This thesis describes preparative and structural work on some silyl and germyl derivatives of iridium(III). The introduction is a review of two aspects of silicon and germanium transition metal chemistry. Initially silicon and germanium hydride compounds are considered, then, after the general chemistry of the iridium complexes, \( \text{Ir(CO)}_2\text{(Ph}_3\text{)}_2 \) and \( \text{IrH(CO)}_3\text{(Ph}_3\text{)}_2 \) has been discussed, iridium derivatives of organosilanes and organogermylates are considered. There is also a discussion of oxidative addition reactions.

The reactions of the silyl and germyl compounds \( \text{MH}_X \text{(4-)}_n \text{(M=Si,Ge; X=H,Cl, Br,I)} \) with \( \text{Ir(CO)}_2\text{(Ph}_3\text{)}_2 \) and with \( \text{IrH(CO)}_3\text{(Ph}_3\text{)}_2 \) are discussed separately. The reaction of \( \text{Ir(CO)}_2\text{(Ph}_3\text{)}_2 \) with \( \text{SiH}_2\text{X} \) and \( \text{GeH}_2\text{X} \) in benzene gives an insoluble as initial product. This product has been identified as \( \text{H.Ir(CO)}_2\text{(Ph}_3\text{)}_2\text{MH}_2\text{X} \); the reaction is slow unless an initial excess of silyl halide is taken. The initial products from the reaction of \( \text{GeH}_2\text{X} \) with \( \text{Ir(CO)}_2\text{(Ph}_3\text{)}_2 \) in benzene are soluble species which are shown to be the equimolar addition \( \text{H.Ir(CO)}_2\text{(Ph}_3\text{)}_2\text{GeH}_2\text{X} \). Precipitation occurs after a few minutes. In some cases there is evidence for the formation of more than one isomer; various ways in which such isomerisation may arise are considered. The nature of the reaction products is shown to be highly dependent on the reaction time, concentration of reactants, reaction conditions and the nature of \( X \) in \( \text{MH}_X \). The long-term reaction between excess \( \text{SiH}_2\text{Cl} \) and \( \text{Ir(CO)}_2\text{(Ph}_3\text{)}_2 \) produces a soluble species, \( \text{IrH}_2\text{(CO)}_2\text{(Ph}_3\text{)}_2\text{SiH}_2\text{Cl} \).

Some soluble silyl and germyl iridium compounds \( \text{IrH}_2\text{(CO)}_2\text{(Ph}_3\text{)}_2\text{MH}_X \) (\( M=\text{Si,Ge; X=H,Cl,Br,I} \)) have been prepared by the reaction of the silyl and germyl species \( \text{MH}_X \) with \( \text{IrH(CO)}_3\text{(Ph}_3\text{)}_2 \). The structure of the products formed depends on \( M \); the addition of \( \text{SiH}_2\text{X} \) results in the formation of dihydride complexes with cis phosphines whereas the addition of \( \text{GeH}_2\text{X} \) gives dihydride complexes having trans phosphines. Reasons for the difference in structure of these complexes are considered. The germyl species, \( \text{IrH}_2\text{(CO)}_2\text{(Ph}_3\text{)}_2\text{GeH}_2\text{X} \), are the first known products from the reaction of a germane with \( \text{IrH(CO)}_3\text{(Ph}_3\text{)}_2 \).

The proton n.m.r. and vibrational spectra of all the silyl and germyl iridium compounds are discussed. Particular reference is made to the use of the 220MHz n.m.r. spectrometer in the analysis of the n.m.r. spectra. Two mechanisms, for the preparative reactions, one for the reaction of \( \text{MH}_2\text{X} \) with Vaska’s compound and the other for the reaction of \( \text{MH}_3\text{X} \) with \( \text{IrH(CO)}_3\text{(Ph}_3\text{)}_2 \) are postulated. The former involves oxidative addition of \( M=\text{H} \) to the square planar
complex, the latter involves prior dissociation of the 5 co-ordinate iridium species to a four co-ordinate complex and subsequent oxidative addition of M-H.

Digermane, disilane, trisilane and trimethylsilylsilane when treated with Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ form digermanyl, disilanyl and trisilanyl species. Addition is in the sense M and H; there is no severance of the H-H bond. Substitution of chlorine at silicon occurs during the reaction of SiHH₃ with Vaska’s compound. Silyl and germycyclopentadiene derivatives of iridium have also been prepared by the reaction of IrH(CO)(PPh₃)₃ with NH₂C₂H₅. The nature of these species has been compared and contrasted with that of analogous platinum species.

The analysis in the gas phase, by electron diffraction, of the molecular structure of nitrosyl-tris(trifluorophosphine) rhodium is described in an Appendix.
SOME SILYL AND GERMYL COMPLEXES OF IRIDIUM (III)

by

Diana Mary Bridges

A Thesis presented for the degree of
Doctor of Philosophy

University of Edinburgh

July 1972
TO MY PARENTS
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SUMMARY

This thesis describes preparative and structural work on some silyl and germyl derivatives of iridium(III).

The introduction is a review of two aspects of silicon and germanium transition metal chemistry. Initially silicon and germanium hydride compounds are considered; then, after the general chemistry of the iridium complexes, Ir(CO)Cl(PPh₃)₂ and IrH(CC)(PPh₃)₃ has been discussed, iridium derivatives of organosilanes and organogermaines are considered. There is also a discussion of oxidative addition reactions.

