SOME GROUP IV-B COMPLEXES OF RHODIUM, IRIDIUM AND PLATINUM

by

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1980
To my husband and my parents
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SUMMARY

This thesis describes the preparation of some silyl and germyl complexes of rhodium, iridium and platinum.

Some silyl and germyl derivatives of rhodium RhY(CO)H(MH$_2$X)(PET$_3$)$_2$ (Y = Cl or I; M = Si or Ge, and X = H, Cl or I) have been prepared by reaction of MH$_3$X with RhY(CO)(PET$_3$)$_2$. When X = Cl or I the products were stable at room temperature; nevertheless when X = H evidence supported the formation of the rhodium(III) adduct only at low temperature. Similar results were obtained when the reactions were performed using H$_2$MRZ (for M = Si: Z = H, R = -CH$_3$ or -CH$_2$-CH=CH$_2$; Z = Cl or I, R = -CH$_3$; For M = Ge: Z = H, R = -CH$_3$); formation of the products occurred at low temperatures, but the adduct dissociated to the starting materials as the temperature was increased. Also, preparation of Rh(III) hydrides of molecular formulae RhYXH(CO)(PET$_3$)$_2$ (X = Cl or I) is described.

Some equilibrium and thermochemical data corresponding to the Rh(I) + H$_2$MRZ $\rightleftharpoons$ Rh(III) conversion was measured and attempts are made in the text to account for the information obtained.

Reactions using some organo-substituted silyl compounds H$_3$SiR (R = -CH$_3$, -C$_6$H$_5$, -CH=CH$_2$ and -CH$_2$-CH=CH$_2$) were carried out with IrY(CO)(PET$_3$)$_2$, t-PtHY(PET$_3$)$_2$ and t-PtY$_2$(PET$_3$)$_2$. The phenylsilane derivatives of iridium and platinum were reacted with the hydrogen halides (HCl or HI), but evidence supporting the breaking of the C-Si bond was not found.

The complexes formed were characterised by $^1$H and $^{31}$P n.m.r. spectroscopy at low or room temperature as appropriate, and where possible, by analysis for C and H.
CHAPTER I

Introduction
There is a large and growing field of Transition Metal Chemistry in which silicon-containing ligands are involved. The work of Hein and his associates (1941) on Sn-Co derivatives established the possibility of forming bonds between a Group IV-B metal and a transition element\(^1\), but it was fifteen years later that \((h_5-C_5H_5)\text{Fe(CO)}_2\text{SiMe}_3\)\(^2\), the first of many silyl derivatives, was synthesized. The interest in these compounds derives from\(^3\):

1. Comparison with the corresponding alkyl- and Ge-, Sn-, and Pb-transition metal (M) complexes, including the role of \(\pi\)-back-bonding from filled \(d\pi\) orbitals of M into empty \(d\pi\) orbitals on Si (or other Group IV-B metal), and
2. expectation of useful catalytic properties from such heteronuclear derivatives.

The major synthetic routes to transition metal silyl fall into four main categories:

1. Salt elimination.
2. The mercurial route, (a modification of 1).
3. Elimination of a covalent molecule (\(H_2, H\) Halogen, or \(R_2NH\)).
4. Oxidative addition.

As previously mentioned, \((h_5-C_5H_5)\text{Fe(CO)}_2\text{SiMe}_3\) was the first compound containing a silicon-metal bond; it was prepared by Peper, Lemal and Wilkinson (1956) using salt elimination (eq. 1).
\[ \text{Na}[\text{h}_5\text{C}_5\text{H}_5\text{Fe(CO)}_2] + \text{Me}_3\text{SiCl} \xrightarrow{\text{THF}} \text{Me}_3\text{SiFe(CO)}_2(\text{h}_5\text{C}_5\text{H}_5) + \text{NaCl} \quad (1) \]

The compound, an orange crystalline solid, was thermally stable up to about 473 K but decomposed within a day when exposed to atmospheric oxygen. Following this observation, several other complexes were prepared using the same technique. Most of them contain one or more \(-\text{SiR}_1\text{R}_2\text{R}_3\) groupings, where \(R\) is usually alkyl, aryl, hydrogen, halogen, alkoxy, silyl or polysilyl.

The nature of such a metal-metal bond is not very clear. It is essentially a \(\sigma\) bond when compared with the organometallic complexes of these metals with carbon, which contain \(\sigma\) bonds. However, the potential availability of low energy empty d orbitals in the heavier Group IV-B elements should be taken into account. Although it is uncertain whether these d-orbitals are actually involved in bonding to the transition metal it is certain that this introduces the possibility of \(\pi\)-bonding.

The work in this thesis deals mainly with the preparation and study by nuclear magnetic resonance of some silyl derivatives of platinum, iridium and rhodium. The rest of the introduction will give a brief account of some of the relevant work done with these metals in this field. The three metals will be discussed individually in separate sections.

**Platinum**

Platinum-silicon chemistry is a vast field and formation of these metal-metal bonds has been achieved by several methods. The first platinum-silicon bond was obtained in 1966, prepared by the
lithium chloride salt elimination method (eq. 2):
\[
cis-[PtCl_2(PMe_2Ph)_2] + 2LiSiMePh_2 \xrightarrow{THF} [Pt(SiMePh_2)_2(PMePh)_2] + 2LiCl \tag{2}
\]
As in the case of the analogous germyl compounds, the reaction took place in two stages, and it was not possible to isolate the monosilyl species. The bis(silyl) complexes were stable as solids in the air, but decomposed when their solutions in tetrahydrofuran or chloroform were exposed to air.

For comparative reactivity and to simplify the spectroscopic studies, Glockling required a method of forming Me₃Si-Pt bond other than by using the salt elimination route, since the alkali-metal derivatives, Me₃SiLi or Me₃SiK are not readily accessible. This problem was overcome by the use of the required mercurial silylating agent (eq. 3):
\[
cis-[PtCl_2(PEt_3)_2] + (Me_3Si)_2Hg \xrightarrow{C_6H_6, \text{Reflex}} t-[Me_3Si]PtCl(PEt_3)_2 + Hg + Me_3SiCl \tag{3}
\]
The stereochemistry of the product was assigned using \(^1H\) n.m.r., which indicated a trans-configuration of phosphine groups in solution. The failure to introduce two trimethylsilyl groups in this way was ascribed to the higher trans effect of the aliphatic (SiMe₃) ligand, when compared with the mixed aromatic-aliphatic (SiMePh₂) ligand.

Another method used to prepare platinum-silicon bonds involves the use of silicon hydrides and Pt(0) complexes, (eqs. 4 and 5):
\[
Pt(PPh₃)_4 + R₃SiH \rightarrow cis-[PtH(SiR₃)(PPh₃)₂] + 2PPh₃ \tag{4}
\]
\[
Pt(PPh₃)_4 + 2R₃SiH \rightarrow cis-[Pt(SiR₃)₂(PPh₃)₂] + 2PPh₃ + H₂ \tag{5}
\]
Whether the reaction followed the course indicated by equations 4 or 5 depended on the nature of the group R and the reaction conditions,

\[ R_3 Si = Cl_3 Si-, Ph_2 HSi-, (m-F C_6 H_4)_3 Si-, (m-CF_3 C_6 H_4)_3 Si- \]

and (p-CF_3 C_6 H_4)_3 Si-]. Trichloro- and diphenylsilane did react with [Pt(PPh_3)_4] according to equation 5, but triarylsilanes (XC_6 H_4)_3 SiH in which X is electron withdrawing (viz. m-F, m-CF_3 and p-CF_3 ) reacted readily with the platinum zero complex in refluxing benzene to give the mono silyl compounds [PtHSi(C_6 H_4 X)_3 (PPh_3)_2] (equation 4). They did not react further with an excess of the triarylsilane, probably because of steric hindrance to attachment of two triarylsilyl groups to the platinum atom. A similar reaction was observed for Pt(diphos)_2 (diphos = Ph_2 P(CH_2)_2 PPh_2), but both types of silyl complex were too insoluble for n.m.r. study; however, the members of these series showed sufficient general similarities to suggest that all have the cis-configuration, which is imposed by the geometry of the ligand on these containing the diphosphine.

The discovery of the reversible hydrogenolysis according to equation 6 has led to the development of a useful synthesis for production of silyl complexes from hydridochloro-complexes of platinum(II), (eq. 6):

\[ \text{trans-}[PtCl(SiMePh_2)(PMe_2 Ph)_2] + H_2 \overset{\text{\(\Delta\)}}{\rightleftharpoons} \text{trans-}[PtHCl(PMe_2 Ph)_2] + MePh_2 SiH \] (6)

The ease of such reactions is dependent on ligands attached to platinum and silicon. Thus, t-[PtHCl(Ph_2 PhP)_2] gave complexes with a number of triarylsilanes, whereas t-[PtHCl(PEt_3)_2] did not react with Ph_3 SiH, and t-[PtHCl(PPh_3)_2] underwent only slow chlorination with Cl_3 SiH. Since the starting materials are readily available and the
reaction gives pure products, the hydrogen elimination method has no obvious limitation and Bentham used it to prepare a series of stable silyl and germyl hydride complexes. Trans-[PtHY(PET$_3$)$_2$], \((Y = \text{Cl, Br or I})\), reacted readily with the compounds H$_3$SiX, \((X = \text{H, Cl, Br or I})\) to form trans-[(H$_2$XSi)PtY(PET$_3$)$_2$], (eq. 7): \[ t-[\text{PtHY(PET}_3)_2] + \text{SiH}_3X \rightarrow t-[\text{Pt(SiH}_2X)Y(\text{PET}_3)_2] + \text{H}_2 \] (7)

When \(X,Y = \text{Cl}\), treatment of the complex with an excess of HCl gave the ultimate product \(t-[\text{PtCl(SiCl}_3)(\text{PET}_3)_2]\), in which H at Si has been replaced by Cl, and only when the solid was treated with liquid HCl was the platinum-silicon bond cleaved$^{14}$.

Six-coordinate platinum(IV) intermediates have been postulated for both of these platinum(II) reactions and such an intermediate has been isolated, (eq. 8):

\[ t-[\text{(H}_2\text{ISi})\text{PtI(PET}_3)_2] + \text{HI} \rightarrow [(\text{H}_2\text{ISi})\text{Pt(H)}\text{I}_2(\text{PET}_3)_2] \] (8)

This yellow crystalline Pt(IV) complex decomposes slowly at 20°C with evolution of hydrogen and formation of \(t-[\text{(HI}_2\text{Si})\text{PtI(PET}_3)_2]\).

The proposed mechanism is shown in the scheme A:
It was suggested that the oxidative addition step of the SiH bond in $X_2SiH_2$ across Pt may proceed through a six-coordinate Pt(IV) complex, as an intermediate, which then eliminates two ligands (H$_2$) to form the product. The intermediate must be unstable and decompose rapidly as it has not been detected experimentally. However, platinum(IV) adducts formed by CH$_3$I addition, such as t-[Pt(CH$_3$)$_2$(PEt$_3$)$_2$], have been known for a long time\textsuperscript{15}.

A series of novel mono and dihydride complexes of six-coordinate platinum(IV) have been reported\textsuperscript{16}. They were prepared by the addition of HX to trans-[PtHY(PEt$_3$)$_2$] or trans-[PtY$_2$(PEt$_3$)$_2$] to give cis-trans-[PtH$_2$XY(PEt$_3$)$_2$] (eq. 9), and [PtHXY$_2$(PEt$_3$)$_2$] respectively.

\[
\begin{align*}
\text{PEt}_3 & \quad \text{H} \quad \text{Pt} \quad \text{Y} + \text{HX} \rightarrow \text{PEt}_3 \quad \text{H} \quad \text{Pt} \quad \text{Y} \\
& \quad \text{PEt}_3
\end{align*}
\]

(X, Y = Cl, Br or I).

Some other silyl and germyl platinum complexes have been reported lately\textsuperscript{17,18,19}. Among them, trans-[Pt(MH$_2$X)Y(PEt$_3$)$_2$], (M = Si or Ge; X = CCH, CCCF$_3$, CN, C$_5$H$_5$; Y = halogen), have been prepared by the reaction of silyl and germyl compounds, MH$_3$X, with platinum hydrides, trans-[PtHY(PEt$_3$)$_2$]; in those cases no interaction between the group X and platinum was observed\textsuperscript{20}. The products in this report have been properly characterised by n.m.r. spectroscopy, using heteronuclear double resonance to determine the parameters for $^{195}$Pt and certain other nuclei\textsuperscript{21}. 
Iridium

The discovery of a four-coordinated iridium(I) complex, \( \text{IrCl(CO)}[\text{P(C}_6\text{H}_5)_3]_2 \) has afforded access to novel chemical reactions.

It has been reported by Vaska\(^{22,23}\) that \([\text{IrCl(CO)}(\text{PPh}_3)_2]\) shows a striking power under normal conditions to react with a large number of molecules (e.g. hydrogen, oxygen, halogen halides, organic halides, organic acids, etc). Yet, it displays properties which are remarkably well suited for a convenient investigation of its chemical behaviour: its crystals are durable in air and thermally stable; its relevant reactions represent additions to the square planar species to yield octahedral complexes of iridium(III).

Such ability stimulated interest in the oxidative addition of Group IV-B hydrides to these complexes. Chalk and Harrocl\(^24\) showed that silanes (\( \text{R}_3\text{SiH} \)) bearing electro-negative substituents \( \text{R} \) such as Cl or OEt add reversibly to the planar complex \( \text{IrCl(CO)(PPh}_3)_2 \) involving addition of Si and H to iridium to give octahedral hydrido-(silyl)iridium(III) adducts of formula \( \text{IrHCl(SiR}_3)(\text{CO)(PPh}_3)_2 \). With an excess of silane, further reaction can occur to give octahedral iridium(III) dihydrides \( \text{IrH}_2(\text{SiR}_3)(\text{CO)(PPh}_3)_2 \), the appropriate chlorosilane being eliminated\(^{25,26,27}\) (scheme B).

\[
\begin{align*}
\text{IrCl(CO)(PPh}_3)_2 + \text{R}_3\text{SiH} & \rightarrow \text{IrHCl(SiR}_3)(\text{CO)(PPh}_3)_2 \\
\text{IrH}_2(\text{SiR}_3)(\text{CO)(PPh}_3)_2 + \text{R}_3\text{SiCl} & \rightarrow \\
\text{Scheme B}
\end{align*}
\]

Similar germyl reactions suggest that there is a difference between the reactions of Vaska's compound with silanes and with germanes as the second step occurs very readily in the reactions of
trialkyl - or triaryl - germanes with IrCl(CO)(PPh₃)₂, leading exclusively to dihydrides of the type IrH₂(GeR₃)(CO)(PPh₃)₂²⁸.

Ebsworth and Leitch²⁷ have found that only the mono-hydride species are obtained when a range of simple silyl and germyl compounds H₃MX were reacted with IrCl(CO)(PPh₃)₂, (eq. 10).

\[
\text{IrCl(CO)(PPh₃)₂ + H₃MX} \rightarrow \text{Cl(CO)IrH(PPh₃)₂(MH₂X)} \quad (10)
\]

(M = Si or Ge; X = H, Cl, Br or I).

They were able to obtain the dihydrides only after prolonged standing with SiH₃Cl or MeSiH₂Cl, and surprisingly SiH₄ does not give a dihydride of this type. In contrast, they had no difficulty in isolating 1:1 adducts of the usual type from Vaska's compound and germanium hydrides, and even on long term reactions they could not obtain germyl iridium dihydrides by this reaction.

Carbonylation of five-coordinate silyliridium(III) complexes was used by Bennett, Charles and Fraser²⁹ as an alternative route to prepare IrHCl(SiR₃)(CO)(PPh₃)₂ complexes, (eq. 11):

\[
\text{IrHCl(SiR₃)(PPh₃)₂ + CO} \rightarrow \text{IrHCl(SiR₃)(CO)(PPh₃)₂ + PPh₃} \quad (11)
\]

\[R₃ = \text{Cl₃, MeCl}_₂ \text{ or (OEt)}₃\].

In nearly all these cases the products are only sparingly soluble in common organic solvents, making n.m.r. work difficult, and unfortunately their structures could only be assigned from infrared spectra and to a lesser extent, from proton n.m.r. spectra.

Since the reactions of Ir(CO)Cl(PPh₃)₂ seem to give such different ranges of products depending on the reactants, it appears interesting to investigate them; but it is imperative to try other
conditions to overcome the insolubility problem.

Aware that changing the phosphine may lead to a different mode of addition and subsequently different products, triphenylphosphine was replaced in Vaska's compound by triethylphosphine, a more basic phosphine with smaller steric requirements than triphenylphosphine, allowing Ebsworth and Fraser\(^\text{30}\) to be more successful in the investigation of \(\text{Ir(CO)}\_2\_\gamma(\text{PET}_3)_2\) (\(\gamma = \text{Cl} \) or \(\text{I}\)), and silyl and germyl \(\text{H}_3\text{MX}\) (\(X = \text{hydrogen or halogen}; M = \text{Si} \) or \(\text{Ge}\)), reactions.

They concluded that all silyl adducts studied are of type I, with mutually trans phosphine ligands and with H trans to \(\text{SiH}_3\); in contrast, most of the germyl adducts are of type II with H cis to \(-\text{GeH}_3\). When a germyl isomer of type I is formed it is in no case the most abundant product. It is a situation not attributable exclusively to steric factors as germyl and silyl groups are not very different in size.

They have no evidence to the mechanism of addition; ionic mechanisms are perhaps unlikely to be important with such hydrides in non-polar solvents; nor do radical mechanisms seem very probable under such very mild conditions. The simplest and safest explanation of the results is that \(\text{SiH}\) adds to this iridium complex in the trans mode, whereas \(\text{GeH}\) can add either trans or cis. They have no evidence at
all to suggest that either type of isomer tends to rearrange and a final suggestion could not be made at this stage.

The little information on unsaturated groups bound to silicon compounds, SiH₂R (R = CH₂ = CH—, CH₂=CH—CH₂—, -C₆H₅), reacting with PtH₂(PEt₃)₂, Pt₂(PEt₃)₂ and Ir₂(CO)(PEt₃)₂, (Y = Cl or I), led us to investigate these reactions to see whether the organic groups which may also attack the transition metal could give us some evidence to propose oxidative addition involving bonds other than Si-H.

Rhodium

RhCl(CO)(PPh₃)₂, the rhodium compound analogous to Vaska's complex was synthesized by Vallarino in 1957.

The report of Vaska that IrCl(CO)(PPh₃)₂ has a great tendency to add covalent molecules, suggested that it might be possible to add alkyl halides to rhodium chlorocarbonyl bistriphenylphosphine and form alkyl rhodium derivatives. Indeed RhCl(CO)(PPh₃)₂ reacts readily with active organic halides producing alkyl rhodium dihalocarbonyl bis-phosphines, air stable complexes, as iridium does. Nevertheless, the reaction was observed to be reversible as the starting material could not be completely removed from the products (eq. 12):

\[
\text{RhCl(CO)(PPh₃)₂ + RX} \rightleftharpoons \text{R RhClX(CO)(PPh₃)₂} \quad (12)
\]

(RX = CH₃I, CH₂ = CH-CH₂I, C₆H₅CH₂Br).

By analogy, attempts to prepare silyl derivatives of rhodium were started. First, Rh(CO)Cl(PPh₃)₂ was reacted with an alkali metal
derivative of silane\(^{33}\), but it failed to produce readily characterizable products. A second approach also failed when \(R_3\text{SiH}^{33,34}\) \((R_3 = \text{Cl}_3, \text{Cl}_2\text{Ph}, \text{Cl}_2\text{Et}, \text{Cl}_2\text{Me and (OEt)}_3\)\), was reacted with \((\text{Ph}_3\text{P})_2\text{Rh(CO)Cl}\). The failure was suggested to be due to the higher energy of oxidation of rhodium(I) compared to iridium(I), as the same reaction gave the complex \(\text{Ir(CO)ClH(SiR}_3\text{)(PPh}_3\text{)}_2\) when \(\text{IrCl(CO)(PPh}_3\text{)}_2\) was used\(^{24}\).

According to other reactions of \((\text{Ph}_3\text{P})_3\text{RhCl}\) complexes, which normally lead to products of the type \((\text{Ph}_3\text{P})_2\text{RhCl(Y)Z}\) when reacted with \(\text{YZ (YZ = H}_2^{35}, \text{HCl}^{36}, \text{O}_2^{35}, \text{etc})\), it was hoped that an increase in the ease of oxidative addition reactions could be brought about by replacement of carbon monoxide by triphenylphosphine in the \(\text{RhCl(CO)(PPh}_3\text{)}_2\) complex. As expected \((\text{Ph}_3\text{P})_3\text{RhX}\) has been found to react with an excess of trichloro – and other silanes to give the first silyl derivatives of rhodium\(^{33,37}\), \(\text{Rh(SiR}_3\text{)XH(PPh}_3\text{)}_2\). (Eq. 13).

\[
\text{RhX(PPh}_3\text{)}_3 + \text{SiHR}_3 + (\text{Ph}_3\text{P})_2\text{RhH(SiR}_3\text{)X + Ph}_3\text{P (13)}
\]

\((X = \text{Cl or Br}; R_3 = \text{Cl}_3, \text{Cl}_2\text{Ph, Cl}_2\text{Et, (OEt)}_3\)\).

The reaction has been carried out at room temperature, and the displaced ligand triphenylphosphine recovered from its solution in the excess of the silane. Reaction rates are very low and are almost certainly caused by the insolubility of \(\text{RhX(PPh}_3\text{)}_3\) in the silanes. Characterisation of the products has been made by molecular weight estimation and infrared spectroscopy.

Wilkinson, G. and co-workers in 1968 got interesting results\(^{34}\) when triethylphosphine, a more basic phosphine than triphenylphosphine, was used as a ligand in the \(\text{RhCl(CO)L}_2\) complex. It reacts readily with \(\text{SiHCl}_3\) and \(\text{SiHCl}_2\text{Me}\) to produce the \(\text{Rh(III) adducts, RhClH(SiCl}_3\text{)(CO)(PEt}_3\text{)}_2\) and \(\text{RhClH(SiCl}_2\text{Me)(CO)(PEt}_3\text{)}_2\) respectively,
both dissociated in solution and stable only in the presence of excess of silane.

Carbonylation was thought to be a good solution to the dissociation problem as dissociation could be inhibited by performing the reactions on the solid complex. Thus attempts to prepare $\text{RhCl(CO)(SiCl}_3\text{H(PPh}_3\text{)}_2$ from carbonylation on $\text{RhClH(SiCl}_3\text{)(PPh}_3\text{)}_2$ have been made, but they failed as such reactions result in the displacement of the silane and the formation of the known complex $\text{trans-Rh(CO)Cl(PPh}_3\text{)}_2$. It might be possible that dissociation of the complex is encouraged by carbon monoxide, a good $\pi$ ligand which would be expected to favour the lower oxidation state for rhodium. In conclusion, the observation of the six coordinate intermediate $\text{RhCl(CO)H(SiCl}_3\text{)(PPh}_3\text{)}_2$ in such reaction at low temperature presents much controversy.

For the platinum, iridium and rhodium the last combination to be known in examples of bonding to Si, Ge and Sn, was that between rhodium and germanium. In 1970, Glockling and Hill reported the first Rh(I) and Rh(III) germyl derivatives, isolated mainly by the following reaction (eq. 14):

$$\text{RhCl(Ph}_3\text{E)}_3 + \text{R}_3\text{GeH \rightarrow RhCl(H)(GeR}_3\text{)(Ph}_3\text{E)}_2 + \text{Ph}_3\text{E} \quad (14)$$

($E = P, \text{As} ; \text{R} = \text{Me, Et, Cl}$).

Such compounds are formed like the silyl analogues; the products dissociate extensively in solution but are mostly air stable as solids. Unfortunately, $^1\text{H}$ and $^{31}\text{P}$ n.m.r. studies on such complexes have been restricted by extensive dissociation or low solubility in inert solvents, and they have not been properly characterized.
As in its reactions with silyl compounds, RhCl(PR$_3$)$_2$(CO) ($R = \text{Ph and Pr}^n$) failed to form stable Rh-Ge complexes with trimethyl- or triethylgermane$^{40}$; this contrasts with the behaviour of the iridium analogue and illustrates the greater stability of the +3 oxidation state for iridium (eqs. 15 and 16):

$$\text{MC}(\text{CO})(\text{PPh}_3)_2 + \text{HGeCl}_3$$

If $M = \text{Ir}$

$$\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}\text{G}(\text{GeCl}_3) \quad (15)$$

If $M = \text{Rh}$

$$[\text{Ph}_3\text{PH}]_2[\text{Rh}(\text{GeCl}_3)_5(\text{CO})] \quad (16)$$

Addition of HGeCl$_3$ to the rhodium complex results in a rapid reaction giving H$_2$ and a phosphonium salt, which was not obtained pure and it was partially characterized with infrared spectroscopy.

