text{HIr(CO)(PPh}_3\text{)}_3$ was prepared by slow addition of an ethanolic solution of NaBH$_4$ to a refluxing solution of ClIr(CO)(PPh$_3$)$_2$ and PPh$_3$ in ethanol under nitrogen$^{21}$. Product was filtered off hot, washed with ethanol then dried and stored under vacuum.
2.4 Solvents

The various solvents used were purified as follows:

- methylene chloride - commercial grade, dried over molecular sieve
- acetone - commercial grade, dried over molecular sieve
- di isopentyl ether - commercial grade, dried over AlLiH₄
- n-pentane - commercial grade, dried over sodium wire
- di ethyl ether - commercial grade, dried over sodium wire
- methanol - commercial grade, dried over molecular sieve
- 2-dichlorobenzene - commercial grade, dried over molecular sieve
- phenyltrichlorosilane - commercial grade, used as supplied
- triethyl phosphine - commercial grade, used as supplied.

Deuterated n.m.r. solvents were dried and distilled prior to use.

2.5 The N.m.r. Experiment

0.1 mM of the required metal substrate was accurately weighed into a 5 mm n.m.r. tube fitted with a B10 cone and a constriction to facilitate sealing. The tube was then connected to the vacuum line and left to pump for at least one hour to ensure dryness. The required solvent was then distilled in at -196°C and the tube warmed to room temperature to allow dissolution. The solution was then refrozen and the required volatile reagent condensed in. The tube was then sealed off at the constriction and stored at -196°C until required.

The tube was placed in the precooled probe of the n.m.r. machine and observed at various temperatures from -90°C upwards until reaction was observed.
REFERENCES - CHAPTER 2

10. S. Cradock, personal communication.
14. F.J. Reid, personal communication.
19. F.J. Reid, personal communication.
21. G. Wilkinson, Inorganic Synthesis XIII, 126,
CHAPTER 3: OXIDATIVE ADDITION REACTIONS OF [HPT(PET$_3$)$_3$]$^+$BPh$_4^-$

3.1 Introduction

Bentham$^1$ found that simple silyl and germyl halides reacted with equimolar quantities of trans HPT(PET$_3$)$_2$X where X = Cl, Br or I to form monohalo silyl or germyl derivatives of platinum with the evolution of hydrogen.

\[
\begin{align*}
\text{PEt}_3 &\quad \text{MH}_3Y + H \quad \text{Pt} \quad X \quad + \quad \text{YH}_2M \quad \text{Pt} \quad X \quad + \quad \text{H}_2 \\
\text{PEt}_3 &\quad \text{PEt}_3 \\
\text{M} = \text{Si} \text{ or Ge}; \text{X, Y} = \text{Cl, Br or I.}
\end{align*}
\]

In these systems, no direct evidence was found to support the formation of an intermediate 6-coordinate Pt(IV) species. Other works$^2,3$ have proven that the oxidative addition reactions proceed via the 6-coordinate Pt(IV) species followed by reductive elimination to the 4-coordinate Pt(II) product. In these works, the reductive elimination has involved elimination of H$_2$ or HX.

This work, using the [HPT(PET$_3$)$_3$]$^+$ cation, introduces a third possible elimination product - the phosphonium salt HPEt$_3^+$BPh$_4^-$. A variety of reagents have been reacted with the cation to study their reactions and to observe the method of reductive elimination of the system.
3.2 Reaction with SiH$_3$Y (Y = H, F, Cl, Br, I)

All the reactions in this chapter were carried out in CD$_2$Cl$_2$ and the $^{31}$P n.m.r. spectra were run proton decoupled unless otherwise stated. N.m.r. parameters are detailed in Tables 3.1 (i) and (ii).

3.2.1 Reaction with SiH$_4$

No low temperature reaction was detected by $^{31}$P n.m.r. but after about 4 hours at ambient temperature reaction began. The $^{31}$P n.m.r. spectra of the product showed a doublet and triplet, both with $^{195}$Pt satellites, typical of a cationic species. The magnitude of the platinum phosphorus coupling constant established the species to contain 4-coordinate Pt(II). The $^1$H n.m.r. spectra showed a narrow doublet with $^{195}$Pt satellites in a region typical of a trans P-Pt-SiH$_3$ species. On the basis of the n.m.r. spectra it appears the species is:

$$\begin{align*}
\begin{array}{c}
\text{PEt}_3 \\
\text{H}_3\text{Si} \\
\text{Pt} \\
\text{PbEt}_3
\end{array}
\end{align*}$$

From the $^{31}$P n.m.r. spectra the maximum yield of this species was about 10%. On standing the species decomposed and the solution turned dark brown. It appears that for this system the mechanism of reductive elimination was via loss of H$_2$. The reaction was so slow that only the occasional bubble of gas was observed during reaction.

3.2.2 Reaction with SiH$_3$F

No reaction could be detected by $^{31}$P n.m.r. even after a period
of weeks at room temperature.

3.2.3 Reaction with SiH₃Cl

This reaction was more rapid than with SiH₄ and at -40°C a small amount of [ClPt(P(t)₃)₃]⁺BPh₄⁻ was identified by its ³¹P n.m.r. spectrum. This is in keeping with a small amount of HCl being present (see Section 3.4.1) either as an impurity in the SiH₃Cl or as a hydrolysis product of the SiH₃Cl. At 0°C the ³¹P n.m.r. spectra showed a doublet and a triplet with ¹⁹⁵Pt satellites typical of a 4-coordinate Pt(II) cationic species. The ¹H n.m.r. spectra showed a narrow doublet with ¹⁹⁵Pt satellites typical of SiH₂X trans to phosphorus. These factors suggest that the species is:

\[
\begin{array}{c}
\text{ClH}_2\text{Si} \\
\text{Pt} \\
\text{P} \_\text{Et}_3 \\
\text{P} \_\text{Et}_3
\end{array}
\]

At room temperature there was still only about 40% of this species present, the remainder being the [H₂Pt(P(t)₃)₃]⁺BPh₄⁻ starting material. A further reaction with excess SiH₃Cl resulted in an extremely complex mixture of products whose ³¹P n.m.r. spectra could not be interpreted.

3.2.4 Reaction with SiH₃Br

Reaction began at -30°C. The ³¹P n.m.r. spectra showed a singlet with ¹⁹⁵Pt satellites. Removal of the tube from the n.m.r. probe revealed a white solid floating on top of the solution. ¹H
n.m.r. spectra showed a low frequency triplet with $^{195}$Pt satellites. A triplet was also observed in the SiH$_2$X region but only the low frequency $^{195}$Pt satellite was observed. The n.m.r. evidence suggests the product to be the neutral species

$$\begin{align*}
\text{P} \quad \text{Et}_3^+ & \\
\text{H} & \quad \text{Pt} & \quad \text{SiH}_2\text{Br} \\
\text{P} \quad \text{Et}_3^- &
\end{align*}$$

Further warming increased the yield of this product to a maximum of about 30%. As in the SiH$_3$Cl system an excess of SiH$_3$Br caused a complex mixture to form.

The n.m.r. tube was frozen and opened under a dry nitrogen atmosphere, and the white solid filtered off and dried on a vacuum line. Analysis for C and H confirmed the solid to be HPEt$_3^+$BPh$_4^-$. 

C$_{30}$H$_{36}$BP  
required  C 82.19%  H 8.22%  
obtained  C 82.01%  H 8.23%

Thus for this system the reductive elimination did not go by H$_2$ elimination but favoured elimination of the phosphonium salt.

3.2.5 Reaction with SiH$_3$I

Reaction began at -60°C. $^{31}$P n.m.r. spectra showed a doublet and a triplet with $^{195}$Pt satellites. The reduced size of the platinum-phosphorus coupling constants showed the species to be a 6-coordinate Pt(IV) complex. The $^1$H n.m.r. spectra showed two distinct low frequency hydride signals. The higher frequency hydride appears as a doublet of triplets with $^{195}$Pt satellites, the large doublet
splitting of 210 Hz arising from a trans two-bond phosphorus coupling. The smaller triplet coupling of 9 Hz arises from two-bond coupling to two cis phosphorus atoms. The lower frequency hydride appears as an apparent quartet with $^{195}$Pt satellites. The SiH$_2$X region was not observed. These facts are in keeping with the structure:

```
\[
\begin{array}{c}
\text{PEt}_3 \\
\text{H}_b \\
\text{Pt} \\
\text{H}_a \\
\text{SiH}_2 \text{I} \\
\text{BPh}_4^-
\end{array}
\]
```

The resonance associated with H$_a$ appears as a quartet and it must therefore be from an overlapping doublet of triplets due to the magnetic inequivalence of the phosphines.

Based on the $^{31}$P n.m.r. spectra the maximum amount of this species present was about 20%. Further warming resulted in the decomposition of this species by the elimination of phosphonium salt - identified by elemental analysis. The $^{31}$P n.m.r. spectra at -20°C showed a singlet with $^{195}$Pt satellites. The $^1$H n.m.r. spectra showed one type of low frequency hydride - a triplet with $^{195}$Pt satellites. The SiH$_2$X region also showed a triplet with $^{195}$Pt satellites. To prove the triplet coupling on the low frequency hydride came from the two cis two-bond phosphorus coupling rather than the trans three-bond SiH$_2$ coupling, a heteronuclear double resonance experiment was carried out. The same $^{31}$P frequency collapsed both the triplet couplings on the hydride and the SiH$_2$ signals. A homonuclear decoupling on the SiH$_2$ region had no effect on the hydride signal. The structure can be assigned as:
Once again only about 40% product was obtained, the remainder being unreacted starting material. Addition of excess SiH₃I, as before, gave a complex mixture.

3.3 Reaction with GeH₃Y (Y = H, F, Cl, Br, I)

N.m.r. parameters are detailed in Tables 3.2 (i) and (ii).

3.3.1 Reaction with GeH₄

Although the tube darkened in colour over a period of twelve hours, the only effect detected by ³¹P n.m.r. was a distinct broadening of all the signals. Cooling down to -60°C sharpened the signals but no new signals could be detected. This tends to suggest some sort of scrambling of the triethyl phosphine signals. The ¹H n.m.r. spectrum appeared to be identical to the spectrum of the cation by itself.

3.3.2 Reaction with GeH₃F

Unlike the SiH₃F system, reaction began at -60°C. ³¹P n.m.r. spectra showed a doublet of doublets and an overlapping doublet of triplets, which appeared as a quintet of relative intensities 1:2:2:2:1 (Figure 3.1), with ¹⁹⁵Pt satellites. From the size of the
TABLE 3.1(ii) \(^1\)H n.m.r. parameters for the products of the reactions between \([\text{HPt} (\text{PET}_3)_3]^+\text{BPh}_4^-\) and \(\text{SiH}_3\text{Y}\). \((\text{Y} = \text{H, Cl, Br and I})\)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>(\delta \text{H}_a) ppm</th>
<th>(\delta \text{H}_b)</th>
<th>(\text{JH}_a) _a Hz</th>
<th>(\text{JH}_b) _b Hz</th>
<th>(\text{JH}_a) _a Hz</th>
<th>(\text{JH}_b) _b Hz</th>
<th>(\delta \text{SiH}_a) ppm</th>
<th>(\text{JHSiPt}_a)</th>
<th>(\text{JHSiPt}_b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiH}_4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.30</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>(\text{SiH}_3\text{Cl})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.04</td>
<td>128</td>
<td>12</td>
</tr>
<tr>
<td>(\text{SiH}_3\text{Br})</td>
<td>-11.55</td>
<td>-</td>
<td>1110</td>
<td>-</td>
<td>10.0</td>
<td>-</td>
<td>4.62</td>
<td>130</td>
<td>n.o.</td>
</tr>
<tr>
<td>(\text{SiH}_3\text{I})</td>
<td>-14.22</td>
<td>-10.45</td>
<td>1178</td>
<td>698</td>
<td>6.0</td>
<td>210</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td></td>
<td>-14.10</td>
<td>-</td>
<td>1190</td>
<td>-</td>
<td>9.5</td>
<td>-</td>
<td>3.29</td>
<td>132</td>
<td>10</td>
</tr>
</tbody>
</table>

Frequencies are all ±1 Hz

n.r. = not resolved
n.o. = not observed
TABLE 3.1

31P n.m.r. parameters for the products of the reactions between [HPt(PEt₃)₃]⁺BPh₄⁻ and SiH₃Y. (Y = H, Cl, Br and I)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>δP_a ppm</th>
<th>δP_b ppm</th>
<th>J_PtP_a Hz</th>
<th>J_PtP_b Hz</th>
<th>J_P a b Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>+18.2</td>
<td>+9.5</td>
<td>2234</td>
<td>2950</td>
<td>19.5</td>
</tr>
<tr>
<td>SiH₃Cl</td>
<td>+10.1</td>
<td>+11.4</td>
<td>2410</td>
<td>1938</td>
<td>26.5</td>
</tr>
<tr>
<td>SiH₃Br</td>
<td>+15.0</td>
<td>-</td>
<td>2380</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiH₃I</td>
<td>-3.2</td>
<td>-31.4</td>
<td>1610</td>
<td>1534</td>
<td>18.5</td>
</tr>
</tbody>
</table>

a) was observed at -50°C. All other species were observed at ambient temperature, frequencies are all +1.2 Hz.
platinum-phosphorus coupling constant it was apparent that the species formed was a 6-coordinate Pt(IV) complex. The normal doublet and triplet pattern found in these systems is further split by the $^{19}\text{F}$ of the coordinated GeH$_2$F group. As the fluorine-phosphorus coupling constant in the overlapping doublet of triplets is much larger than in the doublet of doublets, it is probable that the GeH$_2$F group is trans to the unique phosphorus and cis to the pair of phosphorus atoms. This itself rules out the isomer (I) shown below:

\[
\begin{array}{c}
\text{Et}_3\text{P} \\
\text{GeH}_2\text{F} \\
\text{Pt} \\
\text{BPh}_4^- \\
\end{array}
\]

(I)

as the fluorine phosphorus coupling constant for this isomer would be very similar, if not identical. Thus, from the $^{31}\text{P}$ n.m.r. spectrum it appears that there are two possible isomers:

\[
\begin{array}{c}
\text{Et}_3\text{P} \\
\text{GeH}_2\text{F} \\
\text{Pt} \\
\text{BPh}_4^- \\
\end{array}
\]

(II)

\[
\begin{array}{c}
\text{Et}_3\text{P} \\
\text{GeH}_2\text{F} \\
\text{Pt} \\
\text{BPh}_4^- \\
\end{array}
\]

(III)

The $^1\text{H}$ n.m.r. spectra showed the low frequency hydride resonance as a doublet of triplets (Figure 3.2) with $^{195}\text{Pt}$ satellites. The large doublet coupling obviously arises from a trans phosphorus
Figure 3.1 $^{31}$P n.m.r. spectrom

$$[\text{Hpt(PEt}_3)_3]^+\text{BPH}_4^- + \text{GeH}_3\text{F}^- \text{ at } -60^\circ\text{C}$$
Figure 3.2 $^1$H n.m.r. spectrum

$[\text{HPT(P}E_t_3)_3]^{+}\text{BPh}_4^- + \text{GeH}_3\text{F} - 60^\circ\text{C}$
coupling, the small triplet coupling arising from coupling to two cis phosphorus atoms. This information rules out isomer(II). Isomer (III) however, should show the hydride region as a second order spectrum as the two phosphorus atoms are not magnetically equivalent, nor are the two hydrides. As the actual spectrum appears to be first order, the geometry of the system must be such that the values of $J_{HH}$ and $J_{PP}$ are accidentally near zero. The GeH$_2$F pattern in the $^1$H n.m.r. spectrum consists of a doublet of doublets with $^{195}$Pt satellites. The smaller doublet comes from the three-bond trans phosphorus coupling and the larger doublet arises from the two-bond fluorine coupling.

The $^{19}$F n.m.r. spectra showed an apparent quartet of triplets with $^{195}$Pt satellites. The small triplet arises from coupling to the two cis phosphorus atoms. The quartet is actually an overlapping doublet of triplets; the doublet coupling from the trans phosphorus and the triplet coupling from the two protons on the germanium having the same size, overlap to give a pseudo quartet.

As the sample was warmed further, the concentration of the 6-coordinate Pt(IV) species decreased rapidly and by $-30^\circ$C it had decomposed completely. Phosphonium salt was eliminated and the contents of the tube turned black. Metallic platinum was precipitated and no further spectra were obtained. It appears that if the phosphonium salt is eliminated then the species

\[
\begin{array}{c}
\text{PEt}_3 \\
\text{H} \quad \text{Pt} \quad \text{GeH}_2\text{F} \\
\text{PEt}_3
\end{array}
\]
must also form. This species must be very unstable and despite several attempts to characterise its n.m.r. spectra at low temperature, each attempt met with failure.

3.3.3 Reaction with GeH₃Cl

Reaction began at -60°C. ³¹P n.m.r. spectra showed a doublet and a triplet with ¹⁹⁵Pt satellites. The size of the platinum-phosphorus coupling constant again established the species to be a 6-coordinate Pt(IV) complex. The ¹H n.m.r. spectra showed a doublet of triplets with ¹⁹⁵Pt satellites in the GeH₂X region (Figure 3.3); the large doublet coupling arises from a trans phosphorus coupling and the small triplet from coupling to two cis phosphorus atoms.

The low frequency hydride region showed a second order pattern (Figure 3.4). The basic pattern is a doublet of triplets with ¹⁹⁵Pt satellites. The doublet arises from the trans phosphorus coupling but the cis phosphorus atoms are obviously not quite equivalent. This almost certainly shows the structure to be

\[
\begin{array}{c}
\text{GeH}_2\text{Cl} \\
\text{H} \\
\text{Pt} \\
\text{H} \\
\text{P}_\text{Et}_3 \\
\text{P}_\text{Et}_3
\end{array}
\]

This is directly analogous to the GeH₃F product. However, in the case of GeH₃F, the geometry of the molecule was such that ²JHH and ²JPP were accidentally near zero. In the case of GeH₃Cl, however, the slight change in stereochemistry brought about by the change in size and electronegativities of the halogen involved results in these
Figure 3.3 $^1H$ n.m.r. spectrum

$[\text{HPt(PEt}_3)_3]^+\text{BPh}_4^- + \text{GeH}_3\text{Cl} - 60^\circ\text{C}$
Figure 3.4 $^1$H n.m.r. spectrum

$[\text{Hpt(PEt}_3)_3]^+ \text{BPh}_4^- + \text{GeH}_3\text{Cl} \to -60^\circ\text{C}$
couplings not being zero. The result is that second order effects become apparent in the low frequency hydride region. In order to establish the values of $J_{HH}$ and $J_{PP}$ it would be necessary to use a computer program, e.g. NUMARIT, to simulate the spectrum by an iterative method.