The reactions of the silyl and germyl compounds MHₓXₙ₋₄ (M=Si,Ge; x=H,Cl,Br,I) with Ir(CO)Cl(PPh₃)₂ and with IrH(CC)(PPh₃)₃ are discussed separately. The reaction of Ir(CO)Cl(PPh₃)₂ with SiHₓX and GeH₄ in benzene gives an insoluble species as initial product. This product has been identified as H.Ir(C(:)Cl(rPhMHₓ; the reaction is slow unless an excess of silyl halide is initially taken. The initial products from the reaction of GeH₃X with Ir(CO)Cl(PPh₃)₂ in benzene are soluble species which are shown to be the equimolar adducts H.Ir(C(:)Cl(PPh₃)₂GeHₓX. Precipitation occurs after a few minutes. In some cases there is evidence for the formation of more than one isomer; various ways in which such isomerisation may arise are considered. The nature of the reaction products is shown to be highly dependent on the reaction time, concentration of reactants, reaction conditions and the nature of X in MHₓX. The long-term reaction between excess
SiH$_3$Cl and Ir(CO)Cl(PPh$_3$)$_2$ produces a soluble species, IrH$_2$(CO)(PPh$_3$)$_2$SiH$_2$Cl.

Some soluble silyl and germyl iridium compounds Ir$_2$(CO)(PPh$_3$)$_2$MH$_2$X (M=Si,Ge; X=H,Cl,Br,I) have been prepared by the reaction of the silyl and germyl species MH$_3$X with IrH(CO)(PPh$_3$)$_3$. The structure of the products formed depends on M; the addition of SiH$_3$X results in the formation of dihydride complexes with cis phosphines whereas the addition of GeH$_3$X gives dihydride complexes having trans phosphines. Reasons for the difference in structure of these complexes are considered. The germyl species, Ir$_2$(CO)(PPh$_3$)$_2$GeH$_2$X, are the first known products from the reaction of a germane with IrH(CO)(PPh$_3$)$_3$.

The proton n.m.r. and vibrational spectra of all the silyl and germyl iridium compounds are discussed. Particular reference is made to the use of the 220MHz n.m.r. spectrometer in the analysis of the n.m.r. spectra. Two mechanisms, for the preparative reactions, one for the reaction of MH$_3$X with Vaska's compound and the other for the reaction of MH$_3$X with IrH(CO)(PPh$_3$)$_3$ are postulated. The former involves oxidative addition of M-H to the square planar complex, the latter involves prior dissociation of the 5 co-ordinate iridium species to a 4 co-ordinate complex and subsequent oxidative addition of M-H.

Digermane, disilane, trisilane and trimethysilane when treated with Ir(CO)Cl(PPh$_3$)$_2$ and IrH(CO)(PPh$_3$)$_3$ form digermanyl, disilanyl and tridilanyl species. Addition is in the sense M and H; there is no severance of the M-M bond. Substitution of
chlorine at silicon occurs during the reaction of $\text{Si}_2\text{H}_8$ with Vaska's compound. Silyl and germylcyclopentadiene derivatives of iridium have also been prepared by the reaction of $\text{IrH(CO)(PPh}_3)_3$ with $\text{MH}_2\text{C}_5\text{H}_5$. The nature of these species has been compared and contrasted with analogous platinum species.

The analysis in the gas phase, by electron diffraction, of the molecular structure of nitrosyl-tris(trifluorophosphine) rhodium is described in an Appendix.
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INTRODUCTION

There has been much interest in the last few years in the preparation and reactions of organometallic compounds in general and this has been one of the most widely expanding fields of chemistry recently. The reactions of transition metal compounds with many different systems have been studied in connection with homogeneous catalysis, and included in this study has been reactions with compounds derived from the Group IVB elements, namely silicon, germanium, tin and lead. The complexes resulting from these reactions are interesting because of their possible relevance to hydrosilation and hydrogermanation of olefins. Indeed, olefin complexes of platinum (11) and rhodium (1)\textsuperscript{7} and dicobalt octacarbonyl\textsuperscript{9,10} have been shown to be good hydrosilation catalysts and the addition of alkyl germanes to olefins is catalysed homogeneously by chloroplatinic acid.

The work in this thesis deals with the preparation and properties of silicon and germanium hydride derivatives of iridium, and the introduction presents a brief review of the relevant chemistry in the field. This review is divided into several sections each dealing with a distinct topic of relevance to the overall theme of iridium - Group IVB chemistry. In the section concerned with compounds of Group IVB elements most emphasis will be laid on the reactions of silicon and germanium
rather than tin or lead.

1.1. General introduction to the reactions of Group IV B compounds with transition metal complexes.

The compounds of silicon and germanium whose reactions with derivatives of transition metals have been most thoroughly studied are of the form $R_3MH$ ($M = Si$ or Ge; $R =$ halogen, alkyl, alkoxy or aryl). The first transition metal-silicon complex TiC$_5$H$_5$(CO)$_2$Fe(SiMe$_3$) was prepared by Piper and associates in 1951. Since then, silicon derivatives have been prepared for nearly every transition metal, and several general methods have been formulated for the synthesis of transition metal-silicon bonds. However the best method for a given compound depends more on the particular transition metal concerned than on any other factor.

Cleavage of metal-metal bonds in compounds such as bi- or tri-nuclear carbonyls by reaction with a tri-organo- or trihalogeno-silan•e is one widely-used method. The compounds Cl$_3$SiRe(CO)$_5$ Cl$_3$SiNi(CO)C$_5$H$_5$ and Me$_3$SiRu$_2$(CO)$_8$SiMe$_3$ have been prepared in this way:

$$\text{Cl}_3\text{SiH} + \text{Re}_2(\text{CC})_{10} \rightarrow \text{Cl}_3\text{SiRe}(\text{CO})_5 + \text{Re}(\text{CO})_5$$

$$\text{Cl}_3\text{SiH} + [\text{C}_5\text{H}_5(\text{CO})\text{Ni}]_2 \rightarrow \text{Cl}_3\text{SiNi}(\text{CO})\text{C}_5\text{H}_5 + \text{Ni}(\text{CO})\text{C}_5\text{H}_5$$

$$\text{R}_3\text{SiH} + \text{Ru}_3(\text{CO})_{12} \rightarrow \text{Me}_3\text{Si} - \text{Ru} - \text{Ru} - \text{SiMe}_3$$