Carbonylation of (Ph$_3$P)$_2$Rh(H)Cl(GeEt$_3$), as in the analogous silyl compound, produces Et$_3$MH and the rhodium (I) complex Rh(CO)Cl(Ph$_3$P)$_2$$_4^{40}$, (eq. 17). The reaction may proceed via predissociation to triethyl germane followed by coordination of the neutral ligand to rhodium.

$$\text{Rh}(\text{H})\text{Cl}(\text{GeEt}_3)(\text{Ph}_3\text{P})_2 \xrightarrow{\text{CO}} \text{Et}_3\text{GeH} + (\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl} \quad (17)$$

Other reactions have been performed with (Ph$_3$P)$_2$(CO)RhCl and germanium compounds$^{40}$ but they all produce Rh(I) complexes. (Ph$_3$P)$_2$(CO)Rh(GeCl$_3$) has been obtained from the reaction of caesium trichlorogermainite and (Ph$_3$P)$_2$(CO)RhCl; alternatively with triethylbromogermaine in the presence of carbon monoxide, a carbonylate anion has been produced.
from which \((\text{Ph}_3\text{P})_2\text{CO})_2\text{Rh}(\text{GeEt}_3)\) could be isolated. It loses CO under nitrogen atmosphere, giving the rhodium(I) complex \((\text{Ph}_3\text{P})_2\text{CO})\text{Rh}(\text{GeEt}_3)\).

To compare the reactivity of \(\text{RhY(CO)}(\text{PET}_3)_2\) with its parent \(\text{Ir(CO)}\text{Y(PET}_3)_2\) complex \((Y = \text{Cl or I}),\) we have investigated the reaction of \(\text{RhY(CO)}(\text{PET}_3)_2\) with the most simple silyl and germyl hydrides \(\text{MH}_3\text{X}, (M = \text{Si or Ge; X = H, Cl or I).}\) Moreover, we have studied the reactions of the rhodium complex with \(\text{H}_2\text{MRZ}\) groups, \((\text{for M = Si: Z = H, R = -CH}_3 \text{ or -CH}_2\text{-CH}=\text{CH}_2; Z = \text{Cl or I, R = -CH}_3.\) For \(\text{M = Ge: Z = H, R = -CH}_3),\) to see whether interaction of the organic group with rhodium could be suggested.

The oxidative addition method has been used for the formation of transition metal bonds to both carbon and silicon. For comparative purposes it is noteworthy that analogous oxidative addition of \(\text{CH}_3\text{X}\) \((X = \text{halogen})\) across \([\text{PtI(\text{CH}_3)}\text{PET}_3)_2]\)\(^{15}\), \([\text{Ir(CO)}\text{Cl(PPh}_3)_2]\)\(^{32}\) and \([\text{Rh(CO)}\text{Cl(P(n-C}_4\text{H}_9)_3)]\)\(^{32}\), give six coordinate adducts by addition of \(\text{CH}_3\text{-X instead of CH}_2\text{X-H as in the silyl case. This observation reflects the differing bond strengths of Z-Z, Z-H and Z-X (Z = C, Si; X = halogen) for carbon and silicon. While C-X addition is common and C-H cleavage unusual for carbon, the Si-X addition is unconfirmed for silicon, and Si-H cleavage provided a good synthetic route to numerous complexes.}

Finally, the importance of transition metal-hydrides must be mentioned, as the majority of the synthesized silyl and germyl complexes in this project are hydrides.

Transition metal hydride chemistry has been developed recently
in inorganic and organometallic chemistry. In 1931, Hieber \(^{41}\) discovered the first well-defined, although unstable, transition metal hydrides: \(\text{H}_2\text{Fe(CO)}_4\) and \(\text{HCo(CO)}_4\), but it was not until 1955 that the first stable hydride, \(\text{HRe(C}_5\text{H}_5)_2\), was prepared by Wilkinson and Birmingham \(^{42}\).

Although transition metal hydride complexes have an interesting chemistry of their own, the greatest interest in hydrides comes from their importance to catalyze homogeneously a wide variety of organic reactions such as: hydrogenations, deuterations, olefin-isomerizations, hydroformylation and hydrosilations.

One of the most fruitful techniques for characterization of hydride complexes is n.m.r. spectroscopy. In the n.m.r. spectrum, hydride resonances generally occur in the 12-60 \(\tau\) region, and the magnitude of coupling constants and the splitting patterns often provide valuable evidence for the configuration studies of geometrical isomers.

As mentioned above, the earlier silyl and germyl complexes of platinum, iridium and rhodium contain organo-substituted Group IV-B metals. Although they are more stable to oxidation than the parent hydrides, they have the disadvantage of giving more complex \(^1\text{H}\) n.m.r. spectra; there is always at least one more bond between the nearest proton to the Group IV-B element and the transition metal. Recently with the synthesis of platinum and iridium complexes using \(\text{MH}_3\text{X}\) (\(M = \text{Si or Ge}; X = \text{hydrogen or halogen}\)), facility to analyse the spectra was obtained. The Si-H proton resonances in the \(^1\text{H}\) n.m.r. spectra are chemically shifted from most C-H resonances and are more sensitive to the nature of the transition metal and its substituents.
CHAPTER II

Reactions of some silyl and germyl compounds with
\[ \text{RhY(CO)(PET}_3)_2 \] (Y = Cl or I)
II.1 Introduction

Oxidative addition by trisubstituted silyl and germyl compounds to some rhodium(I) complexes has been studied over the past twelve years\(^\text{33-40}\). The oxidative addition reaction of a d\(^8\) complex has been tried to prepare rhodium-silicon and -germanium compounds using RhCl(CO)(PR\(_3\))\(_2\) (R = Ph, Et).

(PPh\(_3\))\(_2\)Rh(CO)Cl gives a very unstable adduct with trichlorosilane\(^\text{33}\), but the use of a more basic phosphine, e.g. Et\(_3\)P, gives a slightly more stable Rh(III) product\(^\text{34}\). Nevertheless, it was impossible to isolate and properly characterize the silyl rhodium(III) carbonyls before they eliminated silane and formed RhCl(CO)(PEt\(_3\))\(_2\).

A similar reaction failed to form stable Rh-Ge complexes with Me\(_3\)GeH and Et\(_3\)GeH\(^\text{40}\). On the contrary, addition of excess of trichlorogermaine to (Ph\(_3\)P)\(_2\)(CO)RhCl results in a rapid reaction giving hydrogen and a phosphonium salt, which is probably [Ph\(_3\)PH]\(_2\)[Rh(CO)(GeCl\(_3\))\(_5\)], with infrared evidence indicating that rhodium is in the +3 oxidation state. Using another route some Rh(I) germanium complexes have been prepared, but none of them in the +3 oxidation state.

The inability of the germyl triorgano-substituted compounds to form Rh(III) complexes of the type Rh(CO)Cl(H)(GeR\(_3\))(PPh\(_3\))\(_2\) contrasts with silicon, as in this case there is evidence that such Rh(III) complexes exist. Besides, it is noteworthy that in this project there was no difficulty in isolating 1:1 adducts of the usual type with germanium hydrides, despite the rather different reaction.
between Rh(CO)Cl(PPh\textsubscript{3})\textsubscript{2} and triorgano germanes; indeed, no phosphonium salt or germyl rhodium in +1 oxidation state was obtained by this reaction, but of course no conclusions about it can be drawn from this parallel reaction as the change in phosphine from PPh\textsubscript{3} to PET\textsubscript{3} and the use of triorgano-substituted germane will no doubt have an influence in this reaction.

Unfortunately the structure of the silyl adduct mentioned above has been deduced from infrared spectra and only to a limited extent from n.m.r. data, which gives much more specific information about such complexes.

In this chapter will be presented the synthesis of adducts formed by a series of simple silanes and germanes (MH\textsubscript{3}X, where M = Si or Ge, and X = H, Cl or I) with trans-halogen carbonyl bis-(triethyl phosphine)rhodium(I) and the characterization of these products using nuclear magnetic resonance.

The presence of rhodium in these reaction-products gives extra evidence for such characterization. Rhodium is one of the few elements that occur solely as an isotope which has I = \frac{1}{2} and a natural abundance of 100%, but this desirable feature is counterbalanced by a very low magnetogyric ratio\textsuperscript{43}. Despite being an element of major chemical interest, the low resonance frequency and very low sensitivity to n.m.r. detection of the \textsuperscript{103}Rh nucleus (which is only 0.003% of that of the proton), seem to have deterred spectroscopists.

Therefore, further alternatives for the spectroscopic study of this rhodium-phosphine complex are the heteronuclear \textsuperscript{1}H-(\textsuperscript{103}Rh)\textsuperscript{2} double resonance and \textsuperscript{1}H(\textsuperscript{31}P, \textsuperscript{103}Rh) triple resonance experiments;
however, none of these experiments was successful and n.m.r. data dealing with $^{103}\text{Rh}$ are not available in these results.

II.2 Oxidative-Addition Reactions of $\text{MH}_3\text{X}$ ($\text{M} = \text{Si} \text{ or Ge}; \text{X} = \text{Cl} \text{ or I}$)

The reactions of $\text{Rh}(\text{CO})\text{Y(PEt}_3\text{)}_2$ with $\text{MH}_3\text{X}$ ($\text{Y}$ and $\text{X} = \text{Cl} \text{ or I}; \text{M} = \text{Si} \text{ or Ge}$) were carried out in toluene and n.m.r. spectra of those mixtures were recorded from low temperature. Reactions were not expected to be complicated by halide exchange when the halogen on the Group IV-B compound and rhodium are the same ($\text{X} = \text{Y}$).

The addition reaction of $\text{Rh}(\text{CO})\text{Cl(PEt}_3\text{)}_2$ with $\text{SiH}_3\text{Cl}$ was very fast and it began at about $213 \text{ K}$. Complete proton decoupled phosphorus n.m.r. spectra were recorded in $20^\circ\text{C}$ steps; when the mixture was brought up to room temperature the reaction was complete within minutes. An adduct of Rh(III) that was stable at room temperature was obtained, but it was felt to be unwise to bring any further possible complication to the reaction by leaving the products for long periods at room temperature. Therefore the solution was kept cold until characterisation of the adduct was complete.

At $203 \text{ K}$, the phosphorus n.m.r. spectrum contained a doublet, when proton decoupled, with $^{13}\text{C}$ and $^{29}\text{Si}$ satellites. It was due to two equivalent phosphorus atoms split by a $^{103}\text{Rh}$ nucleus, confirming that the phosphines are mutually trans. The phosphorus resonance occurred in the region expected for triethylphosphine bound to Rh(III)$^{43-45}$, and decrease on $^1J_{\text{P-Rh}}$ was obtained, as expected for a change from four to six coordination. When the protons of the ethyl groups were decoupled (off-resonance decoupling), the main
resonance was split into narrow doublets confirming the presence of RhH (see Diagram 1).

\[ 31P\{^1H\} \hspace{1cm} \text{Off-resonance decoupling} \]

Diagram 1

At the same temperature, the proton n.m.r. spectrum of the solution contained three sets of resonance (see Diagram 2); those associated with:

- protons on a silicon atom (4.5 - 5.5 ppm);
- the ethyl groups of a phosphine (0.5 - 2.0 ppm); and
- a proton on the rhodium metal (less than -7 ppm).

The resonances due to the protons on the ethyl groups of the phosphines are complicated and do not yield much information, apart from their overall pattern which indicates that the phosphine molecules are bound to a metal.

The resonance due to the protons on the silicon appeared as a seven line multiplet (1:2:3:4:3:2:1), due to overlapping splittings coming from two $^{31}P$ atoms, one $^{103}Rh$ nucleus and a hydride on the transition metal. By irradiating in the phosphorus region of the spectrum this signal was collapsed into a 1:2:1 triplet with $2J_{H-Si-Rh} = 3J_{H-Si-Rh-H}$, due to two overlapping doublets. Additional irradiation of the hydride proton collapses this triplet into a
The resonance due to the hydride on the rhodium took the form of a 9 line set (1:2:4:6:6:4:2:1) due to overlapping multiplets. By irradiating with a phosphorus frequency corresponding to the same phosphorus chemical shift as that which collapsed the silyl protons multiplet, this hydride resonance was collapsed into a set of 5 lines due to two overlapping triplets from which can be deduced that \( J_{\text{H-Rh}} = 2 J_{\text{Rh-Si-H}} \). Additional irradiation of the silyl protons collapsed this set into a doublet with a separation equal to \( J_{\text{H-Rh}} \). The couplings are of the same magnitude (see Diagram 2).
Integration of both sets of resonances indicate that the silyl resonance is twice as intense as the one for the metal hydride.

The chemical shift of the Rh-H resonance suggests that it could be trans to carbonyl or silicon, but the observation of $^3J_{\text{H-Si-Rh-H}}$ in the silyl and hydride resonance signals implies that the hydride should be in a trans position to the silyl group. Thus the product from this reaction is a I-type isomer with mutually trans-phosphines, hydride trans to silyl and carbonyl trans to chloride.

$$\text{MH}_2\text{X} \quad \text{M} = \text{Ge or Si}$$

$$\text{Et}_3\text{P} \quad \text{Y} \quad \text{PET}_3 \quad X = \text{Cl or I} \quad Y = \text{Cl or I}$$

**I-type isomer**

The $^1\text{H}$ n.m.r. resonances of $\text{Rh} \quad (\text{CO})\text{H(SiH}_2\text{)}\text{(PET}_3\text{)}_2$ at 360 MHz are shown in Figures II.1 and II.2 together with homonuclear resonance experiment.

When the n.m.r. reaction tube was left at room temperature for some time the solution became brown. $^3\text{P}$ n.m.r. spectra showed that a new product with equivalent phosphine groups was present in the solution and $^1\text{H}$ n.m.r. recorded, in addition to a singlet at 3.16, a new silyl and hydride resonance signal. The singlet was possibly due to SiH$_4$. The silyl resonance of the complex was not well resolved and the form of the hydride signal was different from the one found for the initial product. Neither the hydride resonance pattern nor the $\delta$(Rh-H) value was consistent with an isomer having H trans to Cl.
Figure II.1 360 MHz silyl resonance of $\text{H-Rh-SiH}_2\text{I}$ at 243 K
Figure II.2 360 MHz hydride resonance of \( \text{H} \quad \text{Rh} \quad \text{SiH}_2\text{I} \) at 243 K.
These silyl and hydride resonances seemed to be related in a 1:1 intensity ratio, and they could be due to \( \text{RhHCl(SiHCl}_2\text{)(CO)(PEt}_3\text{)}_2 \).

As with the previous reaction, the reaction between \( \text{Rh(CO)Cl(PEt}_3\text{)}_2 \) and GeH\(_3\)Cl was carried out at low temperatures using toluene as solvent. The addition reaction was very fast and it was complete within minutes at 233 K to give a pale brown solution. The reaction solution was kept cool until characterization using n.m.r. was complete.

At 203 K the phosphorus n.m.r. spectrum of the solution contained mainly two signals in a 5:1 ratio in the region of the spectrum associated with triethylphosphine bound to Rh(III). Both signals were doublets when proton decoupled indicating equivalence of phosphorus atoms, and they split into small doublets when observed under off-resonance conditions, suggesting the presence of a hydride attached to rhodium.

At the same temperature, and as in the silyl case, the proton n.m.r. spectrum contained three sets of resonances (see Diagram 3). Those associated with the ethyl groups of a phosphine did not yield much information, but its pattern indicated that the phosphine molecules were bound to a metal.

Those associated with protons on a germanium atom (4.9-5.5 ppm) appeared as a set of 9 lines (1:2:2:1:4:1:2:2:1) due to three overlapping triplets. By irradiation in the phosphorus region of the spectrum this signal was collapsed into a 1:2:1 triplet due to two overlapping doublets with \( ^2J_{H-\text{Ge-Rh}} \neq ^3J_{H-\text{Ge-Rh-H}} \); additional irradiation of the hydride proton collapsed this triplet into a doublet with a separation equal to \( ^2J_{H-\text{Ge-Rh}} \).
The resonances due to a proton on the rhodium metal (less than -8 ppm) took the form of an 8 line multiplet (1:3:5:7:7:5:3:1), because of overlapping splittings. By irradiating with a phosphorus frequency corresponding to the same phosphorus chemical shift as that which collapsed the germyl signal, this hydride resonance was collapsed into a 1:3:3:1 quartet, due to two overlapping triplets with $^{1}J_{H-Rh}$. Additional irradiation of the germyl protons collapsed this quartet into a doublet with a coupling constant equal to $^{1}J_{H-Rh}$ (See Diagram 3).

Due to the resolution of 3 bond coupling constant $^{3}J_{H-Rh-Ge-H}$ it is thought that Rh-H is trans to the germyl group. Consequently these observations indicate that, as in the silyl case, this
reaction has produced mainly a I-type isomer. Differences of the proton n.m.r. resonance patterns of the silyl and germyl halide adducts are due to the big discrepancy of $^1J_{H-Rh}$ for these adducts; the $^1J_{H-Rh}$ separation is smaller for the germyl halide product.

Concentration of the non-predominant species in this reaction solution was not enough to have resolution of the associated signals in the $^1H$ n.m.r. spectra. As mentioned before, the phosphorus spectrum showed equivalence of phosphorus atoms in the species and off-resonance decoupling showed this peak to be due to a species having a hydride on the metal, but as the GeH or RhH resonances in the proton spectrum were not observed, it could not be determined what may be stereochemistry or what is bound to the germanium atom.

The reaction of SiH$_3$I with Rh(CO)I(PEt$_3$)$_2$ was complete at 253 K in toluene. It gave very similar results to those for the analogous reaction of Rh(CO)Cl(PEt$_3$)$_2$ with SiH$_3$Cl; the n.m.r. spectra contained similar resonances to those of this adduct, but with some changes in the chemical shift. When proton decoupled, the phosphorus n.m.r. spectrum contained a doublet in a region associated with triethylphosphine bound to Rh(III). Off-resonance decoupling gave a doublet of doublets on this signal indicating the presence of a metal hydride. The $^1H$ n.m.r. spectra showed resonances matching with an I-type isomer, and their apparently complicated silyl and hydride resonances were analysed with the help of homo- (at 360 MHz) and heteronuclear (at 100 MHz) double resonance.
In the case of the reaction of Rh(CO)I(PE\textsubscript{3})\textsubscript{2} with GeH\textsubscript{3}I different results to those for the analogous reaction of Rh(CO)Cl(PE\textsubscript{3})\textsubscript{2} with GeH\textsubscript{3}Cl were obtained.

At 203 K phosphorus n.m.r. spectra of the reaction solution showed two species (A and B) in a 2:1 ratio; when the temperature was raised to 223 K a drastic change of ratio was observed, 2:3 for A and B respectively. The $^{31}\text{P}\{^1\text{H}\}$ spectrum showed a doublet for both isomers, confirming that the phosphines were mutually trans, and off-resonance decoupling indicated that both species were monohydrides. The resonance region was associated with triethylphosphine bound to Rh(III).

The proton n.m.r. spectrum of this solution contained two sets of resonances associated with protons on a germanium atom, two sets of resonances due to hydrides on a metal atom, and resonances due to the ethyl groups of triethylphosphine (see Diagram 4).

![Diagram 4](image-url)

Note: not at scale; resonance signals denoted as I were represented in Diagram 3
The stronger GeH resonance to lower frequency (corresponding to species B) appears as a set of 9 lines and the RhH resonance to higher frequency as an 8 line multiplet. The couplings on both sets of resonances were collapsed by irradiating at a frequency corresponding to the same phosphorus chemical shift and are therefore associated with the same metal system. The hydride resonance was in a region for RhH trans to carbonyl or germanium, but as $^3J_{\text{H-Ge-Rh-H}}$ is resolved it is thought that the hydride is trans to the germyl group. The $^3J_{\text{H-Ge-Rh-H}}$ couplings were of the same magnitude for both sets of resonance. Comparison of the resonances previously described and marked as (I) in Diagram 4 with the spectrum in Diagram 3, shows that resonances for species B were due to an isomer of type I: mutually trans phosphines, germyl trans to hydride and iodide trans to carbonyl.

The other resonances in the proton n.m.r. spectrum (corresponding to species A) took the form of a triplet in the GeH region and a set of 5 lines in the RhH region. When irradiated in the phosphorus region of the spectrum the triplet in the GeH region collapsed to a singlet and the set of 5 lines in the RhH region, due to two overlapping triplets with $^1J_{\text{H-Rh}} = 2^2J_{\text{H-Rh-P}}$, converted into a doublet with a separation equal to $^1J_{\text{H-Rh}}$.

For both sets of resonances the irradiating frequency used to collapse the signal corresponded to the same phosphorus chemical shift. The chemical shift differs from that used to collapse the couplings in the I-type isomer which was present, and it can therefore be assumed that the simple resonances in the proton spectrum belonged to a system which was independant of the I-type isomer.
Surprisingly $^{2}J_{H-Ge-Rh}$ was not observed and even on expansion of the germyl signal, which is broad, such coupling was not resolved. Evidence that H was cis to the germyl group comes from the failure to observe $^{3}J_{H-Rh-Ge-H}$ coupling in either germyl or hydride resonances. The appearance of this hydride at a lower frequency than the hydride for the isomer type I of this species (with H trans to GeH$_2$I) indicates that H should be trans to halogen.

The value of $^{1}J_{H-Rh}$ for this system is approximately twice that for a type I isomer, but is similar to the one found for Rh-H trans to halides in other rhodium complexes.$^{38}$ Also, $\delta$(Rh-H) for this isomer is similar to the one found for the hydride in Rh(H)I$_2$(CO)-(PET$_3$)$_2$ complex, which is thought to have hydride trans to iodide (see Section II.7).

Therefore, it is suggested that resonances for species A are due to a II-type isomer, with phosphines mutually trans, iodo germyl trans to carbonyl and H trans to iodide.

\[
\begin{align*}
\text{GeH}_2X & \\
\text{Et}_3\text{P} & \quad \text{Rh} & \quad \text{PB} & \quad \text{CO} \\
\text{H} & & \text{Y} & \\
\text{X} & = \text{Cl} \text{ or I} & \text{Y} & = \text{Cl} \text{ or I}
\end{align*}
\]

II-type isomer

The $^1$H n.m.r. resonances of this reaction mixture at 100 MHz are presented in Figures II.3 and II.4.

At this stage, it is impossible to make more precise assignments without presenting other evidence and a further
Figure II.3 GeH resonances of type I and II isomers of RhI(CO)H(H₂GeI)(PEt₃)₂ at 203 K.
Figure 11.4  RhH resonances of type I and II isomers of RhI(CO)H(H₂GeI)(PET₃)₂ at 203 K.
discussion reinforcing this assignment will be given in the next section where comparative evidence from \( \text{MH}_4 \) (M = Si or Ge) adducts are presented.

When \( X \neq Y \) in the reaction of \( \text{RhY(CO)(PEt}_3)_2 \) with \( \text{MH}_3X \) (M = Si or Ge; Y and X = halogen, Cl or I), halide exchange reactions are usually involved, with migration of a heavier halide (e.g. I) from the group IV-B atom onto the metal and a lighter halide (e.g. Cl) from the metal to the group IV-B atom. One way to prevent such a reaction would be to start with the heavier halide on the metal; this means that \( \text{Rh(CO)I(PEt}_3)_2 \) could be used for the study of reactions involving addition only.

The reaction of \( \text{SiH}_3\text{Cl} \) with \( \text{Rh(CO)I(PEt}_3)_2 \) was allowed to occur at low temperature in toluene. The reaction went rapidly to completion at 243 K to give one adduct. The product of this reaction gives \( ^{31}\text{P} \) and \( ^1\text{H} \) n.m.r. spectra of the sort outlined in Diagrams 1 and 2 respectively, and was assigned as a I-type isomer with the silyl halide group trans to \( \text{RhH} \). From this n.m.r. spectrum no trace of any other isomer was observed.

In the case of the reaction of \( \text{Rh(CO)I(PEt}_3)_2 \) with \( \text{GeH}_3\text{Cl} \) similar results to those for the analogous reaction of \( \text{Rh(CO)I(PEt}_3)_2 \) with \( \text{GeH}_3\text{I} \) were obtained. At 198 K the phosphorus n.m.r. spectrum records signals for two species (A and B) in a 2:1 ratio; but species A should be thermodynamically less stable than species B, because as soon as the temperature is raised to 223 K a large change in the ratio of the species was observed: 1:2 ratio for A and B species respectively. The phosphorus spectrum shows that for both isomers the phosphine ligands were equivalent and off-resonance.
decoupling indicates that they were monohydrides. Both phosphorus chemical shifts indicated that iodine was attached to the rhodium metal and resonances occur in a region associated with triethylphosphine bound to rhodium(III).