On further warming to room temperature the 6-coordinate Pt(IV) species decomposed via the reductive elimination of the phosphonium salt to yield a single 4-coordinate Pt(II) species as the only Pt-P compound. A small amount of the phosphonium salt was also detected by its $^{31}\text{P}$ n.m.r. spectrum at +18.1 ppm. This was the first time it had been detected in solution in these systems. The $^1\text{H}$ n.m.r. spectra of the GeH$_2$Cl region (Figure 3.5) appeared as a triplet with $^{195}\text{P}$ satellites. The triplet coupling arises from the two cis three-bond phosphorus atoms. The three-bond trans hydride coupling is not resolved in any of these systems. The low frequency hydride region showed a triplet, due to the two cis phosphines with $^{195}\text{Pt}$ satellites. Attempts to isolate this compound from the n.m.r. tube failed even under the most rigorously dry, oxygen-free conditions. As soon as the solvent was removed, even at reduced temperatures, the dark orange solid turned black and decomposed. The eliminated phosphonium salt analysed for C and H satisfactorily. The reaction may be summarised as follows:
Figure 3.5 $^1$H n.m.r. spectrum

$[\text{HPt(PEt}_3\text{)}_3]^+\text{BPh}_4^- + \text{GeH}_3\text{Cl} \quad 0^\circ\text{C}$
3.3.4 Reaction with GeH₂Br

No reaction was detected until -10°C, at which temperature the $^{31}$P spectrum showed a singlet with $^{195}$Pt satellites. The value of the platinum-phosphorus coupling constant established the species to be a 4-coordinate Pt(II) species. Removal of the tube from the n.m.r. probe showed phosphonium salt (later confirmed by analysis) had been reductively eliminated. The $^1$H n.m.r. showed a low frequency hydride resonance as a triplet with $^{195}$Pt satellites typical of two cis two-bond phosphorus coupling. The GeH₂Br resonance, also a triplet from phosphorus coupling, was detected with $^{195}$Pt satellites. The structure would therefore appear to be
The 6-coordinate Pt(IV) cation was not detected on repeating the experiment. The salt was successfully analysed as HPEt$_3^+$BPh$_4^-$.

3.3.5 Reaction with GeH$_2$I

Reaction began at -60°C. $^{31}$P n.m.r. spectra showed a doublet and a triplet with $^{195}$Pt satellites. The size of the platinum-phosphorus coupling constant established the species as being a 6-coordinate Pt(IV) complex. The $^1$H n.m.r. spectra showed a doublet of triplets with $^{195}$Pt satellites in the GeH$_2$X region. The large doublet coupling arises from a trans phosphorus coupling and the small triplet from two cis phosphorus atoms. The low frequency hydride region showed a doublet of triplets with $^{195}$Pt satellites, the respective couplings again arising from a trans phosphine and two cis phosphines. Like the GeH$_3$F system, the low frequency hydride spectra appear to be first order. These factors suggest the structure to be

$$\begin{array}{c}
\text{H} \\
\text{GeH}_2\text{I}
\end{array} \xrightarrow{\text{Pt}} \begin{array}{c}
\text{H} \\
\text{Pt} \\
\text{H}
\end{array} \xrightarrow{\text{PEt}_3^+} \overbrace{\begin{array}{c}
\text{H} \\
\text{Pt} \\
\text{H} \\
\text{GeH}_2\text{I}
\end{array}}^{+} \begin{array}{c}
\text{PEt}_3 \\
\text{PEt}_3 \\
\text{BPh}_4^-
\end{array}$$

On further warming the 6-coordinate Pt(IV) cation decomposed via the reductive elimination of the phosphonium salt. The room temperature $^{31}$P n.m.r. spectrum showed a singlet with $^{195}$Pt satellites and a platinum-phosphorus coupling constant indicative of a 4-coordinate Pt(II) species. The $^1$H n.m.r. spectra showed a low frequency hydride as a triplet with $^{195}$Pt satellites and a GeH$_2$X resonance, again as a triplet with $^{195}$Pt satellites. This is in keeping with the structure

$$\begin{array}{c}
\text{H} \\
\text{Pt} \\
\text{GeH}_2\text{I}
\end{array} \xrightarrow{\text{Pt}} \begin{array}{c}
\text{H} \\
\text{Pt} \\
\text{H}
\end{array} \xrightarrow{\text{PEt}_3^+} \overbrace{\begin{array}{c}
\text{H} \\
\text{Pt} \\
\text{H} \\
\text{GeH}_2\text{I}
\end{array}}^{+} \begin{array}{c}
\text{PEt}_3 \\
\text{PEt}_3 \\
\text{BPh}_4^-
\end{array}$$
**TABLE 3.2(1):** $^{31}$P n.m.r. parameters for the products of the reaction between $[\text{HPT(PEt}_3\text{)}_3]^+\text{BPH}[\text{4}]$ and GeH$_3$Y. (Y = F, Cl, Br and I)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$\delta_P$ a ppm</th>
<th>$\delta_P$ b ppm</th>
<th>$^1$JPtP$_a$ Hz</th>
<th>$^1$JPtP$_b$ Hz</th>
<th>$^2$JP$_a$,P$_b$ Hz</th>
<th>$^3$JP$_a$ F Hz</th>
<th>$^3$JP$_b$ F Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_3$F</td>
<td>-12.5</td>
<td>-24.7</td>
<td>1330</td>
<td>1446</td>
<td>20.0</td>
<td>6.0</td>
<td>39.0</td>
</tr>
<tr>
<td></td>
<td>-26.7</td>
<td>-10.7</td>
<td>1376</td>
<td>1438</td>
<td>19.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH$_3$Cl</td>
<td>+18.1</td>
<td>-</td>
<td>2354</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH$_3$Br</td>
<td>+9.59</td>
<td>-</td>
<td>2309</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH$_3$I</td>
<td>-26.83</td>
<td>-12.47</td>
<td>1412</td>
<td>1402</td>
<td>19.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+3.02</td>
<td>-</td>
<td>2280</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All frequencies $\pm 1.2$ Hz
TABLE 3.2(ii): $^1$H n.m.r. parameters for the products of the reaction between $[\text{HPt(PEt}_3)_3]^+\text{BPh}_4^-$ and GeH$_3$Y. (Y = F, Cl, Br and I)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>δH$_a$ ppm</th>
<th>δH$_b$ ppm</th>
<th>$^1$JPtH$_a$ Hz</th>
<th>$^2$JH$_a$P$_a$ Hz</th>
<th>$^2$JH$_a$P$_b$ Hz</th>
<th>GeH$_2$ ppm</th>
<th>$^2$JPtGeH Hz</th>
<th>$^3$JHGePtP$_b$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_3$F*</td>
<td>-10.78</td>
<td>-</td>
<td>718</td>
<td>183</td>
<td>9</td>
<td>6.96</td>
<td>216</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>-11.25</td>
<td>-</td>
<td>≈710</td>
<td>184</td>
<td>2nd order</td>
<td>5.53</td>
<td>218</td>
<td>8.0</td>
</tr>
<tr>
<td>GeH$_3$Cl</td>
<td>-12.10</td>
<td>-</td>
<td>915</td>
<td>-</td>
<td>10</td>
<td>4.75</td>
<td>226</td>
<td>9.5</td>
</tr>
<tr>
<td>GeH$_3$Br</td>
<td>-12.31</td>
<td>-</td>
<td>910</td>
<td>-</td>
<td>8.5</td>
<td>4.38</td>
<td>231</td>
<td>8.5</td>
</tr>
<tr>
<td>GeH$_3$I</td>
<td>-13.11</td>
<td>-</td>
<td>709</td>
<td>192</td>
<td>8.5</td>
<td>4.65</td>
<td>223</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>-13.27</td>
<td>-</td>
<td>906</td>
<td>-</td>
<td>10</td>
<td>4.08</td>
<td>231</td>
<td>9.5</td>
</tr>
</tbody>
</table>

*Also determined for GeH$_3$F reaction δF = -215.7 ppm, $^2$JPtF = 188 Hz, $^2$JHGeF = 38.0 Hz, $^3$JFGePtP$_b$ = 39.0 Hz, $^3$JFGePtP$_a$ = 6.0 Hz.

All frequencies ± 1 Hz.
3.4 Reaction with HCl, DCl, HI and Cl₂

N.m.r. parameters are detailed in Table 3.3.

3.4.1 Reaction with HCl

Reaction began at -80°C. $^{31}$P n.m.r. spectra showed a doublet and a triplet with $^{195}$Pt satellites. The platinum-phosphorus coupling constant indicated the species to be a 6-coordinate Pt(IV) complex. As the platinum coupling to the unique phosphorus is smaller than to the pair of phosphorus atoms, it would suggest that the unique phosphorus is trans to a hydride rather than a chloride. This is in keeping with the observed couplings in $[\text{ClPt}(\text{PET}_3)_3]^+\text{BPh}_4^-$ and $[\text{HPt}(\text{PET}_3)_3]^+\text{BPh}_4^-$. The $^1$H n.m.r. spectra showed two distinct types of low frequency hydrides. The higher frequency resonance appeared as a doublet of triplets with $^{195}$Pt satellites. The couplings arising from one trans and two cis phosphorus atoms. The lower frequency resonance appeared as an apparent small quartet with $^{195}$Pt satellites. These facts are in keeping with the structure

![Structure Diagram]

From this structure it is impossible to tell whether the HCl has oxidatively added cis or trans. Further warming to $-10$°C decomposed
the 6-coordinate Pt(IV) cation to produce mainly $[\text{ClPt(PEt}_3^3)]^+\text{BPh}_4^-$ with a small ($\approx 10\%$) amount of $\text{HPtCl(PEt}_3^2$), both of which were identified by their $^{31}\text{P n.m.r. spectra. This shows that the reductive elimination can proceed by either elimination of H}_2 \text{ or phosphonium salt, although the former appears to occur preferentially.}$

\[
\begin{align*}
\text{H-Pt-PEt}_3 + \text{Cl}^- & \rightarrow \text{Cl-Pt-PEt}_3 + \text{H}_2 \\
\text{PEt}_3^3 + \text{PEt}^- \rightarrow \text{H}_2 \\
\end{align*}
\]

**Figure 3.6**

3.4.2 Reaction with DCI$^4$

In order to ascertain whether HCl oxidatively added by a cis or trans mechanism, the reaction was carried out using DCI. This means that the two modes of addition can be distinguished:
The $^1$H n.m.r. spectra showed one hydride resonance with a large trans phosphorus coupling. This means that the DCl has oxidatively added by a trans mechanism.

3.4.3 Reaction with HI

Reaction began at -80°C. $^{31}$P n.m.r. spectra showed a doublet and a triplet with $^{195}$Pt satellites. The size of the platinum-phosphorus coupling constant confirmed the species as being a 6-coordinate Pt(IV) complex. As in the case for HCl the relative sizes of the two platinum phosphorus couplings indicated that the unique phosphorus must be trans to a hydride rather than an iodide. The $^1$H n.m.r. spectra again showed two low frequency hydride resonances. As in the HCl system, one hydride showed a trans phosphorus coupling plus two cis phosphorus couplings. The other resonance showed only cis phosphorus coupling. Thus this system appears to be directly analogous to the HCl system and the structure is probably:
Warming to -60°C showed the presence of an additional species with only a singlet $^{31}$P resonance with $^{195}$Pt satellites. The platinum-phosphorus coupling constant confirmed the species to be a 6-coordinate Pt(IV) complex. Comparison with a previous work confirmed the species to be cis-cis-trans [$\text{PtH}_2\text{I}_2(\text{PET}_3)_2$]. Warming to -10°C showed the presence of $t$-H$\text{PtI(PEt}_3)_2$, confirmed by its $^{31}$P n.m.r. spectrum. To have formed the cis-cis-trans $\text{PtH}_2\text{I}_2(\text{PET}_3)_2$, the cationic 6-coordinate species must have eliminated phosphonium salt and the trans $\text{HPTI(PEt}_3)_2$ so formed, reacted with HI. At room temperature, the products were a mixture of trans $\text{HPTI(PEt}_3)_2$ and trans $\text{I}_2\text{Pt(PEt}_3)_2$, both of which were identified by their $^{31}$P n.m.r. spectra. The reactions with HI are summarised in Figure 3.7.

![Chemical reaction diagram](image)
3.4.4 Reaction with Cl

Reaction began at -80° C. $^{31}$P n.m.r. spectra showed two product species. The first was identified as the HCl adduct of \([\text{HPt(PEt}_3\text{)}_3]^{+}\cdot\text{BPh}_4^{-}\) by its n.m.r. parameters. The second species $^{31}$P n.m.r. spectrum showed a doublet and a triplet with $^{195}$Pt satellites. The platinum-phosphorus coupling constants showed the species to be a 6-coordinate Pt(IV) complex and from the relative sizes of these constants the unique phosphorus was trans to a chlorine, not a hydride. This must mean the mode of oxidative addition was \textit{cis}. The $^1$H n.m.r. spectra showed a low frequency hydride coupled to three \textit{cis} phosphorus atoms. This suggests the species to be

$$\text{Cl-Pt-P-Et}_3^- \cdot \text{BPh}_4^-$$

Warming the sample to room temperature gave \([\text{ClPt(PEt}_3\text{)}_3]^{+}\cdot\text{BPh}_4^{-}\) as the sole product. These observations suggest the reaction proceeds as shown in Figure 3.8.

$$\begin{array}{c}
\text{PEt}_3^+ + \text{PEt}_3^- + \text{Cl}_2 \rightarrow \text{Cl-Pt-P-Et}_3^- \cdot \text{BPh}_4^- + \text{HCl} \\
\text{RT} \\
\text{Cl-Pt-P-Et}_3^- \cdot \text{BPh}_4^- + \text{HCl} \rightarrow \text{Cl-Pt-P-Et}_3^- \cdot \text{BPh}_4^- + \text{H}_2
\end{array}$$

Figure 3.8
TABLE 3.3  N.m.r. parameters for the products of the reactions between [HPt(PEt$_3$)$_3$]+BPh$_4^-$ and HCl, HI and Cl$_2$.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$\delta_{Pa}$ ppm</th>
<th>$\delta_{Pb}$ ppm</th>
<th>$^1$JPt$_a$ Hz</th>
<th>$^1$JPt$_b$ Hz</th>
<th>$^2$JP$_{Pa}$ $^b$ Hz</th>
<th>$^1$JP$_b$ ppm</th>
<th>$^2$JP$_b$ ppm</th>
<th>$^1$JPtH$_a$ Hz</th>
<th>$^1$JPtH$_b$ Hz</th>
<th>$^2$JHP$_a$ Hz</th>
<th>$^2$JH$_b$P$_b$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>+4.43</td>
<td>-18.0</td>
<td>1630</td>
<td>1350</td>
<td>18.0</td>
<td>-17.48</td>
<td>-10.33</td>
<td>1110</td>
<td>730</td>
<td>7</td>
<td>217</td>
</tr>
<tr>
<td>HI</td>
<td>-3.2</td>
<td>-31.3</td>
<td>1610</td>
<td>1380</td>
<td>18.0</td>
<td>-15.90</td>
<td>-10.10</td>
<td>1124</td>
<td>726</td>
<td>6</td>
<td>210</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>+8.8</td>
<td>+12.5</td>
<td>1380</td>
<td>2065</td>
<td>10.5</td>
<td>-17.81</td>
<td>-</td>
<td>1108</td>
<td>-</td>
<td>7</td>
<td>-</td>
</tr>
</tbody>
</table>

All spectra were recorded at -80 in CD$_2$Cl$_2$. $^{31}$P chemical shifts are relative to 85% H$_3$PO$_4$. $^1$H chemical shifts are relative to TMS.
Although the \([\text{ClPt(PEt}_3)_3]^+\text{BPh}_4^-\) was not detected at -80°C to support this scheme a check showed it to be virtually insoluble in CD\(_2\)Cl\(_2\) at below about -60°C. This also accounts for it not reacting with Cl\(_2\) in this scheme.

3.5 Reaction with \(\text{H}_2\text{S}\) and \(\text{H}_2\text{Se}\)

\(\text{H}_2\text{S}\) showed no detectable reaction, even after a period of some weeks at room temperature.

3.5.1 Reaction with \(\text{H}_2\text{Se}\)

No reaction was detected by \(\text{^31P n.m.r.}\) at low temperatures. On standing for c.a. 1 hour at room temperature a white precipitate of, presumably, HPEt\(_3^+\text{BPh}_4^-\) floated on top of the solution. The \(\text{^31P n.m.r.}\) at -50°C showed a singlet with \(\text{^{195Pt satellites}}\). The size of the platinum-phosphorus coupling constant showed the species to be a 6-coordinate Pt(IV) complex. Selectively decoupling the triethyl phosphine protons and retaining the hydrides split the signal into triplets of c.a. 8 Hz. \(\text{^1H n.m.r.}\) spectra showed one type of low frequency hydride resonance, split into a triplet by two cis phosphorus atoms, with \(\text{^{195Pt satellites}}\). A further triplet was also detected at -5.08 ppm. Comparison with previous work confirmed this species to be cis, cis, trans PtH\(_2\)(SeH)\(_2\)(PEt\(_3\))\(_2\). The formation of this species can be accounted for by the mechanism shown in Figure 3.9.
A study at 0°C of a freshly prepared sample showed both species III and another product. The other product was 4-coordinate and selectively decoupling the triethylphosphine protons showed it to be a monohydride (Figure 3.10). It was identified as species II in the scheme shown in Figure 3.9. Repeated attempts were made to observe species I but all met with failure.