Cleavage of a metal-halogen bond to form a metal-silicon bond has been achieved in various ways and some unusual silicon
complexes of the earlier transition metals have been prepared thus. A complex of zirconium was prepared by Lappert and associates and some platinum complexes were prepared by Glockling and his co-workers.  

\[ (\text{THF}) (\text{Me}_3\text{Si})_2\text{ZrCl}_2 + \text{Ph}_3\text{SiLi} \rightarrow (\text{THF}) (\text{Me}_3\text{Si})_2\text{ZrSiPh}_3 + \text{LiCl} \]

\[ \text{trans} (\text{Et}_3\text{P})_2\text{PtCl}_2 + (\text{Me}_3\text{Si})_2\text{Hg} \rightarrow (\text{Et}_3\text{P})_2\text{PtClSiMe}_3 + \text{SiMe}_3\text{Cl} + \text{Hg} \]

Reaction of certain transition metal hydrides with silicon compounds resulting in the elimination of a small molecule (usually \( \text{H}_2 \)) has also proved a useful method and complexes of molybdenum, tungsten, cobalt and platinum have been prepared in this way.  

\[ \text{M=W, Mo} \]

\[ \Pi \text{C}_5\text{H}_5(\text{Co})_2\text{H} + \text{Me}_3\text{Si-NMe}_2 \rightarrow \Pi \text{C}_5\text{H}_5(\text{Co})_2\text{N-SiMe}_3 + \text{Me}_2\text{NH} \]

\[ \text{R}_3\text{SiH} + (\text{PR}_3)_3\text{Co(N}_2\text{)}\text{H} \rightarrow (\text{PR}_3)_3\text{CoH}_2(\text{SiR}_3) + \text{N}_2 \]

\[ \text{R}_3\text{NH} + \text{PtCl}_2 \rightarrow \text{R}_3\text{M-PtCl} + \text{H}_2 \]

\[ \Pi\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_3 \]

was prepared using the general reaction of a transition metal union with a silicon halide:

\[ \Pi\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na} + \text{SiMe}_3\text{Cl} \rightarrow \Pi\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_3 + \text{NaCl} \]

This method has also been used to prepare iron complexes containing Si-Si bonded ligands.

The final general method, which has been used extensively in the preparation of silicon compounds of the Group VIII triad cobalt, rhodium and iridium is that of oxidative addition of the
silicon compound to a transition metal complex in a low oxidation state, normally for Rhodium and Iridium the (1) state.

\[ (\text{PPh}_3)_3\text{Rh} \text{I} \text{Cl} + \text{excess SiHCl}_3 \rightarrow (\text{PPh}_3)_2\text{Rh} \text{II} \text{I} \text{Cl} \cdot \text{SiR}_3 + \text{PPh}_3 \]

There is an increase in oxidation state and co-ordination number during the reaction.

A novel reaction whose postulated mechanism involves oxidative addition is that of Fe(CO)\(_5\), CrC\(_6\)H\(_6\)(CO)\(_3\) or MnC\(_5\)H\(_5\) (CO)\(_4\) with HSiCl\(_3\) under photochemical conditions. The products are thought to arise from oxidative addition of SiHCl\(_3\) to intermediates formed by elimination of a carbonyl group from the starting materials.

\[ \text{Fe(CO)}_5 \xrightarrow{\text{hv}} \text{Fe(CO)}_4 \xrightarrow{\text{HSiCl}_3} \text{Fe(CO)}_4\text{SiCl}_3 \]

\[ \text{CrC}_6\text{H}_6\text{(CO)}_3 \xrightarrow{\text{hv}} \text{Cr} \text{C}_6\text{H}_6\text{(CO)}_2 \xrightarrow{\text{HSiCl}_3} \text{Cr} \text{C}_6\text{H}_6\text{H(CO)}_2\text{SiCl}_3 \]

These methods are also applicable to the formation of transition metal complexes of germanium and a range of germanium compounds as extensive as that of the silicon analogues has been prepared. Generally the metal-metal bonds are of quite high thermodynamic stability but their chemical reactivity varies enormously. As with \(\sigma\)-bonded transition metal carbon complexes, it seems that the heavier transition metals form the more stable complexes (Au \(\gg\) Ag \(\gg\) Cu, Fe \(\gg\) Fe\(^{23,24}\)) and the complexes \(\text{II}\text{C}_5\text{H}_5\) (CO)\(_3\)MM\(^1\)R\(_5\)H(M=Cr, Mo, W; M\(^1\)=Si, Ge; R=Me, Ph) certainly show this increase in stability from Cr\(\rightarrow\)W\(^{25}\).

In almost all of the stable compounds reported, the
transition metal is in a low formal oxidation state. Coordination number, charge on the complex and the effect of \( \Pi \) bonding ligands attached to the transition metal all seem to affect the stability and reactivity of the transition metal-Group IV B complexes. For the series Si, Ge, Sn and Pb there is some indication that the maximum stability occurs with Ge and Sn but instability and reactivity can easily be confused. For example \( \text{Ph}_3\text{P} \text{AuSi(Ph)}_3 \) and \( (\text{Et}_3\text{P})_2\text{Pt(II)Si(Ph)}_3 \) are air and light sensitive whereas the germyl analogues are not.

There have been a few reports of reactions occurring between certain transition metal complexes and the parent hydride systems \( \text{MH}_3\text{X} (\text{M}=\text{Si, Ge}; \text{X}= \) halogen or \( \text{H} \) ) and these have in fact used some of the general preparative methods outlined above.