Proton n.m.r. spectra of these products were of the type described in Diagram 4 and the GeH chemical shifts for both species were in a region associated with chloride attached to germyl.

Resonances corresponding to the major species B were identified as arising from a I-type isomer with mutually trans-phosphines, hydride trans to GeH₂Cl group and iodine trans to carbonyl. Resonance signals for species A were characteristic of a type II isomer and on this basis it probably has mutually trans phosphines, GeH₂Cl trans to carbonyl and hydride trans to iodine. It is noteworthy that when δ(Rh-H) and ²JH-Rh-P of RhHI(CO)(GeH₂I)(PET₃)₂ and RhHI(CO)(GeH₂Cl)(PET₃)₂, type II isomers, are compared with the ones for similar Ir(III) complexes IrHI(CO)(GeH₂I)(PET₃)₂ and IrHI(CO)(GeH₂Cl)(PET₃)₂ with H trans to I, it is observed that as in the iridium case:

- δ(Rh-H) changes 0.5 ppm to lower frequency when X in GeH₂X group changes from iodide to chloride.

- ²JH-Rh-P for these type II isomers are 2 Hz smaller than ²JH-Rh-P for type I isomers of this species.

N.m.r. parameters for the adducts presented in this section are given in Table II.1 for the rhodium silicon compounds and in Table II.2 for the rhodium-germanium compounds.
II.3 Oxidative-addition Reactions of MH₄ (M = Si or Ge)

The reaction of Rh(CO)Cl(PEt₃)₂ with SiH₄ was carried out in toluene and n.m.r. spectra of this mixture were recorded from low temperature in 20 K steps. At 203 K the yellow colour of Rh(CO)Cl(PEt₃)₂ disappeared to give a clear colourless solution; at this temperature a Rh(III) adduct and a very small amount of unreacted starting material were recorded in the ³¹P and ¹H n.m.r. spectrum of this solution, but it was observed that as the temperature was raised the signal corresponding to the Rh(III) species disappeared, and at ca. 298 K the only observed species was RhCl(CO)(PEt₃)₂, i.e. this reaction has a temperature dependant equilibrium in which the Rh(III) adduct is stable at low temperature only (see Chapter V).

At 198 K the phosphorus n.m.r. contained a doublet when proton decoupled; the splitting is due to two equivalent phosphorus atoms and ¹⁰³Rh nuclei, confirming that the phosphines are mutually trans. The resonance region is associated with triethylphosphine bound to Rh(III)⁴⁴,⁴⁵ and ¹J_P-Rh is smaller as expected for a change from four to six coordination. Off-resonance decoupling confirmed that the adduct was a monohydride. At the same temperature, the ¹H n.m.r. spectrum contained three sets of resonances associated with protons on a silicon atom (3.0-3.5 ppm), the ethyl groups of the phosphine (0.5-2.0 ppm), and a proton on the rhodium metal (less than -7 ppm) (see Diagram 5).

The resonances due to the protons on the ethyl groups of phosphine do not yield much information, apart from their overall pattern which indicates that the phosphine molecules were bound to
The resonance due to the protons on the silicon appeared as a 1:2:1 triplet. The triplet coupling was due to equivalent, or near equivalent, phosphorus atoms and was reduced to a singlet by irradiating in the phosphorus region of the spectrum. For the phosphines to be apparently equivalent with respect to the silyl protons they must be cis to the silyl group. Surprisingly, the two bond splitting of the silyl proton with $^{103}\text{Rh}$ nuclei, $^{2}J_{H-Si-Rh}$, was not observed even when the limit of resolution was 0.5 Hz.

The resonance due to the hydride on the rhodium took the form of a 1:3:3:1 quartet due to two overlapping triplets with $^{1}J_{H-Rh} = ^{2}J_{H-Rh-P}$, and integration suggested that it is three times smaller than the silyl resonance. The triplet coupling, as with the silyl resonance, was due to the phosphines and was collapsed.
into a doublet by irradiating at a frequency corresponding to the same phosphorus chemical shift as that which collapsed the triplet coupling on the silyl protons. The doublet coupling is thought to be due to coupling with the $^{103}$Rh nucleus, but it could not be proved as a $^{103}$Rh irradiation experiment was unsuccessful.

The silane adduct with RhI(CO)(PEt$_3$)$_2$ gave similar results and n.m.r. spectra of this adduct will be described first in order to analyse the stereochemistry of both RhY(CO)H(SiH$_3$)(PEt$_3$)$_2$ ($Y = \text{Cl or I}$) adducts. Again, a thermodynamic equilibrium between the Rh(I) starting material and Rh(III) adduct was observed and the Rh(III) adduct was found to be stable at low temperature only.

At 203 K, the $^{31}$P and $^1$H n.m.r. spectra contained similar resonance patterns, but with changes in the chemical shifts of the resonances. Phosphorus n.m.r. spectra contained a doublet, when proton decoupled, in a region associated with triethylphosphine bound to Rh(III) and off-resonance decoupling indicated the presence of a metal hydride. Proton n.m.r. spectra showed a 1:2:1 triplet in the SiH region, resonances due to the ethyl protons of bound triethylphosphine, and a 1:3:3:1 quartet in the Rh-H region. When phosphorus decoupled the silyl resonance was collapsed to a singlet and the hydride to a doublet. Once more $^3J_{H-Si-Rh-H}$ was not resolved in this set of resonances.

In similar cases the failure to observe $^3J_{H-Si-Rh-H}$ coupling suggests that the silyl group was cis to the hydride, but since some interesting values of $^1$H n.m.r. parameters were observed when compared with the ones for RhYH(CO)(SiH$_2$X)(PEt$_3$)$_2$ (type I isomer) and RhY$_2$H(CO)(PEt$_3$)$_2$ (X and Y = Cl or I) adducts, a definite assignment
of H cis to SiH₃ for the silane adduct should not be made. Moreover, it is noteworthy that experimental evidence supports the view that the failure to observe $^3J_{H-TM-Si-H}$ (TM = Transition Metal) should not be a definite assignment to conclude that H is cis to SiH₃, as in iridium isomers of the kind:

\[
\begin{align*}
\text{SiH}_2Q \\
\text{Ph}_3P \quad \text{Ir} \quad \text{PPH}_3 \\
\text{H}_b \quad \text{H}_a \\
\end{align*}
\]

$^3J_{H_a-Ir-Si-H}$ has not been observed when Q = H, but a clear splitting is resolved when Q = Cl or I. Consequently, in RhY(CO)H(SiH₃)(PEt₃)₂ the possibility that H is trans to SiH₃ should not be discarded and some arguments supporting this are:

- $\delta$(Rh-H) of this species is similar to the one for RhH(CO)Y(SiH₂X)(PEt₃)₂ (type-I isomer), meaning that H could be trans to SiH₃ as in these isomers. The possibility that H is trans to halogen (Y) should be discounted as changes of the hydride chemical shift to a lower frequency from iodide to chloride were not observed. Moreover, the $\delta$(Rh-H) values are different to the one found for RhHY₂(CO)(PEt₃)₂ adducts where H is believed to be trans to halogen (see Section II.7).

- $^1\text{J}_{H-Rh}$ of this species is equal to those obtained for RhY(CO)R(SiH₂X)(PEt₃)₂ complexes where H is trans to a SiH₂X group, but it is smaller than those for RhHY₂(CO)(PEt₃)₂
species where H is trans to the halogen.

As in the Ir(III) isomers\textsuperscript{30}, where the SiH\textsubscript{2}X (X = H, Cl or I) group is trans to H, it was observed that \( ^2J_{H-Rh-P} \) does not depend on the element (X) bound to silicon and \( ^3J_{H-Si-Rh-P} \) is smaller when X = H than when X = Cl or I.

The only alternative left for a ligand trans to hydride is carbonyl, as the halogen possibility has been eliminated already, but unfortunately Rh-H chemical shift values for a hydride trans to carbonyl are not available in the literature to draw comparison.

Therefore, with the information gathered so far, it is not possible to be certain about the geometry of these adducts, but in spite of that two suggestions can be proposed:

- A first possibility, and the most likely, is a I-type isomer, i.e. mutually trans phosphines, carbonyl group trans to halide and hydride trans to SiH\textsubscript{3} group.

\[
\begin{align*}
\text{Et}_3\text{P} & \quad \text{Rh} \\
\text{MH}_2\text{X} & \quad \text{CO} \\
\text{PET}_3 & \quad \text{Y} \\
& \quad \text{H}
\end{align*}
\]

\( M = \text{Si or Ge} \)  
\( X = \text{H} \)  
\( Y = \text{Cl or I} \)

I-type isomer

- A second alternative is an adduct with trans-phosphines, SiH\textsubscript{3} group trans to halide and hydride trans to carbonyl.

\[
\begin{align*}
\text{Et}_3\text{P} & \quad \text{Rh} \\
\text{MH}_3 & \quad \text{CO} \\
\text{PET}_3 & \quad \text{Y} \\
& \quad \text{H}
\end{align*}
\]

\( M = \text{Si or Ge} \)  
\( Y = \text{Cl or I} \)

III-type isomer
N.m.r. parameters for RhY(CO)H(SiH₃)(PEt₃)₂ adducts are given in Table II.1 and a 360 MHz ¹H n.m.r. spectrum of RhCl(CO)H(SiH₃)–(PEt₃)₂ adduct is represented in Figure II.5.

The reaction of Rh(CO)Cl(PEt₃)₂ with GeH₄, as with the previous reactions, was allowed to occur in toluene and n.m.r. spectra were recorded from low temperature in 20°C steps. Again a temperature-dependant equilibrium between the Rh(I) and the Rh(III) adduct was obtained in which at low temperature the Rh(III) product was stable.

At 198 K, the ¹H n.m.r. spectrum contained resonances due to the ethyl groups of triethylphosphine, which from the pattern seemed to be bound to a metal. The GeH resonance appeared as a 1:2:1 triplet as in the silane case and the RhH resonance as a 1:1:2:2:1:1 triplet of doublets. (See Diagram 6).

\[
\text{RhY(CO)(GeH₃)H(PEt₃)₂}
\]

Note: not at scale

Diagram 6
Figure II.5 360 MHz silyl and hydride resonances of RhCl(CO)H(H₃Si)(PEt₃)₂ at 203 K.
The triplet couplings in both resonances were due to the phosphorus atoms which are equivalent, or nearly equivalent, to RhH and GeH and must therefore be cis to both groups.

The two triplet couplings were collapsed by irradiating at frequencies corresponding to the same phosphorus chemical shift and are therefore associated with the same metal system. When phosphorus was irradiated the hydride signal collapsed into a doublet due to coupling with the $^{103}$Rh nucleus, and the germyl resonance into a singlet. Integration of both resonances showed that the germyl signal was 3 times more intense than the Rh-H resonance.

At the same temperature, the $^{31}$P$^{1H}$ spectrum showed a doublet due to splitting by two equivalent phosphorus atoms and $^{103}$Rh nuclei; when only the ethyl protons were decoupled, the main doublet resonance was split into small doublets due to Rh-H, proving the presence of a hydride ligand. This resonance occurred in a region associated with triethylphosphine bound to Rh(III) and $^{1}J_{P-Rh}$ had a value corresponding to a six coordinate Rh(III) species.

Similar results were obtained for the reaction of GeH$_4$ with RhI(CO)(PET$_3$)$_2$ and a description of n.m.r. spectra for this product will be presented first, in order to deduce the stereochemistry of both germane adducts. Once more a thermodynamic equilibrium between the Rh(I) and Rh(III) adducts was observed and the Rh(III) product was stable at low temperature only.

At 203 K, the bright yellow colour of Rh(CO)I(PET$_3$)$_2$ was discharged to give a pale one, and the n.m.r. spectra contained similar resonance patterns to those of RhCl(CO)H(GeH$_3$)(PET$_3$)$_2$ with the expected changes in the chemical shift of such resonances. The
\[ ^{31}P\{^1H\} \] spectrum showed a doublet, in a region associated with triethylphosphine bound to Rh(III); off-resonance decoupling recorded the presence of a hydride and \(^{1}J_{P-Rh}\) was characteristic for a six coordinate rhodium(III) species. The proton n.m.r. spectrum showed a 1:2:1 triplet in the GeH region, resonances due to the ethyl protons of bound triethylphosphine, and a 1:2:1 triplet of narrow doublets in the RhH region. When phosphorus was decoupled the germyl resonance was converted to a singlet and the hydride to a doublet with a separation equal to \(^{1}J_{H-Rh}\).

As in the silane case, at 203 K the \(^{1}H\) n.m.r. spectra of the germane adducts showed: intriguing values in the trends of n.m.r. parameters [\(\delta(Rh-H)\) and coupling constants], and neither the two bond coupling \(^{2}J_{H-Ge-Rh}\), nor the three bond splitting \(^{3}J_{H-Ge-Rh-H}\) was observed when the limit of resolution was 0.6 Hz. Therefore, using the same arguments as in the silane case, a definite conclusion about the ligand trans to the hydride could not be made.

As previously mentioned, the failure to observe \(^{3}J_{H-GeRh-H}\) should not be used as absolute evidence to suggest that H is cis to GeH₃, especially if other n.m.r. parameters do not agree with the assignment.

The \(\delta(Rh-H)\) values for the GeH₄ and SiH₄ adducts are very similar to those found for all the silyls and corresponding germyls (type I isomers), hence these species are very likely to have the same structures. Also, this \(\delta(Rh-H)\) mismatch those found for RhHY₂(CO)(PET₃)₂ adducts where H is trans to halogen.
As in the Ir(III) isomers, where a GeH₂X group is trans to H (X = H, Cl or I), it was observed that the value of $^2J_{H-Rh-P}$ is independent of the element (X) bound to germanium and the value of $^3J_{H-Si-Rh-P}$ is smaller when X = H than when X = Cl or I.

A new argument in favour of a type I structure for the germane adduct is given by the fact that $^1J_{H-Rh}$ of this product is equal to the one obtained for RhY(CO)H(GeH₂X)(PET₃)₂ type I isomer (where H is trans to GeH₂X group), and in contrast it is between 3 and 4 times smaller than the value recorded for RhY(CO)H(GeH₂X)(PET₃)₂ type II isomer (where H is trans to halogen).

Therefore, as for the SiH₄ adduct, two geometries can be suggested for the GeH₄ adduct: first a type I isomer where the main characteristic is that H is trans to GeH₃ group, and second a type III isomer where H is trans to carbonyl and cis to GeH₃ group.

N.m.r. parameters of RhY(CO)H(GeH₃)(PET₃)₂ (Y = Cl or I) adducts are given in Table II.2 and the $^1H$ n.m.r. spectra of RhHCl(CO)(GeH₃)-(PET₃)₂ is represented in Figure II.6.

II.4 Oxidative Addition Reactions including Halide Exchange

Halide exchange reactions usually imply migration of a heavier halide from the group IV-B atom onto the metal and a lighter halide from the metal to the group IV-B atom. Such halide exchange is expected to happen in the oxidative addition reaction between
Figure II.6 Silyl and hydride resonance of RhCl(CO)H(GeH₃)(PEt₃)₂ at 203 K.
RhY(CO)(PET₃)₂ and MH₃X (M = Si or Ge; X and Y = Cl or I) if x ≠ y and Rh(CO)Cl(PET₃)₂ is used as starting material.

Exchange is normally faster in four coordinated compounds than in six coordinated derivatives, so it is reasonable to suppose that any exchange is more likely to occur before rather than after addition.

In the reaction of SiH₃I with Rh(CO)Cl(PET₃)₂ four species could be formed if a common stereochemical relationship between the ligands is assumed.

Species A will predominate if oxidative addition is faster than exchange but species D will be the major product if the halogen exchange reaction between SiH₃I and the square planar rhodium complex is faster than addition.

The reaction between Rh(CO)Cl(PET₃)₂ and SiH₃I was allowed to occur at low temperature in toluene. At 198 K the ³¹P{¹H} n.m.r. spectrum showed that reaction had started to take place. At this stage the predominant signal corresponded to unreacted Rh(CO)Cl(PET₃)₂ and two Rh(III) species, A and B in a 1:1 ratio. At 223 K remaining Rh(I) intermediate species of Rh(CO)Cl(PET₃)₂ were not observed, and A and B species were present in a 1:3 ratio.
Both Rh(III) species had equivalent phosphorus and off-resonance decoupling showed that they contained one metal hydride.

The phosphorus chemical shift suggested that iodine was attached to rhodium in species B. The $^1$H n.m.r. spectrum showed one set of resonances with patterns as in Diagram 2 (type I isomer), and the SiH chemical shift was compatible with SiH$_2$Cl trans to RhH. Therefore, species B should correspond to RhH(CO)I(PEt$_3$)$_2$(SiH$_2$Cl).

The $\delta^{31P}$ of the less abundant species A suggested that chloride was attached to rhodium, but unfortunately its concentration in the solution was not sufficient for resolution of the proton n.m.r. spectrum and it was not possible to determine whether the species present was RhH(CO)Cl(SiH$_2$Cl)(PEt$_3$)$_2$ or RhH(CO)Cl(PEt$_3$)$_2$-(SiH$_2$I), i.e. which halogen (chloride or iodide) was on the -SiH$_2$ group.

On warming to 243 K, the species A disappeared completely and no further reactions were apparent when the reaction mixture was warmed to room temperature.

Work described earlier with Rh(CO)Cl(PEt$_3$)$_2$ and SiH$_3$Cl, and with Rh(CO)I(PEt$_3$)$_2$ and both SiH$_3$I and SiH$_3$Cl have made it possible to establish the presence of RhH(CO)I(PEt$_3$)$_2$(SiH$_2$Cl), type I isomer, as the main product in this reaction.

Due to the formation of two types of isomers (I and II) in the germyl addition reactions, when RhCl(CO)(PEt$_3$)$_2$ was reacted with GeH$_3$I several species were expected to be produced.

Reaction was very rapid and at 198 K the $^{31}$P n.m.r. spectra showed the presence of seven species, all of them with mutually
trans-phosphines. Surprisingly, the two most abundant species had not been identified in previous reactions, and the \( \delta^{(31} \text{P}) \) indicated that chlorine was attached to the metal in one of them. Off-resonance decoupling showed that all of the Rh(III) species were monohydrides.

At the same temperature the \(^1\text{H} \text{n.m.r.}\) spectra detected seven sets of resonances in the GeH region and six in the region associated with Rh-H. Their resonance patterns indicated that four of them were type I isomers and the other three type II (see Diagrams 3 and 4). Similarly, the \((\text{GeH})\delta\) values suggested that while iodine was attached to germanium in four of them, chlorine was bound to that element in three of the species.

Irradiation at the frequencies of lines in the \(^{31}\text{P}\) spectrum made it possible to connect GeH and RhH resonances from the different species present, and to correlate them with the resonances in the \(^{31}\text{P}\) spectrum.

By comparison of this \(^1\text{H}\) and \(^{31}\text{P}\) n.m.r. data with that previously recorded for other germyl halide systems, it was possible to establish the presence of five species: RhHCl(CO)(PET\(_3\))\(_2\)(GeH\(_2\)Cl), RhHI(CO)(PET\(_3\))\(_2\)(GeH\(_2\)I) (type I and II of isomers), and RhHI(CO)(PET\(_3\))\(_2\)(GeH\(_2\)Cl) (type I and II of isomers), the last being the predominant species of this group.

The \(^1\text{H}\) n.m.r. resonance patterns showed that the two additional species were two isomers of a different type containing iodine attached to germanium. \( \delta^{(31} \text{P}) \) of the type I isomer indicated that chlorine was attached to rhodium, and on this basis the main species
at 198 K was identified as the type I isomer of RhHCl(CO)(PEt₃)₂⁻
(GeH₂I). Because the δ³¹P of the type II isomer was shifted ca.
6 ppm to lower frequency from that for the type I adduct described
above, it is believed that this resonance corresponds to a type II
isomer of RhHCl(CO)(PEt₃)₂(GeH₂I), having chlorine attached to
rhodium and GeH₂I group cis to H. Similar behaviour has been
observed in other type I and II germyl complexes (see Section II.5).

Both species appeared to be thermally unstable, as when this
solution was allowed to warm to 213 K their signals were lost in the
n.m.r. spectra; presumably they dissociate to their reactant
materials or rearrange to give more stable products. At room
temperature, the spectrum showed that intensive reaction had occurred
and the predominant species were the type I and II isomers of
RhH₁(CO)(PEt₃)₂(GeH₂Cl), type I being the most abundant. Also,
traces of RhHCl(CO)(PEt₃)₂(GeH₂Cl) and RhH₁(CO)(PEt₃)₂(GeH₂I)
type I and II isomers) were present.

Although the final products of this system were those for an
ordinary halide exchange reaction, halide distribution in the initial
RhHCl(CO)(PEt₃)₂(GeH₂I) adducts implies that oxidative addition took
place before exchange. Such results contrast with the above
described silyl reaction as, under the same conditions, exchange on
the square planar rhodium starting material appeared to be faster
than addition.

II.5 Trends in N.M.R. Parameters

The n.m.r. data for the compounds discussed in Sections II.2,
II.3 and II.4 are tabulated in Tables II.1 and II.2.
TABLE II.1

$^{31}$P and $^1$H n.m.r. data of some RhH(CO)Y(PEt$_3$)$_2$(SiH$_2$X) complexes.

$$\text{RhY(CO)(PEt}_3)_2 + \text{SiH}_3X \rightarrow \text{RhH(CO)(PEt}_3)_2(\text{SiH}_2X)$$

![Diagram of RhH(CO)Y(PEt$_3$)$_2$(SiH$_2$X) complex]

I-type isomer

<table>
<thead>
<tr>
<th>Y = Cl$^a$</th>
<th>Cl$^b$</th>
<th>Cl</th>
<th>I</th>
<th>I</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = Cl</td>
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<td>H</td>
<td>Cl</td>
<td>I</td>
<td>H</td>
</tr>
<tr>
<td>$^1J(P-\text{Rh})$</td>
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<td>85.5</td>
<td>88.7</td>
<td>85.9</td>
<td>85.0</td>
</tr>
<tr>
<td>$\delta(^{31}P)$</td>
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<td>27.1</td>
<td>28.4</td>
<td>19.4</td>
<td>17.3</td>
</tr>
<tr>
<td>$\nu(^{31}P)$</td>
<td>27.6</td>
<td>-</td>
<td>28.7</td>
<td>19.5</td>
<td>17.5</td>
</tr>
<tr>
<td>$\delta(\text{SiH})$</td>
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<td>5.9</td>
<td>3.3</td>
<td>5.1</td>
<td>4.0</td>
</tr>
<tr>
<td>$\delta(\text{RhH})$</td>
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<td>-8.3</td>
<td>-8.3</td>
<td>-10.0</td>
<td>-9.8</td>
</tr>
<tr>
<td>$^2J(H-\text{Si-Rh})$</td>
<td>5.5</td>
<td>-</td>
<td>N.O</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>$^3J(H-\text{Si-Rh-P})$</td>
<td>11.0</td>
<td>-</td>
<td>6.0</td>
<td>10.0</td>
<td>10.5</td>
</tr>
<tr>
<td>$^3J(H-\text{Si-Rh-H})$</td>
<td>5.5</td>
<td>-</td>
<td>N.O</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>$^1J(H-\text{Rh})$</td>
<td>12.0</td>
<td>-</td>
<td>12.0</td>
<td>11.0</td>
<td>10.0</td>
</tr>
<tr>
<td>$^2J(H-\text{Rh-P})$</td>
<td>12.0</td>
<td>-</td>
<td>11.5</td>
<td>11.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Type of isomer = I

$^a$ main product; $^b$ minor product.

N.m.r. parameters obtained at 203 K using d-toluene as solvent.

Units and abbreviations:

$^{31}$P and $^1$H coupling constant in Hz.

$^{31}$P and $^1$H chemical shifts in ppm; measured as positive to high frequency of SiMe$_4$ for $^1$H or 85% H$_3$PO$_4$ for $^{31}$P.

$\nu^{31}P$ = in ppm, shifts obtained from indirect observations.