3.6 Discussion of Results

The \(\text{[HPt(PET}_3\text{)}_3]^+\) cation undergoes oxidative addition reaction with a variety of reagents, as has been shown. The most common method of reductive elimination is the elimination of the phosphonium salt \(\text{HPEt}_3^+\text{BPh}_4^-\) rather than elimination of \(\text{H}_2\) (Figure 3.11).
Figure 3.10 $^{31}$P n.m.r. spectrum

$$[\text{HPr(PEt}_3)_2]^+\text{BPh}_4^- + \text{H}_2\text{Se} \text{ O}^\circ\text{C}$$
This observation must, in general, reflect the relative stabilities of (I) and (II) and seems to suggest that the cationic species with ligands other than simple halides and hydrides are less stable than their neutral counterparts. The halo cations are quite stable and recent work in this department on the iodo cation with fluorophosphines also showed the reductive elimination to go via the elimination of phosphonium salt. SiH₄ and SiH₃Cl react and eliminate H₂. This probably reflects the instability of a hydride trans to an SiH₃ or SiH₂Cl group. The adduct with HCl showed both modes of reductive elimination but preferred H₂ elimination to about 90%. In this case however the two products PtHCl(PEt₃)₂ and [ClPt(PEt₃)₃⁺BPh₄⁻] are both very stable compounds and the presence of both in the reaction mixture must be a reflection of just how similar in energy are the two reductive elimination pathways. Chlorine involved a very complex reaction (Figure 3.8) but no matter which way the reaction proceeds the final product is always the chlorocation.

The SiH₄ reaction is very slow and the GeH₄ reaction did not proceed at all. This is not unique to the cation system and Chatt et al suggested that the slow reactions of SiH₄ and GeH₄ in oxidative addition reactions could be attributed to the lack of electron withdrawing substituents. This theory would suggest that SiH₃F should react very rapidly due to high electron withdrawing properties of the fluorine. In fact SiH₃I reacts most rapidly of all the SiH₃X systems and is the only case in which a 6-coordinate Pt(IV) species is observed.

The tendency of the silyl compound containing a heavy halide to form 6-coordinate complexes has been observed by previous workers. In contrast even GeH₃F forms a 6-coordinate Pt(IV) intermediate. The 4-coordinate
GeH$_2$F species was not observed but there are very few stable platinum complexes involving fluorine. The unexpected inability of GeH$_3$Br to form a 6-coordinate Pt(IV) species remains a mystery for which no satisfactory explanation can be offered. The absence of reaction with H$_2$S is not altogether surprising as previous workers found that -SH complexes of platinum were generally more difficult to prepare than the -SeH analogues. They found that elimination of H$_2$S seemed to be the driving force in the very rapid decomposition of platinum(IV) hydrogen sulphides which are formed. This would block the formation of the initial 6-coordinate species in the cation reaction. In keeping with their results, the H$_2$Se formed a relatively stable 6-coordinate Pt(IV) species.

The mode of oxidative addition is most commonly cis$^{10}$ and while this has not been proven for this system it is the most likely mechanism. Reaction using either the deuto cation or MD$_3$X would elucidate the mode of addition as the $^1$H n.m.r. spectra would be quite different for the two possible products in each case (see below).
HCl has been shown to undergo trans oxidative addition with the cation but this cannot be taken as typical due to the small size of HCl compared with the other ligands used.

The cation undergoes oxidative addition reactions in a manner typified by incomplete reactions on an equimolar basis and extremely complex manner when an excess is used. The reductive elimination is typically via loss of the phosphonium salt unless another route produces a more stable compound. The rate of reaction between the cation and silyl or germyl halides is, in general, no faster than the reactions between the same silyl or germyl species and the neutral complexes PtH(PEt$_3$)$_2$X.

The n.m.r. spectra show some unexpected features. The absence of marked second-order effects in the PtH resonances of the 6-coordinate adducts with GeH$_3$F and GeH$_3$I is a little surprising. It is strange to observe $^3$J$_{HSiPtP}$ when there is no trans phosphine ligand, as in the 4-coordinate GeH$_3$Cl adduct, yet to observe no such coupling when phosphorus is also trans to Si, as in the 4-coordinate SiH$_3$Cl adduct. It is possible that the positive charge on the latter makes a significant difference. It is disappointing to have failed to isolate any of these complexes, but the spectroscopic parameters leave little room for doubt as to their identities.
REFERENCES (CHAPTER 3)


4. K. Worville and A. Quirt, N.m.r. Program Library, University of East Anglia.


CHAPTER 4: OXIDATIVE ADDITION REACTIONS OF SOME ANIONIC PLATINUM(II) SPECIES

4.1 Introduction

As an extension to the study of the platinum(II) cationic species detailed in the previous chapter, it was decided to investigate some oxidative addition reactions of the \( [X_3Pt(PEt_3)]^- \) anion. The compounds studied were \( Pr_4N^+[Cl_3Pt(PEt_3)]^- \), \( Pr_4N^+[I_3Pt(PEt_3)]^- \) and \( Me_4N^+[Cl_3Pt(PEt_3)]^- \). Previous workers have observed a wide variation in the reactivity of Platinum halo phosphine complexes by varying the halogen. Generally, the species with the heavier halogen atom tends to be the more reactive. This effect should be greatly enhanced in the anionic species as they contain three halogen atoms. Thus the original idea was to study the reactions of the chloro and iodo anions and see how pronounced the difference in reactivities would be. The study could only be carried out by \( ^{31}P \) n.m.r. spectroscopy as the \( Pr_4N^+ \) counter cation has a very broad set of resonances in the \( ^1H \) n.m.r. spectrum and in a large number of cases these obscured product resonances. Accordingly it was decided to extend the study by preparing the chloro and iodo anions with an \( Me_4N^+ \) counter cation. The chloro species was synthesised without problem, but when the normal halogen metathesis was carried out the product obtained was \( Pt_2I_4(PEt_3)_2 \). (See Section 4.5).

Thus, the study was carried out using the aforementioned species, mainly on the basis of \( ^{31}P \) n.m.r. spectroscopy. Where applicable, \( ^1H \) n.m.r. spectroscopy and occasionally elemental analysis for halogen were utilised.
4.2 Reactions of \( \text{Pr}_4^+\text{Cl}_3\text{Pt(PET}_3) \)

All reactions were carried out in \( \text{CD}_2\text{Cl}_2 \) and \( ^{31}\text{P} \) n.m.r. spectra were recorded with protons decoupled unless otherwise stated. N.m.r. parameters are detailed in Table 4.1.

4.2.1 Reaction with \( \text{SiH}_4 \)

After 10 minutes at room temperature reaction was detected by \( ^{31}\text{P} \) n.m.r. spectroscopy. From the size of the platinum-phosphorus coupling constant the product species was a 6-coordinate Pt(IV) complex. The species was produced in low concentration and after ca. two hours at room temperature had disappeared and was replaced by about 10% yield of a 4-coordinate Pt(II) species. Attempts to observe a low frequency hydride resonance in the \( ^1\text{H} \) n.m.r. spectrum of the initial product were unsuccessful even at low temperature, due to the presence of solid in the tube giving very low levels of resolution. On the basis of previous reactions it was thought the two species could be:

\[
\begin{align*}
\text{Pr}_4^+\text{Cl}_3\text{Pt(PET}_3) & - \text{SiH}_3 \\
\text{Pr}_4^+\text{Cl}_3\text{Pt(H)SiH}_3 & - \text{PET}_3
\end{align*}
\]

The 6-coordinate isomer showed no apparent trans \( ^2J_{PH} \) coupling on selective decoupling of the triethyl protons in the \( ^{31}\text{P} \) n.m.r. spectra. The only result of this experiment was a slight broadening
of the resonances. Attempts at isolation all met with failure.

4.2.2 Reaction with SiH$_3$F

After about three hours at room temperature, two species were detected by $^{31}$P n.m.r. spectroscopy. From the size of their platinum-phosphorus coupling constants it was apparent that one was a 6-coordinate Pt(IV) and the other a 4-coordinate Pt(II) species. After standing at room temperature overnight, the $^{31}$P n.m.r. spectrum showed the presence of another 6-coordinate Pt(IV) species in addition to the two species already observed. The $^{19}$F n.m.r. spectrum showed three fluorine containing species, none of which showed triplet coupling from an SiH$_2$. The lowest frequency signal was a doublet with $^{195}$Pt satellites. The doublet coupling of 76 Hz is as expected for a coordinated SiHF$_2$ group. This would suggest the compound to be:

This is the most likely species following HCl elimination of a 6-coordinate intermediate. The phosphine would be expected to show coupling if it was trans to the SiHF$_2$ group. The absence of an -SiH$_2$F species is not completely surprising as this effect has been observed before$^1$. (See Section 4.5). The highest frequency signal was a doublet of doublets with $^{195}$Pt satellites but no two bond H-F coupling. This would suggest that the ligand was actually
an SiF$_3$ group. The n.m.r. parameters are compatible with the product being one of the three isomers:

$I$: $\text{Pr}_4\text{N}^+\left[\begin{array}{c} \text{Cl} \\ \text{SiF}_3 \\ \text{Cl} \\ \text{PET}_3 \end{array}\right]$ or $\text{Pr}_4\text{N}^+\left[\begin{array}{c} \text{Cl} \\ \text{Pt} \\ \text{Cl} \\ \text{PET}_3 \end{array}\right]$ or $\text{Pr}_4\text{N}^+\left[\begin{array}{c} \text{Cl} \\ \text{H} \\ \text{Pt} \\ \text{Cl} \end{array}\right]$

(II) (III)

It did not prove possible to decide which isomer actually was present as the Varian XL100 could not decouple $^1\text{H}$ or $^{31}\text{P}$ from the $^{19}\text{F}$ spectrum at this time. On the basis of the sizes of coupling constants by another worker in this department, it seems most likely that the larger doublet coupling of 6 Hz arises from a cis phosphorus and the narrow doublet coupling of 2 Hz from a cis hydride. Thus it would appear that isomer III is the most likely candidate. Selectively decoupling only the ethyl protons from the $^{31}\text{P}$ n.m.r. spectrum resulted in a slight broadening of the lines, which implies the hydride and phosphine are mutually cis.

The third species in the $^{19}\text{F}$ n.m.r. spectrum is a narrow triplet with $^{195}\text{Pt}$ satellites. Assuming that this was the third species observed in the $^{31}\text{P}$ n.m.r. spectrum, it too is a 6-coordinate Pt(IV) complex. Due to the absence of a two bond proton coupling in the $^{19}\text{F}$ n.m.r. spectrum, it appears that this is also an SiF$_3$ species. The small triplet coupling in the $^{19}\text{F}$ n.m.r. spectrum can be explained as an overlapping doublet of doublets arising from a trans hydride and a cis phosphine coupling, both of
4 Hz, giving rise to an apparent triplet. Repeating the experiment and observing the $^{19}$F n.m.r. spectrum at low temperature again failed to show any SiH$_2$F species. Attempts to observe any low frequency hydride resonances also met with failure. The structure was assigned as:

$$\text{Pr}_4\text{N}^+\left[\begin{array}{c}
\text{SiF}_3 \\
\text{Cl} \\
\text{Pt} \\
\text{Cl} \\
\text{H} \\
\text{P} \\
\end{array}\right]^-$$

4.2.3 Reaction with SiH$_3$Cl

Reaction was observed after two hours at room temperature by $^{31}$P n.m.r. spectroscopy. Two species formed in about 1:2 ratio. The more abundant species was a 4-coordinate Pt(II) complex and the other a 6-coordinate Pt(IV) complex assigned on the sizes of their platinum-phosphorus coupling constants. Comparison of the $^{31}$P n.m.r. parameters showed that the 4-coordinate Pt(II) species was clearly the same as that detected in the reaction with SiH$_4$ (Section 4.2.1). This implies the structure to be:

$$\text{Pr}_4\text{N}^+\left[\begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{SiH}_2\text{Cl} \\
\text{PET}_3 \\
\end{array}\right]^-$$

Although the 6-coordinate Pt(IV) species in the two reactions
appear to be different, it seems most likely that the final 4-coordinate Pt(II) species are the same. This type of reaction has been observed by a previous worker. Assuming the 6-coordinate Pt(IV) species is not the same as that observed for the SiH₄ system it seems likely that the structure is:

\[
\begin{align*}
\text{Pr}_4N^+ &\quad \text{SiH}_2\text{Cl} \\
&\quad \text{PEt}_3 \\
\text{Cl} &\quad \text{Pt} \\
&\quad \text{Cl} \\
&\quad \text{Cl}
\end{align*}
\]

or an isomer thereof.

4.2.4 Reactions with SiH₃Br and SiH₃I

Both of these were slow to react, but after about two hours at room temperatures, reactions were detected by $^{31}$P n.m.r. spectroscopy. In both cases a large number of different species was observed. This can be explained by the halogen on the silyl group exchanging with the various chlorine atoms bound to platinum. The tendency of the heavier halogen to bind to platinum rather than the silicon is well documented. Due to the number of isomers possible in these systems, no further work was carried out on them.

4.2.5 Reaction with GeH₄

Although the reaction was faster than the corresponding SiH₄ reaction, the sample had to be warmed to room temperature before reaction was detected by $^{31}$P n.m.r. spectroscopy. The only product
detected was a 4-coordinate Pt(II) species. No further information could be obtained as regards the structure of the species at this stage.

4.2.6 Reaction with GeH₃F

After one hour at room temperature, reaction was detected by ³¹P n.m.r. spectroscopy. From the size of the platinum-phosphorus coupling constant the species was a 4-coordinate Pt(II) complex. The ¹⁹F n.m.r. spectrum was a narrow doublet with ¹⁹⁵Pt satellites. The absence of a two bond proton coupling confirmed the species to contain a GeF₃ group rather than GeH₂F. The narrow doublet must arise from coupling to a cis phosphine as ¹H n.m.r. in the low frequency region failed to show a hydride. This suggests the structure to be:

\[
\begin{array}{c}
\text{GeF}_3 \\
\text{Pr}_4N^+ \\
\text{Cl} \\
\text{Pt} \\
\text{P} \\
\text{Cl}
\end{array}
\]

4.2.7 Reactions with GeH₃Cl

Reaction was detected at 0°C by ³¹P n.m.r. spectroscopy. The product obtained in low yield, was a 4-coordinate Pt(IV) species from the size of its platinum-phosphorus coupling constant. The ³¹P n.m.r. parameters were identical to those of the species obtained in the reaction with GeH₄ (Section 4.2.5). This is directly analogous to the case of SiH₄ and SiH₃Cl. On standing
overnight at room temperature the reaction went to completion. The $^{31}$P n.m.r. spectrum showed the species to be the sole product. Attempts to isolate the product, even at reduced temperatures, met with failure despite rigorous exclusion of air and moisture. Accordingly the reaction was repeated on a larger scale and as soon as the reaction was complete the solvent and any volatiles were removed, 2MNaOH added, and the mixture refluxed under nitrogen for ten minutes. The solution was then acidified with dilute nitric acid and silver nitrate solution added to precipitate the chloride. The silver chloride was filtered off and dried under vacuum. The results shown below confirm the presence of three chlorines per molecule. After removal of solvent and volatiles, a significant weight increase was also noted on another sample, showing reaction had occurred.

Analysis for Chlorine:

<table>
<thead>
<tr>
<th>Weight of Pru$^4 N^+$[Cl$_3$Pt(PEt$_3$)]$^-$</th>
<th>0.1105 (\equiv) 0.1825 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of AgCl precipitated</td>
<td>0.0778 (\equiv) 0.5422 mM</td>
</tr>
<tr>
<td>% error for 3 chlorines per molecule</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

These results confirm the product to contain three chlorine atoms, i.e.

\[
\begin{align*}
\text{Pr}_4 N^+ & \quad \text{Cl} \quad \text{Pt} \quad \text{PEt}_3 \\
& \quad \text{GeH}_2 \text{Cl} \\
\end{align*}
\]

or

\[
\begin{align*}
\text{Pr}_4 N^+ & \quad \text{Cl} \\
& \quad \text{Pt} \quad \text{Cl} \\
& \quad \text{Pet}_3 \\
\end{align*}
\]
4.2.8 Reactions with GeH$_3$Br and GeH$_3$I

These reactions were analogous to those with SiH$_3$Br and SiH$_3$I and once again a mixture of products was obtained. This again shows halogen exchange and no further work was carried out on these systems.

4.2.9 Reaction with Cl$_2$

Reaction began at room temperature and the sole product was detailed by $^{31}$P n.m.r. spectroscopy. The $^{31}$P n.m.r. spectrum showed 100% conversion to a 6-coordinate Pt(IV) species, confirmed by the size of the platinum phosphorus coupling constant. The product was stable at room temperature but decomposed on removal of solvent. This structure is probably:

\[
\text{Pr}_4\text{N}^+ \quad \text{Cl} \quad \text{Pt} \quad \text{PEt}_3 \quad \text{Cl} \quad \text{Cl}
\]

Decomposition products appeared to contain platinum and no n.m.r. data could be obtained.

4.2.10 Reactions with HCl and HI

No reaction with HCl was detected by $^{31}$P n.m.r. spectroscopy, even after a period of weeks at room temperature. The reaction with HI was detected at -60°C by $^{31}$P n.m.r. spectroscopy when a 4-coordinate Pt(II) species was the only phosphorus species present.
The value of the platinum-phosphorus coupling constant for this species of 3515 Hz is between the values for the \([\text{Cl}_3\text{Pt(PEt}_3\text{)}]\) anion (3696 Hz) and the \([\text{I}_3\text{Pt(PEt}_3\text{)}]\) anion (3428 Hz). The species is presumably one of the complexes with mixed halogens. Purely on the basis of a linear change of coupling constant between the trichloro and triodo anions, it looks as if the species contains two iodines and one chlorine. This cannot be taken as more than an indication and no proof can be offered. On warming the sample, a complex mixture of products was obtained from which no further information could be obtained but neither the trichloro or the triodo anion was detected.