The first such reaction was reported\(^{26}\) by Aylett in 1965 who prepared an air-sensitive, pale yellow liquid by treating \( \text{NaCo(CO)}_4 \) with \( \text{SiH}_3\text{I} \); the product was shown to be \( \text{SiH}_3\text{Co(CO)}_4 \). An electron diffraction determination of the molecular structure in the gas phase indicated a trigonal bipyramid structure with \( C_3v \) symmetry.\(^{27}\) The liquid disproportionated slowly at room temperature to \( \text{SiH}_4 \) and \( \text{SiH}_2[\text{Co(CO)}_4]_2 \) although the vapour was stable at this temperature. A similar reaction has been used to prepare silylene-bis(tetracarbonyl cobalt):\(^{28}\)

\[
\text{SiH}_4-x \text{I}_x + \text{NaCo(CO)}_4 \xrightarrow{230^\circ C} \text{SiH}_4-x[\text{Co(CO)}_4]_x + x \text{NaI}.
\]

Cleavage of the Si-Co bond was found to be effected...
relatively easily by reaction with a number of different compounds including HF, HCl, H2O and HgX2. The hydrogen halides form HCo(CO)5 and the corresponding silyl halide; water forms solid (SiO2)x polymers; mercuric halides react rapidly and completely to form silyl halides and Hg(Co(CO)4)2. Tri-phenyl phosphine slowly replaced CO to give a compound which was probably trans SiH3Co(CO)3PPh3. Air reacted slowly at reduced pressure with SiH3Co(CO)4 to give (SiH3)2O and HCo(CO)4 as products. In general the complex could be said to possess many of the reactions common to silicon hydride compounds. Silyl chloride or iodide form adducts with tertiary amines and SiH3Co(CO)4 was observed to react in the same way. The infrared spectra of the products indicated that they are probably ionic and of the form [H3Si2B]+[Co(CO)4]⁻ where B is NMe3 or pyridine.

Subsequently, SiH3Mn(CO)5, a colourless, volatile solid melting at 250°C was prepared using a method similar to that for the cobalt complex:

$$\text{SiH}_3\text{I} + \text{NaMn(CO)}_5 \xrightarrow{250\degree\text{ether}} \text{SiH}_3\text{Mn(CO)}_5 + \text{NaI}$$

The product was found to be more thermally stable than the cobalt complex and the cleavage of the Si-Mn bond was effected less readily by the same reactants. Water only reacted slowly to produce disiloxane and HMn(CC)5 and the other reagents gave no reaction under normal conditions. When the liquid compound was heated with HCl an unusual reaction involving
chlorination at the silicon atom occurred:

\[
\text{SiH}_3\text{Mn(CO)}_5 + x\text{HCl} \rightarrow \text{SiH}_{3-x}\text{Cl}_x\text{Mn(CO)}_5 + x\text{H}_2
\]

Normally a Lewis acid is needed as catalyst for halogenation of a silyl compound by HCl. As with the cobalt complex, adducts were formed with tertiary amines and these reacted rapidly with HCl even at low temperatures giving support to the ionic structures which had been postulated for them.

\[
\text{SiH}_3\text{Mn(CO)}_5 + 3\text{HCl} \rightarrow \text{SiH}_3\text{Cl} + \text{H}_2\text{Mn(CO)}_5 + 2\text{pyHCl}
\]

To complete the study of the reactions of SiH\textsubscript{3}X with the transition metal series Mn, Fe and Co the compound (SiH\textsubscript{3})\textsubscript{2}Fe(CO)\textsubscript{4} was prepared using an analogous method:-

\[
\text{SiH}_3\text{I} + \text{Na}_2\text{Fe(CO)}_4 \rightarrow (\text{SiH}_3)_2\text{Fe(CO)}_4 + 2\text{NaI}
\]

The main product was a white solid readily sublimable at room temperature. Its reactions were similar to those of the manganese and cobalt complexes but it was intermediate in reactivity; hydrolysis was reasonably fast to give (SiH\textsubscript{3})\textsubscript{2}O and H\textsubscript{2}Fe(CO)\textsubscript{4} and it reacted violently with air at atmospheric pressure. HCl reacted slowly at room temperature giving 90% cleavage of the Si-Fe bonds. Reaction with tertiary bases gave a 1:2 adduct which had an ionic structure: \(((\text{SiH}_3\text{B})_2)_2^+[\text{Fe(CO)}_4]^2^-

Russo and Hagen have prepared in 25% yield, again by the reaction of the corresponding unions and a silyl halide the silyl derivatives of Mo and Cr. Mo(CO)\textsubscript{3}(C\textsubscript{5}H\textsubscript{5})SiH\textsubscript{3} and
Cr(CO)$_3$(C$_5$H$_5$)SiH$_3$ were prepared from the potassium salts and SiH$_2$Br:

$$\text{K}[\text{M(CO)}_3(\text{C}_5\text{H}_5)] + \text{SiH}_2\text{Br} \rightarrow \text{M(CO)}_3(\text{C}_5\text{H}_5)\text{SiH}_3 + \text{KBr}$$

These compounds gave a characteristic Si-H stretch in the I.R. spectrum at 2125 cm$^{-1}$. Both solids were readily sublimable and were instantly oxidized by air. The molybdenum compound could be stored at room temperature for a long time but the chromium one decomposed to a green solid after 48 hours. HCl attacked the Si-M bond producing SiH$_3$Cl and HM(CO)$_3$(C$_5$H$_5$).

Bentham$^{36, 37}$ has shown that compounds of the form XPt(PEt$_3$)$_2$SiH$_3$-nY$_n$ (x=Cl, Br, I; Y=Cl, Br, I; n=1-3) containing silyl ligands co-ordinated to platinum or palladium can be prepared. These differed from the previously described complexes in not containing carbonyl ligands. Many platinum species were prepared; the methods of preparation were fairly standard for such systems, involving the reaction of a platinum (II) hydride or dihalide species with SiH$_3$X to form a four co-ordinate platinum(II) silyl species:

$$\text{trans Pt(PEt}_3)_2\text{HY} + \text{SiH}_3\text{X} \rightarrow \text{Pt(PEt}_3)_2\text{Y.SiH}_2\text{X + H}_2$$

Similarly, trans ClPd (PEt$_3$)$_2$ SiH$_{3-x}$Cl$_x$ (x=1 or 2) has been formed by the treatment of trans ClPd(PEt$_3$)$_2$ Cl with SiH$_3$Cl.