N.O = not observed.
### TABLE II.2

$^{31}P$ and $^1H$ n.m.r. data of some $\text{RhH(CO)}Y(\text{PET}_3)_2(\text{GeH}_2X)$ complexes.

$$\text{RhY(CO)}(\text{PET}_3)_2 + \text{GeH}_2X \rightarrow \text{RhH(CO)}Y(\text{PET}_3)_2(\text{GeH}_2X)$$

| Y = Cl     | Cl | Cl | Cl | Cl | I | I | I | I | I |  |  |  |  |  |  |  |  |  |
|------------|----|----|----|----|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X = Cl     | I  | I  | H  | Cl | Cl | Cl | I | I | H |  |  |  |  |  |  |  |  |  |  |

- $^1J(\text{P-Rh})$: 85.0 84.7 86.9 88.7 84.3 85.8 83.6 85.6 88.0
- $\delta^{31}P$: 26.2 24.9 18.8 27.8 19.1 14.3 17.3 12.1 21.1
- $J^{31}P$: 25.5 24.5 - 27.1 19.5 - 17.8 12.6 20.4
- $\delta(\text{SiH})$: 5.2 3.6 3.7 2.8 5.4 5.6 3.9 4.2 3.1
- $\delta(\text{RhH})$: -9.3 -9.0 - -8.6 -10.3 -12.6 -10.0 -12.1 -9.7
- $^2J(\text{H-Ge-Rh})$: 5.0 6.0 - N.O 6.0 N.O 6.0 N.O N.O
- $^3J(\text{H-Ge-Rh-P})$: 9.5 11.0 - 6.0 10.0 10.0 10.0 10.0 6.0
- $^3J(\text{H-Ge-Rh-H})$: 5.0 6.0 - N.O 6.0 N.O 6.0 N.O N.O
- $^1J(\text{H-Rh})$: 5.0 6.0 - 6.0 6.0 22.0 6.0 21.0 6.0
- $^2J(\text{H-Rh-P})$: 12.0 12.0 - 13.0 13.0 11.0 13.0 11.0 12.0

Type of isomer = I I II ? I II I II ?

N.m.r. parameters obtained at 203 K using d-toluene as solvent.

For units and abbreviations see Table II.1.
A surprising feature of the many coupling constants recorded is the very wide range of values of $^1J_{H-Rh}$ for those adducts. This coupling depends on the Group IV-B metal (M) and the type of isomer, but for a given M it is independent of the atom (hydrogen or halogen) directly attached to the Group IV-B atom. For type I isomers $^1J_{H-Rh}$ is bigger when $M = Si$ than when $M = Ge$; for $GeH_3X$ adducts this coupling is considerably bigger for type II isomers than for those of type I.

As in the similar iridium complexes it was observed that for $M = Ge$, $^2J_{H-Rh-P}$ is about 2 Hz bigger for type I isomer than for type II, which seems to reflect a difference in the electronic distribution between the two configurations.

The most unexpected characteristics were observed for the two and three bond coupling constants, $^2J_{H-M-Rh}$ and $^3J_{H-M-Rh-H}$. They were not resolved either for $MH_4$ (M = Si or Ge) adducts, or for $GeH_3X$ (X = Cl or I) products, type II isomers. Nevertheless, they were clearly recorded for type I isomers of $MH_3X$ adducts. Both coupling constants are independent of changing M or X and they are transmitted to a very similar extent by silicon and germanium.

The three bond coupling constant $^3J_{H-M-Rh-P}$ is similar for $MH_3X$ adducts, type I and II isomers, where X = Cl or I and $M = Si$ or Ge. But when X = H, this coupling is smaller for the silane and germane adducts.

Changes of the halide on the Group IV-B metal do not produce particular effects on the phosphorus chemical shift, but it was observed that the $MH$ resonances move to low frequency as the halide
increases in atomic weight. On changing the halide directly attached to Rh the chemical shift $\text{MH}$ is not greatly changed; the phosphorus chemical shift moves between 6.0 and 10.0 ppm to lower frequency on going from Cl to I, and the rhodium hydrides trans to the halides (type II isomers of $\text{GeH}_3X$ adducts) move to lower frequency on going from I to Cl while the hydrides cis to the halides move to higher frequency.

In the $^{31}\text{P} \{^1\text{H}\}$ n.m.r. spectra, the peak due to the isomer with cis $\text{GeH}_2X$ to H in a given system (type II isomers) is always to lower frequency of the resonance corresponding to the isomer with trans $\text{GeH}_2X$ to H (type I isomer). If the structural assignment is correct for this type of isomer the changes in $\text{Rh-H}_3$ with $Y$ follow regular trends; the hydride resonances move to a higher frequency as $Y$ changes from Cl to I.

II.6 Conclusions about $\text{MH}_3X$ ($X = \text{H, Cl or I}$) Oxidative Additions

The complex trans-$\text{RhY(CO)(PEt}_3)_2$ ($Y = \text{Cl or I}$) reacts with the silyl and germyl halide compounds $\text{MH}_3X$ ($M = \text{Si or Ge}; X = \text{Cl or I}$) at room temperature to form an adduct, and there is evidence for the existence of a stable $\text{MH}_4$ product at low temperature as well. These reactions are analogous to the addition reactions of silanes and germanes with $\text{IrY(CO)(PEt}_3)_2$ studied by Ebsworth and Fraser$^{30}$, with the difference that $\text{RhY(CO)(PEt}_3)_2$ is much less susceptible to such oxidative addition than is the iridium complex, illustrating the greater stability of the +3 oxidation state for this metal.
The equilibrium in solution can be expressed as:

\[ \text{RhCl}(\text{CO})(\text{PET}_3)_2 + \text{MH}_4 \rightleftharpoons \text{RhCl}(\text{CO})(\text{MH}_3)(\text{PET}_3)_2 \]

This equilibrium can be displaced to the right by decreasing the temperature down to 198 K, and changing the halide coordinated to the rhodium has no influence on the stability of the adducts. The instability of these Rh(III) adducts is difficult to explain; it is very unlikely that steric factors are playing a role in it as silyl and germyl halide compounds produce stable adduct, even though they are bulkier. Analogous results are discussed in Chapter V and some thermodynamic calculations have been performed for several cases.

The \( ^1 \text{H} \) and \( ^{31} \text{P} \) n.m.r. spectra of the solution tell us a great deal about the geometries of the reaction-products, and confirm the formulation of the products. However, conclusions about the structure of \( \text{MH}_4 \) adducts are tentative because some unexpected features in the \( ^1 \text{H} \) n.m.r. spectra could not be completely analysed; isolation of these adducts was not tried as they dissociate at temperatures higher than 203 K, and consequently separation of the Rh adduct from the Rh starting material would be very difficult, impeding obtaining the crystallographic information.

As expected the reaction of the silyl and germyl compounds is always by M-H addition, instead of M-X addition as with the methyl halides\(^ {32} \); similar results have been found in silyl and germyl additions to platinum\(^ {13,14} \) and iridium complexes\(^ {27,30} \), and as mentioned in the introduction it is due to the differing bond strengths of M-H compared to C-H and M-X compared to C-X for silicon, germanium and carbon.
Beside the clear differences in the mode of addition of MeX (M = methyl) and of silyl or germyl halides, there is also a clear difference between the mode of addition of silyl and of germyl halides. They both produce products in which the phosphines are mutually trans, but the silyl halides species tend to add in a predominantly trans mode (MH₂X group trans to H) to give type I isomers, while germyl halide compounds tend to add initially in a cis mode (type II isomers) which converts to trans as the temperature is increased. Such germyl halide adducts with the GeH₂X group cis to H (type II isomer) are formed faster (as they are the abundant product at the lowest temperature) but they must be thermodynamically less stable than the adducts with GeH₂X trans to H (type I isomer), as the former tend to rearrange to trans as the temperature increases; the ratio of both isomers tends to remain stable after being left at room temperature.

No evidence supporting any specific type of mechanism for the oxidative addition or reductive elimination was obtained. It is very risky to base conclusions about the stereochemistry of the initial attack upon the stereochemistry of the ultimate product, but the simplest explanation of these results is that for germyl and silyl reactions GeH adds initially to the rhodium complex in the cis mode and rearranges to trans, because where an isomer of type II is formed it is in no case the most abundant product, even though it is the main adduct at 198 K. Although isomers of type II (H cis to SiH₂X) were not detected in the silyl reactions, it is possible that SiH adds initially in the cis mode and rearranges very fast to the trans isomer obtained.
II.7 Reactions of HX with trans-RhY(CO)(PEt$_3$)$_2$ (X and Y = Cl or I)

The hydride complexes RhHCl$_2$(CO)(PPh$_3$)$_2$\textsuperscript{45,53} and RhHBr$_2$(CO)(PPh$_3$)$_2$\textsuperscript{54} have been prepared and characterized by infrared spectroscopy. A clear assignation of the element trans to H was not well produced, but since $v_{M-H}$ is sensitive to changes in X it was likely that the hydride ligand was trans to a halide.

In this section some rhodium monohydrides with general formula RhHXY(CO)(PEt$_3$)$_2$, where X and Y are halogens, will be described. The adducts have been characterized by $^{31}$P and $^1$H n.m.r. spectroscopy, using heteronuclear double resonance.

As observed in this chapter, a signal in the low frequency region can usually be regarded as a transition metal hydride. Also, coupling of the hydride hydrogen to $^{103}$Rh nucleus, together with phosphorus n.m.r. spectra to which nuclei the hydride proton was coupled provided further strong evidence for a direct metal-hydrogen bond.

These rhodium complexes were produced by reaction of a gaseous sample of HX with RhY(CO)(PEt$_3$)$_2$ in a deuterated solvent, and they involved a formal oxidation of Rh(I) to Rh(III).

When X and Y were the same halogen, the $^{31}$P n.m.r. spectra showed a doublet, conforming the mutually trans arrangement of the phosphine ligands. By selective irradiation of the ethyl protons of the phosphine, the signal was converted to a doublet of doublets indicating the presence of a hydride attached to rhodium.

The $^1$H n.m.r. spectrum showed in addition to PEt$_3$ resonances, a pair of overlapping triplets at low frequency, assigned to Rh-H.
The large doublet coupling was due to $^1 J_{(\text{Rh-H})}$; the PEt$_3$ groups must both be equivalent to split into a triplet and the magnitude of $^2 J_{\text{H-Rh-P}}$ was consistent with this. By irradiating in the phosphorus region of the spectrum at a frequency corresponding to the chemical shift of the signal in the $^{31}$P n.m.r. spectra, the Rh-H resonance was collapsed to a doublet with a separation equal to $^1 J_{\text{H-Rh}}$. These complexes are assumed to have H trans to a halogen because of the regular way in which the shift of the (Rh-H)δ as the halogen trans to H varies from Cl to I (-13.4 to -10.8 ppm); similar trends were observed for the analogous Ir(III) complexes (see Table II.2.3). Therefore, these complexes must have mutually trans phosphine and halogen trans to carbonyl and hydride.

Knowing that H tends to arrange trans to a halogen instead of carbonyl, it was thought that some of the addition products of HX to RhY(CO)(PEt$_3$)$_2$, when X and Y were different halogens, were likely to have geometry A or B, depending on the halogen (Cl or I) trans to H.

![Diagram of complexes](image)

Reactions were carried out under the conditions described above. At 198 K, the $^{31}$P n.m.r. spectra of the product of reaction of RhI(CO)(PEt$_3$)$_2$ with HCl, showed the presence of four Rh(III)
adducts and two Rh(I) complexes (identified as unreacted RhI(CO)-(PEt$_3$)$_2$ and RhCl(CO)(PEt$_3$)$_2$, formed by exchange). Off-resonance experiments showed that the Rh(III) species were monohydrides.

The $^1$H n.m.r. spectra detected four signals at low frequency in the region associated with Rh-H resonances. Their patterns took the form described above which by phosphorus irradiation were collapsed to doublets; the phosphorus frequencies corresponded to the $\delta(^{31}P)$ of the signals in the phosphorus n.m.r. spectrum. Using this information, resonances due to the complexes RhHCl$_2$(CO)(PEt$_3$)$_2$ and RhHI$_2$(CO)(PEt$_3$)$_2$ were identified; the other two signals were probably due to the mixed halides A and B. Their hydride signals were in different places and the $\delta$(Rh-H) values indicated that chloride was trans to H in the most abundant species (A), while iodide was in the other (B). The calculated phosphorus chemical shifts were consistent with these assignments; their values were between those for RhHCl$_2$(CO)(PEt$_3$)$_2$ and RhHI$_2$(CO)(PEt$_3$)$_2$ indicating that both halides were attached to rhodium.

As the temperature was raised the n.m.r. signals for both Rh(I) complexes together with the one for species A vanished, and at room temperature the $^{31}$P n.m.r. spectrum recorded the presence of species B (H trans to I) as predominant, and RhHI$_2$(CO)(PEt$_3$)$_2$ and RhHCl$_2$(CO)(PEt$_3$)$_2$ in minor amounts.

A cis or trans mode of addition for the formation of B as final product can not be suggested, as RhCl(CO)(PEt$_3$)$_2$ complex and species A had been observed in the n.m.r. spectra. Therefore, it is reasonable to think that exchange and addition gave rise to the products obtained. It is likely that species A was formed
initially by trans addition of HCl to RhI(CO)(PEt₃)₂.

Reaction of RhCl(CO)(PEt₃)₂ with HI proceeded faster; at 198 K the ³¹P n.m.r. spectrum showed signals corresponding to three Rh(III) species, and changes were not observed as the temperature of the mixture was raised. The predominant signal corresponded to species B (H trans to I), and the minors to RhHI₂(CO)(PEt₃)₂ and RhHCl₂(CO)(PEt₃)₂ species. Formation of species B could be due to trans addition of HI in the starting material.

For both reactions the ultimate products are those in which H is trans to I (the heavier halogen), and it appears that oxidative addition usually took place by trans addition of the hydrogen halide.

The ¹H n.m.r. spectrum of the reaction products is shown in Figure II.7, and the n.m.r. parameters are recorded in Table II.3.
Figure II.7 Hydride resonance of $\text{RhCl(CO)HI(PEt}_3)_2$ and $\text{RhI}_2H(CO)(\text{PEt}_3)_2$ complexes at 263 K.
TABLE II.3

$^31P$ and $^1H$ n.m.r. data of some RhHXY(CO)(PEt$_3$)$_2$ complexes

\[
\begin{align*}
\text{H} & \quad \text{CO} \\
\text{Et}_3\text{P} & \quad \text{Rh} & \quad \text{PEt}_3 \\
\text{Y} & \quad \text{X}
\end{align*}
\]

<table>
<thead>
<tr>
<th>X</th>
<th>Cl</th>
<th>Cl</th>
<th>I</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Cl</td>
<td>I</td>
<td>Cl</td>
<td>I</td>
</tr>
</tbody>
</table>

$^1J(P-Rh)$  
$^31P$  
$\delta$(Rh-H)  
$^1J(H-Rh)$  
$^2J(H-Rh-P)$

\[
\begin{align*}
\text{X} = \text{Cl} & \quad \text{Cl} & \quad \text{I} & \quad \text{I} \\
\text{Y} = \text{Cl} & \quad \text{I} & \quad \text{Cl} & \quad \text{I} \\
1J(P-Rh) & \quad 80.6 & \quad 80.6 & \quad 80.6 & \quad 80.6 \\
\delta(31P) & \quad 26.7 & \quad 22.5 & \quad 21.9 & \quad 13.7 \\
\delta$(Rh-H) & \quad -13.4 & \quad -13.0 & \quad -10.4 & \quad -10.8 \\
1J(H-Rh) & \quad 17.0 & \quad 18.0 & \quad 19.0 & \quad 16.0 \\
2J(H-Rh-P) & \quad 10.0 & \quad 9.0 & \quad 9.0 & \quad 10.0
\end{align*}
\]

N.m.r. parameters obtained at 253 K using d-toluene as solvent.

For units see Table II.1
CHAPTER III

Reactions of some organo substituted Group IV-B compounds with rhodium, iridium and platinum complexes.
The work in this chapter deals with the reactions of some organo-substituted silyl and germyl compounds with four-coordinated rhodium, iridium and platinum complexes.

The chapter will be subdivided, according to the transition metal used, into three parts:

Part 1: Reactions of some organo-substituted silyl and germyl compounds with RhY(CO)(PEt$_3$)$_2$ (Y = Cl or I).

Part 2: Reactions of some organo-substituted silyl compounds with IrY(CO)(PEt$_3$)$_2$.

Part 3: Reactions of some organo-substituted silyl compounds with t-PtHY(PEt$_3$)$_2$ and t-PtY(PEt$_3$)$_2$.

Conclusions will be given at the end of the chapter.

A review of some of the work done in this field has been presented in Chapter I.
PART 1

III.1.1 Introduction

Silyl and germyl hydrido carbonyl rhodium(III) complexes of the type RhH(CO)(HMRZ)Y(PEt$_3$)$_2$ are readily obtained by treating the complex t-Rh(CO)Y(PEt$_3$)$_2$ (Y = Cl or I) with H$_2$MRZ (for M = Si: Z = H, R = H, -CH$_3$, or -CH$_2$-CH=CH$_2$; Z = Cl or I, R = -CH$_3$). For M = Ge: Z = H R = H, or -CH$_3$) in a 1:1 molar ratio.

In general, these Rh(III) adducts are formed by oxidative addition at ca. 203 K, but they dissociate by reductive elimination to the Rh(I) starting material at temperatures higher than 253 K. In toluene solution these thermodynamic equilibria can be expressed as:

\[ \text{RhY(CO)(PEt}_3\text{)}_2 + \text{H}_2\text{MRZ} \rightleftharpoons \text{RhH(CO)(HMRZ)Y(PEt}_3\text{)}_2 \]

The low temperature $^{31}$P and $^1$H n.m.r. spectra of these solutions permitted some deductions about the stereochemistry of each Rh(III) adduct, and consequently the n.m.r. data was collected for these products at 203 K. At this temperature, the $^{31}$P n.m.r. spectrum was characteristic for all of these species. It showed a doublet when fully proton decoupled, due to two equivalent phosphorus atoms coupled to $^{103}$Rh, proving that the phosphines are mutually trans. When the protons of the ethyl groups are decoupled (off-resonance decoupling) each line in the main resonance was split into a small doublet, indicating the presence of one H bound to Rh (see Diagram 1, Chapter II), which was definitely verified by the $^1$H n.m.r. spectrum. The phosphorus resonance occurred in the region expected.
for triethylphosphine bound to Rh(III)\(^{43,45}\), and \(^1J(P-Rh)\) was less than in the starting material, as expected for a change from four to six coordination. Therefore, these six coordinate Rh(III) adducts are monohydrides in which both phosphine groups are mutually trans.

Variable temperature \(^{31}P\) and \(^{1}H\) n.m.r. spectroscopy allowed the following of both rhodium species in the equilibrium and some thermodynamic determinations corresponding to these reactions are discussed in Chapter V.

Providing that reactions were carried out in a 1:1 molar ratio, the \(^{31}P\) n.m.r. spectra of the chloride and iodide systems showed that the six coordinate adduct was the main species at low temperature (ca. 203 K), but that it dissociated as the temperature increased, leaving the starting material as only P-containing species at high temperature (ca. 283 K). For the chloride systems, the resonance signals of both rhodium species were observed at intermediate temperatures; nevertheless, for the iodide only one signal, with a coupling constant (\(^1J_{P-Rh}\)) that was intermediate between the values for the six coordinate adduct and the RhI(CO)(PET\(_3\))\(_2\) starting material, was observed. The doublet, caused by spin-spin coupling, was sharp at low and high temperatures, but broad at the intermediate temperatures, as illustrated in Diagram III.1.1. It is believed that the effect originated because the \(\delta(^{31}P)\) of the Rh(III) and Rh(I) complexes are very similar, but their \(J_{P-Rh}\) are different; in particular, one line of the doublet due to the adduct coincided almost exactly at all temperatures studied with the analogous line in the spectrum of the starting material. Therefore, while the temperature was changed, complete overlapping of one of the lines of both signals
Diagram III.1.1

Typical $^{31}$P($^1$H) spectrum at various temperatures of the systems:

$$\text{RhY(CO)(PET}_3)_2 + H_2MZR \rightleftharpoons \text{RhHY(CO)(HMZR)(PET}_3)_2$$

For $Y = \text{Cl}$, see set A; for $Y = \text{I}$, see set B.

(For $M = \text{Si}$, $Z = \text{H}$, $R = \text{H}$, $-\text{CH}_3$ or $-\text{CH}_2-\text{CH}=$ or $-\text{CH}_3$; $Z = \text{Cl}$ or $\text{I}$, $R = -\text{CH}_3$. For $M = \text{Ge}$, $Z = \text{H}$, $R = \text{H}$ or $-\text{CH}_3$)
produced a peak of high intensity, and averaging of the other line in each signal produced the observed "hump".

It is believed that the components of this compound have been identified by proton magnetic resonance spectroscopy, but this identification must be, to some extent, tentative since none of the compounds has been isolated in a pure state.

The resonance pattern of the $^1$H n.m.r. spectra for these complexes, formed from a given set of organo-Group IV-B compound, do not depend on the halogen attached to rhodium, hence $^1$H n.m.r. spectra of the Rh(III) adducts will be described for each silyl and germyl compound and n.m.r. parameters will be given in Tables III.1.1 and III.1.2 for the chloride and iodide systems respectively.

III.1.2 Oxidative Addition Reactions of $\text{H}_3\text{MCH}_3$ ($\text{M} = \text{Si}$ or $\text{Ge}$)

III.1.2.a Oxidative addition reactions of $\text{H}_3\text{SiCH}_3$

$\text{RhY(CO)(PEt}_3)_2$ was reacted with $\text{H}_3\text{SiCH}_3$ in toluene. At 203 K the proton decoupled phosphorus n.m.r. spectrum of the reaction solution consisted of a doublet in the region associated with triethylphosphine bound to Rh(III), indicating the mutually trans arrangement of the phosphines.

The proton n.m.r. spectrum contained three sets of resonances. The pattern of the set due to the ethyl protons of the triethylphosphine groups indicated that they were bound to a metal.

The signal in the region associated with a metal hydride trans to carbonyl or silyl (see Chapter II) appeared as a nine-line pattern that could be interpreted as an overlapping 1:3:3:1 quartet
of triplets; this signal was collapsed into a set of five lines by irradiating in the \(^{31}\text{P}\) region of the spectrum at a frequency corresponding to the chemical shift of the signal in the \(^{31}\text{P}\) n.m.r. spectra and it is assumed that the five-line pattern was due to two overlapped triplets with \(J(\text{H-Rh}) = 2J(\text{H-Rh-Si-H})\). While phosphorus decoupled, irradiation of the silyl protons collapsed this resonance to a doublet with a separation equal to \(J_{\text{H-Rh}}\).

The resonance due to the silyl protons was complicated and a clear pattern could not be obtained even at 360 MHz. This probably arose from additional couplings of the silyl with the methyl protons, and also from differences among \(J(\text{H-C-Si-H})\), \(J(\text{H-Si-Rh-H})\), \(J(\text{H-Si-Rh-P})\) and \(2J(\text{H-Si-Rh})\) resulting in a proliferation of many more peaks giving an unresolvable "hedgehog". It contrasts with the analogous Ir(III) complexes\(^{48}\) (see Part 2) where \(J(\text{H-C-Si-H})\) and \(J(\text{H-Si-Ir-H})\) were similar. Phosphorus irradiation gave a great narrowing effect on this complex multiplet, although there was no real improvement in resolution.

It was unfortunate that the resonance due to the -\(\text{CH}_3\) protons bound to silicon, possibly to low frequency of the resonances due to triethylphosphine, could not be observed. It is believed that observation of \(J(\text{H-Si-Rh-H})\) from the \(\text{H}(^{31}\text{P})\) experiment in the hydride resonance indicates that \(\text{H}\) is trans to the -\(\text{SiH}_2\text{CH}_3\) group instead of carbonyl. The species produced by the reaction would then have mutually trans triethylphosphine groups, carbonyl trans to halide (Y) and -\(\text{SiH}_2\text{CH}_3\) trans to Rh-H.
III.1.2.b Oxidative addition reactions of $\text{H}_3\text{GeCH}_3$

At 203 K the proton decoupled $^{31}\text{P}$ n.m.r. spectrum of the toluene solution of $\text{H}_3\text{GeCH}_3$ with $\text{RhY(CO)(PEt}_3)_2$ showed a doublet in the region associated with triethylphosphine bound to Rh(III); therefore the compound has mutually trans phosphine.

The proton n.m.r. spectrum contained three sets of resonances due to the product. The resonances corresponding to the triethylphosphine groups showed them to be bound to a metal. The resonance due to the metal hydride was in a region associated with RhH trans to carbonyl or germyl, and appeared roughly as a 1:2:1 triplet of doublets, which indeed was three overlapping quartets. By irradiating in the $^{31}\text{P}$ region of the spectrum at a frequency corresponding to the chemical shift of the signal in the $^{31}\text{P}$ n.m.r. spectra, this signal was collapsed into a 1:3:3:1 quartet. Simultaneous irradiation of phosphorus and decoupling of the silyl protons converted the resonance to a doublet with a separation equal to $^{1}\text{J}_{\text{H-Rh}}$ (see Figure III.1.1).

The resonance due to the germyl protons is complicated and a clear pattern could not be obtained from it, even at 360 MHz. Such a complex multiplet might arise from the different values of $^{3}\text{J(H-Ge-C-H)}$, $^{3}\text{J(H-Ge-Rh-H)}$, $^{3}\text{J(H-Ge-Rh-P)}$ and $^{2}\text{J(H-Ge-Rh)}$. The signal was sharpened by phosphorus irradiation, but even then, splittings could not be identified. When iodine was attached to rhodium, this resonance was underneath the signal due to free $\text{H}_3\text{GeCH}_3$ impeding its observation.