4.2.11 Reaction with \(\text{H}_2\text{S}\)

Reaction was detected at -40°C by \(^{31}\text{P}\) n.m.r. spectroscopy. The species observed was a singlet with two sets of \(^{195}\text{Pt}\) satellites. The normal satellites were augmented by long range satellites of coupling constant 10 Hz. This pattern is indicative of an (AX)_2 binuclear platinum species (see Section 4.5). A very small amount of this species was detected and further warming decomposed it, leaving starting material as the only species detected by \(^{31}\text{P}\) n.m.r. spectroscopy. Repeating the experiment with a large excess of \(\text{H}_2\text{S}\) present gave the same result. It proved impossible to obtain an \(^1\text{H}\) n.m.r. spectrum of this species and no further information about its structure could be obtained.
Figure 4.1 Reaction of $\text{Pr}_4\text{N}^+[\text{Cl}_3\text{Pt(PEt}_3\text{)}]^- + \text{H}_2\text{Se} \quad -40^\circ\text{C}$
4.2.12 Reaction with $\text{H}_2\text{Se}$

Reaction was detected at $-40^\circ\text{C}$ by $^{31}\text{P}$ n.m.r. spectroscopy. The species once again was obviously a symmetrical binuclear platinum(II) complex from the two sets of $^{195}\text{Pt}$ satellites. Unlike the $\text{H}_2\text{S}$ system (4.2.11), the yield of this product was about 60% based on the $^{31}\text{P}$ n.m.r. spectrum. Attempts to obtain an $^1\text{H}$ n.m.r. spectrum at low temperature met with failure because of incomplete dissolution interfering with the resolution of the high field spectrometer. Warming the sample sufficiently to remove the problem unfortunately decomposed the species.

4.3 Reactions of $\text{Me}_4\text{N}^+\left[\text{Cl}_3\text{Pt(PEt}_3)\right]^-$

All reactions were carried out in $\text{CD}_2\text{Cl}_2$ and $^{31}\text{P}$ n.m.r. spectra were recorded with protons decoupled unless otherwise stated. N.m.r. parameters are detailed in Table 4.2. Only the more interesting reactions from Section 4.2 were studied with the different counter cation in an attempt to gain more information about the systems. Little change was anticipated in either the manner or rate of reaction with the different counter cation.

4.3.1 Reaction with $\text{SiH}_4$

After 15 minutes at room temperature, reaction was detected by $^{31}\text{P}$ n.m.r. spectroscopy. As the contents of the tube were darkening fairly rapidly, the spectra were observed at $-50^\circ\text{C}$. The $^{31}\text{P}$ n.m.r. spectra showed two species to be present and from the
TABLE 4.1  N.m.r. parameters for the products of the reaction between Pr\textsubscript{4}N\textsuperscript{+}[Cl\textsubscript{3}Pt(Pe\textsubscript{3})]\textsuperscript{-} and L

<table>
<thead>
<tr>
<th>L</th>
<th>P ppm</th>
<th>$^{1}$J\textsubscript{PtP} Hz</th>
<th>Other parameters observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH\textsubscript{4}</td>
<td>+12.31</td>
<td>2436</td>
<td>δF = -96.85 ppm. $^{2}$J\textsubscript{FSiPt} = 1050 Hz. $^{3}$J\textsubscript{PPtSiF} = 6 Hz. $^{3}$J\textsubscript{FSiPtH} = 2 Hz</td>
</tr>
<tr>
<td></td>
<td>+ 9.24</td>
<td>3507</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+12.32</td>
<td>2397</td>
<td>δF = -99.52 ppm. $^{2}$J\textsubscript{FSiPt} = 904 Hz. $^{3}$J\textsubscript{PPtSiF} = 4 Hz. $^{3}$J\textsubscript{FSiPtH} = 2 Hz.</td>
</tr>
<tr>
<td>SiH\textsubscript{3}F</td>
<td>+11.94</td>
<td>2369</td>
<td>δF = -101.28 ppm. $^{2}$J\textsubscript{FSiPt} = 752 Hz. $^{2}$J\textsubscript{HSiF} = 76 Hz.</td>
</tr>
<tr>
<td></td>
<td>+ 9.90</td>
<td>3557</td>
<td></td>
</tr>
<tr>
<td>SiH\textsubscript{3}Cl</td>
<td>+13.31</td>
<td>2399</td>
<td></td>
</tr>
<tr>
<td>GeH\textsubscript{4}</td>
<td>+ 7.61</td>
<td>3426</td>
<td></td>
</tr>
<tr>
<td>GeH\textsubscript{3}F</td>
<td>+10.53</td>
<td>3390</td>
<td>δF = -109.39 ppm. $^{2}$J\textsubscript{FGePt} = 705 Hz. $^{2}$J\textsubscript{PPtGeF} = 2 Hz.</td>
</tr>
<tr>
<td>GeH\textsubscript{3}Cl</td>
<td>+ 7.61</td>
<td>3426</td>
<td></td>
</tr>
<tr>
<td>HI</td>
<td>+ 6.05</td>
<td>3515</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>+ 4.96</td>
<td>3219</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}Se</td>
<td>+ 4.63</td>
<td>3365</td>
<td>$^{3}$J\textsubscript{PPtSePt} = 11 Hz</td>
</tr>
</tbody>
</table>

Frequencies are all +1.2 Hz except $^{19}$F parameters +1.0 Hz. $^{19}$F chemical shifts are relative to CCl\textsubscript{3}F. $^{31}$P chemical shifts are relative to 85% H\textsubscript{3}PO\textsubscript{4}. 
sizes of their platinum-phosphorus coupling constants, they were assigned as a 6-coordinate Pt(II) and a 4-coordinate Pt(IV) species. The $^1$H n.m.r. spectrum at $-50^\circ$ proved to be unattainable as dissolution had not fully occurred at this temperature and the crystals in the solution adversely affected the resolution of the high field spectrometer. When the temperature was raised to $-40^\circ$C only one product species was observed. A rather broad singlet with $^{195}$Pt satellites was observed in the region associated with SiH$_2$X protons. It did not prove possible to resolve a three-bond coupling to the phosphine and this would almost certainly mean that the phosphine is cis to the SiH$_2$X group. Allowing the sample to stand at room temperature resulted in the contents of the tube turning dark brown and decomposing.

4.3.2 Reactions with SiH$_3$Cl

Reaction was detected after 5 minutes at room temperature by $^{31}$P n.m.r. spectroscopy. From the size of the platinum-phosphorus coupling constant, the species was a 4-coordinate Pt(II) complex. The chemical shifts of the phosphorus and the value of the platinum-phosphorus coupling constants were, within experimental error, the same. The $^1$H n.m.r. parameters also transpired to have the same values. This is in keeping with the hypothesis put forward in Section 4.2.3 and confirms that reaction of the anion with either SiH$_4$ or SiH$_3$Cl yields the same product:
The chemical shift of the SiH₂X resonance in the ¹H n.m.r. spectrum also confirms that X is a halogen rather than a hydride.

4.3.3 Reaction with GeH₄

After a short time at room temperature, reaction was detected by ³¹P n.m.r. spectroscopy. The species was confirmed as a 4-coordinate Pt(II) complex by the size of its platinum-phosphorus coupling constant. The ¹H n.m.r. spectrum showed a broadened singlet with ¹⁹⁵Pt satellites in the region associated with a GeH₂X resonance (X = halogen). This is in keeping with the observations for the SiH₄ system (Section 4.3.1).

4.3.4 Reaction with GeH₃Cl

Reaction was detected after 5 minutes at room temperature by ³¹P n.m.r. spectroscopy. From ³¹P and ¹H n.m.r. spectra the species was confirmed to be the same as that detected in the GeH₄ reaction (Section 4.3.3). Once again, this is in keeping with the hypotheses suggested in Section 4.2.3 and the structure is probably:

\[
\begin{array}{c}
\text{Me₄N⁺} \\
\text{Cl} \\
\text{Pt} \\
\text{SiH₂Cl}
\end{array}
\quad [-]
\begin{array}{c}
\text{PEt₃} \\
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{Me₄N⁺} \\
\text{Cl} \\
\text{Pt} \\
\text{GeH₂Cl}
\end{array}
\quad [-]
\begin{array}{c}
\text{PEt₃} \\
\text{Cl}
\end{array}
\]
4.3.5 Reaction with $\text{H}_2\text{S}$

Reaction was detected at $-40^\circ\text{C}$ by $^{31}\text{P}$ n.m.r. spectroscopy. The spectrum showed no long range $^{195}\text{Pt}$ satellites and was assigned as a simple 4-coordinate Pt(II) species. The $^1\text{H}$ n.m.r. spectrum showed a singlet with $^{195}\text{Pt}$ satellites at $-1.07$ ppm, which was assigned as a Pt-SH resonance on the basis of results obtained by other workers. The structure is probably

$$\begin{array}{c}
\text{Me}_4\text{N}^+ \\
\text{Cl} \\
\text{Pt} \\
\text{SH} \\
\text{Cl} \\
\text{PEt}_3
\end{array}$$

Allowing the sample to stand at room temperature did not increase the yield above about 40% (based on the $^{31}\text{P}$ n.m.r. spectrum). Addition of an excess of $\text{H}_2\text{S}$ had no effect on the yield and even heating the sample failed to produce a binuclear species. It is likely that formation of this type of species is intermediate in the formation of the binuclear system (see Section 4.3.6). There seems to be no simple explanation as to why reducing the size of the counter cation should stop the reaction at this intermediate stage.

4.3.6 Reaction with $\text{H}_2\text{Se}$

Reaction was detected at $-50^\circ\text{C}$ by $^{31}\text{P}$ n.m.r. spectroscopy. The product singlet had two sets of $^{195}\text{Pt}$ satellites typical of an $[\text{PtP}]_2$ spin system and the species was assigned as being a 4-coordinate, symmetrical, binuclear Pt(II) complex. The $^1\text{H}$ n.m.r.
spectrum at -45°C showed a narrow triplet at -1.8 ppm and what appeared to be rather weak $^{195}$Pt satellites (see Section 4.5). Irradiation with a broad band (3 KHz) of $^{31}$P frequency radiation collapsed both the main triplet coupling and the triplet on the $^{195}$Pt satellites. This decoupling also helped to show the $^{77}$Se satellites. This would suggest that the structure is probably:

$$\begin{align*}
\text{Pr}_4^+ 
\begin{array}{c}
\text{Cl} \\
\text{Et}_3^p \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{H} \\
\text{Se} \\
\text{Pt} \\
\text{Pt} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{PEt}_3 \\
\end{array}
\end{align*}$$

The isomer with the phosphines both cis to the bridge cannot be ruled out solely on the basis of the size of the coupling $^3J_{PPtSeH}$ as three bond coupling constants are very sensitive to twist angles.

The formation of this binuclear species can be accounted for by the mechanism in Figure 4.2:

$$\begin{align*}
\text{Me}_4^+ 
\begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{PEt}_3 \\
\end{array}
\end{align*} + H_2 Se + \text{Me}_4^+ 
\begin{align*}
\text{Cl} & \begin{array}{c}
\text{Pt} \\
\text{SeH} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{PEt}_3 \\
\end{array} & \begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{SeH} \\
\end{array}
\end{align*} + \text{HCl}

\text{(I)}

\text{(II)}

+ \text{Me}_4^+ - [\text{Cl}_3^3\text{Pt(PEt}_3^-)]$$

$$\begin{align*}
\text{Me}_4^+ 
\begin{array}{c}
\text{Cl} \\
\text{Et}_3^p \\
\text{Pt} \\
\text{Cl} \\
\text{Cl} \\
\text{PEt}_3 \\
\end{array} + \text{Me}_4^+ \text{Cl}
\end{align*}$$

Figure 4.2
A selective decoupling experiment showed that irradiating at the frequency of the high frequency $^{195}\text{Pt}$ satellite in the $^{31}\text{P}$ n.m.r. spectrum collapsed the low frequency $^{195}\text{Pt}$ satellite of the SiH resonance in the $^{1}\text{H}$ n.m.r. spectrum. This showed that $^{1}_J\text{PtP}$ and $^{2}_J\text{HSePt}$ are of opposite signs and as $^{1}_J\text{PtP}$ is known to be positive, means that $^{2}_J\text{HSePt}$ is negative. Despite repeated attempts at low temperature, it did not prove possible to observe either species (I) or (II) in Figure 4.2 by either $^{31}\text{P}$ or $^{1}\text{H}$ n.m.r. spectroscopy.

4.4 Reactions of Pr$_4$N$^+\text{I}_2\text{Pt(PEt}_3\text{)}$-

All reactions were carried out in CD$_2$Cl$_2$ and $^{31}\text{P}$ n.m.r. spectra were recorded with protons decoupled unless otherwise stated. N.m.r. parameters are detailed in Table 4.3.

4.4.1 Reaction with SiH$_4$

Reaction was detected at $-30^\circ\text{C}$ by $^{31}\text{P}$ n.m.r. spectroscopy. The size of the platinum-phosphorus coupling constant proved the product species to be a 6-coordinate Pt(IV) complex. The $^{1}\text{H}$ n.m.r. spectrum could not be observed in the SiH$_2$X region due to the counter cation but the low frequency region showed a singlet with $^{195}\text{Pt}$ satellites. The absence of a doublet coupling implies the presence of a cis, rather than trans, phosphorus. The chemical shift of the hydride is compatible with the trans ligand being a halogen. This would suggest the structure to be:
<table>
<thead>
<tr>
<th>L</th>
<th>δP ppm</th>
<th>$^1J_{\text{PtP}}$ Hz</th>
<th>δMH ppm</th>
<th>$^2J_{\text{HMPt}}$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_4$</td>
<td>+12.30</td>
<td>2396</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>SiH$_3$Cl</td>
<td>+ 8.14</td>
<td>3658</td>
<td>+4.69</td>
<td>113</td>
</tr>
<tr>
<td>GeH$_4$</td>
<td>+ 9.08</td>
<td>3415</td>
<td>+5.11</td>
<td>211</td>
</tr>
<tr>
<td>GeH$_3$Cl</td>
<td>+ 9.11</td>
<td>3413</td>
<td>+5.12</td>
<td>212</td>
</tr>
<tr>
<td>*H$_2$S</td>
<td>+ 4.83</td>
<td>3681</td>
<td></td>
<td></td>
</tr>
<tr>
<td>†H$_2$Se</td>
<td>+ 5.83</td>
<td>3221</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All $^{31}$P frequencies ±1.2 Hz; all $^1$H frequencies ±1.0 Hz.

* also determined for H$_2$S reaction - δSH = -1.07 ppm, $^2J_{\text{HSPt}}$ = 54 Hz.

† also determined for H$_2$Se reaction - δSeH = -1.82 ppm, $^1J_{\text{SeH}}$ = 82 Hz, $^2J_{\text{HSePt}}$ = 42 Hz, $^3J_{\text{HSePtP}}$ = 7 Hz.

n.o. = not observed.
It was thought unlikely that an iodine was bonded to the silicon as an -SiH₂I, but this cannot be ruled out. On warming to -20°C the 6-coordinate species decomposed and was replaced by a 4-coordinate Pt(II) species. It is not possible to prove the structure of this species but it is most likely that the reductive elimination proceeds via the loss of HI. On warming to room temperature the contents of the n.m.r. tube turned black and decomposed.

4.4.2 Reaction with SiH₃F

At -50°C a trace of a 6-coordinate Pt(IV) species was detected by its ³¹P n.m.r. spectrum. This decomposed very rapidly and on repeating the experiment a satisfactory ¹⁹F n.m.r. spectrum still could not be obtained. No further reaction was detected by either ³¹P or ¹⁹F n.m.r. spectroscopy until 0°C when a narrow quartet with ¹⁹⁵Pt satellites was detected by ³¹P n.m.r. spectroscopy. The ¹⁹F n.m.r. spectrum of this 4-coordinate Pt(II) species consisted of an equally narrow doublet with ¹⁹⁵Pt satellites. The size of the narrow doublet coupling was typical of a cis phosphorus coupling to the fluorine. As no two-bond hydrogen coupling was observed, the species is presumably an SiF₃ complex. This would suggest the structure to be:
This is in keeping with the observed result for the reaction of the trichloro anion with SiH$_3$F.

4.4.3 Reaction with SiH$_3$Cl

At -50°C reaction was detected by $^{31}$P n.m.r. spectroscopy. The size of the platinum-phosphorus coupling showed the species to be a 6-coordinate Pt(IV) complex. The $^1$H n.m.r. spectrum showed a broad low frequency resonance with $^{195}$Pt satellites. The chemical shift of the hydride resonance is typical for the trans ligand being a halogen. The breadth of the resonance was probably caused by the problem of crystals disturbing the homogeneity of the magnetic field but confirms that the phosphorus is in a cis position to the hydride.

On warming the sample to -10°C a 4-coordinate Pt(II) species was detected by its $^{31}$P n.m.r. spectrum. Further warming to room temperature eventually led to decomposition of this species and formation of a complex pattern which could not be assigned. From the information obtained the species formed were probably:

\[ \text{Pr}_4N^+ \left[ \begin{array}{c} \text{PEt}_3 \\ \text{I} \\ \text{H} \\ \text{I} \end{array} \right] \text{Pt} \left[ \begin{array}{c} \text{SiH}_2\text{Cl} \\ \text{I} \end{array} \right] \text{Pr}_4N^+ \left[ \begin{array}{c} \text{PEt}_3 \\ \text{I} \end{array} \right] \text{Pt} \left[ \begin{array}{c} \text{SiH}_2\text{Cl} \\ \text{I} \end{array} \right] + \text{HI} \]
4.4.4 Reaction with SiH₂Br

Reaction was detected at -50°C by $^{31}$P n.m.r. spectroscopy and two species were formed. From the sizes of their platinum-phosphorus coupling constants both were identified as 6-coordinate Pt(IV) species. The coupling constants for the two species are very similar and probably arise from two isomers of the same compound, e.g:

$$\begin{align*}
\text{Pr}_4N^+ & \quad \text{SiH}_2\text{Br}^- \\
& \quad \text{H} \quad \text{Pt} \quad \text{PEt}_3
\end{align*}$$

and

$$\begin{align*}
\text{Pr}_4N^+ & \quad \text{SiH}_2\text{Br}^- \\
& \quad \text{H} \quad \text{Pt} \quad \text{I}
\end{align*}$$

Due to problems with resolution, it again proved impossible to obtain a low frequency $^1$H n.m.r. spectrum. Warming to -10°C resulted in the decomposition of these species and the formation of a 4-coordinate Pt(II) complex. Although no proton data could be obtained for this species, it is most likely that reductive elimination proceeds via the loss of HI in the normal manner. Warming to room temperature for an hour resulted in decomposition and the appearance of a large number of unassigned resonances in the $^{31}$P n.m.r. spectrum.