These compounds were identified by analysis, I.R., Raman
and n.m.r. spectroscopy. When X differed from Y, halogen exchange occurred leading to a product with the heavier halogen on platinum. This exchange is energetically favourable and is supported by evidence from bond energies of $M-X$ in $MX_4^{38}$ ($M=Si, Ge; \ X=Cl, Br, I$) where the lighter halogen atom is favourably attached to $M$:

<table>
<thead>
<tr>
<th>$MX_4$</th>
<th>$E(M-Cl)$</th>
<th>$E(M-Br)$</th>
<th>$E(M-I)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>97.2</td>
<td>75.6</td>
<td>56</td>
</tr>
<tr>
<td>Ge</td>
<td>81</td>
<td>66</td>
<td>51</td>
</tr>
</tbody>
</table>

$E$ values in kcal/mole.

fig. 1.

Although there is no absolute bond energy data for $Pt-X$ bonds stability constant values $^{39}$ and other data $^{40}$ indicate that the order is $E(Pt-I) > E(Pt-Br) > E(Pt-Cl)$.

The mechanism which was postulated was that of oxidative addition followed by elimination.

Although it is likely that all the reactions proceed via these six co-ordinate species $^{41}$ they have only in fact been isolated and identified for the most stable case when $Y = I$.

The four co-ordinate compounds were found to be relatively
stable as solids and could be isolated and handled under vacuum or an atmosphere of nitrogen, but were unstable over long periods in solution. They were sensitive to moisture, producing $\text{H}_2\text{SiO}_2$ and $\text{Si}_2\text{Pt}(\text{PEt}_3)_2\text{H}_2$, but only decomposed slowly in dry air. This behaviour in air contrasted sharply with that of the compounds of Mn, Fe and Co $^{28,32,34}$ and since all compounds containing silicon-hydride groups are thermodynamically unstable with respect to oxidation then kinetic factors must be involved. Their reactions could be divided into two groups: those involving the silyl group (and the Pt-Si bond) and those involving the other ligands in the complex. HCl gas gave further reaction with a solution of the complex presumably via an addition/elimination process until full chlorination of the silyl ligand was obtained:

$$\text{ClPt(PEt}_3)_2\text{SiH}_2\text{Cl} + \text{HCl} \rightarrow \text{ClPt(PEt}_3)_2\text{SiHCl}_2 + \text{H}_2$$

Liquid HCl permanently cleaved the Pt-Si bond giving $\text{SiHCl}_3$ and $\text{Cl}_2\text{Pt(PEt}_3)_2$ and a little trans $\text{ClPt(PEt}_3)_2\text{SiCl}_3$. MeOH cleaved this bond, giving a mixture of products including silane and methoxychlorosilanes as volatiles and a platinum compound, possible $\text{ClPt(PEt}_3)_2\text{SiHCl(OMe)}$. The nature of these products indicated that a complex reaction was occurring probably involving attack by methanol at the Si-Cl bond liberating HCl, which would then react further as discussed above.
Reaction of MeOH in the presence of Me3N produced the simple platinum methoxysilyl compound trans Cl(PEt3)2PtSiH2(OMe) since the HCl would be removed as the trimethylammonium salt:

\[ \text{Me}_3\text{N} + \text{transCl(PEt}_3\text{)}_2\text{PtSiH}_2\text{Cl} + \text{MeOH} \rightarrow \text{Me}_3\text{NH}^+\text{Cl}^- + \text{transCl(PEt}_3\text{)}_2\text{PtSiH}_2(\text{OMe}) \]

Addition of triethylphosphine to the complex caused collapse of \( J(\text{H}-\text{Si}-\text{Pt}-\text{P}) \) and simplification of the resonances due to the ethyl protons, indicating that an exchange of free and bound PEt3 which was fast with respect to the n.m.r. time scale was probably occurring. Phosphine exchanged very slowly with PEt3 in the complex to form an unstable, insoluble platinum-phosphine complex.

Whereas, in the compounds described in the earlier part of this section the ligand which became attached to the transition metal was SiH3, in the platinum and palladium species it was SiH2X. This difference however is probably reflected in the difference in methods of preparation since the former method produces preferentially an alkali halide salt and the latter H2.

One notable feature of the platinum silyl work was the variation in rate of reaction of the different silicon compounds; SiH4 < SiH3X ~ SiH2X2 > SiHCl3. However, this type of oxidative addition reaction is thought to be assisted by the presence of electron withdrawing groups on the silicon atom since the rate
The determining step is postulated to be electrophilic attack by Si or H on platinum and this would explain the slowness of the reaction with silane. In the case of SiHCl₃ it is possible that steric hindrance to reaction causes an increase in the activation energy of the reaction and reduces the rate of the reaction so that in fact opposing effects are occurring during the overall reaction.

So far, relatively few complexes of germanium hydrides with transition metals have been prepared, and this may reflect the fact that the compounds and starting materials are inherently less thermally stable. The bond energy $E(\text{Ge}-\text{H})$ in GeH₄ is 69.8 kcal/mole in comparison with 76.5 kcal/mole for $E(\text{Si}-\text{H})$ in SiH₄. However if formed they do appear to be less resistant to oxidation. This is in agreement with the observation that although both silicon-hydrogen and germanium-hydrogen bonds are thermodynamically unstable with respect to oxidation, in most compounds Ge-H bonds are less readily oxidized than Si-H bonds. (Oxidation of GeH₄ by O₂ occurs on heating to 150°-230°, depending on conditions, but SiH₄ can explode with O₂ even at -140°). The difference in reactivity may be because the Si-H bond is less thermodynamically stable than the Ge-H bond; furthermore the Si-O bond energy is greater than that of the Ge-O bond. [$E(\text{Si}-\text{O})$ in SiO₂ is $\sim$112 kcal/mole in comparison with 85 kcal/mole for $E(\text{Ge}-\text{O})$ in GeO₂].