A definite proof that the $\text{CH}_3$ group was bound to germanium would have been to find, directly to low frequency of the resonances
Figure III.1.1 RhH resonance at 203 K of $\text{H} - \text{Rh} - \text{GeH}_{3}\text{CH}_{3}$

$\delta$ -9.2 -9.4 -9.6 -9.8 -10.0 ppm

10 Hz/cm
due to triethylphosphine, a signal associated with -CH₃ protons; nevertheless it must have been overlapped by the ethyl protons as such a resonance was not observed. It would have been of interest to see whether or not coupling is observed between these -CH₃ protons and rhodium, as such splittings have been reported for Pt-silyl complexes to be about 25 Hz.

It is supposed that the observation of ³J(H-Rh-GeH) from the ¹H(³¹P) experiment in the Rh-H signal indicates that the species produced by this reaction has H trans to the -GeH₂CH₃ group, carbonyl trans to halide and mutually trans phosphines.

For both types of CH₃MH₃ (M = Si or Ge) adducts, integration of the Rh-H signal relative to those for the phosphine and Group IV-B resonance showed that only one hydride ligand was present per rhodium atom and that the M-H resonance was twice as strong as the one for Rh-H.

III.1.3 Oxidative Addition Reactions of H₂SiCH₃Z (Z = Cl or I)

H₂SiCH₃Z was reacted with RhY(CO)(PEt₃)₂ (Y = Cl or I) in toluene solution. Because of the presence of a halide on the silicon group this reaction is expected to be complicated by halide exchange when Z ≠ Y and the heavier halide (I) is bound to the silicon compound.

At 203 K, the phosphorus n.m.r. spectrum when completely proton decoupled contained a doublet in the region associated with triethylphosphine bound to Rh(III) implying the trans position of the phosphine groups.
At the same temperature, three sets of resonances were recorded in the proton n.m.r. spectrum. Those resonances associated with the ethyl protons of the triethylphosphine groups denoted that they were bound to a metal.

A single resonance related to a hydride directly attached to a metal was recorded in the low frequency region. The signal was a clear 1:3:3:1 quartet of doublets which by irradiating in the $^{31}$P region of the spectrum at a frequency corresponding to the phosphorus chemical shift was collapsed into a doublet of doublets due to the one bond coupling of this hydride with $^{103}$Rh nucleus ($^{1}J_{H-Rh}$), and the three bond splitting with the proton on the silicon ($^{3}J_{H-Rh-Si-H}$). While phosphorus was irradiated, additional irradiation of the silyl proton converted this signal into a doublet with a separation equal to $^{1}J_{H-Rh}$ (see Figure III.1.2).

The resonance due to the silyl protons was not clear, and could not be resolved even on separation of the signal; the splittings are assumed to arise from extra couplings of the silyl protons with the methyl ones. Phosphorus irradiation sharpened the signal, but regardless of it clear patterns were not resolved.

The presence of $^{3}J_{H-Rh-Si-H}$ was evident from the hydride resonance pattern, and on this basis it is assumed that RhY(CO)(HSiCH$_3$Z)H(PEt$_3$)$_2$ adducts have: H trans to the silyl group, carbonyl trans to Y and mutually trans phosphines.

For these adducts, integration of the Rh-H signal relative to those for the phosphine and silyl resonance showed that only one hydride ligand was present per rhodium atom and that the silyl
Figure III.1.2 RhH resonance at 203 K of $\text{H-Rh-SiH(CH}_3\text{)Cl}$

$\begin{array}{c}
\text{Cl} \\
\text{PEt}_3 \\
\text{Et}_3\text{P} \\
\text{CO}
\end{array}$

$\delta$ -7.8 -8.0 -8.2 ppm

10 Hz/cm
resonance was as strong as the Rh-H, i.e. they were related in a 1:1 ratio.

When RhCl\text{(CO)}(\text{PET}_3)_2 was reacted with H_2\text{SiCH}_3\text{I}, halide exchange was observed with migration of the heavier halide from the silicon atom onto the metal and the lighter halide from the metal to the silicon.

This reaction was allowed to occur at low temperature; phosphorus n.m.r. spectrum at 198 K showed that reaction was starting to take place: in addition to two Rh(III) species (A and B), both halides of RhY\text{(CO)}(\text{PET}_3)_2 starting material were observed. On warming the solution to 223 K, both Rh(I) species disappeared and both A and B Rh(III) products were present, A being 85% more abundant than B.

The patterns of the resonances in the $^{31}\text{P}$ and $^1\text{H}$ n.m.r. spectra were of the same nature as those described in the previous section, and confirmed the mutually trans position of both phosphines, and the presence of a metal hydride trans to the silyl group.

For both species deduction of which halogen was attached to rhodium and to silicon was made using the $^{31}\text{P}$ and $^1\text{HSiCH}_3\text{Z}$ chemical shift values. In the proton decoupled $^{31}\text{P}$ n.m.r. spectra the abundant species (A) was at the lower frequency and $\delta(^{31}\text{P})$ indicated that iodine was attached to Rh (Y = I), while chloride was the halogen (Y = Cl) in the trace product (B) at higher frequency.

$^1\text{H}$ n.m.r. spectra showed a set of resonances corresponding to only one product; the silyl resonance was in a region associated with chloride attached to this group and on this basis it is
suggested that the main reaction species (A) has: -HSiCH₃Cl group trans to H, iodine trans to carbonyl and mutually trans phosphines. Observation of the silyl peak, connected with the less abundant species (B), was not possible; however it could be underneath the main SiH signal because chlorine is likely to be attached to silicon.

The previously described reactions of RhCl(CO)(PEt₃)₂ and RhI(CO)(PEt₃)₂ with H₂SiCH₃Cl ratified the assignments for species A, and helped to confirm that the less abundant species B has: -HSiCH₃Cl group trans to H, chloride trans to carbonyl and mutually trans phosphines.

The reasons explained in Chapter II suggest that the main species was formed because halogen exchange reaction on the square planar Rh(I) complex was faster than addition. The ratio of the products indicates that reaction was not in a 1:1 molar ratio, and that excess of RhCl(CO)(PEt₃)₂ was initially present in the mixture.

II.1.4 Oxidative Addition Reactions of H₃Si-CH₂-CH = CH₂

RhY(CO)(PEt₃)₂ complex was reacted with H₃Si-CH₂-CH = CH₂. At 203 K, the proton decoupled phosphorus n.m.r. resonance appeared as a simple doublet due to couplings with a ¹⁰³Rh nucleus, and thus the two phosphorus atoms in the adduct must be magnetically equivalent.

In the proton n.m.r. spectra, besides the resonances due to PEt₃, silyl protons and allyl structure (the aliphatic -CH₂-, and the vinyl -CH= and =CH₂) signals were detected in the low frequency
region indicating the presence of a direct Rh-H bond. This hydride resonance appeared roughly as a 1:3:3:1 quartet of triplets which by irradiating in the $^{31}$P region of the spectrum at a frequency corresponding to the phosphorus chemical shift was collapsed into a set of five lines due to two overlapping triplets. Irradiation of the silyl protons, while simultaneously decoupling, converted this set of lines to a doublet with a separation equal to $^{1}J_{H-Rh}$.

The silyl resonance pattern was complicated and coupling constants could not be worked out from it. Such complications are assumed to arise from differences among the values of $^{3}J_{H-Si-C-H'}$, $^{3}J_{H-Si-Rh-H'}$, $^{3}J_{H-Si-Rh-P}$ and $^{2}J_{H-Si-Rh}$, leading to the confused signal observed. Phosphorus irradiation produced a narrowing effect on this signal but resolution was not improved.

Analyses of the $^{31}$P and $^{1}$H n.m.r. spectra and recording of the $^{3}J_{H-Rh-Si-H}$ suggest that these allyl silane adducts have H trans to the $-H_2Si-CH_2=CH_2$ group, halogen trans to carbonyl and mutually trans phosphines.

The total integrated intensity of the hydride peaks, relative to those due to the silane and phosphine, corresponds to one hydride proton per rhodium atom and two silyl protons per hydride.

III.1.5 Trends in N.M.R. Parameters

Chemical shift and coupling constant data from the $^{31}$P and $^{1}$H n.m.r. spectra for the chloride and iodide Rh(III) adducts are presented in Tables III.1.1 and III.1.2 respectively. Data for the rhodium(I) starting materials are also given in these tables, as they were the products of the reductive eliminations of the adducts.
TABLE III.1.1

$^{31}P$ and $^1H$ n.m.r. data of some RhH(CO)Cl(PEt$_3)_2$(HMRZ) complexes

\[
\begin{align*}
\text{Cl} & \quad \text{PEt}_3 \\
\text{Et}_3\text{P} & \quad \text{CO} \\
\text{H}_2\text{MRZ} & \quad \text{Rh} \\
\text{MHRZ} & \quad \text{Et}_3\text{P} \\
\end{align*}
\]

$I$-type isomer

\[
\begin{array}{cccccc}
M & = & \text{Si} & \text{Si} & \text{Si} & \text{Ge} \\
Z & = & \text{H} & \text{Cl} & \text{H} & \text{H} \\
R & = & \text{-CH}_3 & \text{-CH}_3 & \text{-CH}_2\text{-CH} = \text{CH}_2 & \text{-CH}_3 \\
\end{array}
\]

$^1J_{P-Rh}$

\[
\begin{array}{cccc}
90.3 & 90.0 & 90.9 & 90.9 \\
\end{array}
\]

$\delta(^{31}P)$

\[
\begin{array}{cccc}
27.1 & 27.3 & 27.4 & 27.4 \\
\end{array}
\]

$\nu(^{31}P)$

\[
\begin{array}{cccc}
- & 27.4 & 27.8 & 27.1 \\
\end{array}
\]

$\delta(MH)$

\[
\begin{array}{cccc}
3.7 & 5.3 & 3.6 & 3.3 \\
\end{array}
\]

$\delta(RhH)$

\[
\begin{array}{cccc}
-8.1 & -8.0 & -8.1 & -8.4 \\
\end{array}
\]

$^1J(H-Rh)$

\[
\begin{array}{cccc}
12.0 & 12.0 & 12.0 & 6.0 \\
\end{array}
\]

$^2J(H-Rh-P)$

\[
\begin{array}{cccc}
12.0 & 11.9 & 12.0 & 13.0 \\
\end{array}
\]

$^3J(H-Rh-M-H)$

\[
\begin{array}{cccc}
4.0 & \text{N.M.} & 4.0 & 5.0 \\
\end{array}
\]

N.m.r. parameters obtained at 203 K using d-toluene as solvent.

$^{31}P$ n.m.r. parameters of RhCl(CO)(PEt$_3)_2$ at R.T. in d-benzene:

$^1J_{P-Rh} = 117.2$ Hz; $\delta(^{31}P) = 23.5$ ppm.

Units and abbreviations:

$^{31}P$ and $^1H$ coupling constant in Hz.

$^{31}P$ and $^1H$ chemical shifts in ppm, measured as positive to higher frequency of SiMe$_4$ for $^1H$ or 85% H$_3$PO$_4$ for $^{31}P$.

$\nu^{31}P$: in ppm; shifts obtained from indirect observations.

N.M.: Not Measured.
TABLE III.1.2

$^{31}_P$ and $^1_H$ n.m.r. data of some RhH(CO)Cl(PEt$_3$)$_2$(MHRZ) complexes.

\[
\begin{array}{ccc}
 \text{Rh} & \text{PEt} & \text{CO} \\
 \text{Et}_3\text{P} & \text{PEt}_3 & \text{CO} \\
\end{array}
\]

\[+ \text{H}_2\text{MRX} \rightarrow \]

\[
\begin{array}{ccc}
 \text{Rh} & \text{PEt}_3 & \text{CO} \\
 \text{ET}_3\text{P} & \text{PEt}_3 & \text{CO} \\
\end{array}
\]

I-type isomer

\[
\begin{array}{cccccc}
 \text{M} & \text{Si} & \text{Si} & \text{Si} & \text{Si} & \text{Ge} \\
 \text{Z} & \text{H} & \text{I} & \text{Cl} & \text{H} & \text{H} \\
 \text{R} & \text{-CH}_3 & \text{-CH}_3 & \text{-CH}_3 & \text{-CH}_2\text{-CH=CH}_2 & \text{-CH}_3 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 1^J_{(P-Rh)} & 86.6 & 90.1 & 89.6 & 89.8 & 89.6 \\
 \delta(31^P) & 18.6 & 20.3 & 20.6 & 20.6 & 20.2 \\
 \nu(31^P) & 18.8 & 20.3 & 20.2 & 20.2 & 20.6 \\
 \delta(\text{M-H}) & 3.9 & 3.9 & 5.3 & 3.8 & 3.5 \\
 \delta(\text{Rh-H}) & -9.1 & -9.3 & -9.2 & -9.3 & -9.6 \\
 2^J(\text{H-Rh}) & 10.0 & 11.0 & 12.0 & 9.3 & 6.0 \\
 2^J(\text{H-Rh-P}) & 10.0 & 11.0 & 12.0 & 11.3 & 14.0 \\
 3^J(\text{H-Rh-M-H}) & 5.0 & 4.0 & 4.0 & 4.4 & 5.0 \\
\end{array}
\]

N.m.r. parameters obtained at 203 K using d-toluene as solvent.

$^{31}_P$ n.m.r. parameters of RhI(CO)(PEt$_3$)$_2$ at 283 K in d-toluene:

\[1^J_{(P-Rh)} = 114.4 \text{ Hz} \]

\[\delta(31^P) = 19.9 \text{ ppm.} \]

For units and abbreviations see Table III.1.1.
in each case.

For these adducts, more satisfactory n.m.r. spectra could not be obtained, as increasing the temperature to improve resolution led to the dissociation of the adduct and lowering the temperature to augment the concentration of the adduct occasioned troubles because of the increasing viscosity of the solvent near the melting point. Consideration of the n.m.r. data leads to the conclusion that regardless of the organic group attached to M (M = Si or Ge), all of the reaction products have the same kind of structures, which are analogous to the I-type isomer described in Chapter II.

Apart from the reaction in which halide exchange was involved, $^3$P and $^1$H n.m.r. spectra gave no evidence of other products present in any of the solutions. Deduction that H is trans to the Group IV-B compound was determined from the hydride resonance pattern, as the splittings in the silyl resonance signal were unresolved.

Coupling constant values are very similar to those recorded for the silyl and germyl halide type-I isomer, confirming the assignment of H trans to the M-H group for these adducts. In general, $^1J_{H-Rh}$ depends on the Group IV-B atom trans to the hydride, being bigger when M = Si than when M = Ge; in contrast $^3J_{H-Rh-M-H}$ does not depend on M, i.e. silicon and germanium transmit couplings to the same extent.

On changing the halide directly attached to rhodium:

- $\delta(MH)$ does not change appreciably, except in the SiH$_2$CH$_3$Cl cases (where chloride is attached to silicon), in which the MH proton chemical shift moves to higher frequency.
The $\delta^{31}P$ moves between 6.0 to 9.0 ppm to lower frequency as the halide changes from Cl to I.

At room temperature, $^{31}P$ n.m.r. spectra showed resonance signals corresponding to the Rh(I) starting material. $^1H$ n.m.r. spectra gave no evidence of resonances due to Group IV-B complexes or rhodium hydrides, only the ones corresponding to the free silyl or germyl compound and triethylphosphine bound to a metal.
III.2.1 Introduction

The formation of equimolar adducts by the simple silanes $\text{H}_3\text{SiX}$ ($\text{X} = \text{H, Cl, B, I or CH}_3$) with trans-carbonyl halogen bis(triethylphosphine)iridium(I), analogous to Vaska's compound, has been reported\(^\text{30}\). Structural assignments of the adducts were based on $^{31}\text{P}$ and $^1\text{H}$ n.m.r. spectra, indicating that these silyl adducts studied are of type-I, with silyl trans to hydride, halogen trans to carbonyl and mutually trans phosphine ligands.

![I-type isomer](attachment:image.png)

In this part it will be reported that organo-substituted silanes $\text{H}_3\text{SiR}$ ($\text{R} = -\text{C}_6\text{H}_5, -\text{CH} = \text{CH}_2, -\text{CH}_2\text{-CH} = \text{CH}_2$ or $-\text{CN}$) add rapidly and irreversibly to the planar complex $\text{IrY(CO)(PEt}_3)_2$ ($\text{Y} = \text{Cl or I}$) to give octahedral hydrido(silyl)iridium(III) adducts of formula $\text{IrHY(SiH}_2\text{R(CO)(PEt}_3)_2$.

By evaporation of the solvent at 253 K, most of these products were isolated as solid and characterised by its n.m.r. spectrum and analysis. The phosphorus n.m.r. spectra gave identical signals for all of the reaction products. When proton coupling was eliminated, resonances appeared as singlets with $^{13}\text{C}$ and $^{29}\text{Si}$ satellites and if only the triethylphosphine protons were irradiated (off-resonance decoupling), doublets were resolved. These
observations indicate that the two phosphorus nuclei are apparently equivalent under these conditions and therefore mutually trans; also that there is one proton bound to iridium. The phosphorus resonance occurred in the region expected for triethylphosphine bound to iridium(III).

Proton resonance patterns of the products formed from this reaction did not depend on the halogen(Y) attached to iridium, but on the organic group bound to silicon. Thus, spectra will be described for each silyl adduct, and the n.m.r. parameters given in Table III.2.1 and III.2.2 for the chloride and iodide products respectively.

Reactions were carried out in deuterated organic solvents in a 1:1 molar ratio, but the same results were obtained when excess of the silyl compound was used.

III.2.2 Oxidative Addition Reaction of H_3SiC_6H_5

The reaction of IrY(CO)(P(Et)_3)_2 with phenylsilane was observed at low temperatures; at 203 K the addition reaction was slow, but it took place fast at room temperature where the yellow colour of the Ir(I) starting material vanished within a few minutes to give a clear colourless solution.

The phosphorus n.m.r. spectrum showed a singlet, when proton decoupled, in the region associated with triethylphosphine bound to Ir(III). Off-resonance decoupling converted the signal to a doublet showing the presence of a single hydride ligand.

The proton n.m.r. spectrum contained mainly sets of resonances associated with: ethyl groups of the phosphine, signals between 7.0
and 7.85 due to phenyl group resonances, protons on a silicon atom, and a proton on iridium.

The resonances due to the protons on the ethyl groups of the phosphine did not give much information, apart from their overall pattern which indicated that the phosphine molecules were bound to a metal.

The resonance corresponding to the protons on the silicon appeared as a 1:2:1 triplet of doublets. The triplet coupling was due to equivalent phosphorus atoms and could be collapsed by irradiating in the phosphorus region of the spectrum. The doublet splitting obtained was due to coupling with the hydride bound to iridium, and the separation was equal to $3J(H-Si-Ir-H)$. For the phosphines to be equivalent with respect to the silyl protons they must be cis to the silyl group.

The resonance due to the hydride on the iridium took the form of a triplet of triplets. The larger triplet coupling, as in the silyl resonance, was due to the phosphine ligands and was collapsed by irradiating at a frequency corresponding to the same phosphorus chemical shift as that which collapsed the triplet coupling of the silyl signal. The coupling in the small triplet was of the same magnitude as the doublet splitting on the silyl resonance ($3J_{H-Si-Ir-H}$) and confirmed the presence of two equivalent protons on the silicon.

The chemical shift of the Ir-H resonance indicated that H could be trans to a ligand of high trans influence such as carbonyl or silicon, and it is thought that observation of $3J_{H-Ir-Si-H}$ confirms that H is trans to the silyl group. The species produced by the
reaction would then have mutually trans phosphine ligands, H trans to $H_2SiC_6H_5$ and carbonyl trans to halogen.

**III.2.3 Oxidative Addition Reaction of $H_3Si-CH = CH_2$**

The proton decoupled phosphorus n.m.r. spectrum of the deuterated solution of this reaction contained a singlet in the region associated with triethylphosphine bound to Ir(III); therefore the compound has mutually trans phosphines.

In the proton n.m.r. spectrum the resonances due to the ethyl protons of the triethylphosphine groups indicated they were bound to a metal. The peak in the region associated with a metal hydride trans to carbonyl or silyl was a triplet of triplets. By irradiating at a frequency corresponding to the chemical shift of the singlet in the phosphorus spectrum, the larger triplet coupling was collapsed; simultaneous decoupling of phosphorus and irradiation of the silyl protons converted the signal to a singlet.

The resonance in the region associated with Si-H appeared as a 1:2:3:4:3:2:1 septet, and was possibly due to three overlapping triplets caused by similarities in the values of $^3J(H-Si-Ir-H)$ and $^3J(H-Si-C-H)$, thus giving a triplet rather than a doublet of doublets.

Irradiating in the phosphorus region of the spectrum gave a triplet with coupling of the same magnitude as the small triplet coupling on the Ir-H resonance, proving that $^3J_{H-Si-Ir-H}$ is equal to $^3J_{H-Si-C-H}$.

The resonances corresponding to the vinyl group were observed
as a complicated set of signals between 5.5 and 6.5. By irradiating the silyl protons, it was observed that some peaks were disturbed converting the resonance to a set of four lines. Analysis of the patterns indicated that, as expected, the vicinal -CH₂ protons are non-equivalent to the -CH= proton and because of this coupling between the vinyl and -CH₂ protons produce two doublets with different coupling constants, the larger being assigned to ³J_{HH} trans and the smaller to ³J_{HH} cis. When silyl protons were not irradiated each line split into triplets with couplings equal to the one observed in the silyl triplet. The usual triplet of doublets pattern for the silyl resonance was obtained while the vinyl proton was irradiated.

This n.m.r. information suggests that the product should have hydride trans to -SiH₂-CH=CH₂, halogen trans to carbonyl and mutually trans phosphine ligands.

III.2.4 Oxidative Addition Reaction of \( \text{H}_3\text{Si} = \text{CH}_2 - \text{CH} = \text{CH}_2 \)

The proton decoupled phosphorus n.m.r. spectrum of the deuterated solution of this product contained a singlet due to an Ir(III) species with mutually trans triethylphosphine.

The proton n.m.r. spectrum showed resonances due to the triethylphosphine groups indicating that they are bound to a metal. The silyl proton region contained an octet which was reduced to a quartet when phosphorus decoupled, indicating that the total multiplet was due to three overlapping quartets. The quartets were thought to originate from similarities between ³J(H-C-Si-H) and ³J_H-Si-Ir-H.
A complete set of resonances due to the vinyl protons on the allyl group were recorded between 4.5 and 6.0¢. Resonances due to the \(-\text{CH}_2\)- protons, next to the silicon atom, were observed ca. 1.7¢. The signal appeared as a clear set of five lines which by irradiation of the silyl protons was converted to a doublet, indicating that the original resonance was caused by two overlapping triplets where \(3J_{\text{H-C-C-H}}\) was twice as big as \(3J_{\text{H-C-Si-H}}\); hence, it is likely that the triplets are due to \(-\text{CH}_2-\) protons bound to a silicon atom which bears two protons. When these \(-\text{CH}_2-\) protons were decoupled the expected triplet of doublets pattern was obtained in the silyl region.

The signal in the hydride region consisted of a triplet of triplets, the large triplet splitting being collapsed by phosphorus irradiation. Couplings in the small triplet were similar to those in the SiH signal and were collapsed by irradiating the silyl protons (see Figure III.2.1). Thus, the species produced by this reaction has \(-\text{SiH}_2-\text{CH}_2-\text{CH}==\text{CH}_2\) group trans to H, carbonyl trans to halide and mutually trans phosphines.

### III.2.5 Oxidative Addition Reactions of \(\text{H}_3\text{SiCN}\)

\(\text{IrY(CO)(PET}_3)_2\) was reacted with \(\text{H}_3\text{SiCN}\) in deuterated solvent; phosphorus n.m.r. spectra were collected from 198 K showing the presence of one adduct. At room temperature, the spectrum of the solution contained one peak in the region of the spectrum associated with triethylphosphine bound to Ir(III). This peak was a singlet when proton decoupled, and a doublet when observed under off-resonance conditions.
Figure III.2.1 Silyl and hydride resonances of $\text{H}_{\text{Ir-SiH}_2-\text{CH}_2-\text{CH}==\text{CH}_2}$

\begin{align*}
\text{SiH} & \quad \text{IrH} \\
\delta & \quad 3.8 \quad 3.6 \quad 3.4 \\
\text{ppm} & \quad -9.6 \quad -9.8 \quad -10.0
\end{align*}

10 Hz/cm
The proton n.m.r. resonance patterns were of the same type found for the $\text{SiH}_3X$ adducts or $\text{H}_3\text{SiC}_6\text{H}_5$ product; there was a triplet of doublets in the silyl region and a triplet of triplets at low frequency for a hydride trans to $\text{SiH}_2$Q ($Q = Y$ or CN) group. Whether CN was attached to silicon or iridium was the main question in the structure assignment of this product. Recording of the $^{31}\text{P}$ n.m.r. spectra from low temperature gave no evidence to suggest exchange or the presence of other isomers in this reaction. If CN instead of chlorine or iodine was directly attached to iridium, a change of the $^{31}\text{P}(\delta)$ would be expected; nevertheless, the recorded values do not differ from those obtained for other silyl adducts where Cl or I is bound to iridium, suggesting that CN is on the silicon atom. Hence, the species produced in this reaction should have the $-\text{SiH}_2\text{CN}$ group trans to H, halogen trans to carbonyl and mutually trans phosphine ligands.