4.4.5 Reaction with SiH₃I

Reaction was detected at -50°C by $^{31}$P n.m.r. spectroscopy. From the size of the platinum-phosphorus coupling constant, the species was a 6-coordinate Pt(IV) complex. After standing at
-50°C for one hour, a second 6-coordinate Pt(IV) species was observed in the $^{31}P$ n.m.r. spectrum. As in the SiH$_3$Br system, these two 6-coordinate species have very similar coupling constants and it seems likely that they are analogous to the isomers obtained with SiH$_3$Br. The low frequency $^1$H n.m.r. spectrum could not be observed until the sample had been warmed to -30°C to allow complete dissolution. No low frequency hydride resonances were observed at this temperature and the $^{31}P$ n.m.r. spectrum showed that the two 6-coordinate species had decomposed and a large number of weak resonances had developed. Warming to room temperature for a short time resulted in the only species detected by $^{31}P$ n.m.r. spectroscopy being a 4-coordinate Pt(II) complex whose n.m.r. parameters were identical to those observed for the 4-coordinate product with SiH$_4$ (Section 4.4.1). This suggests that the complex obtained by reaction of the triodo anion with either SiH$_4$ or SiH$_3$I is:

$$\text{Pr}_4\text{N}^+ \begin{array}{c} \text{I} \\ \\
\text{Pt} \\
\text{SiH}_2\text{I} \\
\text{I} \end{array} \text{PET}_3^-$$

This is analogous to the products observed in the reactions between the trichloro anion and either SiH$_4$ or SiH$_3$Cl.

4.4.6 Reaction with GeH$_4$

Reaction was detected at -40°C by $^{31}P$ n.m.r. spectroscopy. The spectrum contained a large number of resonances which could not be
assigned. A number had no associated $^{195}$Pt satellites. Warming to
-20°C resulted in the contents of the tube turning black with
fizzing and no further n.m.r. spectra could be obtained.

4.4.7 Reaction with GeH₃F

Reaction was detected at -50°C by $^{31}$P n.m.r. spectroscopy. The
product was assigned as a 6-coordinate Pt(IV) complex on the basis
of the value of its platinum-phosphorus coupling constant. The
lines were rather broad and initially this was thought to be due to
a poorly resolved coupling to fluorine, but removal of the n.m.r.
tube from the probe showed the reason to be effervescence. No $^1$H
n.m.r. spectra could be obtained for the 6-coordinate species and
the $^{19}$F n.m.r. showed broad humps spanning a range of over 20 ppm.
Warming the sample to -30°C resulted in the effervescence stopping
and the $^{31}$P n.m.r. spectrum showed a 4-coordinate Pt(II) species.
The lines were slightly broadened and this was probably genuine
broadening from $^{19}$F coupling. The $^{19}$F n.m.r. spectrum showed a very
narrow doublet with $^{195}$Pt satellites. The absence of a two bond
fluorine hydrogen coupling confirmed the species to contain a
-GeF₃ group. The narrow coupling probably arises from a cis
phosphorus and means that the structure is most probably:

$$\begin{array}{c}
\text{Pr}_4N^+ \\
\text{I} \\
\text{Pt} \\
\text{GeF}_3 \\
\text{I} \\
\text{PET}_3
\end{array}$$
4.4.8 Reaction with GeH₃Cl

Reaction was detected at -60°C by ³¹P n.m.r. spectroscopy. Two species were formed in roughly equal amounts and were confirmed to be 6-coordinate Pt(IV) species by the size of their platinum-phosphorus coupling constants. As with the reactions between SiH₃Br or SiH₃I and the anion, these species had very similar platinum-phosphorus coupling constants and are probably analogous isomers to those suggested in Section 4.4.4. Due to solid in the n.m.r. tube, it once again proved impossible to observe the low frequency region of the ¹H n.m.r. spectrum. Warming the n.m.r. tube to -40°C resulted in the decomposition of the two 6-coordinate species and the formation of a 4-coordinate Pt(II), identified by its ³¹P n.m.r. spectrum. No further information could be obtained about this system but it seems likely that the final 4-coordinate Pt(II) species is formed by reductive elimination of HI from the 6-coordinate Pt(IV) intermediates to give an analogous product to that obtained with SiH₃I.

4.4.9 Reaction with GeH₃Br

Reaction was detected at -60°C by ³¹P n.m.r. spectroscopy. Unlike the reaction with GeH₃Cl, only one 6-coordinate Pt(IV) species was observed. Warming to -30°C decomposed this species and a large number of unassigned lines were observed in the ³¹P n.m.r. spectrum. Warming to room temperature for a short time then cooling to -50°C showed a 4-coordinate Pt(II) species to be the major product but leaving at room temperature resulted in the contents of the tube turning black and decomposing, and no further
spectra could be obtained.

4.4.10 Reaction with GeH$_3$I

Reaction was detected at -50°C by $^{31}$P n.m.r. spectroscopy when two 6-coordinate Pt(IV) species were observed. Once again these have very similar platinum-phosphorus coupling constants, as experienced in previous reactions. Warming to -30°C decomposed both these species, the tube darkened in colour and what appeared to be metallic platinum dropped out of solution. Although it proved possible to observe a very low quality $^{31}$P n.m.r. spectrum, no $^1$H n.m.r. spectra could be observed. The $^{31}$P n.m.r. spectra showed mainly a 4-coordinate Pt(II) species but also contained a little of a new 6-coordinate Pt(IV) species. Further standing at -30°C resulted in further decomposition and not even $^{31}$P n.m.r. spectra could be observed. This suggests that whilst the first stage of this reaction is typical, the latter stages are involved with decomposition products which could not be identified.

4.4.11 Reaction with HCl

Reaction was detected at -80°C by $^{31}$P n.m.r. spectroscopy when a 6-coordinate Pt(IV) species was observed. The $^1$H n.m.r. spectrum showed a singlet with $^{195}$Pt satellites in the low frequency hydride region. No coupling to phosphorus was observed and it must therefore be assumed that the hydride is cis to the phosphine. The chemical shift of the hydride is also consistent with the trans ligand being an iodide. Warming to room temperature showed this species to be present but only in small (20%) amounts. The structure
can probably be assigned as

\[
\text{Pr}_4\text{N}^+ \left[ \begin{array}{c} \text{I} \\
\text{Cl} \\
\text{I} \end{array} \right] \text{Pt} \left[ \begin{array}{c} \text{I} \\
\text{H} \end{array} \right] \left[ \begin{array}{c} \text{PEt}_3 \\
\text{I} \\
\text{Cl} \end{array} \right] - \quad \text{or} \quad \left[ \begin{array}{c} \text{Cl} \\
\text{I} \\
\text{I} \end{array} \right] \text{Pt} \left[ \begin{array}{c} \text{H} \\
\text{I} \end{array} \right] \left[ \begin{array}{c} \text{PEt}_3 \\
\text{I} \\
\text{Cl} \end{array} \right] -
\]

### 4.4.12 Reaction with HI

Reaction began while the n.m.r. tube was being fitted with a spinner and by the time the sample was placed in the probe the sample had visibly reacted, by changing colour to deep red. The $^{31}\text{P}$ n.m.r. spectrum at $-80^\circ\text{C}$ showed the only species present to be a 6-coordinate Pt(IV) complex. The $^1\text{H}$ n.m.r. spectrum in the low frequency region at this temperature showed a singlet with $^{195}\text{Pt}$ satellites. No phosphorus coupling was observed and this was taken to mean that the hydride and phosphine were mutually cis. The chemical shift of the hydride was consistent with the trans ligand being an iodide. The structure can almost certainly be assigned as:

\[
\text{Pr}_4\text{N}^+ \left[ \begin{array}{c} \text{I} \\
\text{I} \end{array} \right] \text{Pt} \left[ \begin{array}{c} \text{H} \end{array} \right] \left[ \begin{array}{c} \text{PEt}_3 \\
\text{I} \end{array} \right] -
\]

Warming to room temperature resulted in decomposition to unassigned species which had virtually no $^{31}\text{P}$ n.m.r. spectrum.
4.4.13 Reaction with \( \text{H}_2\text{S} \) and \( \text{H}_2\text{Se} \)

No reaction could be detected by \( ^{31}\text{P} \) n.m.r. spectroscopy with \( \text{H}_2\text{S} \), even after a period of some weeks at room temperature. \( \text{H}_2\text{Se} \) showed a reaction at \(-45^\circ\text{C}\), detected by \( ^{31}\text{P} \) n.m.r. spectroscopy. The product, a 6-coordinate Pt(IV) species, showed only a singlet with \( ^{195}\text{Pt} \) satellites in the \( ^{31}\text{P} \) n.m.r. spectrum. There was no sign of any binuclear species and further warming resulted in the appearance of a large number of resonances which could not be assigned. Removal of the tube from the probe showed the contents to be dark and some solid particles floating in the solution. Due to this solid, it proved impossible to obtain a good \( ^1\text{H} \) n.m.r. spectrum and no further characterisation could be carried out. The most likely product in the 6-coordinate Pt(IV) adduct with \( \text{H}_2\text{Se} \) is:

\[
\begin{array}{c}
\Pr_4\text{N}^+ \\
\text{I} \\
\text{Pt} \\
\text{SeH} \\
\text{H} \\
\text{I} \\
\text{I}
\end{array}
\]

or an isomer.

However, no evidence can be offered at this stage to establish the actual structure.

4.5 Discussion

The purpose behind this work was to compare the reactions of the \( [\text{Cl}_3\text{Pt(PEt}_3)\text{]}^- \) and \( [\text{I}_3\text{Pt(PEt}_3)\text{]}^- \) anions. Previous works\(^3\) have noted the dependence of reactivity on the halogen in the reactions of
<table>
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<th>L</th>
<th>δP (ppm)</th>
<th>$^{1}J_{PtP}$ (Hz)</th>
<th>Other parameters observed</th>
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<td>SiH$_4$</td>
<td>-10.20</td>
<td>2742</td>
<td>$\delta_{Pth} = -15.21$ ppm, $^{1}J_{PtH} = 1160$ Hz</td>
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<tr>
<td></td>
<td>-6.43</td>
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<td>+14.84</td>
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<td>$\delta_{F} = -75.68$ ppm, $^{2}J_{FSiPt} = 609$ Hz, $^{3}J_{FSiPtP} = 4$ Hz</td>
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<tr>
<td></td>
<td>+12.57</td>
<td>3628</td>
<td></td>
</tr>
<tr>
<td>SiH$_3$Cl</td>
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<td>2578</td>
<td>$\delta_{Pth} = -10.29$ ppm, $^{1}J_{PtH} = 1178$ Hz</td>
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<td>3452</td>
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<tr>
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<td>+9.14</td>
<td>3413</td>
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</tr>
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<td></td>
<td>-1.01</td>
<td>574</td>
<td></td>
</tr>
<tr>
<td>SiH$_3$I</td>
<td>-15.83</td>
<td>2576</td>
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</tr>
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<td></td>
<td>+6.43</td>
<td>3579</td>
<td></td>
</tr>
<tr>
<td>GeH$_3$F</td>
<td>-22.40</td>
<td>1687</td>
<td>$\delta_{F} = -81.34$ ppm, $^{2}J_{FSiPt} = 679$ Hz, $^{3}J_{FGePtP} = 2$ Hz</td>
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<td>+14.1</td>
<td>3236</td>
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<td></td>
<td>+6.71</td>
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<td>+16.02</td>
<td>2571</td>
<td></td>
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<tr>
<td>HCl</td>
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<tr>
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<td>$\delta_{Pth} = -16.88$ ppm, $^{1}J_{PtH} = 800$ Hz</td>
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<tr>
<td>H$_2$Se</td>
<td>+6.04</td>
<td>2278</td>
<td></td>
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HPtX(PEt$_3$)$_2$ with simple silyl and germyl species. It would be predicted that the triodo anion would be more susceptible to oxidative addition reactions as the iodine, being a softer base than chlorine, would withdraw less charge from the platinum. Thus, the more localised charge on the platinum makes it more susceptible to attack by a molecule which is slightly polar, e.g. MH$_3$X. The reactions detailed indeed confirm the triodo anion to react much more rapidly than the trichloro anion. The most surprising feature of the reactions of the [Cl$_3$Pt(PEt$_3$)]$^-$ anion was that it did not react with HCl but reacted with HI. This proved to be most fortuitous as the reductive elimination proceeded by the loss of HCl. If the trichloro anion had reacted with HCl, this would have further complicated the n.m.r. spectra. The reaction of the trichloro anion with MH$_3$Br and MH$_3$I (M = Si or Ge) led to complex mixtures. For the reactions between MH$_3$X and HPt(Y)(PEt$_3$)$_2$ where the halogen (X) bound to M (Si or Ge) is different to the halogen bound to platinum (Y), reaction is accompanied by halogen exchange resulting in the final product in which the heavier halogen is bound to platinum, irrespective of the original halogen locations. Thus, it was to be expected that the reaction of MH$_3$Br or MH$_3$I (M = Si or Ge) with the [Cl$_3$Pt(PEt$_3$)]$^-$ anion would result in halogen exchange resulting in either bromide or iodide bound to the platinum and chloride to the silicon or germanium. It was hoped that fairly clean reactions would occur but in fact complex mixtures were obtained. This probably indicates stepwise halogen exchange and results in a large number of possible species. Addition of excess MH$_3$X (M = Si or Ge; X = Br or I) failed to produce the
products expected from complete halogen exchange. The reaction mixtures so obtained were actually more complex than when equimolar amounts were used. The halogen exchange can be explained in terms of the bond energies of the M-X bond as the lighter halogen bonded to M is strongly favoured. The bond energies for the platinum halogen bonds are not well defined but it does appear from other factors that the most favourable is the bond to iodine.

The reaction of \([X_3Pt(PEt_3)^-]^-\) with \(MH_4\) (M = Si or Ge) always resulted in the final product containing a Pt-MH₂X rather than a Pt-MH₃. This can be accounted for by the mechanism proposed in Figure 4.3.

![Figure 4.3](image)

NB. The isomers shown are not necessarily those produced.

Of all the reactions studied, the most surprising were those involving \(H_2S\) and \(H_2Se\). With the triodo anion the structure of
the product can only be speculated upon but it is probable that it is the expected $\text{H}_2\text{Se}$ adduct. It was to be expected that the reactions with the trichloro anions would produce similar reactions but that the rates would be slower. Contrary to this, the trichloro anions reacted rapidly at low temperatures to produce bridged binuclear species. If the mechanism postulated in Section 4.3.6 is correct, then the reaction proceeded beyond the simple adduct. Previous workers observed that for the species $[\text{H}_2\text{PtX(SeH)(PEt}_3)_2]$ the case where $X = \text{I}$ is the one least likely to reductively eliminate $\text{HX}$ to form the four-coordinate Pt(II) complex. This may mean that the 6-coordinate species produced by the reaction of the triodo anion and $\text{H}_2\text{Se}$ decomposed before the reductive elimination, necessary in the proposed mechanism, could occur. No reaction was detected between the triodo anion and $\text{H}_2\text{S}$ yet reaction with the trichloro anion produced a bridged binuclear species. This is puzzling and no satisfactory explanation can be offered at this time.

The $^1\text{H}$ n.m.r. spectrum of the bridged binuclear species produced by the reaction of $\text{Me}_4\text{N}^+[\text{Cl}_3\text{Pt(PEt}_3)_2]^-$ and $\text{H}_2\text{Se}$ showed some novel features. The product was formulated in Section 4.3.6 as being:

![Chemical structure](image-url)

although the $^1\text{H}$ n.m.r. spectrum of the SeH region was compatible with the structure being:
the $^{31}$P n.m.r. spectrum ruled out this isomer on the basis of the $^{195}$Pt satellites. The satellite pattern was clearly that of an (AX)$_2$ rather than an [A$_2$XY] spin system. The $^1$H n.m.r. spectrum of the SeH (Figure 4.4) resonance showed the platinum satellites to be much less intense than expected and also significantly broader than the central resonance. This phenomenon has been recently reported$^8$ for a related binuclear platinum species. The most likely explanation is that the rate of relaxation is enhanced by chemical shift anisotropy to such an extent that the $^{195}$Pt appears to lose some of its magnetic character. This can lead to the loss of a coupling or, in less extreme cases, to broadening and loss of intensity. The relaxation process is known to be strongly dependant on the observing magnetic field and has been reported to be significant in the case of heavy metal ions such as $^{207}$Pb$^9$. Accordingly the spectrum was recorded at 360 MHz (Figure 4.5) and a further reduction in the intensity of the $^{195}$Pt satellites was observed. Broad band decoupling of the phosphorus couplings showed the $^{77}$Se satellites much more clearly (Figure 4.6).

The reaction between the triodo anion and MH$_3$X (M = Si or Ge) generally produced two 6-coordinate Pt(IV) isomers. When the trichloro anion was reacted with silyl halides only one 6-coordinate Pt(IV) species was observed. Reaction with germyl halides did not show any 6-coordinate Pt(IV) species. This is the reverse of the
Figure 4.4 $^1$H n.m.r. spectrum at 100 MHz

$\text{Me}_4\text{N}^+[\text{Cl}_3\text{Pt(P}E\text{t}_3)] + \text{H}_2\text{Se} \quad -50^\circ \text{C}$
Figure 4.5 $^1H^{31P}$ n.m.r. spectrum at 100 MHz

$\text{Me}_4\text{N}^+[\text{Cl}_3\text{Pt}(\text{PEt}_3)]^- + \text{H}_2\text{Se} \quad -50^\circ \text{C}$
\[ \text{Me}_4N^+\text{[Cl}_3\text{(PPh}_3)]^- + H^+ \rightarrow \text{H}_2\text{Se} \]

Figure 4.6: \( ^1H \) n.m.r. spectrum at 360 MHz
observation for the reactions of silyl and germyl halides with the
cation studied in Chapter 3. Presumably the triodo anion systems
produced two isomers because they are energetically similar but
with the trichloro anion one isomer is formed preferentially to
the other.