\[ E(\text{Ge}-\text{H}) = 69.8 \text{ kcal/mole} \]

\[ E(\text{Si}-\text{H}) = 76.5 \text{ kcal/mole} \]
However, GeH₄ is thermodynamically unstable to O₂ at room temperature; therefore kinetic stability factors must be of importance. This resistance to oxidation is shown by the compound H₂Ge[Cr(CO)₅]₂ prepared in 1963, which is an air stable solid formed by the reaction of GeH₄ and HMn(CO)₅. 45

\[
\text{GeH}_4 + \text{HMn(CO)}_5 \xrightarrow{8 \text{ days}} H_2\text{Ge[Cr(CO)}_5)_2 + H_2
\]

It is interesting that the reaction of SiH₄ and HMn(CO)₅ to give a similar product did not occur. 45 It was postulated that the mechanism might involve the formation of GeH₂ because no H Ge[Cr(CO)₅]₃ or H₃Ge[Cr(CO)₅] was formed. The latter compound was prepared, at a later date, 46 using a reaction analogous to that for the formation of the silyl complex SiH₃Cr(CO)₅.

\[
\text{GeH}_3\text{Br} + \text{NaMn(CO)}_5 \rightarrow \text{GeH}_3\text{Mn(CO)}_5 + \text{NaBr}
\]

This volatile, colourless solid which could be distilled on a vacuum line differed from SiH₃Mn(CO)₅ in its great resistance to oxidation, remaining unchanged after contact with air for a long time.

The second germyl complex to be prepared was an iron compound which was prepared by the reduction of Cl₂Ge[Fe(CO)]₂(η₅C₅H₅)₂ with NaBH₄. 47

\[
\text{Cl}_2\text{Ge[Fe(CO)}_2(\eta_5\text{C}_5\text{H}_5)_2]_2 + \text{GeCl}_4 \rightarrow \text{Cl}_2\text{Ge[Fe(CO)}_2(\eta_5\text{C}_5\text{H}_5)_2]_2 + \text{GeCl}_4
\]

This compound, which was an air-sensitive solid soluble in chloroform, was identified by its germyl hydride stretch, v(Ge-H) at 2012 cm⁻¹.
A cobalt analogue of SiH₃Co(CO)₄ has also been reported and was prepared by the exchange reaction of GeH₃F and SiH₃Co(CO)₄. This complex, which is air-sensitive, has also been prepared using the reaction of GeH₃Br and NaCo(CO)₄.

GeH₃Br + NaCo(CO)₄ → GeH₃Co(CO)₄ + NaBr.

From the I.R. spectrum it is shown to have C₃ᵥ symmetry. It exists as a colourless, volatile liquid which becomes reddish on exposure to light although the decomposition of the complex is slow. A rhenium complex, GeH₃Re(CO)₅, is known. It is prepared using a similar method and is found to be an air stable, colourless, crystalline solid. This complex is more thermally and photochemically stable than the manganese analogue.

Using preparative techniques similar to those for his platinum and palladium silyl compounds, Benthall prepared many germyl hydride complexes of platinum XPt(PEt₃)₂GeH₃₋₉Yₙ:

e.g. XPt(PEt₃)₂H + GeH₃₋₉ -→ XPt(PEt₃)₂GeH₃₋₉ + H₂

(X=Cl, Br, I; Y=Cl, Br, I, H)

These compounds were again identified by I.R., Raman and n.m.r. spectroscopy and were of the same form as the silyl analogues. However the products seemed to be less thermally stable since they decomposed rapidly (between 15 minutes and 1 hour) in solution and were not isolable as solids at room temperature but rather gave brown tars. By careful evaporation
of the solvent at -22° a pale yellow solid was obtained in the case of the most stable product, ClPt(P₃Et)₂GeH₂Cl. Most of the products were in fact only identified by their spectroscopic properties in solution. A 6 co-ordinate platinum species I₂(P₃Et)₂Pt.H.GeH₂I was also obtained. As for the monosilane reaction the monogermane reaction with trans ClPt(P₃Et)₂H was slower than with the halogen substituted germanes, but it was much faster than the analogous reaction with silane being complete in one hour instead of one week. The product however could not be isolated and rapidly decomposed even in solution.

As well as the simpler germyl platinum species which have been described, Bentham\textsuperscript{36,51,52} prepared and identified, by the use of n.m.r. spectroscopy, several six co-ordinate tris (germyl) platinum species (fig. 3) which were prepared by the reaction of ClPt(P₃Et)₂GeH₂Cl or ClPt(P₃Et)₂H with excess GeH₃Cl. A very complex addition/elimination mechanism has been postulated to explain this occurrence.

The reactions of all these transition metal - Group IVB compounds can be divided into two broad categories: those due to the hydride groups and those depending on the nature of the silicon or germanium transition metal bond. The bonding between
a co-ordinated transition metal and a Group IVB moiety creates nothing new in the stereochemistry observed for either the transition metal or the Group IVB atom. Therefore it is only the effects causing distortions of co-ordination and the lengths of metal-metal bonds which need to be considered. Mono-substituted complexes, such as Cl₃SiCo(CO)₄, show slight deviations from regular tetrahedral co-ordination about Si. The nature of the metal-metal bond has been the subject of some speculation. Reported metal-metal distances provide evidence for multiple bonding since nearly all observed metal-metal bonds show appreciable shortening from the theoretical bond lengths calculated from metallic covalent radii. It is possible of course that other electronic and steric factors could be affecting the bond length. The R₃M group (where M is Si or Ge; R is alkyl, aryl or halogen) is essentially a σ donor, forming a σ bond with a transition metal however M has an unfilled d orbital of the correct symmetry for overlap with a filled orbital on the metal. There is thus a possibility of Π bonding. Graham and his co-workers have claimed that in some manganese carbonyl complexes, R₃Si- and R₃Ge- act as good Π acceptors as well as σ donors. By comparison with analogous R₃Sn-complexes the order of Π-bonding ability appears to be Cl₃Sn > Ph₃Sn > Ph₃Ge; the presence of the highly electronegative chlorine atom attached to M is expected to increase the Π acceptor properties of the group. Similar Π acceptor properties have
been proposed by MacDiarmid for the $R_3M$ group in $R_3MCo(CO)_4$ and Aylett's work supported the results with the manganese complexes. He has, however, cast doubt on the validity of MacDiarmid's calculations. A comparison of the molecular structure for SiH$_3$Co(CO)$_4$ with that for the Cl$_3$SiCo(CO)$_4$ has provided some stereochemical evidence for (d-d)π bonding in the trichloro compound. As might be expected for a stronger π acceptor, in the latter, the Si-Co bond is shorter and the out of plane displacement of the equatorial carbonyls is less compared with the hydride compound.