### III.2.6 Trends in N.M.R. Parameters

The n.m.r. parameters for the species outlined in the last sections are listed in Tables III.2.1 and III.2.2 for the chloride and iodide systems respectively.

$^{31}\text{P}$ and $^1\text{H}$ n.m.r. spectra gave evidence of only one product. Although the size of the organic groups (R) attached to silicon were different, only the isomer with the $-\text{SiH}_2\text{R}$ group trans to the hydride was obtained.

Couplings did not show modifications on varying the organic group attached to silicon; and in general they followed the same trend as in the reported $^{48}$ $\text{SiH}_3X$ ($X = \text{Cl}, \text{Br}$ or I) adducts of
TABLE III.2.1

$^{31}P$ and $^1H$ n.m.r. data of some $\text{IrH(CO)Cl(PEt}_3)_2(H_2\text{SiR})$ complexes

<table>
<thead>
<tr>
<th></th>
<th>$\text{PEt}_3$</th>
<th>$\text{H}_2\text{SiR}$</th>
<th>$\text{Ir}$</th>
<th>$\text{SiHR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta(^{31}P)$</td>
<td>-5.7</td>
<td>-5.0</td>
<td>-4.9</td>
<td>-5.9</td>
</tr>
<tr>
<td>$\nu(^{31}P)$</td>
<td>-5.7</td>
<td>-4.8</td>
<td>-5.5</td>
<td>-5.8</td>
</tr>
<tr>
<td>$\delta(\text{SiH})$</td>
<td>4.0</td>
<td>3.5</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>$\delta(\text{IrH})$</td>
<td>-7.9</td>
<td>-8.0</td>
<td>-8.1</td>
<td>-8.7</td>
</tr>
<tr>
<td>$^2J(\text{H-Ir-P})$</td>
<td>16.0</td>
<td>16.0</td>
<td>16.0</td>
<td>15.0</td>
</tr>
<tr>
<td>$^3J(\text{H-Si-Ir-P})$</td>
<td>6.5</td>
<td>7.5</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>$^3J(\text{H-Si-Ir-H})$</td>
<td>2.0</td>
<td>2.5</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>$^3J(\text{H-Si-C-H})$</td>
<td>-</td>
<td>2.5</td>
<td>3.5</td>
<td>-</td>
</tr>
</tbody>
</table>

a. $^3J_{\text{H-H}}$ trans = 18.0; $^3J_{\text{H-H}}$ cis = 14.5.

b. $^3J_{\text{H-C-C-H}}$ = 8.0.

N.m.r. parameters obtained at room temperature using CD$_2$Cl$_2$ as solvent.

Units and abbreviations:

$^{31}P$ and $^1H$ coupling constants in Hz.

$^{31}P$ and $^1H$ chemical shifts in ppm, measured as positive to higher frequency of SiMe$_4$ for $^1H$ or 85% H$_3$PO$_4$ for $^{31}P$.

$\nu^{31}P$: In ppm; shifts obtained from indirect observation.
### TABLE III.2.2

$^{31}$P and $^1$H n.m.r. data of some IrH(CO)I(PEt$_3$)$_2$(H$_2$SiR) complexes

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>R</th>
<th>-C$_6$H$_5$</th>
<th>-CH=CH$_2$</th>
<th>-CH$_2$-CH=CH$_2$</th>
<th>-CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$(P)</td>
<td>-15.7</td>
<td>-15.0</td>
<td>-14.8</td>
<td>-16.5</td>
</tr>
<tr>
<td>$\nu$(P)</td>
<td>-15.7</td>
<td>-15.0</td>
<td>-14.9</td>
<td>-16.5</td>
</tr>
<tr>
<td>$\delta$(SiH)</td>
<td>4.3</td>
<td>3.8</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>$\delta$(IrH)</td>
<td>-10.0</td>
<td>-10.0</td>
<td>-9.9</td>
<td>-10.7</td>
</tr>
<tr>
<td>$^2$J(H-Ir-P)</td>
<td>16.0</td>
<td>16.0</td>
<td>16.0</td>
<td>15.0</td>
</tr>
<tr>
<td>$^3$J(H-Si-Ir-P)</td>
<td>8.0</td>
<td>8.0</td>
<td>7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>$^3$J(H-Si-Ir-H)</td>
<td>3.0</td>
<td>3.5</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>$^3$J(H-Si-C-H)</td>
<td>-</td>
<td>3.5</td>
<td>3.0</td>
<td>-</td>
</tr>
</tbody>
</table>

a. $^3$J$_{H-C-C-H}$ = 8.0

N.m.r. parameters obtained at room temperature using CDCl$_3$ as solvent.

For units and abbreviations see Table III.2.1.
Ir(CO)Y(PEt₃)₂ (Y = Cl or I).

Although the halide on the iridium did not have influence on the coupling constants, it certainly did on the ³¹P and ¹H chemical shifts. On changing the halide from Cl to I it was observed that:

- SiH and IrH resonances moved to low frequency, and
- phosphorus chemical shifts moved ca. 10 ppm to lower frequency.

III.2.7 Reactions of IrHY(CO)(H₂SiC₆H₅)(PEt₃)₂ with HX (X = Cl or I)

In general, the reactions of some silyl transition metal complexes with hydrogen halides (HX) proceed either with cleavage of the Si-M (M = transition metal) bond⁸,¹¹,¹³,³⁸,⁵⁰, or with replacement of the H in H-Si-M by the halogen (X) of HX¹³,⁵¹,⁵².

III.2.7.a Reaction of IrHCl(CO)(H₂SiC₆H₅)(PEt₃)₂ with HCl

Reaction between an excess of gaseous hydrogen chloride and IrHCl(CO)(SiH₂Ph)(PEt₃)₂ (Ph = -C₆H₅) did not take place at low temperature. At 273 K, the ³¹P n.m.r. spectrum recorded, apart from the predominant signal for the Ir(III) starting material, the presence of three Ir(III) products: A, B and C, A being the most abundant species.

After two hours at room temperature most of the starting material had reacted, and species A was the most abundant. The phosphorus n.m.r. signals for the species were singlets, confirming the trans position of the phosphine ligands. Resonances appeared in
the region associated with triethylphosphine bound to Ir(III). When the ethyl protons of the phosphines were selectively decoupled, the species showed to be monohydrides, except species A whose signal split into a triplet instead of a doublet as for the other, indicating the presence of a dihydride.

In the region between 0 and 10.0δ, the proton n.m.r. spectrum of the solution showed resonances corresponding to the ethyl protons of the phosphine ligands, indicating they were bound to a metal, a singlet at 3.9δ, and no silyl resonance. At low frequency (-8.0 to -22.0δ) three hydride signals were detected: a triplet and two triplets of doublets.

The triplet at -16.9δ was collapsed by a phosphorus frequency corresponding to the phosphorus chemical shift for species B in the n.m.r. spectrum. Its hydride chemical shift value indicated that H was trans to a halide and n.m.r. experiment performed with the adduct formed from IrCl(CO)(PET₃)₂ and HCl gave similar parameters, confirming the product to be IrHCl₂(CO)(PET₃)₂, with both phosphine groups trans to each other, chloride trans to carbonyl and hydride trans to chloride.

The two stronger triplets of doublets were of the same intensity and are supposed to be due to the two hydrides of the abundant species A. The chemical shift values (-8.5 and -20.7δ) indicated that the hydrides were trans to different ligands and by using the same phosphorus frequency both signals were collapsed to triplets. While phosphorus decoupled, irradiation of the hydride proton at -8.5δ collapsed the signal at -20.7δ to a singlet and vice versa, corroborating the relation between both signals.
The hydride signal at lower frequency (-20.76) is supposed to be trans to chlorine, and the other to carbonyl (-8.56). These values are consistent with those reported\textsuperscript{28} for IrH\textsubscript{2}Cl(CO)(PEt\textsubscript{3})\textsubscript{2}, confirming that species A should have: H trans to carbonyl, H trans to chloride and mutually trans phosphine ligands.

Unfortunately resonances originated for species C were not detected in the \textsuperscript{1}H n.m.r. spectrum, probably due to its low concentration in solution; the \textsuperscript{31}P n.m.r. spectrum indicated it was a monohydride.

After a few days at room temperature the dihydride species disappeared slowly and n.m.r. evidenced the presence of IrHCl\textsubscript{2}(CO)(PEt\textsubscript{3})\textsubscript{2} as the sole species present; the signal at 3.96 in the \textsuperscript{1}H n.m.r. spectra was identified as H\textsubscript{2}SiPhCl. No further reaction or decomposition was observed after solution was left for several weeks at room temperature.

If assignments are correct, the nature of these products suggests that HCl initially cleaves the iridium-silicon bond, with liberation of H\textsubscript{2}SiPhCl and subsequent formation of the dihydride IrH\textsubscript{2}(CO)Cl(PEt\textsubscript{3})\textsubscript{2} species by reaction of HCl with the intermediate Ir(I) species. Formation of the ultimate product could be accounted from reaction of the dihydride adduct with hydrogen chloride to yield hydrogen and the monohydrido complex (see Diagram III.2.1).

\textbf{III.2.7.b Reaction of IrH\textsubscript{I}(CO)(H\textsubscript{2}SiC\textsubscript{6}H\textsubscript{5})(PEt\textsubscript{3})\textsubscript{2} with HI}

At 203 K, the \textsuperscript{31}P n.m.r. spectrum showed signals for a predominant species and two other Ir(III) compounds, one of them being
the starting material. On warming the solution 20 K the small signals corresponding to the minor species disappeared, leaving only a product with $^{31}$P and $^1$H n.m.r. parameters similar to the one for IrH$_2$(CO)(PEt$_3$)$_2$ complex, obtained from the oxidative addition of IrI(CO)(PEt$_3$)$_2$ with a gaseous sample of HI.

Reaction appeared to be faster than in the chloride system and, although it could not be proved if the minor Ir(III) species ($\delta(^{31}$P) = 7.5 ppm) was a monohydride or dihydride, the formation of the monohydride Ir(III) product seems to be consistent with the previous explanation for the chloride reaction. The $^1$H n.m.r. spectra recorded a singlet at 4.65, which did not correspond to the resonance signal of H$_3$SiPh, but that was obtained in the analogous reaction of t-PtI(H$_2$SiC$_6$H$_5$)(PEt$_3$)$_2$ with HI, and could be due to H$_2$SiPhI compound.

The n.m.r. parameters for the hydride species are represented in Table III.2.3.
TABLE III.2.3

$^{31}\text{P}$ and $^1\text{H}$ n.m.r. data of $\text{IrHX}_2(\text{CO})(\text{PEt}_3)_2$ ($X = \text{Cl}$ or $\text{I}$) and $\text{IrH}_2\text{Cl}(\text{CO})(\text{PEt}_3)_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{(31}\text{P})$ ppm</th>
<th>$\delta(\text{IrH})$ ppm</th>
<th>$^2J_{\text{H-Ir-P}}$ Hz</th>
<th>$^2J_{\text{H-Ir-H}}$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{IrHI}_2(\text{CO})(\text{PEt}_3)_2$</td>
<td>-20.8</td>
<td>-14.5</td>
<td>11.0</td>
<td>-</td>
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<tr>
<td>$\text{IrHCl}_2(\text{CO})(\text{PEt}_3)_2$</td>
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<td>-17.0</td>
<td>11.0</td>
<td>-</td>
</tr>
<tr>
<td>$\text{IrH}_2\text{Cl}(\text{CO})(\text{PEt}_3)_2$</td>
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<td>-20.7</td>
<td>14.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Values measured at room temperature in:

- a. $\text{CDCl}_3$/TMS
- b. $\text{CD}_2\text{Cl}_2$/TMS
III.3.1 Introduction

As discussed in Chapter I, the reactions between $\text{H}_3\text{SiX}$ and trans-$\text{PtHY}$(PEt$_3$)$_2$ ($X$ and $Y = \text{Cl, Br or I}$) have been used to prepare silicon compound of four-coordinated platinum with elimination of hydrogen$^{13}$. These reactions are believed to occur through oxidative addition, leading to an unstable complex of six-coordinated platinum.

\[
\begin{align*}
\text{PEt}_3 & \quad \text{H} \quad \text{Pt} \quad Y \quad \text{PEt}_3 \\
\text{H}_3\text{SiX} & \quad \rightarrow \quad \text{H} \quad \text{Pt} \quad \text{PEt}_3 \\
\text{Et}_3\text{P} & \quad \text{SiH}_2\text{X} \\
\end{align*}
\]

No direct evidence was found for such an intermediate, but in similar reactions between $\text{H}_3\text{SiX}$ and trans-$\text{PtI}_2$(PEt$_3$)$_2$, the first product was a derivative of six-coordinated platinum which decomposed slowly at room temperature$^{14}$.

\[
\begin{align*}
\text{PEt}_3 & \quad \text{H}_2 \\
\text{Y} \quad \text{Pt} \quad \text{SiH}_2\text{X} \\
\text{PEt}_3 & \\
\end{align*}
\]
The formation of t-PtI(PEt₃)₂(SiH₂I₂) was assumed to happen by elimination of SiH₂I₂, subsequent readdition of H-SiH₂ and elimination of hydrogen.

In this Part, the reactions of some organo-substituted silyl hydrides with four-coordinated platinum complexes will be described, and their products characterized by ³¹P and ¹H n.m.r. spectroscopy.

The reactions considered are those of H₃SiR (R = -C₆H₅, -CH=CH₂, and -CH₂-CH=CH₂) with trans-PtHY(PEt₃)₂ and trans-Pt₂Y(PEt₃)₂ (Y = Cl or I) in a 1:1 molar ratio.

III.3.2 Reactions of trans-PtHY(PEt₃)₂ with H₃SiR

Organo-substituted silyl compounds reacted with trans-PtHY(PEt₃)₂ in deuterated solvent with evolution of hydrogen and formation of a silyl complex of four-coordinated platinum:
trans-PtHY(PEt$_3$)$_2$ + H$_3$SiR $\rightarrow$ trans-PtY(SiH$_2$R)(PEt$_3$)$_2$ + H$_2$

(Y = Cl or I; R = -C$_6$H$_5$, -CH=CH$_2$ or =CH$_2$=CH=CH$_2$).

When R = -C$_6$H$_5$, the reaction was complete after ca. 2 hr at room temperature, being faster for Y = I. Nevertheless, it was slow at temperatures lower than 253 K. The complexes were isolated by evaporation of the solvent as white (Y = Cl) or pale yellow (Y = I) solids, and characterized by analysis as well as by their n.m.r. spectra. The amount of hydrogen evolved in these reactions was measured using a Toepler pump. The solutions were stable for several days at room temperature.

When R = -CH=CH$_2$ or -CH$_2$-CH=CH$_2$, the reactions appeared to be complete after ca. 20 min at room temperature, but the solutions darkened after being left for one hour at room temperature, and $^1$H n.m.r. spectrum detected broadening of the SiH resonances, indicating that some decomposition had occurred.

All the complexes were characterized by their n.m.r. spectra and these are discussed in Section III.3.5.

III.3.3 Reactions of trans-PtY$_2$(PEt$_3$)$_2$ with H$_3$SiR

Di-haloplatinum complexes t-PtY$_2$(PEt$_3$)$_2$ reacted with an equimolar amount of the organo-substituted silyl compounds. In general the reactions when Y = I proceeded faster than when Y = Cl.

Treatment of a solution of t-PtI$_2$(PEt$_3$)$_2$ in deuterated methylene chloride with an equimolar proportion of H$_3$SiC$_6$H$_5$ gave a yellow solution and no gas was evolved. A series of proton-decoupled $^{31}$P spectra was recorded in steps of 20 K from 203 to 283 K, showing
how the reaction progressed.

At 273 K, in the $^{31}$P n.m.r. spectra three Pt(II) and one Pt(IV) species were detected, identified as: t-PtI$_2$(PEt$_3$)$_2$; t-PtHI(PEt$_3$)$_2$; t-PtI(SiH$_2$Ph)(PEt$_3$)$_2$; and cis-cis-trans-PtH$_2$I$_2$(PEt$_3$)$_2$.

When the reaction mixture was allowed to warm gradually to room temperature, hydrogen was evolved. The $^{31}$P n.m.r. spectrum recorded the decreasing of intensity of the resonance signals associated with the Pt(IV) species, as well as those resonances associated with the starting material and with t-PtHI(PEt$_3$)$_2$; the signal associated with t-PtI(SiPhH$_2$)(PEt$_3$)$_2$ increased in intensity and a new signal appeared whose $^1$J(P-Pt) was characteristic of a Pt(II) species; the signal was assigned tentatively to t-PtI(SiPhHI)(PEt$_3$)$_2$.

After the mixture was left for fifteen hours at room temperature $^{31}$P spectra showed a decrease in the intensity of the signal due to t-PtI(SiPhH$_2$)(PEt$_3$)$_2$ and a considerable amount of t-PtI(SiPhHI)-(PEt$_3$)$_2$ which was characterized by n.m.r. (see Section III.3.5).

This result supports the mechanism discussed in the introduction. It seems likely that reaction initially proceeded by addition of H$_2$PhSi-H to platinum forming a six-coordinate intermediate; although there was no proof for such an intermediate the products formed can be explained by the following reactions:

\[
\begin{align*}
\text{I} & \\
\text{Pt} & \\
\text{HI} + t-\text{PtI}(\text{SiH}_2\text{Ph})(\text{PEt}_3)_2 & \\
\text{H}_2\text{SiPhI} + t-\text{PtIH(PEt}_3)_2
\end{align*}
\]
t-PtIH(PET₃)₂ + HI ⇌ cis-cis-trans-PtI₂H₂(PET₃)₂

t-PtIH(PET₃)₂ + H₂SiPhI → t-PtI(SiPhHI)(P ET₃)₂ + H₂

also, t-PtI₂(PET₃)₂ + H₂SiPhI → [PtI₂H(SiPhHI)(P ET₃)₂] → HI + t-PtI(SiPhHI)(P ET₃)₂

It must be pointed out that ¹H n.m.r. spectra recorded a singlet at 4.7δ which is believed to correspond to H₂SiPhI (a singlet at the same position has been obtained in other reactions which analogously seems to proceed by H₂SiPhI elimination—see Section III.2.7b and III.3.4). Since HX was generated during the process breaking of the Si-C bond could take place, but no evidence supporting the formation of benzene or H₃SiII was present; also the n.m.r. parameters of the platinum products did not correspond with that reported¹³ for this iodine silyl derivative.

An attempt to obtain different reaction-products using a twofold excess of H₃SiPh was unsuccessful. The resulting n.m.r. parameters were similar to those for the products of the 1:1 molar reaction.

The reaction of t-PtCl₂(PET₃)₂ with phenylsilane was slow. When the reaction mixture was left for one hour at room temperature, a small amount of t-PtCl(SiPhH₂)(P ET₃)₂ was detected. After twelve hours a signal corresponding to a new platinum(II) species was observed and tentatively assigned to t-PtCl(SiPhHCl(P ET₃)₂. Reaction was complete after three days at room temperature; the product was characterized by its n.m.r. spectra and identified as t-PtCl-(SiPhHCl)(P ET₃)₂.

A similar pattern of reactions was followed when t-PtY₂(PET₃)₂ reacted with H₃SiR (R = -CH=CH₂ and -CH₂-CH=CH₂). In addition to
t-PtCl(SiRCl)(PET$_3$)$_2$, a new Pt(II) species was observed, with $\delta$(P) and $^1$J(P-Pt) analogous to the organo-monochlosilyl-platinum(II) complex, and it was believed to correspond to t-PtCl(SiRCl$_2$)(PET$_3$)$_2$. Nevertheless, at this stage a change of colour in the reaction mixture was noticed and n.m.r. spectra deteriorated, suggesting that some decomposition had occurred. No evidence supporting the presence of platinum hydride was obtained.

N.m.r. parameters for these products are collected in Table III.3.1.

### III.3.4 Reaction of t-PtY(H$_2$SiC$_6$H$_5$)(PET$_3$)$_2$ with HX (X = Cl or I)

The reactions of hydrogen halides with similar silyl platinum compounds have been reported to involve a six-coordinated intermediate$^{14,17}$.

The following reactions were undertaken to see if the Si-C bond could be broken under the conditions used. Hydrogen iodide reacted with t-PtI(H$_2$SiC$_6$H$_5$)(PET$_3$)$_2$ very fast. At 193 K, the $^{31}$P n.m.r. spectra recorded, in addition to some unreacted starting material, the presence of two platinum(IV) species; the less abundant identified as cis-cis-trans-PtI$_2$H$_2$(PET$_3$)$_2$.

The $^1$H n.m.r. spectra at this stage showed in addition to the characteristic hydride resonance of cis-cis-trans-PtI$_2$H$_2$(PET$_3$)$_2$, one SiH and a PtH resonance signals, both of them with the corresponding $^{195}$Pt satellites. The resonances corresponding to this silyl-platinum(IV) intermediate were too broad as to indicate how H and SiH were arranged. Nevertheless, the $\delta$(Pt-H) was consistent
with similar six-coordinated Pt species for which H is proposed to be trans to iodine and hence cis to the silyl group$^{13,17}$.

Due to the broadness of the Pt-H signal, assignment of the number of protons attached to silicon could not be made, therefore whether the intermediate corresponds to \( \text{PtH}_2(\text{H}_2\text{SiPh})(\text{PEt}_3)_2 \) or \( \text{PtH}_2(\text{HSiPhI})(\text{PEt}_3)_2 \) is not certain.

When the temperature of the mixture was raised, \( ^{31}\text{P} \) n.m.r. spectra at 258 K detected that the intensity of the signal due to the silyl-platinum(IV) intermediate decreased, and that of cis-cis-trans-PtI\(_2\text{H}_2(\text{PEt}_3)_2\) increased. Small amounts of some other platinum(II) species appeared: t-PtIH(PEt\(_3\))\(_2\); t-PtI\(_2\)(PEt\(_3\))\(_2\); and t-PtI(\text{HSiPhI})(\text{PEt}_3)_2. At this stage a singlet at 4.75 was detected in the \( ^1\text{H} \) n.m.r. spectrum; it is believed the signal corresponds to H\(_2\text{SiPhI}\) because a peak at the same position has been obtained during the reactions of H\(_3\text{SiPh}\) with t-PtI\(_2\)(PEt\(_3\))\(_2\) and of IrH(CO)I(\text{H}_2\text{SiPh})(\text{PEt}_3)_2 with HI, both of them were believed to occur by elimination of this silyl compound. Reaction was complete after two days and t-PtI(\text{HSiPhI})(\text{PEt}_3)_2 was identified as the only Pt-containing product.

The reaction proceeded faster when a twofold excess of HI was used; the silyl-Pt(IV) intermediate was not observed, but in addition to cis-cis-trans-PtI\(_2\text{H}_2(\text{PEt}_3)_2\), a signal for trans-trans-PtI\(_3\text{H}(\text{PEt}_3)_2\)\(^{16}\) was detected. t-PtI(\text{HSiPhI})(\text{PEt}_3)_2 and a small amount of a new Pt(II) species were observed after one day at room temperature, and the reaction was complete after two days. The predominant species was assigned tentatively as t-PtI(\text{SiPhI}_2)(\text{PEt}_3)_2 on the view that no SiH or PtH resonances were observed in the \( ^1\text{H} \)
n.m.r. spectra.

The formation of these platinum complexes suggests that initially HI added to the platinum starting material; it seems probable that the intermediate corresponds to \( \text{PtHI}_2(\text{H}_2\text{SiPh})(\text{PET}_3)_2 \) which then eliminates \( \text{H}_2\text{SiPhI} \). Cis-cis-trans-PtI\(_2\text{H}_2\)(PET\(_3\)) was formed but it loses HI on warming the reaction mixture; subsequent addition of \( \text{H}_2\text{SiPhI} \) to \( \text{t-PtHI(PET}_3)_2 \) gave the \( \text{t-PtI(HSiPhI)(PET}_3)_2 \) product.