The reactions involving $\text{MH}_3\text{F}$ ($M = \text{Si or Ge}$) failed to produce
any $\text{Pt-MH}_2\text{F}$ system. One $\text{Pt-MHF}_2$ species was formed but all the
other complexes contained coordinated $-\text{MF}_3$ groups. The tendency
of $\text{MH}_3\text{F}$ ($M = \text{Si or Ge}$) to disproportionate is well known and the
metal substrates may have some affect on this tendency. Another
worker in this department has observed the same effect using some
iridium species. When the $^{19}\text{F}$ n.m.r. spectrum of the reaction
between the triodo anion and $\text{SiH}_3\text{F}$ was observed at $-70^\circ\text{C}$, both
$\text{SiH}_3\text{F}$ and $\text{SiH}_2\text{F}_2$ were observed before any reaction occurred with the
anion. $^{19}\text{F}$ n.m.r. spectroscopy was used to check the purity of the
$\text{SiH}_3\text{F}$ used in the reaction but no trace of $\text{SiH}_2\text{F}_2$ could be
detected. This tends to support the theory that the presence of
the metal substrate increases the tendency of the $\text{SiH}_3\text{F}$ to
disproportionate.

The $\text{Pr}_4\text{N}^+$ counter cation was found to have resonances which
overlapped the regions of the $^1\text{H}$ n.m.r. spectrum associated with
silyl or germyl signals. Accordingly $\text{Me}_4\text{N}^+\text{[Cl}_3\text{Pt(PET}_3\text{)}_2\text{]}^-$ was
prepared as the methyl resonances are well to low frequency of the
region. When a normal halogen metathesis reaction was carried
out using this species and excess sodium iodide in acetone, the
iodo analogue was not obtained. The product was identified as
$\text{Pt}_2\text{I}_4(\text{PET}_3)_2$ by its $^{31}\text{P}$ n.m.r. parameters, mass spectrum and
elemental analysis for C and H. Presumably this was formed by the mechanism:

\[
2\text{Me}_4\text{N}^+\left[\begin{array}{c} \text{PEt}_3 \\
\text{Cl} & \text{Pt} & \text{Cl}
\end{array}\right]^- + 6\text{NaI} \rightarrow 2\text{Me}_4\text{N}^+\left[\begin{array}{c} \text{PEt}_3 \\
\text{I} & \text{Pt} & \text{I}
\end{array}\right]^- \rightarrow \text{Pt}_2 \text{I}_4 (\text{PEt}_3)_2 + 2\text{Me}_4\text{N}^+\text{I}^-.
\]

It was thought possible that the small size of the Me_4N^+ cation was responsible for the instability of the desired product, but on treatment of Ph_4P+[Cl_3Pt(PEt_3)]^- with sodium iodide in acetone the products were a mixture of Ph_4P+[I_3Pt(PEt_3)]^- (10%) and Pt_2I_4(PEt_3)_2 (90%). Treatment of Pt_2I_4(PEt_3)_2 with Me_4N^+I^- or Ph_4P^+I^- in acetone gave no detectable reaction, even after refluxing overnight. The only other cations which were found to give the desired type of product were Bu_4N^+ and t-Bu_4N^+ and, as both of these have resonances in the silyl and germyl regions, were of no help.

One possible way to overcome this problem would be to study the reactions of the anions using MD_3X and observe the $^2$D n.m.r. spectrum.

It is disappointing to have failed to isolate any of these species but the reactions did not lend themselves to isolations. A crystal structure would be necessary to establish the stereochemistry of the species obtained. Although most of the structures have been assigned as being of the type:

\[
\text{R}_4\text{N}^+\left[\begin{array}{c} \text{PEt}_3 \\
\text{X} & \text{Pt} & \text{MH}_2\text{Y}
\end{array}\right]^- \quad \text{or} \quad \text{R}_4\text{N}^+\left[\begin{array}{c} \text{PEt}_3 \\
\text{H} & \text{Pt} & \text{X} & \text{MH}_2\text{Y}
\end{array}\right]^-.
\]
this stereochemistry has been assigned on the basis of not observing the three bond coupling $J_{\text{PPh}_{2}M}$. The isomer with the phosphine trans to the $\text{MPh}_{2}$ group cannot be ruled out as three bond coupling constants are very sensitive to angle change.
REFERENCES (CHAPTER 4)

1. H.M. Ferrier, unpublished work.
2. J.E. Bentham, unpublished work.
CHAPTER 5: REACTIONS OF HIr(CO)(PPh₃)₃ WITH SIMPLE SILANES AND GERMANES

5.1 Introduction

Ebsworth and Leitch\(^1\) reported the reaction between simple silanes and germanes (MH₃Q, where M = Si or Ge and Q = F, Cl, Br or I) with IrCl(CO)(PPh₃)₂ to produce 6-coordinate Ir(III) adducts. The conclusions drawn regarding the stereochemistry of these species were tentative as low solubility restricted n.m.r. studies, and adequate crystals for an X-ray diffraction study could not be obtained. Harrod et al\(^2\) formed adducts by reacting HIr(CO)(PPh₃)₃(I) with a variety of silicon hydrides. It has been suggested\(^2\),\(^3\),\(^4\) that triorganosilanes, germanes and stannanes react with (I) to give products which contain two mutually cis phosphines and silicon trans to one phosphine. A study of the reaction of (I) with MH₃X (M = Si or Ge, X = H, F, Cl, Br or I) was carried out in 1973\(^5\) but as the facilities for pulsed n.m.r. (FT) were not available the \(^1\)H n.m.r. spectra were obtained by continuous wave methods and the quality of resolution was poor. This resulted in assignments of configuration being tentative. Another worker\(^6\) studied the same reactions using mainly \(^3\)¹P n.m.r. (and \(^1\)⁹F where applicable) but again was unable to completely characterise the products.

This study was undertaken to establish the exact nature of these reactions and it was hoped that the high field 360 MHz n.m.r. spectrometer would prove capable of obtaining sufficiently high quality spectra to do so.

Unless otherwise stated, all reactions were carried out in
C₆D₅CD₃ as the sole solvent. 0.05 mM of HIr(CO)(PPh₃)₃(I) was weighed into the n.m.r. tube and attached to the vacuum line. Solvent and 0.05 mM of MH₃Q were condensed in at -196°C and the tube sealed under vacuum. The reaction was carried out at -30°C until the yellow colour of (I) was discharged. The tube was then warmed to ambient temperature for one hour before the n.m.r. spectra were recorded at 28°C. N.m.r. parameters are detailed in Tables 5.1 and 5.2. Unless otherwise stated, all ³¹P n.m.r. spectra were recorded with protons decoupled.

PPh₃ was detected in all the ³¹P n.m.r. spectra and the overall reaction can be summarised:

\[
\text{H} \text{Ir(CO)(PPh₃)}₃ + \text{MH₃Q} \rightarrow \text{Ir(CO)}\text{H₂(PPh₃)}₂(\text{MH₂Q}) + \text{PPh₃}
\]

The iridium product can have six isomeric forms (Figure 5.1). Species (A) and (B) have equivalent phosphine ligands and so should give singlet ³¹P n.m.r. resonances; similarly, the phosphines in isomer (F) are also equivalent when phosphorus decoupled. Isomers (C), (D) and (E) should give ³¹P n.m.r. spectra which are AB patterns. The ¹H n.m.r. spectra are much more complex but can be used to distinguish between at least some of the isomeric forms once the ³¹P n.m.r. spectra had been used to assign general type.

Unlike the preceding two chapters, the reactions are dealt with in order of complexity of ¹H n.m.r. spectra rather than working through the silyl and then the germyl species.
Figure 5.1
5.2 Results

With a few exceptions, all the reactions produced a mixture of isomers. The $^{31}$P n.m.r. spectra showed that isomers with both non equivalent (AB) and equivalent (singlet) phosphines were present. When $M = Ge$, the predominant isomer produced had equivalent phosphines, i.e. (A), (B) or (F) isomer type, whereas when $M = Si$ the main product had non equivalent phosphines, i.e. (C), (D) or (E) isomer type. Reaction of (I) with $SiH_3F$ gave a $^{31}$P n.m.r. spectrum with 8 lines associated with the AB part of an [ABX] spin system. No product with equivalent phosphines could be detected for this reaction. Reaction of (I) with $MeSiH_3$ gave a product whose $^{31}$P n.m.r. spectrum consisted of an AB quartet showing that the species is of type (C), (D) or (E) and no other isomer type could be detected. The product of the reaction between (I) and $GeH_3I$ was also mono isomeric but this time the $^{31}$P n.m.r. spectrum showed a singlet, plus the triphenyl phosphine signal, and some very weak and complex multiplets. The product was assumed to be of type (A), (B) or (F).

5.2.1 Reaction with $GeH_3I$

The $^1$H n.m.r. spectrum (Figure 5.2) showed two low frequency hydride signals of equal intensity, which suggests two hydrides, each trans to a different ligand. The GeH region showed a signal, twice as strong as either hydride resonance, which appeared as a 1:3:3:1 quartet of narrow doublets. This was clarified by a homonuclear decoupling experiment. Irradiation at the centre of the lower frequency of the two IrH resonances collapsed the GeH resonance to a
Figure 5.2 $^1$H n.m.r. spectrum
IrH(CO)(PPh$_3$)$_3$ + GeH$_3$I

$\delta = -10.50$ ppm

$\delta = -9.97$ ppm

$\delta = 3.27$ ppm
1:2:1 triplet of narrow doublets. Irradiation at the other IrH resonance collapsed the narrow doublet coupling, leaving a 1:3:3:1 quartet. This means that the quartet is actually an overlapping doublet of triplets. The doublet arises from coupling to the lower frequency IrH (H_a) and the triplet coupling is assigned as being \( ^3J_{HGeIrP}\). These two couplings are coincidentally equal. The narrow doublet arises from coupling to the higher frequency IrH (H_b). Both of the IrH resonances can be analysed as overlapping triplets of triplets of doublets. Irradiation at the centre of the GeH resonance collapsed the signals to triplets of doublets, the small doublet couplings being the same in each signal and can be assigned as \(^2J_{HIrP}\). The large triplet coupling must arise from \(^2J_{HIrP}\) and the other triplet coupling from \(^3J_{HGeIrP}\). Thus the structure can definitely be assigned as being isomer (A). The only feature which cannot be assigned at this point is which IrH resonance corresponds to which hydride in structure (A). This point will be clarified once the whole series of spectra has been described. N.m.r. parameters are detailed in Table 5.1.

5.2.2 Reaction with GeH_4

The \(^{31}P\) n.m.r. spectrum of the product showed that the major species contained equivalent phosphines and the minor product showed an [AB] quartet. In the \(^1H\) n.m.r. spectrum the GeH resonance (Figure 5.3) of the major product appeared as a triplet of triplets under normal resolution but using a line narrowing technique, under very high resolution, resolved into a triplet of doublets. The narrow doublets had nearly equal couplings.
Figure 5.3 $^1$H n.m.r. spectrum

IrH(CO)(PPh$_3$)$_3$ + GeH$_4$ GeH$_3$ region
Irradiation of the IrH region showed that both of these doublet couplings arose from $^3J_{HGeIrH}$. As the larger triplet was not affected by any homonuclear decoupling experiments it was assigned as arising from coupling to the equivalent phosphines, i.e. $^3J_{HGeIrP}$. The low frequency hydride region (Figure 5.4) showed two very similar resonances of equal intensity, each of which was one third the intensity of the GeH resonance. These resonances were of a very complex nature but simplified upon homonuclear decoupling. Each showed the expected triplet pattern from coupling to the equivalent phosphines, i.e. $^2J_{PIrH}$. Irradiation of one IrH resonance removed a further doublet coupling from the other IrH resonance and is attributed to $^2J_{HIrH}$. Irradiation at the centre of GeH resonance collapsed both IrH resonances to triplets of doublets caused by the removal of $^3J_{HGeIrH}$. The overall appearance of the IrH region was that of a two triplets of sextets or septets, but since $^2J_{HIrH}$ is between two and three times the size of $^3J_{HGeIrH}$ the actual IrH resonances each consist of a triplet of doublets of overlapping quartets.

The $^1H$ n.m.r. spectrum of the minor isomer is much more complicated. The low frequency hydride region showed two distinct types of IrH resonances, one of which showed a large coupling of 121 Hz which was assigned as arising from coupling to a trans phosphine. On this basis the isomer type must be either (C) or (D). Thus the large doublet coupling is assigned as being $^2J_{H_tP_t}$ (see Figure 5.1 for notation). The doublet coupling of 18.3 Hz was unaffected by homonuclear decoupling and was assigned as being $^2J_{H_tP_c}$. Each of these lines appear to be a sextet but irradiation
Figure 5.4 $^1$H n.m.r. spectrum

$\text{IrH(CO)(PPh}_3\text{)}_3 + \text{GeH}_4$, $\text{IrH}$ region
in the centre of the GeH resonance collapsed the sextet to a doublet. Restoring the GeH couplings and irradiating the other IrH resonance collapsed the sextet to a quartet. Thus the apparent sextets are actually overlapping quartets of doublets arising from the couplings $3J_{\text{HGeIrP}}^t$ and $2J_{\text{HIrH}}^c$ respectively. The resonance associated with H is simplified by irradiation in the centre of the GeH resonance. The IrH resonance collapsed to a doublet of doublet of doublets. Selectively irradiating the H peaks enabled these couplings to be assigned as $2J_{\text{HIrP}}^t$, $2J_{\text{HIrP}}^c$, and $2J_{\text{HIrH}}^t$. If the GeH protons are not decoupled there is a further quartet coupling which is not very well resolved due to overlap. The GeH resonance appears, even under the highest resolution, to be a triplet of doublets of doublets. The two doublet couplings can be collapsed by irradiating the two IrH resonances in turn. The triplet pattern is not affected by any homonuclear decoupling experiments and the conclusion which must be drawn is that the values of $3J_{\text{HGeIrP}}^c$ and $3J_{\text{HGeIrP}}^t$ are coincidentally equal. As was mentioned in Chapter 4, three bond coupling constants are very sensitive to angle and it appears that in this case the trans coupling happens to have the same value as the cis coupling. N.m.r. parameters of the two isomers are detailed in Tables 5.1 and 5.2, and rough relative abundances of the isomers in Table 5.3.

5.2.3 Reaction with SiH$_4$

The products obtained from this reaction were similar to those obtained with GeH$_4$, except that the $^{31}$P n.m.r. spectrum showed that about 12 times as much of the isomer with cis-phosphines was
formed as of the other. A third species was also detected in this mixture. This species contained two phosphines and two hydrides bonded to iridium, with one of the phosphines trans to a hydride. No trace could be found of an associated SiH resonance and no further work was carried out on this species. The $^1$H n.m.r. spectrum of the major isomer confirmed the species to be of either (C) or (D) type and the IrH resonances are of similar type to those obtained in the hydride region of the GeH$_3$ complex. The SiH resonance however appeared to be quite different. Homonuclear decoupled revealed that $^3$J$_{H,IrSiH}$ is about half the size of $^2$J$_{H,IrH}$ and that values of $^3$J$_{HSiIrP_c}$ and $^3$J$_{HSiIrP_t}$ are substantially different. Thus, although the SiH resonance appears to be different from the GeH resonance in the GeH$_4$ reaction, this is due to removal of some coincidences which arise in the GeH but not in the SiH region. N.m.r. parameters are detailed in Table 5.2.

The $^1$H n.m.r. spectrum of the minor isomer was complicated in the IrH region by partial overlap with the IrH resonance of the unidentified impurity mentioned previously. The other IrH of the trans isomer showed no detectable coupling to the SiH$_3$ protons. The isomer type could easily be identified as type (A) and the relationships between the peaks was easily established by irradiating across the lower frequency hydride resonance which contained the partial overlap from the impurity. The n.m.r. parameters of this isomer are detailed in Table 5.1, and rough relative abundancies detailed in Table 5.3.
5.2.4 Reaction with $\text{SiH}_3\text{Br}$

The $^{31}\text{P}$ n.m.r. spectrum showed that most of the product was a species with cis phosphines giving rise to an AB quartet. A small amount of an isomer with equivalent phosphines was also detected. Although the $^1\text{H}$ spectrum confirmed the minor product to be of isomer type (A), part of the resonance for the lower frequency hydride was obscured by an overlap of an IrH resonance from the major isomer. Despite this, it still proved possible to measure most of the parameters which are listed in Table 5.1.