Certain techniques have been used to investigate the existence and extent of π bonding. Shortening of metal-metal bonds has been used as one criterion. I.R. data has also been used: an increase in the value of $\nu$(C-O) in the complex SiH$_3$Co(CO)$_4$, for instance, (compared with the value in HCo(CO)$_4$) indicates that there is less back donation from Co to CO. This is taken as an indication of π-bonding between Si and Co.

Use of nuclear quadrupole resonance has been suggested. A change from the normal negative temperature coefficient of NQR frequencies, associated with 6-bonded complexes, to a positive temperature coefficient is said to indicate the presence of complexes involving bonds with π-bond character.
For many complexes much of the evidence is inconclusive. It is possible that Mössbauer spectroscopy could be of importance in investigations on iron complexes.

Although, as will be described later, several iridium compounds containing \( R_3M(M=Si, Ge, Sn) \) ligands, have been prepared, very little comment has been made about the nature of the metal-metal bond.

1. 2. Oxidative Addition Reactions.

Since the formation of many complexes of the Group VIII triad Co, Rh and Ir depends on the oxidative addition of covalent molecules to complexes of these metals in low oxidation states, this type of reaction is discussed in some detail. It has been mentioned previously, (section 1.1.) as one of the general methods of preparation of silicon or germanium complexes of transition metals.

When discussing oxidative addition reactions it is possible for instances to occur of indefinite oxidation states in complexes. This difficulty arises since the definition of oxidation state as 'the charge left on the central metal after the ligands have been removed in their 'normal' closed shell configurations' is based on valence-bond formalism. However the concept of oxidation state is a useful one for considering such reactions.
Complexes of metals with a $d^8$ electronic configuration can add a covalent molecule (hereafter referred to as the addendum) to form octahedral complexes with the metal having a $d^6$ electronic configuration. Different mechanisms occur depending whether the initial complexes are 4- or 5-co-ordinate.

a) 4 co-ordinate species

Square planar, 4 co-ordinated $d^8$ species are co-ordinatively unsaturated and undergo oxidative addition of the addendum by a one-step process which is generally reversible. 

\[
\begin{array}{c}
\text{M} + \text{A} \rightarrow \text{M} \\
\text{B} \\
\end{array}
\]

The behaviour of $d^8$ complexes in this reaction has been compared to that of carbenes. The addendum may be a polar or non-polar molecule and can add to the complex in a cis or trans manner. As will be seen later Ir$^+$\((CO)Cl(\text{PPh}_3)_2\) falls into this category.

b) 5 co-ordinate species

Trigonal bipyramidal, five co-ordinate $d^8$ species are co-ordinatively saturated and generally undergo oxidative addition of the addendum by a two-step process, the second step being irreversible and involving the loss of a neutral ligand from the ionic intermediate. These complexes only add polar or
electrophilic molecules such as $HX$, $RX$ or $X_2$ by this mechanism and the final products usually result from cis addition to the addendum. The behaviour of these $d^8$ complexes has been compared to that of olefins in such a reaction.

In the addition of mercuric halides to these complexes the reaction often stops at the intermediate stage where $HgX^+$ has formed a bond with the central atom to afford a cationic $d^6$ complex.

An alternative pathway for oxidative addition to 5 co-ordinate $d^8$ species involves the prior dissociation of a neutral ligand $L$ to form a more reactive 4 co-ordinate species which will then react with non-polar molecules such as $H_2$. This labilisation of one ligand is thought to be brought about by irradiation or heating.
As will be seen later, \[ \text{Li}[(\text{CO})_2\text{PPh}_3] \text{ fails into this class of complexes. Since 4- and 5- co-ordinated } \text{d}^8 \text{ complexes read by different mechanisms a comparison of the kinetics of reaction cannot be made.} 

The tendency for oxidative addition to a particular complex is highly dependent on the nature of the metal and the ligands attached to it, but the thermodynamic driving force for such a reaction follows closely the pattern observed for Group VIII metals. Therefore this tendency increases down a triad and across a series, and the tendency towards 5-co-ordination in \text{d}^8 \text{ complexes increases across a series and up a triad as shown in fig. 8.}

In the triad, Co, Rh, Ir, products from oxidative addition would be expected to be more stable for Ir complexes than Rh complexes, but since the nature of the ligands is so important, an increase in 5-co-ordination in oxidative addition fig. 8.
only direct comparisons between metals is possible if the complexes are isostuctural. Therefore Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ products would be expected to be more stable than those from Rh(CO)Cl(PPh₃)₂ and RhH(CO)(PPh₃)₃. This has been observed as will be discussed later and has been associated with much work on addition complexes of iridium.

If the ligands attached to M increase the electron density at M then an increase in ease of oxidation is observed. This observation is not unexpected for attack by electrophilic molecules.