The identification of \( \text{t-PtI}_2(PET)_3 \) during this reaction indicated that the addition of \( \text{H}_3\text{SiPh} \) can be reversed; addition of HI to this Pt(II) complex has been reported\(^{16}\) to produce the detected \( \text{t-t-PtI}_3\text{H(PET}_3)_2 \) species.

Analogous results were obtained when \( \text{t-PtCl(SiH}_2\text{Ph})(\text{PET}_3)_2 \) was reacted with HCl, but then the silyl-platinum(IV) intermediate was not detected. Similarly, the final product was believed to correspond to \( \text{t-PtCl(SiPhCl}_2)(\text{PET}_3)_2 \).

It is noteworthy that benzene was not detected in these reactions. Also, the n.m.r. parameters of the products differed from those of the Pt complexes of \( \text{SiH}_3\text{I} \), \( \text{SiH}_3\text{Cl} \) and \( \text{SiH}_2\text{Cl}_2 \).\(^{13,17}\) These products would be formed if the Si-C bond was broken in the presence of HX.

III.3.5 \( ^{31}\text{P} \) and \( ^1\text{H} \) n.m.r. spectra of the products

The stereochemistry of most of the products could easily be determined by consideration of the n.m.r. spectra.

The \( ^{31}\text{P} \) n.m.r. spectra of all the products consisted of a
singlet which was split into a 1:4:1 triplet due to coupling to the platinum isotope, $^{195}\text{Pt}$ (I = $1/2$ and 33.7\% natural abundance). Therefore, both phosphorus atoms are apparently equivalent with respect to the silyl group, which is hence trans to the halogen (Y).

The $^1\text{H}$ n.m.r. spectrum recorded SiH resonances and complicated patterns between 0.5 and 2.5$\delta$ due to the protons of the ethyl groups of the phosphine. Those signals were characteristic of mutually trans $\text{PET}_3$ groups in square planar or octahedral platinum complexes.

**III.3.5a SiH resonance in t-PtY(SiH$_2$R)(PET$_3$)$_2$ and t-PtY(SiXC$_6$H$_5$)-(PET$_3$)$_2$ complexes**

The SiH resonance of t-PtY(H$_2$SiC$_6$H$_5$)(PET$_3$)$_2$ was characteristic of those observed for t-PtY(PET$_3$)$_2$SiH$_2$X complexes $^{13}$ (X = Cl, Br or I). It consisted of three triplets with intensities in the ratio 1:4:1; the satellites due to coupling of the SiH proton with $^{195}\text{Pt}$ nucleus. The small 1:2:1 triplet in each peak was due to coupling with two equivalent phosphorus atoms and was collapsed by phosphorus irradiation.

A similar resonance pattern was obtained for t-PtY(PET$_3$)$_2$-(HSiXC$_6$H$_5$), but substitution of hydrogen by a halide at the silicon atom affected the $\delta$(SiH) position and the magnitude of $^3J_{H-Si-Pt}$ was greater.

For t-PtY(H$_2$Si-CH=CH$_2$)(PET$_3$)$_2$, the main SiH resonance was a 1:2:1 triplet of narrow doublets with satellites due to $^{195}\text{Pt}$ nuclei. A complex set of peaks between 5.5 and 6.5$\delta$ corresponded to
the resonance of the vinyl protons. The small triplet splitting was assigned to coupling with the two phosphorus atoms as by irradiating in the phosphorus region of the spectrum the main signal was collapsed to a doublet; the doublet was shown by double irradiation to derive from coupling with the -CH= proton.

The SiH resonance of t-PtY(H$_2$Si-CH$_2$-CH=CH$_2$)(PEt$_3$)$_2$ took the form of a seven line multiplet with $^{195}$Pt satellites to each side of it. The septet was easily analysed by homo- and heteronuclear spin decoupling experiment showing it was due to three overlapping triplets with $^3J_{H-Si-Pt-P} = 2^3J_{H-Si-C-H}$.

Phosphorus irradiation converted the signal to a triplet, which was collapsed to a singlet by irradiating at the multiplet at 1.7δ ascribed to the -CH$_2$- protons resonance.

SiH resonances due to t-PtI(HISi-CH$_2$-CH=CH$_2$)(PEt$_3$)$_2$ and t-PtI(HISi-CH$_2$-CH=CH$_2$)(PEt$_3$)$_2$ could not be measured; decomposition of the reaction mixture was rapid and it deteriorated the resolution of the spectra.

III.3.6 Trends in N.M.R. Parameters

The n.m.r. parameters for the Pt(II) products and Pt(IV) intermediate are collected in Table III.3.1.

$^{31}$P and $^1$H n.m.r. spectra indicated that all the products formed have mutually trans phosphines, and hence that halogen is trans to the silyl group.

$^1J_{Pt-P}$ depended on the coordination number of platinum, it being larger for the platinum(II) complexes. Variations in the $\delta(^{31}P)$
### TABLE III.3.1

$^{31}$P and $^1$H n.m.r. data of some silyl-platinum complexes:

![Diagram](image)

<table>
<thead>
<tr>
<th>Y</th>
<th>Z'</th>
<th>R</th>
<th>$^1$$J$(P-Pt)</th>
<th>$\delta(^{31}$P)</th>
<th>$\delta$(SiH)</th>
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<th>$^3$$J$H-Si-Pt-P</th>
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N.m.r. parameters obtained at room temperature using CD$_2$Cl$_2$ as solvent.

- **a.** Tentative assignment.
- **b.** Parameters recorded at 203 K; $\delta$(Pt-H) = -13.1; $^1$$J$H-Pt = 1120.0.

For units see Table III.2.1.
were influenced by the halogen attached to platinum.

On the contrary, $\delta$(SiH) values were observed to be independent of the halogen attached to the metal, but they were greatly modified when a halogen was bound to silicon, as in $t$-PtY(HSiXC$_6$H$_5$)(PEt$_3$)$_2$.

$^2J_{H-Si-Pt}$ was similar among the $t$-PtY(H$_2$SiR)(PEt$_3$)$_2$ complexes, but its magnitude was larger for $t$-PtY(HSiXR)(PEt$_3$)$_2$. Similar trends have been observed for other silyl platinum(II) complexes.$^{13,17}$
PART 4

Conclusions

It was observed that for the reactions studied among the organo-substituted Group IV-B compounds and the rhodium, iridium and platinum complexes, there was no evidence of interaction between the organic group attached to the Group IV-B element and the transition metal. They added as $H^-$, and Group IV-B element.

The rhodium and iridium carbonyls, $M(CO)Y(PEt_3)_2$ ($M = Rh$ or $Ir$; $Y = Cl$ or $I$) behave differently in their reactions with the organo-substituted Group IV-B compounds. Whereas iridium forms adducts $IrH(CO)Y(H_2SiR)(PEt_3)_2$ that are stable at room temperature and can be isolated, addition to $Rh(CO)Y(PEt_3)_2$ results in a rapid reaction giving a six-coordinate Rh(III) adduct stable at low temperatures only, which dissociates to the Group IV-B compound and Rh(I) starting material as the temperature is increased. For both systems, the same results were obtained when an excess of the Group IV-B compound was used and reaction was left for long periods at room temperature. Evidence suggested that only one isomer was formed during these reactions.

The results obtained when the rhodium complex was used contrasts with the behaviour of the iridium analogue $Ir(CO)Y(PEt_3)_2$, and illustrates the greater stability of the +3 oxidation state for iridium.

The tendency of these Rh(III) complexes to dissociate in solution giving $H_2MRZ$ ($M = Si$: $Z = H$, $R = H$, $-CH_3$ or $-CH_2-CH=CH_2$; $Z = Cl$, $R = -CH_3$, $M = Ge$: $Z = H$, $R = H$ or $-CH_3$) and the Rh(I)
starting material depends on the groups (R and Z) bound to M, as Rh(III) adducts stable at room temperature were obtained when \( \text{H}_3\text{MX} \) (\( X = \text{Cl} \) or \( I \)) was used (see Chapter II). Some factors accounting for these results will be discussed in Chapter V.

The reactions between \( \text{H}_3\text{SiR} \) and platinum gave Si-Pt products, which were suspected to involve oxidative addition of Si-H to Pt forming a six-coordinate intermediate. Although detection of any complex other than derivatives of four-coordinate platinum was very difficult and only when t-PtI(\( \text{H}_2\text{SiC}_6\text{H}_5 \))(PEt\(_3\)_2) was reacted with HI the formation of a Pt(IV) intermediate containing Si-Pt-H bond could be observed, a different type of mechanism should not be postulated as the products are what would have been expected by analogy with reactions of other silanes.

Finally it must be pointed out that when IrHY(CO)(\( \text{H}_2\text{SiC}_6\text{H}_5 \))(PEt\(_3\)_2) and t-PtY(\( \text{H}_2\text{SiC}_6\text{H}_5 \))(PEt\(_3\)_2) were reacted with the hydrogen halides, there was no evidence supporting the breaking of the Si-C bond.
CHAPTER IV

Experimental
IV.1 General Experimental Methods

All volatile compounds were handled in a Pyrex vacuum system of conventional design. The vacuum line was built up from detachable sections; apiezon L and N greases were used on taps and ground glass joints respectively. Most of the detachable reaction ampoules were fitted with Rotaflo or Sovirel teflon greaseless taps. A high vacuum, necessary for the exclusion of air and moisture from the materials being handled, was maintained by a mercury diffusion pump assisted by a rotary oil pump. The pressures of the materials inside the apparatus were measured using a spiral gauge with a mirror, employed as a null point instrument with a lamp and scale and the pressure in the system was checked by a pirani gauge. Using a molecular weight bulb the line was calibrated for volume which, combined with pressure readings, allowed rapid calculation of the amount of volatile materials present.

Air sensitive solids were manipulated on a different type of vacuum line called a Schlenk line. This line allowed nitrogen gas to be passed over the sample while solvents were added or taken out; the facility for removing solvents and unwanted gases by suction was available.

Preparations were carried out in Pyrex reaction vessels and agitated with teflon coated magnetic stirrer bars. Solutions and slurries were transferred between vessels using Pyrex syringes with stainless steel needles. Air sensitive solids were transferred between vessels in a V.A.C. Model HE-493 glove box equipped with a V.A.C. Model HE-493 Dri-Train (sic). Dry nitrogen gas was supplied directly from a cylinder into the box and then continually
circulated through the Dri-Train to remove contaminants. The pressure in the box was maintained marginally above atmospheric pressure by means of a Pedatrol attachment provided by V.A.C. (California, U.S.A.).

IV.2 Instruments

$^{31}$P n.m.r. spectra were recorded using a Jeol FX60Q or a Varian Associates XL-100 spectrometer, both of them operating in the Fourier transform mode and providing selective proton decoupling facilities. A deuterated solvent was employed as lock; variable temperature facilities were provided by both spectrometers.

$^1$H n.m.r. spectra of some Rh(III) adducts were measured using a Bruker WH360 Fourier transform spectrometer; the $^1$H n.m.r. spectrum of the remaining complexes were recorded in a Varian Associates HA100 spectrometer. Both instruments provided facilities for recording the spectra at low temperatures. All proton resonances were measured using a reference frequency which was locked to the resonating frequency of T.M.S.

The heteronuclear double resonance or "spin tickling" technique provided a very convenient means of obtaining chemical shifts and coupling constants for nuclei other than hydrogen from the proton spectra. The HA100 instrument was used for this experiment; the technique involved connecting a second radio frequency, provided by a Schlumberger FS 30 frequency synthesiser, to the probe. Operating on frequency sweep, the spectrometer chart recorder pen was positioned over the peak to be decoupled, the second radio
frequency was then varied until the pen dropped toward the base line. More selective "tickling" was achieved by decreasing the power of the decoupling frequency.

Various corrections have to be made to the observed decoupling frequency to allow for T.M.S. not resonating at exactly 100 MHz, to relate the observed frequency to the T.M.S. centre band rather than to a sideband, and to counteract any instrumental offsets. For homonuclear double resonance experiments, the modulating frequency was generated by a Muirhead decade oscillator.

Infra-red spectra were recorded using a Perkin Elmer 457 double-beam spectrometer (250-4000 cm\(^{-1}\)). Gas phase spectra were obtained using a gas cell fitted with KBr plates.

Analyses for carbon and hydrogen were carried out using a Perkin Elmer 240 elemental analyser.

IV.3 Preparation of Starting Materials

Procedures for the preparation of the compounds used during this work are described in this section. The compounds were generally prepared by documented techniques, the appropriate references and any modifications being given.

IV.3.a Criteria of purity

Samples and impurities were identified by infrared spectroscopy, the impurities being removed by trap-to-trap distillation through traps surrounded by slush-baths of known temperature. For less well-characterized samples, vapour phase molecular weight determinations were made together with \(^1\)H n.m.r. spectra to determine any
impurities.

Purity of the transition metal complexes was checked by $^{31}$P n.m.r. spectroscopy and C and H analysis.

IV.3.b Preparation of the rhodium, iridium and platinum starting materials

**RhCl(CO)(PET$_3$)$_2$**

17.8 ml of 1 M aqueous KOH solution was added to a mixture of 1.57 g RhCl$_3$.3H$_2$O, 1.8 ml PET$_3$, 15 ml methyl alcohol and 15 ml ethyl alcohol. The resultant mixture was heated under reflux for 45 minutes and acidified with 2.5 ml of concentrated hydrochloric acid. The mixture was cooled over ice for some minutes until the yellow crystals precipitated. The solids were filtered off from the solution, dried under vacuum and sublimed in vacuum at 120°C. The yellow crystals were stored under nitrogen.

**RhI(CO)(PET$_3$)$_2$**

100% excess of NaI was added to an acetone solution of RhCl(CO)(PET$_3$)$_2$ at room temperature; the mixture was stirred for some minutes and the acetone evaporated off. Sublimation of the solid at 130°C produced the pure crystals.

**IrCl(CO)(PET$_3$)$_2$**

Under nitrogen, 0.45 g of Ir$_2$Cl$_2$(C$_8$H$_{14}$)$_4$ was stirred in 5 ml of degassed acetone. 0.24 g of triethylphosphine was dissolved in 5 ml of acetone, degassed and kept under nitrogen. At room temperature, CO was bubbled at a slow rate through the Ir$_2$Cl$_2$(cyclo-octene)$_4$
slurry until the orange colour was replaced by a deep blue. The solution of \( \text{Et}_3\text{P} \) was added gradually and the reaction stirred rapidly until a yellow solution was obtained. The solvent was pumped off and the product maintained at \( 80^\circ \text{C} \) for 90 minutes. The product was sublimed at \( 120^\circ \text{C} \) in vacuum giving yellow crystals which could be handled for short periods in air\(^4\).

\[ \text{IrI(CO)(PEt}_3)_2 \]

\( \text{IrCl(CO)(PEt}_3)_2 \) was dissolved in degassed acetone and reacted with a 100% excess of NaI. The acetone was evaporated off and sublimation of the product at \( 140^\circ \text{C} \) produced the crystals which were handled in the Dri-Train (sic).

\[ \text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4 \]

The dimer was prepared under nitrogen by refluxing \( \text{IrCl}_3\cdot\text{3H}_2\text{O} \) with cyclo-octene in isopropyl alcohol and \( \text{H}_2\text{O} \)\(^6\).

Cis- and trans-\( \text{PtCl}_2(\text{PEt}_3)_2 \)

The complexes were made by reacting either \( \text{PtCl}_2 \) or \( \text{K}_2\text{PtCl}_4 \) with \( \text{PEt}_3 \). 2.0 g of \( \text{K}_2\text{PtCl}_4 \) was dissolved in water and 1.4 ml of \( \text{PEt}_3 \) added. This mixture was left stirring for one hour, giving a pink-brown mixture of cis- and trans-\( \text{PtCl}_2(\text{PEt}_3)_2 \). This mixture can be converted entirely to the cis isomer by suspending it in hexane, adding one drop of \( \text{PEt}_3 \) and leaving the system stirring for several hours. The pure sample of cis-\( \text{PtCl}_2(\text{PEt}_3)_2 \) could then be collected. When \( \text{PtCl}_2 \) was used the first stage of the method was carried out in acetone; otherwise the procedure was the same.
The t-PtCl$_2$(PET$_3$)$_2$ complex was obtained by heating the pink-brown solution for 20 minutes and filtrating the yellow-brown solid. By addition of ether to the solid, a yellow solution was collected which gave the t-PtCl$_2$(PET$_3$)$_2$ product. The brown-white solid left after extraction was the cis product$^{64}$.

Trans-PtHCl(PET$_3$)$_2$

A suspension of 2.0 g of cis-dichloride in 20 ml of H$_2$O and 1.0 ml of hydrazine hydrate was refluxed for one hour, during which time an oil formed. On cooling, the oil solidified to give the impure product$^{65}$. This was purified using activated charcoal and a final recrystallisation from methanol.

Trans-PtHI(PET$_3$)$_2$ and trans-PtI$_2$(PET$_3$)$_2$$^{66}$

The corresponding chloride sample was dissolved in acetone and treated with 100% excess of NaI. The mixture was boiled for 10 minutes and the acetone evaporated to dryness. The product was then washed with water and the solid filtered off. The yellow solids were recrystallised from methanol.

IV.3.c Preparation of the Group IV-B compounds

Monosilane

SiH$_4$ was prepared by the standard method$^{67}$. The reduction was carefully carried out in diethyl ether.
Phenylsilane

PhSiH$_3$ was prepared by the method of Kummer and Fritz$^{68}$. The reduction was carried out in di-n-butyl ether.

Silyl chloride

ClSiH$_3$ was prepared by streaming silyl bromide through an excess of dried mercuric chloride$^{69}$.

Silyl cyanide

Similarly SiH$_3$CN was prepared by streaming small samples of silyl bromide over silver cyanide.

Methylsilane$^{70}$, Vinylsilane and Allylsilane$^{71}$

These compounds were prepared by reducing their corresponding trichloro species with lithium aluminium hydride in di-n-butyl ether under 50 cm of nitrogen pressure kept constant as the reaction proceeded.

Methylchlorosilane

CH$_3$SiH$_2$Cl was prepared by the chlorination of methylsilane with stannic chloride at room temperature$^{72}$.

Germane

Germane was obtained by the reaction of an aqueous solution of potassium hydroxide, germanium(IV) oxide and potassium hydroborate with glacial acetic acid under nitrogen. The apparatus was maintained
at a pressure of 10 cm, and the crude product was collected at liquid nitrogen temperature\textsuperscript{73}.

**Germyl chloride**

$\text{GeH}_3\text{Cl}$ was obtained by reaction of germane with the stannic chloride at room temperature\textsuperscript{72}.

**Germyl iodide**

$\text{GeH}_3\text{I}$ was prepared by the reaction of germyl chloride with a slight excess of gaseous hydrogen iodide at room temperature.

Samples of $\text{H}_3\text{SiBr}$\textsuperscript{68}, $\text{H}_3\text{SiI}$\textsuperscript{74}, $\text{CH}_3\text{SiH}_2\text{I}$, $\text{H}_3\text{GeCH}_3$, $\text{HI}$ and $\text{HCl}$ were kindly provided by members of the Inorganic research group.

**IV.3.d Solvents**

The solvents used were of commercial grade and dried over lithium aluminium hydride, sodium wire or molecular sieves as appropriate.

Deuterated n.m.r. solvents and tetramethylsilane were stored over molecular sieves.

**IV.4 Details of Experiments**

In a typical experiment 0.15 mmol of the transition metal complex was weighed into a 5 mm n.m.r. tube and evacuated. The solvent and a small amount of $\text{SiMe}_4$ were distilled off into the tube and once the complex had been dissolved the required amount of the Group IV-B compound was condensed at -196°C. The tube was then
sealed off and kept cool until required.

Usually the first spectra was obtained at 193 K; the system was then slowly allowed to warm in steps of ca. 10°, and spectra were recorded until reaction was complete.

When appropriate, attempts were made to isolate the products. The n.m.r. tube was opened, the solution transferred to a Schlenk tube where nitrogen was being passed and the solvent was pumped at ca. -10°C.

Analyses of the solid compounds isolated are presented in Table IV.1.

IV.4.a  \( \text{RhY(CO)(PET}_2)_2 + \text{MH}_2X \) (X = halogen)

N.m.r. samples were made up as in IV.4 in equimolar ratio. After reaction was complete and the n.m.r. recorded, the tubes containing products where exchange had not taken place and only one isomer was formed, were tried to be isolated. On evaporation of the solvent a yellow gum remained which gave a yellow or orange solid when washed with diethyl ether (see Table IV.1). The productswere air unstable.

As the silane, germanes and organo-substituted Group IV-B adducts are thermally unstable, attempts to isolate these products were not made.

IV.4.b  \( \text{IrY(CO)(PET}_2)_2 + \text{SiH}_3R \)

N.m.r. samples were prepared as in IV.4. The contents of the n.m.r. tubes were transferred to the Schlenk tube and the solvent removed, giving white or yellow gums, the colour depending on the
halogen attached to the iridium metal. By washing the products with n-hexane, solids were obtained. The Ir(III) complexes were air unstable (see Table IV.1).

IV.4.c \[ t-\text{PtHY(PEt}_3\text{)}_2 + H_3\text{SiC}_6\text{H}_5 \]

N.m.r. tubes were made up as in IV.4. A white or pale yellow powder was obtained directly on removing the solvent at 273 K from the solution after it had been characterized by n.m.r. (see Table IV.1).

IV.4.d \[ \text{IrHY(CO)(H}_2\text{SiC}_6\text{H}_5)(\text{PEt}_3\text{)}_2 + HX \]

0.15 mmol of IrY(CO)(PEt)_3 was weighed into a greaseless tap ampoule with an n.m.r. tube attached to its side arm. A non-deuterated solvent was distilled into the ampoule and the solids were dissolved; this mixture was reacted with an equimolar ratio of PhSiH₃ and left at room temperature until completion of the reaction (ca. 15 minutes). The solvent and any excess of PhSiH₃ were evaporated leaving the C₆H₅SiH₃-Ir(III) adduct which was dissolved in a deuterated solvent and a small amount of T.M.S. and transferred to the side arm n.m.r. tube. The system was then frozen at liquid nitrogen temperature and the corresponding HX added. The n.m.r. tube was sealed off and kept cool until required.

IV.4.e \[ t-\text{PtY(H}_2\text{SiC}_6\text{H}_5)(\text{PEt}_3\text{)}_2 + HX \]

0.2 mmol of t-PtHY(PEt)_3 was used. After addition of PhSiH₃, reaction was left for one hour at room temperature to secure formation of t-PtY(H₂SiC₆H₅)(PEt₃)₂. Otherwise the preparation of the n.m.r. tube was as described in IV.4.d.
TABLE IV.1
Analyses of some Group IV-B derivatives of rhodium, iridium and platinum

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Found</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
</tr>
<tr>
<td>RhHCl(H₂GeCl)(CO)P₂</td>
<td>30.5</td>
<td>6.2</td>
</tr>
<tr>
<td>RhHI(H₂SiCl)(CO)P₂</td>
<td>27.5</td>
<td>5.6</td>
</tr>
<tr>
<td>RhHI(H₂SiI)(CO)P₂</td>
<td>24.3</td>
<td>5.0</td>
</tr>
<tr>
<td>IrHCl(H₂SiCN)(CO)P₂a</td>
<td>30.4</td>
<td>6.1</td>
</tr>
<tr>
<td>IrHCl(H₂Si-CH=CH₂)(CO)P₂</td>
<td>32.4</td>
<td>6.5</td>
</tr>
<tr>
<td>IrHCl(H₂Si-CH₂-CH=CH₂)(CO)P₂</td>
<td>33.8</td>
<td>6.6</td>
</tr>
<tr>
<td>IrHI(H₂SiCN)(CO)P₂b</td>
<td>26.1</td>
<td>5.2</td>
</tr>
<tr>
<td>IrHI(H₂Si-CH₂-CH=CH₂)(CO)P₂</td>
<td>29.2</td>
<td>5.7</td>
</tr>
<tr>
<td>IrHI(H₂Si-C₆H₅)(CO)P₂</td>
<td>32.9</td>
<td>5.6</td>
</tr>
<tr>
<td>t-PtCl(H₂SiC₆H₅)P₂</td>
<td>37.5</td>
<td>6.5</td>
</tr>
<tr>
<td>t-PtI(H₂SiC₆H₅)P₂</td>
<td>32.3</td>
<td>5.7</td>
</tr>
<tr>
<td>t-PtI(HISiC₆H₅)P₂</td>
<td>27.6</td>
<td>4.7</td>
</tr>
</tbody>
</table>

For the complexes P = PEt₃

a. %N found = 2.8; required = 3.2
b. %N found = 2.2; required = 2.2
CHAPTER V

Stability of some Organo-Group IV-B Rhodium(III) Complexes
V.1 Introduction

Oxidative addition to $\text{RhY(CO)(PEt}_3^2$ ($Y = \text{Cl or I}$) of the simple Group IV-B halides ($\text{MH}_3X$; $M = \text{Si or Ge}$; $X = \text{Cl or I}$) produced Rh(III) derivatives stable at room temperature; nevertheless, this reaction failed to produce adducts that were stable at room temperature when $H_2\text{MRZ}$ (for $M = \text{Si}$, $Z = \text{H}$ and $R = \text{H}, -\text{CH}_3$, or $-\text{CH}_2-\text{CH}=\text{CH}_2$; or $Z=\text{Cl}$ or I and $R = -\text{CH}_3$; for $M = \text{Ge}$, $Z = \text{H}$ and $R = \text{H}$, or $-\text{CH}_3$) was used. In these cases temperature-dependent equilibrium among the Rh(III) adduct and Rh(I) starting material was obtained, in which the Rh(III) species was predominant at low temperatures but dissociated as the temperature was raised to give the Group IV-B compound and the Rh(I) complex.