Having accounted for the peaks from the minor isomer an apparent anomaly was observed: two SiH and two IrH resonances, all of equal intensity, remained unexplained. The two SiH resonances were designated as L and Q (Figure 5.5) and the two IrH resonances (Figure 5.6) as C and T, in order of decreasing frequency. Under normal resolution L and C appeared as complex multiplets, Q as a broad quartet with structure and T as a large (112 Hz) doublet of doublets of triplets. These observations could only be explained after a series of homonuclear decoupling experiments had been carried out. Irradiation in the low frequency region at either C or T affected both L and Q. Thus it follows that L, Q, C and T all arise from the same species. The iridium in isomer type (C) or (D) is a chiral centre and the conclusion which must be drawn is that the two resonances, L and Q, arise from the two protons of the SiH$_2$ group becoming non equivalent because of this chirality. When L was decoupled, resonance T simplified to a doublet of doublets of doublets. Applying a line narrowing technique under very high resolution, it became apparent that each line showed a
Figure 5.5 $^1$H n.m.r. spectrum

IrH(CO)(PPh$_3$)$_3$ + SiH$_3$Br  SiH$_2$ region

$\delta = 4.89$ ppm

$\delta = 5.68$ ppm
Figure 5.6  $^1$H n.m.r. spectrum

$\text{IrH(CO)(PPh}_3)_3 + \text{SiH}_3\text{Br}$  IrH region
further very narrow doublet coupling which could be removed by 
irradiating at Q. It was concluded that T was therefore due to 
H_t in a species of isomer type (C) or (D). Assuming this to be 
correct the region, T, can be assigned as follows. The largest 
doublet coupling is due to $2J_{H_t IrP_t}$, the next doublet coupling to 
$2J_{H_t IrP_c}$, the couplings $2J_{H_t IrH}$, and that to one of the SiH 
protons (H_l) are nearly equal and produce an apparent triplet which 
is actually an overlapping doublet of doublets, while coupling to 
the other SiH proton (H_q) is very small and can only just be 
detected. The IrH resonance can now be explained as arising from 
coupling to two different phosphines (20.2 and 14.5 Hz), two 
different SiH protons (1.5 and 5.0 Hz) and the other IrH proton 
(4.0 Hz). Each of these was confirmed by homo- and heteronuclear 
double resonance experiments. The heteronuclear ($^{31}$P) decouplings 
had to be carried out on the Varian XL100 as the Bruker WH360 could 
not perform this experiment.

Of the two SiH resonances, L could be resolved into a set of 
32 overlapping lines (Figure 5.7). Applying a line narrowing 
technique to Q under high resolution (Figure 5.8) clarified the 
four couplings, $2J_{H_l H_t}$, $3J_{H_l P}$, $3J_{H_l H}$, and $3J_{H_l P}$. The remainder 
of the couplings could not be detected. The n.m.r. parameters of 
this isomer are detailed in Table 5.2, the relative abundancies 
of the isomers in Table 5.3, and some relative signs of coupling 
constants in Table 5.4.
Figure 5.7  $^1$H n.m.r. spectrum

$\text{IrH(CO)(PPh}_3\text{)}_3 + \text{SiH}_3\text{Br}$  Si$_2$H region

i) expansion of region L

ii) expansion, with line narrowing, of region L
Figure 5.8 $^1$H n.m.r. spectrum

$\text{IrH(CO)(PPh}_3)_3 + \text{SiH}_3\text{Br}$

$\text{SiH}_2$ region

expansion of $Q$

line narrowed, high resolution spectrum of $Q$

$\delta = 4.89$ ppm
5.2.5 Reaction with SiH$_3$Cl

The reason for carrying out these reactions at -30°C was to minimise impurities. The reaction of (I) with SiH$_3$Cl is not clean, even carrying out the reaction over a period of ca. 15 hours at -45°C. The products included the adduct of SiH$_4$ and the $^1$H n.m.r. spectrum showed resonances which could be assigned to a complex of isomer type (C) or (D) with SiHCl$_2$ as a ligand. It proved possible to analyse the spectra, even with these impurities, as containing an isomer of type (C) or (D) as the major product and an isomer of type (A) as the minor product.

The $^1$H n.m.r. spectrum of the minor isomer was very similar to that obtained with SiH$_3$Br and again problems arose in the low frequency region where part of the resonance associated with $H_b$ was overlapped by the stronger resonance associated with $H_c$ from the major isomer. Most of the parameters were easily measured and are detailed in Table 5.1.

The $^1$H n.m.r. spectrum of the major isomer again showed two SiH and two IrH resonances, all of equal intensity. The same nomenclature was adopted as in the preceding section. In general the resonances were very similar to the analogous resonances in the spectrum of the adduct of SiH$_3$Br and homonuclear decoupling experiments showed the same basic patterns. The only noticeable differences were that it did not prove possible to distinguish $^2$J$_{H, IrH}$ from $^3$J$_{H, SiIrH}$, $^3$J$_{H, SiIrH}$ was not clearly resolved and the differences in coupling to $H_1$ made the appearance of $H_1$ rather different. The n.m.r. parameters of this isomer are detailed in Table 5.2 and rough values for the relative abundances of the
isomers in Table 5.3.

5.2.6 Reaction with CH₃SiH₃

The product from this reaction was monoisomeric and the ³¹P n.m.r. spectrum showed only an AB quartet in addition to the free triphenyl phosphine resonance. The ¹H n.m.r. spectrum was initially recorded at 100 MHz and the SiH₂ resonance was an unresolved complex multiplet, the CH₃ resonance appeared as a quartet which collapsed to a triplet on ³¹P heteronuclear decoupling. The size of this coupling constant (4.2 Hz) suggests that the silicon is trans to the phosphine and shows that the isomer type must be (C). Further evidence of this was gained from the ²⁹Si ¹H n.m.r. spectrum which showed only a large (99 Hz) doublet and was assigned as being 2J₁SiIrP. The ¹³C{¹H} n.m.r. spectrum of the CO region showed no coupling larger than a 2-3 Hz. Collectively, these facts show that the isomer type for this reaction is (C). The low frequency IrH region of the ¹H n.m.r. spectrum showed Hₜ as a large doublet of doublets of doublets. The large doublet can be assigned as 2JₜIrP, the second doublet as arising from ²JₜIrP and the smallest doublet arising from the coupling ²JₜIrH. These explanations can be confirmed by hetero- and homonuclear decoupling experiments. Hₜ, however, showed coupling to the two different phosphines Pₜ and Pₖ and an apparent triplet coupling. The triplet, under high resolution, was actually an overlapping doublet of doublets of very similar coupling constants. Homonuclear decoupling showed that the two doublets arise from ²JₜIrH and coupling to one of the SiH protons. Realising that
the two SiH protons must be different, the SiH$_2$ resonance was studied under high resolution at 360 MHz. The SiH region showed as two distinct resonances. The higher frequency signal was a poorly resolved, complex multiplet. The lower frequency signal was an overlapping triplet of doublets of quartets. Irradiation on the CH$_3$ signal removed the quartet coupling which was therefore assigned as $^3J_{HSiCH}$. The remaining couplings were with the two phosphorus and the other SiH nuclei. By analogy with the other systems, it seems likely that $^2J_{HSiH}$ is roughly equal to $^3J_{HSp}$.

5.2.7 Reaction with SiH$_3$SiH$_3$

The $^{31}$P n.m.r. spectrum showed that isomers both with equivalent and with non-equivalent phosphines had been produced. In the $^1$H n.m.r. spectrum these were two products of type (A) and (C). The minor product (A) was of standard type and its n.m.r. parameters are detailed in Table 5.1. The major isomer showed peaks in the IrH and SiH regions which were qualitatively very similar to those given by the product obtained from (I) and CH$_3$SiH$_3$. The main difference was that, unlike the CH$_3$ resonance, the resonances associated with SiH$_3$ were to high frequency of the SiH$_2$ peaks. This resulted in the SiH$_3$ resonance associated with the (A) type isomer overlapping one of the SiH$_2$ peaks from the (C) type isomer. The result of this unfortunate coincidence was that a number of the n.m.r. parameters normally obtained could not be measured. N.m.r. parameters which were obtained are detailed in Table 5.2 and rough relative abundances of the isomers
in Table 5.3.

5.2.8 Reaction with GeH$_3$Cl

The $^{31}$P n.m.r. spectrum of the products of this reaction showed mainly an isomer with equivalent phosphines but also a small amount of a species with inequivalent phosphines. The major product was identified as being of isomer type (A) from homonuclear decoupling experiments in the $^1$H n.m.r. spectrum. The n.m.r. parameters are detailed in Table 5.1.

The minor isomer showed a large internal chemical shift between the two GeH protons and two IrH resonances. The GeH resonance, H', showed no coupling to either of the IrH protons but coupled to the two inequivalent phosphines and also to the other GeH proton, H. The other GeH resonance showed coupling to both IrH protons in addition to these couplings. Homonuclear decoupling experiments enabled all of these couplings to be determined. N.m.r. parameters for the minor isomer, of type (C), are detailed in Table 5.2 and rough relative abundances of the isomers in Table 5.3.

5.2.9 Reaction with GeH$_3$F

The $^{31}$P n.m.r. spectrum showed the major product to contain mutually trans phosphines and a minor product with cis phosphines (Figure 5.9). Both the $^{31}$P and $^1$H n.m.r. spectra were complicated by the additional coupling to fluorine but unlike most of the reactions with the ionic platinum species in the previous chapters, the ligand was shown to be SiH$_2$F and no trace could be found of a coordinated SiHF$_2$ or SiF$_3$ group. One of the IrH resonances of the
Figure 5.9 $^{31}$P n.m.r. spectrum

IrH(CO)(PPh$_3$)$_3$ + GeH$_3$F
The major species appeared rather unsymmetrical due to an overlap with one of the IrH resonances from the species containing cis-phosphines. The major product was of isomer type (A) and all the parameters were obtained with the aid of homonuclear decoupling experiments and are listed in Table 5.1.

The $^1$H n.m.r. resonances of the minor isomer were not fully resolved but it proved possible to identify about three-quarters of the complex overlapping multiplets arising from $H_t$ and $H_c$. With the aid of homonuclear decoupling experiments it was possible to establish values for the couplings that are consistent with the observed patterns. The couplings involving $H_t$ were well-determined because one of the two multiplets arising from coupling to $P_t$ was separate from other resonances. The GeH resonance was difficult to analyse as it appeared on the edge of the strong peaks due to the phenyl protons. The value for the chemical shift of the GeH protons was given as the position of the strongest line in the resonance. The assignments and parameters of this region must be regarded as somewhat tentative. N.m.r. parameters for the minor product are detailed in Table 5.2 and rough relative abundances of the isomers in Table 5.3.

5.2.10 Reaction with SiH$_3$F

The $^{31}$P n.m.r. spectrum showed the product to be monoisomeric and to contain cis phosphines. The coupling $^3J_{FSiIrP}$ is roughly double the size of $^3J_{FSiIrPt}$ which suggests that the silyl group is trans to $P_t$ and that the product is of isomer type (C). The $^1$H n.m.r. spectrum of the IrH region (Figures 5.10 and 5.11) showed the
Figure 5.10 $^1$H n.m.r. spectrum

$\text{IrH(CO)(PPh}_3\text{)}_3 + \text{SiH}_3\text{F}$ IrH region
Figure 5.11 ¹H n.m.r. spectrum
IrH(CO)(PPh₃)₃ + SiH₃F
Half of the resonance associated with Hₜ - line
narrowed under high resolution
expected two IrH protons. The resonance assigned as arising from 
H_t appeared as a doublet of triplets of quintets. The large doublet 
arises from the coupling $2J_{Ht IrP}$, the apparent triplet is caused 
by the values of $2J_{Ht IrP}$ and $3J_{Ht IrSiF}$ being similar, giving rise 
to an overlapping doublet of doublets. Both SiH protons couple 
equally to H_t and because $3J_{Ht IrSiH}$ is approximately half the value 
of $2J_{Ht IrH}$, a pseudo quintet is produced by their overlap. The 
resonance assigned at H_c was complex but with the aid of homonuclear 
decoupling experiments it proved possible to assign all the 
couplings except those involving phosphorus and fluorine which 
required heteronuclear decoupling to assign them. The resonance 
associated with SiH was much more complicated and could not be 
assigned purely from the spectrum. The values of $3J_{Hc IrSiH}$ and 
$3J_{Ht IrSiH}$ were obtained from the IrH region, $2J_{HSiF}$ from the $^{19}F$ 
n.m.r. spectrum and broad band $^{31}P$ decoupling of the SiH region 
showed two narrow multiplets separated by $2J_{HSiF}$. This implies that 
the internal chemical shift of the two SiH protons must be small and 
decoupling the IrH protons from the SiH resonance gave values of 
$2J_{HSiH}$. Using all these parameters it proved possible to simulate 
the spectrum of the SiH region using the computer program NUMARIT^7. 
The parameters from this simulation and those obtained directly 
are detailed in Table 5.2.

5.2.11 Reaction with SiH₃I

The $^{31}P$ n.m.r. spectrum showed that two isomers had been formed. 
The minor isomer, with trans phosphines, was assigned as being of 
type (A) and n.m.r. parameters are detailed in Table 5.1.
The $^1$H n.m.r. spectrum of the major isomer was assigned as belonging to an isomer type (C) or (D) species. The IrH resonances were very similar to those obtained for the species containing $-\text{SiH}_2\text{Br}$ or $-\text{SiH}_2\text{Cl}$. The resonances associated with the SiH protons were separated by over 1 ppm and while the lower frequency resonance appeared as a broad quartet (c.p. SiH$_3$Br reaction) the other resonance was a featureless hump which showed some sharp components if one or other of the IrH resonances was irradiated. When an attempt was made to decouple one SiH from the other, both resonances disappeared (Figure 5.12). This was interpreted as being a case of saturation transfer and was more efficient than decoupling. It did not prove possible to observe Q without quartet structure at room temperature irrespective of how low the decoupling power used was. Lowering the temperature to $-40^\circ\text{C}$ reduced the efficiency of the saturation transfer sufficiently to collapse Q into a rather broad triplet by irradiation at the other SiH resonance L. Careful experiments, using peaks due to the trans isomer as standards, showed that irradiation at Q or L does not lead to any transfer of saturation to the IrH resonances. Analogous experiments show that with irradiation at L at about 0.05 W decoupler power, the transfer leads to loss of about 60% of the intensity of Q in the spectrum of the adduct of SiH$_3$Br and 40% for the adduct of SiH$_3$Cl at ambient temperature. In each of these two spectra, Q could be reduced to a near-triplet by irradiation at L. N.m.r. parameters of this isomer are detailed in Table 5.2 and rough relative abundancies of the isomers in Table 5.3.
(i) no decoupling

(ii) effect of irradiation at L with 0.05 W power

δ = 5.14

δ = 4.08

50Hz
5.3 Discussion

The final remaining question of assignment in these spectra concerned the two IrH resonances in the isomers of type (A). In the spectra of the adduct of GeH₄, the two resonances looked very similar but in all of the other cases the IrH resonance labelled Hₐ shows a much larger coupling to the MH protons than does the other. While it is known that three bond coupling constants are very sensitive to angle, the consistency of this size difference tends to suggest that Hₐ is trans to M. In the cis isomers, Hₜ must be cis to M and so must Hₖ if the assignment of structure (C) to all the cis isomers is correct. The resonances due to both Hₜ and Hₖ move more or less to high frequency for a given M as Q increases in atomic weight from H to I. In the case of the (A) type isomers, one of the IrH resonances shifts to higher frequency and the other to lower frequency for the same change. The former is assigned to Hₜ cis to M and the latter to H tran to M. This assignment coincides with the one based on the values of the coupling constant ³J₁₁₁HMIRH.

The proportions of each type of isomer (Table 5.3) appear to be constant with time. Correlation between the size of the group MH₃Q and the type of isomer formed is difficult. Although the trend of a small MH₃Q to form a low proportion of (A) type isomer seems at first apparent, the radical difference between M = Si and M = Ge for such a small difference in size between Si and Ge appears to rule out any simple correlation. Furthermore, CH₃ presents a major discrepancy in this analysis as it produces only a (C) type isomer.

The ³¹P n.m.r. parameters show no unusual features and typically the chemical shift of an isomer with trans phosphines is
always to higher frequency than either of the phosphines in a cis complex. The chemical shifts of the two phosphines in a cis complex have to be calculated from the positions of the four lines that form the AB quartet. One such calculation is shown as an example.

Calculation of $^{31}\text{P}$ chemical shifts for $\text{Ir(CO)}_2\text{H}_2(\text{PPh}_3)_2(\text{SiH}_2\text{CH}_3)$. From the $^{31}\text{P}^1\text{H}$ n.m.r. spectrum (Figure 5.13), the frequencies of the four lines a, b, c and d were measured ±0.2 Hz. The positions of these lines are given by:

\[
\begin{align*}
a &= \frac{1}{2}(v_A + v_B) - \frac{1}{2}J - \frac{1}{4}D \\
b &= \frac{1}{2}(v_A + v_B) + \frac{1}{2}J - \frac{1}{4}D \\
c &= \frac{1}{2}(v_A + v_B) - \frac{1}{2}J + \frac{1}{4}D \\
d &= \frac{1}{2}(v_A + v_B) + \frac{1}{2}J + \frac{1}{4}D
\end{align*}
\]

where $v_A = \text{frequency of } P_A$, $v_B = \text{frequency of } P_B$

\[
\begin{align*}
J &= v_b - v_a = v_d - v_c, D = v_B - v_A \\
D^2 &= [(v_A - v_B)^2 + J^2] \\
\frac{1}{2}(v_A + v_B) - \frac{1}{2}J - \frac{1}{4}D &= 180.4 \\
\frac{1}{2}(v_A + v_B) + \frac{1}{2}J + \frac{1}{4}D &= 65.1 \\
\frac{1}{2}(v_A + v_B) &= 245.5 \text{ Hz} \\
\frac{1}{2}(v_A - v_B) + \frac{1}{2}J + \frac{1}{4}D &= 65.1 \\
\frac{1}{2}(v_A - v_B) - \frac{1}{2}J - \frac{1}{4}D &= 180.4 \\
J + D &= -113.5 \text{ Hz}
\end{align*}
\]
from the spectrum \( J = 16.5 \text{ Hz} \)

\[ \therefore D = -99.0 \text{ Hz (the sign is irrelevant for a difference)} \]

\[ D^2 = \left( v_A - v_B \right)^2 + J^2 \]

\[ \therefore v_A - v_B = \pm 97.7 \text{ Hz} \]

\[ v_A + v_B = 245.5 \]

\[ v_A - v_B = +97.7 \]

\[ \therefore v_A = 171.6 \text{ or } 73.9 \text{ Hz} \]

if \( v_A = 171.6 \text{ Hz} \) then \( v_B = 73.9 \)

\[ \therefore \delta P_A = +7.07 \text{ ppm} \]

\[ \delta P_B = +3.04 \text{ ppm} \]

The most striking feature in relationship to chemical shifts in the \(^1\text{H n.m.r.}\) spectra is the internal shift between \( H_1 \) and \( H_q \) in isomers of type (C). The magnitude of this internal shift was found to depend on \( Q \) and is small when \( Q = F, \text{CH}_3 \) and \( \text{SiH}_3 \) but increases in the order Cl, Br, I. The reason for this shift is probably a conformational effect and it was fortunate that it allowed a number of germinal HH coupling constants to be recorded. Isomer type (C) also provided the most unexpected feature of the many coupling constants recorded - the wide variation of values of \( J_{\text{H}1\text{IrM}} \). When the substituent at silicon was fluorine, \( J_{\text{H}1\text{IrSiH}_1}^{\text{t}} \) and \( J_{\text{H}1\text{IrSiH}_q}^{\text{t}} \) are effectively equal, whereas \( J_{\text{H}1\text{IrSiH}_1}^{\text{c}} \) and \( J_{\text{H}1\text{IrSiH}_q}^{\text{c}} \) are 1.7 and 4.4 Hz respectively. In the complex containing \( \text{SiH}_3 \), \( J_{\text{H}1\text{IrSiH}}^{\text{t}} \) is not detected, while of the two possible values of \( J_{\text{H}1\text{IrSiH}_1}^{\text{c}} \), one is
Figure 5.13 $^{31}P$ n.m.r. spectrum

$\text{IrH(CO)(PPh}_3)_3 + \text{SiH}_3\text{CH}_3$
4.3 Hz and the other too small to be detected. When the substituent at silicon is either chloride or bromide, the couplings from $H_1$ and $H_q$ to both $H_c$ and $H_t$ are substantially different. Here too the differences can probably be related to conformational effects. These differences led to resonances whose appearances were in some cases both simple and misleading. For the adduct between (I) and $\text{SiH}_3\text{Br}$, the relative signs of some of the coupling constants were determined using low power hetero- and homonuclear double resonance experiments. These signs are listed in Table 5.4 and have been related to the sign of $2J_{\text{HSiH}}$ which was assumed to be negative on the basis of previous experience with related systems. All of the three bond couplings were found to be negative and all but two of the two bond couplings were positive. Apart from $2J_{\text{HSiH}}$ the other negative two bond coupling involved mutually trans hydride and phosphine.

Isomer type (C) also produced another interesting effect - the saturation transfer. The condition for saturation transfer is that the exchange rate between the nuclei involved must be faster than the relaxation time $T_1$ which is of the order of 5 sec. Experiments showed that there was no transfer of saturation to either of the $\text{IrH}_2$ protons, thus ruling out a process involving the reductive elimination of $\text{SiH}_3\text{I}$. This suggests that the mechanism simply involves the interchange of $H_1$ and $H_q$. As the saturation transfer is dependent upon the nature of the other group bound to the silicon, the most obvious explanation is that the halogen becomes ionised, possibly under the influence of the excess of $\text{PPh}_3$ which is present in solution. If the coordination around the silicon became planar,
interchange of $H_1$ and $H_q$ would become possible. Another possibility
is that the excess PPh$_3$ may coordinate to the silicon and allow
interchange of $H_1$ and $H_q$ by pseudo-rotation in a species containing
5 coordinate silicon. At this time no definite conclusions can be
drawn and further experiments will have to be performed to establish
the mechanism.

Harrod$^4$ studied the reaction between (I) and $R_3$SiH and
suggested that this reaction was stereoscopic, $H_t$ coming from the
silane. He also proposed that reaction between the product and
free $R_3$SiH led to equilibration between $H_t$ and $H_c$. For the systems
studied in this chapter it appears that the processes are more
complex than suggested by this simple scheme. An experiment using
(I) and CH$_3$SiD$_3$ led to the initial product containing D trans to
P but then randomisation distributed the D between the positions
cis and trans to the phosphine (Figure 5.14). In this reaction,
no trace of an SiH species was detected which would be formed if
Harrod's analysis applied to these systems.

\[
\begin{align*}
\text{Ph}_3\text{P} & \xrightarrow{\text{Ir}} \text{PPh}_3 \quad + \quad \text{CH}_3\text{SiD}_3 \xrightarrow{\text{H}} \text{Ir} \quad \text{CO} \\
\text{CO} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad
The mechanism of addition was discussed by Harrod who carried out a kinetic study on the addition of $R_3SiH$ to (I). He suggested that the mechanism proceeded by a predissociation of (I) followed by oxidative addition of the $R_3SiH$ to the 4-coordinate intermediate:

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Ir} \quad \text{PPh}_3 \\
\quad & \quad \text{CO} \quad \text{PPh}_3 \\
\quad & \quad \text{PPh}_3 \\
R_3\text{SiH} & \quad \text{Ir} \quad \text{R}_3\text{Si} \\
\quad & \quad \text{H} \quad \text{H} \\
\end{align*}
\]

The other possibilities involved formation of an ionic intermediate or the reaction to proceed via a 7-coordinate species. The formation of an ionic intermediate had an analogue in the similar osmium system described by Collman and Roper:

\[
\begin{align*}
\text{OC—Os} & \quad \text{P} \quad \text{CO} \quad \text{O} \\
\quad & \quad \text{P} \quad \text{CO} \quad \text{O} \\
\quad & \quad \text{I} \\
\text{I} & \quad \text{OC—Os—I} \quad \text{I} + \text{CO} \\
\end{align*}
\]

If the reaction between (I) and SiH$_3$Cl was carried out in CD$_2$Cl$_2$ at -80°C the $^31$P n.m.r. spectrum (Figure 5.15) showed a small amount of product which appears as a doublet and a triplet of relative intensities 2:1. It is probable that this species is the intermediate in the reaction and was formulated as being:

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Ir} \quad \text{PPh}_3 \\
\quad & \quad \text{CO} \quad \text{PPh}_3 \\
\quad & \quad \text{H} \quad \text{H} \\
\end{align*}
\]

\[
\text{SiH}_2\text{Cl}^- + \text{I}^+ + \text{OC—Os—I} \quad \text{I} + \text{CO}
\]

\[
\text{OC—Os} \quad \text{P} \quad \text{CO} \quad \text{O} \\
\quad \text{P} \quad \text{CO} \quad \text{O} \\
\quad \text{I} \\
\text{I} \\
\end{align*}
\]
Figure 5.15 \(^{31}\text{P}\) n.m.r. spectrum - CD\(_2\)Cl\(_2\) -80°C

H\text{Ir}(CO)(PPh\(_3\))\(_3\) + SiH\(_3\)Cl
This cation was produced by Vaska\textsuperscript{10} from the reaction of (I) with HX. It seems likely that the mechanism of the reaction of (I) with MH\textsubscript{3}Q proceeds via this type of ionic intermediate followed by rearrangement to the final products. Once again, further studies of the reactions at low temperatures are required to elucidate the mechanism of reaction fully.
TABLE 5.1  N.m.r. parameters for products of type (A) from the reaction of IrH(CO)(PPh 3 ) 3  with MH 3 Q

<table>
<thead>
<tr>
<th></th>
<th>SiH 4</th>
<th>SiH 3 Cl</th>
<th>SiH 3 Br</th>
<th>SiH 3 I</th>
<th>SiH 3 SiH 3 a</th>
<th>GeH 4</th>
<th>GeH 3 F b</th>
<th>GeH 3 Cl</th>
<th>GeH 3 Br</th>
<th>GeH 3 I</th>
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</thead>
<tbody>
<tr>
<td>δH a ppm</td>
<td>8.39</td>
<td>8.73</td>
<td>8.89</td>
<td>8.19</td>
<td>9.21</td>
<td>9.97</td>
<td>9.87</td>
<td>10.24</td>
<td>10.50</td>
<td></td>
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<tr>
<td>δH b ppm</td>
<td>-10.42</td>
<td>-10.21(ca)</td>
<td>-10.15</td>
<td>-10.06</td>
<td>-10.19</td>
<td>-10.37</td>
<td>-10.25</td>
<td>-10.33</td>
<td>-10.26</td>
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<tr>
<td>δMH ppm</td>
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<td>4.59</td>
<td>3.68</td>
<td>2.67</td>
<td>2.39</td>
<td>6.09</td>
<td>5.09</td>
<td>4.42</td>
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<tr>
<td>δP ppm</td>
<td>12.47</td>
<td>12.12</td>
<td>11.97</td>
<td>11.52</td>
<td>12.52</td>
<td>12.49</td>
<td>11.77</td>
<td>11.44</td>
<td>11.37</td>
<td></td>
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</table>

\[ J_{H_a}^{IrH_b} \text{ Hz} \]

2.1 4.2 4.2 4.0 4.0 4.3 4.1 4.0 4.0 n.m. 3.9

\[ J_{H_a}^{IrP} \text{ Hz} \]

17.0 17.8 17.7 17.1 16.9 15.9 15.9 15.8 16.0 15.7

2.2 17.9 17.3 16.0 17.1 17.5 18.1 17.8 17.7 17.7 17.5

3.3 4.7 5.5 5.5 5.1 n.m. 4.2 2.8 5.4 5.2 5.4

\[ J_{H_a}^{HMIrP} \text{ Hz} \]

<0.4 2.4 2.8 3.8 <0.4 1.5 5.3 5.6 5.5 5.9

3.4 2.0 1.8 1.8 2.1 2.2 1.8 1.6 1.5 1.5 1.5

\[ \delta(SiH 3) = 3.50 \text{ ppm}, \quad J_{HH} = 3.2 \text{ Hz}; \quad \delta F = -224.8 \text{ ppm}, \quad J_{HF} = 41.3 \text{ Hz}, \quad J_{FH_a} = 9.4 \text{ Hz}, \quad J_{FH_b} = 4.0 \text{ Hz}, \quad J_{FP} = 3.2 \text{ Hz} \]

All measurements in d 8 toluene. Chemical shifts are ± 0.01 ppm, coupling constants to ±0.2 Hz unless otherwise stated. n.m. = not measured.
<table>
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<th>SiH₄</th>
<th>SiH₃CH₃</th>
<th>SiH₃Br</th>
<th>SiH₃I</th>
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<td>-10.53</td>
<td>-10.81</td>
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<td>Si₂ ppm</td>
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<td>4.08</td>
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<td>3.15</td>
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<td>5.79(4)</td>
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<td>2.77(4)</td>
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<th>²JₑIrP_c Hz</th>
<th>²JₑIrPₜ Hz</th>
<th>²JₑIrPₗ Hz</th>
<th>²JₑIrPₙ Hz</th>
<th>²JₑIrP₁ Hz</th>
<th>²JₑIrP₂ Hz</th>
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<td>14.0</td>
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<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
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<td>n.m.</td>
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<td>&gt;4.0</td>
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<td>&lt;0.4</td>
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<td>&lt;0.4</td>
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</tr>
</tbody>
</table>

---

*a = -173.5 ppm, ²JₑIrH = 49.9 Hz, ³JₑIrP₉ = 13.6 Hz, ³JₑIrP₃ = 24.3 Hz, ³JₑIrP₇ = 12.2 Hz, ³JₑIrP₅ = 16.4 Hz.

*b ²JₑIrP₉ = 0.7 ppm, ³JₑIrP₉ = 4.2 Hz, ²JₑIrP₇ = 4.2 Hz, ³JₑIrP₃ = 21.8 ppm relative to TMS, ³JₑIrP₇ = 99 Hz, ³JₑIrP₃ = 1.3 ppm

*c ²JₑIrP₉ = 181.2 ppm, ³JₑIrP₉ = 5 Hz

*d ²JₑIrP₅ = 4.06 ppm, ³JₑIrP₅ = 3.6 Hz, ²JₑIrP₇ = 2.8 Hz

*e ²JₑIrP₉ = -211.5 ppm, ²JₑIrP₅ = 41.5 Hz, ³JₑIrP₇ = 12.5 Hz, ³JₑIrP₉ = 22.5 Hz, ³JₑIrP₃ = 12.3 Hz, ³JₑIrP₉ = 9.0 Hz

**₅JₑIrP₉ = 2.8 ppm, ³JₑIrP₉ = 2.8 Hz

n.m. = not measured; n.o. = not observed.

All measurements in d₈ toluene. Chemical shifts are ±0.01 ppm and coupling constants ±0.2 Hz unless otherwise stated. Values in brackets were obtained from simulations of spectra.
TABLE 5.3  Percentages of isomers of type (A) and (C) formed by the reaction between Ir(CO)(PPh₃)₃ and MH₃Q

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<th>MH₃Q</th>
<th>% of type (A)</th>
<th>% of type (C)</th>
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<tbody>
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<td>92</td>
</tr>
<tr>
<td>SiH₃F</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>SiH₃Cl</td>
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<td>90</td>
</tr>
<tr>
<td>SiH₃Br</td>
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</tr>
<tr>
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<tr>
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<td>100</td>
</tr>
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<td>SiH₃SiH₃</td>
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<td>90</td>
</tr>
<tr>
<td>GeH₄</td>
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<td>35</td>
</tr>
<tr>
<td>GeH₃F</td>
<td>ca 80</td>
<td>ca 20</td>
</tr>
<tr>
<td>GeH₃Cl</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>GeH₃Br</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>GeH₃I</td>
<td>100</td>
<td>0</td>
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In the case of the reaction with GeH₃F, there was so much overlap of the resonances that accurate integration was not possible. The lower value in each case is probably accurate to at least ±2.
TABLE 5.4 Relative signs of coupling constants in Ir(CO)\textsubscript{2}(PPH\textsubscript{3})\textsubscript{2}(SiH\textsubscript{2}Br)

<table>
<thead>
<tr>
<th>Coupling</th>
<th>Sign</th>
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<tr>
<td>$2J_{H_1H_{q}}$</td>
<td>$-$\text{ve (assumed)}</td>
</tr>
<tr>
<td>$2J_{H_tH_{c}}$</td>
<td>$+$\text{ve}</td>
</tr>
<tr>
<td>$2J_{H_tP_{t}}$</td>
<td>$-$\text{ve}</td>
</tr>
<tr>
<td>$2J_{H_cP_{c}}$</td>
<td>$+$\text{ve}</td>
</tr>
<tr>
<td>$2J_{P_cP_{t}}$</td>
<td>$+$\text{ve}</td>
</tr>
<tr>
<td>$3J_{H_{q}H_{t}}$</td>
<td>$-$\text{ve}</td>
</tr>
<tr>
<td>$3J_{H_{q}H_{c}}$</td>
<td>$-$\text{ve}</td>
</tr>
<tr>
<td>$3J_{H_{q}P_{t}}$</td>
<td>$-$\text{ve}</td>
</tr>
<tr>
<td>$3J_{H_{q}P_{c}}$</td>
<td>$-$\text{ve}</td>
</tr>
<tr>
<td>$3J_{H_{1}P_{t}}$</td>
<td>$-$\text{ve}</td>
</tr>
</tbody>
</table>

The relative signs were determined by homo- and heteronuclear double resonance, irradiating peaks due to $H_1$, $H_q$, $H_c$, $H_t$, $P_t$, and $P_c$ at low power. $2J_{H_{q}H_{1}}$ was assumed to be negative by analogy to other molecules where this coupling constant has been determined.
REFERENCES (CHAPTER 5)

7. NUMARIT, K. Norville and A. Quirt, N.m.r. Program Library, University of East Anglia.
CHAPTER 6: SUGGESTIONS FOR FUTURE WORK

The study of the reactions of the \( [\text{HPt(PEt}_3]_3]^+ \) cation left two main points to be finished. The first, and most important, is the question of isolation. This may be accomplished by the use of organosilyl or germyl groups which will almost certainly be more thermally stable and could be handled fairly easily once isolated. Care would be required to ensure the products were of the same type. The second point is the mode of oxidative addition. This could be clarified by the use of either the deutero-cation or of \( \text{MD}_3^X \). A further series of reactions which could be studied would be the hydride cation with fluorophosphine species, e.g. \( \text{F}_2\text{PX} \) (\( X = \text{Cl, Br, I} \)). Indeed, fluorophosphines could also be reacted with the anions detailed in Chapter 4 of this work. The anionic species require synthesising with a counter cation which either does not interfere with the \( ^1\text{H n.m.r.} \), e.g. \( \text{Cs}^+ \) or alternatively one of the more soluble species, e.g., \( \text{Bu}_4^+\text{X}[\text{Pt(PEt}_3]_3]^- \) could be reacted with \( \text{MD}_3X \) and the \( ^2\text{H n.m.r.} \) spectrum used to trace the reaction pathway. It would also help if the bridged species obtained in Section 4.3.6 could be isolated and its structure determined by X-ray crystallography in order to determine whether the phosphines are cis or trans to the SeH bridge.

Some work is currently being undertaken in this department to investigate the reactions of the 5-coordinate iridium complex detailed in Chapter 5 with fluorophosphine species. Further to this, the reaction between Vaska’s compound and certain fluorophosphine species may produce novel 5-coordinate iridium complexes or alternatively may undergo oxidative addition with the
formation of a terminal \(-\text{PF}_2\) group.

Although a great deal of works have been published on the reaction of platinum species, one of the most neglected groups of complexes are the dimeric species:

\[
\begin{array}{c}
\text{Et}_3\text{P} \\
\text{Pt} \\
\text{Pt} \\
\text{PEt}_3 \\
\end{array}
\]

\[
\begin{array}{ccc}
X & X & X \\
\text{Pt} & \text{Pt} & \text{PEt}_3 \\
\end{array}
\]

\(X = \text{halogen}\)

The reaction between this species and \(\text{PF}_2\text{X}\) (\(X = \text{Cl, Br, I}\)), \((\text{PF}_2)_2\text{E}\) (\(E = \text{O, S, Se}\)) and \(\text{SiH}_3\text{X}\) (\(X = \text{H, F, Cl, Br, I}\)) may produce some novel types of complexes.
LIST OF COURSES ATTENDED

<table>
<thead>
<tr>
<th>Course</th>
<th>Lectures</th>
<th>Instructors</th>
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<td>Aspects of Inorganic Chemistry</td>
<td>22</td>
<td>E.A.V. Ebsworth</td>
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<td>Aspects of Fluorine Chemistry</td>
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<tr>
<td>Fortran IV Programming</td>
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Attendance at Inorganic Seminars: 3 years