In the literature, there is no reliable thermodynamic data for species containing transition metals bound to silicon or germanium, and in view of the instability to dissociate of these Group IV-B Rh(III) complexes compared with the adducts of $\text{MH}_3X$, calculation of some thermodynamic information for these complexes was of interest.

The equilibrium:

$$\text{RhY(CO)(PEt}_3^2 + H_2\text{MRZ} \rightleftharpoons \text{RhHY(CO)(HMZR)(PEt}_3^2$$

was such that both rhodium species existed in easily detectable amounts in solution over a useful range of temperatures, a favourable situation which permitted the acquisition of the data.

It was found that the systems could be studied by $^{31}\text{P}$ and $^1\text{H}$ n.m.r. over a range of temperatures. In addition, low temperature spectra of the complexes permitted the determination of the
stereochemistry in solution of the Rh(III) adducts (see Chapters II and III. Part 1).

V.2 Experimental

V.2.a Equilibrium constants

The reactions (equation 1) were carried out in sealed n.m.r. tubes in a 1:1 molar ratio. Provided that the initial amounts of reactants taken are well known, the concentration of the Rh(I) and Rh(III) species could be computed by $^{31}$P and $^1$H n.m.r. spectroscopy at temperatures in which both species were present in appreciable quantity. A routine treatment of this information produced the variable temperature equilibrium constants data:

$$\text{RhY(CO)(PET}_3)_2 + \text{H}_2\text{MZR} \rightleftharpoons \text{RhHY(CO)(HMZR)(PET}_3)_2$$  \hspace{1cm} (1)

(For $M = \text{Si}$, $Z = \text{H}$ and $R = \text{H}$, -CH$_3$ or -CH$_2$-CH=CH$_2$; or $Z = \text{Cl}$, or I and $R = \text{-CH}_3$. For $M = \text{Ge}$, $Z = \text{H}$ and $R = \text{H}$ or -CH$_3$).

If: $\text{Rh(I)} = \text{RhY(CO)(PET}_3)_2$

$Q = \text{H}_2\text{MZR}$

$\text{Rh(III)} = \text{RhHY(CO)(HMZR)(PET}_3)_2$

Then,

$$\text{Keq} = \frac{[\text{Rh(III)}]}{[\text{Rh(I)}][Q]}; \text{ or } \text{Keq} = \frac{[\text{Rh(III)}]}{[\text{Rh(I)}]^2}$$  \hspace{1cm} (2)

For the chloride and iodide systems, such concentrations can be measured using the integrated $^1$H n.m.r. spectra, but this method was only used for the systems when $Y = \text{Cl}$.

The chemical shifts of the M-H, Rh-H and triethylphosphine
protons of the rhodium(III) complex differed sufficiently at 360 MHz from those of the organic group bound to M, that the area underneath each peak could be readily determined. In general it was observed that when the temperature was raised the intensity of the M-H and Rh-H signals from the Rh(III) complex decreased, and that of H₂MZR increased as a consequence of the dissociation of the Rh(III) species.

All of the adducts formed were monohydrides. The number of ethyl protons for two P(C₂H₅)₃ ligands are thirty, therefore independently of the temperature the relation between the proportion of ethyl protons and the total amount of rhodium in the equilibrium is:

\[
\frac{1}{30} [\text{PET}_3] = [\text{Rh(III)}] + [\text{Rh(I)}]
\]

[\text{Rh(III)}] is measured by [RhH in complex], hence the proportion of Rh(I) in the equilibrium could be calculated by substituting the integral values in equation 3. Providing that the concentration of the solution is known, and having the Rh(I)/Rh(III) ratio, the concentration of both rhodium species could be obtained at different temperatures.

The results were consistent if the relation of equation 3 was established using the integral values of the M-H protons, provided that the different numbers of protons bound to M in the complex were taken into account. Thus equation 3 was converted to:

\[
\frac{1}{30} [\text{PET}_3] = \frac{1}{3} [\text{MH in complex}] + [\text{Rh(I)}] \text{ for MH₄ adducts}
\]

\[
(M = \text{Ge})
\]
\[ \frac{1}{30} [\text{PET}_3] = \frac{1}{2} [\text{MH in complex}] + [\text{Rh(I)}] \] for H₃MR adducts

(M = Si, R = -CH₃ or -CH₂-CH=CH₂; M = Ge, R = -CH₃) and equation 3 for H₂SiZR adducts (R = -CH₃, Z = Cl or I).

Regardless of the consideration used to establish the equation 3, it was quantitatively proved that the ratios of the integrals of:

(a) M-H:R-H was -

3:1 for H₄M adducts
2:1 for H₃MR adducts, and
1:1 for H₂SiZR adducts.

(b) PET₃: total SiH in H bound to Si and Rh was consistent during the experiments at different temperatures, so that the value was -

7.5:1 for H₄M reactions
10.0:1 for H₃MR reactions, and
15.0:1 for H₂SiZR reactions, provided that the equimolar ratio of the starting materials was exactly 1:1.

As explained in Chapter III (Section III.1.1), the ³¹P n.m.r. spectra of the iodine systems were very particular when measured from low to room temperature: separate resonance signals for both rhodium species were not observed at any temperature; instead a gradual expansion of \(^{1}J_P-\text{Rh}\) was observed, the values varying from something typical of a six-coordinate species at low temperatures to that for the starting material at room temperature. For each intermediate temperature, the value of \(^{1}J_P-\text{Rh}\) was between those
expected for the six-coordinated complex and for the starting material. Thus, the observed $^{1}J_{p-Rh}$ values were used to measure the proportions of six- and four-coordinated species in the system if the true $^{1}J_{p-Rh}$ for the six- and four-coordinated species, at the temperature of the measurement, were known.

A graph of the changes of $^{1}J_{p-Rh}$ (Hz) against a full range of temperatures (193 to 303 K) was plotted for the starting material RhI(CO)(PET$_{3}$)$_{2}$, and for a six-coordinated Rh(III) species RhIII(CO)(H$_{2}$SiI)(PET$_{3}$)$_{2}$ (which appears to be undissociated). For these species, $dJ/dT$ was observed to be 0.011 and 0.014 Hz/K respectively. With the four-coordinated species, no special considerations were needed to get $^{1}J_{p-Rh}$ at a required temperature, as it was the starting material. Nevertheless for the Rh(III) species studied, it was necessary to assume that $^{1}J_{p-Rh}$ would change with temperature by about the same amount as the SiH$_{3}$I adduct did; therefore corrections were applied to each adduct using the $J_{p-Rh}$ value at the lowest temperature.

Consequently the proportions of Rh(I) and Rh(III) species at a particular temperature were calculated from two simple equations. At 243 K, a particular example could be:

$^{1}J_{p-Rh}$ at equilibrium = 96.3 Hz

$^{1}J_{p-Rh}$ of the starting material = 113.9 Hz

Corrected $^{1}J_{p-Rh}$ of the studied adduct = 90.8 Hz.

Therefore:
96.3 = 113.9 - Rh(III) proportion at equilibrium

96.3 = 90.8 + Rh(I) proportion at equilibrium

Those equations enable the Rh(I)/Rh(III) ratio to be evaluated and concentrations of both species were found provided that the initial concentration of the solution was known.

Regardless of the method used to calculate the concentration of the rhodium species in solution, estimation of the equilibrium constants (Keq) at different temperatures was made by substitution of the Rh(I) and Rh(III) concentration in equation 2.

Integrals were obtained from the $^1$H n.m.r. spectra recorded on a Bruker WH-360 n.m.r. spectrometer. $^{31}$P($^1$H) spectra were measured using a Jeol-FX60 or a Varian Associates XL-100 spectrometer from which $^{1}J_{P-Rh}$ was calculated. The spectrometers were equipped with a variable temperature probe permitting the experiments between 303 and 193 K. The temperature measurements could not take place within the sample tube itself for technical reasons. In practice the temperature was determined by a thermocouple placed in the nitrogen stream directly below the n.m.r. tube when the Jeol FX60 or VA XL-100 spectrometers were used. In the Bruker WH-360 the temperatures were measured by recording the spectra of a standard sample of methanol before and after the spectrum of the rhodium sample under investigation was measured. With the methanol, the chemical shift differences $\Delta \nu$ (in Hz), between the resonances of the CH$_3$ protons and OH proton, are temperature dependent. Precise measurements have led to know relationships from which the temperature of the studied compound could be determined.
The measurements of equilibria, taken over a range of temperature, provided information on enthalpy changes $\Delta H^o_{\text{t}_1 \rightarrow \text{t}_n}$, entropy changes $\Delta S^o_{\text{t}_1 \rightarrow \text{t}_n}$ and therefore on changes of free energy ($\Delta G^o_{\text{t}}$) at a determined temperature.

The Van't Hoff equation can be expressed as:

$$\log_{10} \text{Keq} = \frac{-\Delta H^o_{\text{t}}}{2.303 \, R} \times \frac{1}{T} + \frac{\Delta S^o_{\text{t}}}{2.303 \, R}$$

but it can be modified and written simply as:

$$\log_{10} \text{Keq} = \frac{\Delta H^o_{\text{t}}}{2.303 \, R} \times \frac{1}{T} + \frac{C}{2.303}$$

where $C$ is a constant, equal to $\Delta S^o_{\text{t}}/R$.

If equation 5 is valid a graph of $\log_{10} \text{Keq}$ against $1/T$ will be linear, and the slope equal to $-\Delta H^o_{\text{t}_1 \rightarrow \text{t}_n}/2.303 \, R$.

Hence, $\Delta H^o_{\text{t}_1 \rightarrow \text{t}_n}$ was calculated from the gradient and substitution of this value in equation 5 allowed determination of $C$ from which $\Delta S^o_{\text{t}_1 \rightarrow \text{t}_n}$ could be evaluated.

Equilibrium constant data at various temperatures for the reactions studied here are presented in Tables V.1 and V.2 for the chloride and iodide systems respectively.

The tables show that the equilibrium constants decrease as the temperature is raised. Thus the very large equilibrium constant
TABLE V.1
Equilibrium constants\textsuperscript{a} at various temperatures for the equilibrium
\[ \text{RhCl(CO)(PET}_3\text{)}_2 + H_2\text{MZ} \rightleftharpoons \text{RhHCl(CO)(HMZR)(PET}_3\text{)}_2 \]

<table>
<thead>
<tr>
<th>M</th>
<th>Si</th>
<th>Si</th>
<th>Si</th>
<th>Ge</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>R</td>
<td>-CH\textsubscript{3}</td>
<td>-CH\textsubscript{3}</td>
<td>-CH\textsubscript{2}-CH=CH\textsubscript{2}</td>
<td>H</td>
<td>-CH\textsubscript{3}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>\text{Keq, l.mol}\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>263</td>
<td>3.8</td>
</tr>
<tr>
<td>253</td>
<td>8.4</td>
</tr>
<tr>
<td>243</td>
<td>3.0 21.0</td>
</tr>
<tr>
<td>233</td>
<td>0.3 5.9 0.8 52.3 1.5</td>
</tr>
<tr>
<td>223</td>
<td>0.8 12.9 3.2 4.1</td>
</tr>
<tr>
<td>213</td>
<td>1.2 30.5 14.3 12.2</td>
</tr>
<tr>
<td>203</td>
<td>2.9 80.8 42.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Equilibrium constants determined by the integral method.
TABLE V.2

Equilibrium constants\(^a\) at various temperatures for the equilibrium

\[
\text{RhI(CO)(PEt}_3\text{)}_2 + \text{H}_2\text{MZR} \rightleftharpoons \text{RhHI(CO)(HMZR)(PEt}_3\text{)}_2
\]

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Keq, l.mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>8.6</td>
</tr>
<tr>
<td>273</td>
<td>14.7</td>
</tr>
<tr>
<td>263</td>
<td>0.5</td>
</tr>
<tr>
<td>253</td>
<td>1.2</td>
</tr>
<tr>
<td>243</td>
<td>3.1</td>
</tr>
<tr>
<td>233</td>
<td>8.1</td>
</tr>
</tbody>
</table>

\(^a\) Equilibrium constants determined by the \(^1\)\(^J\)\(_{P-Rh}\).
for the adducts at low temperature should result from the stability to dissociation of the Rh(III) adduct at this temperature while the reactants are unstable. A reverse situation was observed at higher temperatures.

By using equation 6 and considering from the tables that $T_n > T_1$ and $K_1 > K_n$, reactions can be deduced to be exothermic ($\Delta H^0_{\text{t}_1 \rightarrow \text{t}_n} < 0$) indicating that the formation of the adducts is favoured with a greater $K_{eq}$ at the lower temperature.

\[
2.303 \log_{10} \frac{K_n}{K_1} = -\frac{\Delta H^0_{\text{t}_1 \rightarrow \text{t}_n}}{R} (\frac{1}{T_n} - \frac{1}{T_1})
\]  

(6)

Plots of $\log_{10} K_{eq}$ against $T^{-1}$ yielded straight lines with gradients of $-\Delta H^0_{\text{t}_1 \rightarrow \text{t}_n}/2.303$ R, evidencing that $\Delta H^0_{\text{t}_1 \rightarrow \text{t}_n}$ was constant over the temperature range concerned; two of these graphs are represented in Figures V.1 and V.2 and they are characteristic of the other reactions. From this information the thermodynamic data for the systems studied here (equation 1) were calculated and are presented in Table V.3; $\Delta H^0_{\text{t}_1 \rightarrow \text{t}_n}$ and $\Delta S^0_{\text{t}_1 \rightarrow \text{t}_n}$ at different temperature intervals and $\Delta G^0_{t}$ at 233 and 263 K for the chloride and iodide systems respectively.

The high value of $K_{eq_{233}}$ for the GeH₄ system reflects that, of the chloride adducts, RhH(H₃Ge)(CO)Cl(PEt₃)₂ was the most stable to dissociation at that temperature and stability of the GeH₄ complex when compared with the other adducts may be explicable on the basis of steric factors arguments; the importance of such a factor in reduction elimination reactions is well known for iridium(III)⁵⁷,⁵⁸,⁵⁹ and rhodium(III)³⁴,³⁷,³⁸,⁶⁰ complexes. Differences were not so sharp for the iodide systems; for these
Figure V.1  Graph of $\log_{10} K_{eq}$ versus $1/T$ from 198 to 248 K for the system:

$$\text{RhCl} \text{(CO)} \text{P}_2 + (\text{CH}_3) \text{SiH}_2 \text{Cl} \neq \text{PhHCl} \text{(CO)} (\text{CH}_3 \text{SiHCl}) (\text{PET}_3)_2$$
Figure V.2  Graph of $\log_{10} K_{eq}$ versus $1/T$ from 233 to 273 K for the system:

$$\text{RhI(CO)(PET}_3)_2 + H_3\text{Si-CH}_2\text{-CH=CH}_2 \rightleftharpoons \text{RhI(CO)(H}_2\text{Si-CH}_2\text{-CH=CH}_2\text{)(PET}_3)_2}$$
TABLE V.3

Equilibrium and thermochemical data in deuterated toluene for the reversible equilibrium.

\[
\text{RhY(CO)(PET}_3)_2 + \text{H}_2\text{MRZ} \rightleftharpoons \text{RhHY(CO)(HMRZ)(PET}_3)_2
\]

<table>
<thead>
<tr>
<th>No</th>
<th>Y</th>
<th>M</th>
<th>Z</th>
<th>R</th>
<th>(\Delta H^o_{t_1 \rightarrow t_n})</th>
<th>(\Delta S^o_{t_1 \rightarrow t_n})</th>
<th>(K_{eq_t})</th>
<th>(\Delta G^o_{t})</th>
</tr>
</thead>
<tbody>
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<td>-139</td>
<td>0.3</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>Si</td>
<td>Cl</td>
<td>-CH(_3)</td>
<td>-34(1)</td>
<td>-132</td>
<td>5.9</td>
<td>-3.4</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>Si</td>
<td>H</td>
<td>-CH(_2)-CH=CH(_2)</td>
<td>-60(1)</td>
<td>-259</td>
<td>0.8</td>
<td>0.4</td>
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<tr>
<td>4</td>
<td>Cl</td>
<td>Ge</td>
<td>H</td>
<td>H</td>
<td>-45(1)</td>
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<td>-7.7</td>
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<tr>
<td>5</td>
<td>Cl</td>
<td>Ge</td>
<td>H</td>
<td>-CH(_3)</td>
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</tr>
<tr>
<td>6</td>
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<td>Si</td>
<td>H</td>
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<td>-184</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>7</td>
<td>I</td>
<td>Si</td>
<td>I</td>
<td>-CH(_3)</td>
<td>-55(2)</td>
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<td>-8.2</td>
</tr>
<tr>
<td>8</td>
<td>I</td>
<td>Si</td>
<td>H</td>
<td>-CH(_2)-CH=CH(_2)</td>
<td>-66(2)</td>
<td>-232</td>
<td>10.0</td>
<td>-4.6</td>
</tr>
<tr>
<td>9</td>
<td>I</td>
<td>Ge</td>
<td>H</td>
<td>-CH(_3)</td>
<td>-61(2)</td>
<td>-204</td>
<td>24.2</td>
<td>-7.6</td>
</tr>
</tbody>
</table>

a. \(t_1 \rightarrow t_n = 203-243\) K for systems no. 1, 2, 3 and 5.
\(t_1 \rightarrow t_n = 233-273\) K for systems no. 4, 6, 7, 8 and 9.

b. \(t = 233\) K for \(Y = \text{Cl}\); \(t = 263\) K for \(Y = \text{I}\).

Units:

\(\Delta H^o_{t_1 \rightarrow t_n} = \text{kJ mol}^{-1}\)

\(\Delta S^o_{t_1 \rightarrow t_n} = \text{J.K}^{-1}.\text{mol}^{-1}\)

\(\Delta G^o_{t} = \text{kJ.mol}^{-1}\)

\(K_{eq_t} = \text{mol}^{-1}\)
RhH(HSiICH₃)(CO)I(PÉt₃)₂ seemed to be the most stable of the adducts at 263 K.

As expected the enthalpy changes of the Rh(III) ≠ Rh(I) dissociation are exothermic. The entropy changes are small and negative, and should reflect the reduction of the number of molecules in the system as the temperature is decreased and the Rh(III) adduct is formed. The individual differences in these values could, to some extent, be related to the corresponding differences in the structures. For example, the entropy changes for the reactions of RhI(CO)(PÉt₃)₂ and RhCl(CO)(PÉt₃)₂ with H₃Si-CH₂=CHCH₂ are more negative than those of the other adducts, and it can be concluded that these allylsilane complexes should be more constrained than the other adducts, i.e. the allylsilane products are more crowded and the internal rotational motion of the adducts are slower.

V.4 Discussion

Several new Group IV-B Rh(III) derivatives of the type RhHY(CO)(HMZR)(PÉt₃)₂ have been obtained by the oxidative addition reaction of H₂MZR with the rhodium(I) complex RhY(CO)(PÉt₃)₂; but in no case could the complexes be isolated.

The variable temperature n.m.r. study of the 1:1 molar reactions showed that in these cases the Group IV-B complexes are unstable to dissociation (i.e. reductive elimination of the Group IV-B compound). The same results were obtained when an excess of the Group IV-B compound was used; hence it can not be suggested
that this process was inhibited by a deficiency of the \( \text{H}_2\text{MZR} \) compound. Also, change of the halide coordinated to the rhodium had no effect on the stability.

It is noteworthy that the similar silyliridium(III) adducts obtained from IrY(CO)(PEt\(_3\))\(_2\) and H\(_3\)SiR (R = -CH\(_3\), -CH=CH\(_2\) or -CH\(_3\)-CH=CH\(_2\)) showed no tendency to lose silane on warming the reaction solution. Therefore, comparison of the stability of these Rh(III) and Ir(III) complexes seems to reflect:

- the greater tendency of iridium(I) relative to rhodium(I) to undergo oxidative addition; and

- that the instability at room temperature of such Rh(III) adducts may be a result of a lower Rh Group IV-B bond strength.

The ease with which the Group IV-B Rh(III) adducts reductively eliminate the Group IV-B compound to form RhY(CO)(PEt\(_3\))\(_2\) is related markedly to the groups bound to the Group IV-B atom, as six-coordinate derivatives of this type could be isolated only when the Group IV-B atom bore electron-withdrawing substituents such as Cl or I; presumably by forming the most stable rhodium Group IV-B bond\(^{24,38}\).

It seems from the results obtained that the stability of the complexes RhH(CO)\(Y(\text{HMRZ})(\text{PEt}_3)_2\) to dissociation increases as the groups on M become more electronegative, in the order:

\[
\text{MH}_3R \approx \text{SiH}_2\text{RX} < \text{MH}_4 << \text{MH}_3\text{X}
\]

Nevertheless, steric effects arising from the bulky organic groups
attached to M should have also an effect and they should not be ruled out; six-coordinate compounds of the type RhHY(CO)(HMZR)(PEt₃)₂ (R = -CH₃, -CH₂-CH=CH₂) would undoubtedly be more crowded than would RhHY(CO)(H₂MX)(PEt₃)₂ (X = Cl, I), but the effect should not be dominant as there is no apparent correlation with the position of equilibrium for the MH₄ system. The difference in stability of the MH₄ and MH₃X adducts probably reflects electronic instead of steric effects as the MH₃X groups should be larger than MH₄, but the X element induce more electronegativity to the group than H giving the obtained results. The rhodium(III) Group IV-B bond may be strengthened by electron-withdrawing substituents on the Group IV-B atom as a consequence of enhanced rhodium Group IV-B dπ-π back-bonding.

Therefore, this reductive elimination or oxidative addition reaction seems to be influenced by a combination of steric and electronic factors, which are not readily separated and appears to cause the elimination of MH₄ and H₂MRZ from the coordination sphere of rhodium(III).

The comparison and evaluation of the enthalpy changes is a complicated task since this energy term is related to several others and these are mostly of unknown magnitudes.

Factors to be considered in the formation of the Rh(III) adducts include the energies of the formation of the M-Rh and Rh-H bonds and the dissociation energy of the M-H bond:

\[ \Delta H^\circ_T = E(M-Rh) + E(Rh-H) - E(M-H). \]
Except for $E(M-H)$, the values of the other terms are not at present available (i.e. readily calculable), and the important question of the relation of the enthalpy change to the Rh-H and Rh-M bonds energy can not be directly answered. Nevertheless, a comparison of the difference in the overall values of $\Delta H^0_{t_1 \rightarrow t_n}$ can be done. For instance: $\Delta H^0_{t_1 \rightarrow t_n}$ for $H_3SiCH_3$ and $H_3GeCH_3$ adducts are similar; knowing that $E(M-H)$ is different for $M = Si$ and $M = Ge$, and assuming that Rh-H is affected to the same extent in these complexes, it seems likely that the Si-Rh and Ge-Rh bonds are of comparable energy. Analogously, for the adducts of $H_3SiCH_3$ and $H_2ClSiCH_3$ the $\Delta H^0$ values are very similar and it appears that the change of H for Cl bound to Si affects to about the same extent the factors involved in $\Delta H^0$. On the contrary, changing $CH_3^-$ for $CH_2=CH-CH_2^-$ bound to Si makes $\Delta H^0_{t_1 \rightarrow t_n}$ more negative by about 30 kJ mol$^{-1}$, therefore the allyl group either weakens the Si-H bond or strengthens the Si-Rh bond, for its effect on the Rh-H bond will be remote.
REFERENCES


41. W. Hieber and F. Lentent, Naturwissenschaften, 19, 360 (1931).


LIST OF COURSES ATTENDED

Multiple Resonance N.M.R. Spectroscopy
  Dr. W. McFarlane

Aspects of Inorganic Chemistry
  Dr. G. Heath

Mass Spectrometry
  Professor J.H. Beynon

Industrial Inorganic Chemistry
  Dr. H.L. Roberts (ICI)

University of Strathclyde Inorganic Club Conferences
  (3 years)

Departmental and Group Seminars