As mentioned previously, many different types of addenda such as O₂, olefins, H₂, HX or alkyl or alkoxy halides take part in the oxidative addition reaction. Certain generalisations can be made about these reactions and reflect the ability of certain complexes to undergo oxidative addition reactions. For instance, the addition of H₂, HX, HgX₂ and CH₃I occurs to a specific iridium complex but not to the analogous rhodium complex. This reluctance of Rh complexes to undergo oxidative addition has been attributed to the greater instability of Rh in the higher oxidation state. Such reactions are discussed in greater detail in section 1.3. Even in the iridium complexes the tendency towards oxidative addition can be increased by a small change in the nature of the ligand in the complex. Soft σ-donor ligands favour addition, an increase occurring in the order I>Br>Cl, and...
acids reduce the tendency towards addition. Replacement of a CO ligand by $\text{PPh}_3$ therefore will cause an increase in the rate of reaction: $\text{RhCl(PPh}_3)_3$ will add $\text{H}_2$, whereas $\text{Rh(CO)Cl(PPh}_3)_2$ will not.

Oxidative addition may only be the first step in a more complicated reaction process for certain transition metals. Elimination of a molecule from the six co-ordinate $d^6$ complex may occur as a second step to form a new 4 co-ordinate $d^8$ complex. 66, 67

\[ \begin{align*}
\text{M} + \text{A} - \text{B} & \rightleftharpoons \text{M} \rightleftharpoons \text{M} + \text{A} - \text{C} \\
\text{fig. 9.}
\end{align*} \]

Such a mechanism can be the only simplest interpretation of certain experimental results obtained and in some cases e.g. $\text{I}_2\text{Pt(PEt}_3)_2\text{H,SiH}_2\text{I}$ the 6 co-ordinate intermediates themselves have been isolated. 36, 37

1.3. General chemistry of the iridium complexes $\text{Ir(CO)Cl(PPh}_3)_2$

and $\text{IrH(CO)(PPh}_3)_3$

Iridium, one of the rarer platinum metals, 68 occurs in many complexes where the oxidation state of the iridium can vary from (VI) to (-II), the 'normal' state being (III). The stereochemistry can vary from square planar to seven co-ordinate and the type of ligands can vary from strong $\Pi$ donor
ligands such as $F^-$ to 6 donor ligands such as $H_2O$ and $NH_3$.

Combination of all these variations gives rise to numerous complexes and one of these which has been studied quite extensively for its possible importance in homogeneous catalysis and thus industrial importance is the compound $\text{Ir(CO)}\text{Cl(PPh}_3\text{)}_2$, commonly known as Vaska's compound. (fig. 10).

This square planar complex of $\text{Ir}^1$ occurs as lemon yellow crystals and was first prepared in 1959 by Angoletta from $\text{Ir(CO)}_3\text{Cl}$ although this process was superseded in 1961 by Vaska's method of reacting $\text{IrCl}_3$ or $(\text{NH}_4)_2\text{IrCl}_6$ with triphenylphosphine in refluxing 2-methoxyethanol.

Various reaction conditions and solvents have been quoted but in each case carbonylation occurs from the solvent giving rise to the air stable iridium compound. The low oxidation state of iridium is stabilised by the strong $\Pi$ acceptor ligands CO and PPh$_3$ and the square planar stereochemistry is, as mentioned previously, one commonly exhibited by $d^8$ electronic configurations of iridium. Other preparative methods for the iridium compound have been devised, notably that of Collmann and Kang, and from this complex the related analogues
Ir(CO)X(PPh₃)₂(X=Br, I, SCN) have been prepared. On these complexes and those containing different tertiary phosphine ligands, many reactions have been carried out which indicate the relative ease with which oxidative addition reactions occur and how in most cases the conversion of the d⁸ square planar complex to a d⁶ octahedral species occurs. The rhodium analogue had been prepared in 1957 by Vallarino.

Vaska's compound reacts with X₂ (X=Cl, Br, I), H₂, or D₂ or HD and HX (X=Cl, Br, I) to give air-stable six co-ordinate species some of which have been prepared previously from other iridium complexes by different reactions. Molecular oxygen and ethylene also add and in these cases the addendum does not dissociate. The adducts can be considered as five co-ordinate d⁸ complexes or six co-ordinate d⁶ complexes as shown by X-ray work. The reversible addition of oxygen is possibly of importance in research on reversible oxygen carriers and the latter to homogeneous catalysis.

\[ \text{fig. 11} \]
The rate of addition of $O_2$ increases rapidly as $X$ in $\text{Ir}(\text{CO})X(\text{PPh}_3)_2$ changes from $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$, representing the tendency to increasing ease of oxidation with soft $d$ donor ligands that was mentioned in the previous section. $\text{SO}_2$ is reported to form reversibly a 1:1 adduct with a tetragonal pyramidal structure, $\text{SO}_2$ being at the apex. $\text{CO}$ and $\text{PH}_3$ add to form $5$ co-ordinate $\text{Ir}^I$ species by direct molecular addition. Azides cause the CO ligand to be replaced by an $\text{N}_2$ group to form $\text{Ir}^I(\text{N}_2)\text{Cl}(\text{PPh}_3)_2$ via a reactive intermediate:

![Chemical structure diagram](image)

**fig. 12**

$\text{Hg-Ir}^{62}$ and $\text{C-Ir}^{86}$ bonds have been formed by the addition of $\text{HgCl}_2$ and $\text{CH}_3\text{I}$ respectively to Vaska's compound. In the methyl halide series, methyl iodide is the only member which adds to $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$. This addition will be referred to in greater detail later.

In nearly all these cases the products have proved too insoluble for n.m.r. work and the structures have been determined on the basis of evidence from I.R., X-ray and other techniques. Obviously n.m.r. evidence would help in structure determination since the presence of a resonance line at a high value (10-40 $\tau$) would indicate the presence of a hydride ligand.
directly bonded to a transition metal. Characteristic splitting by phosphorus nuclei of other observed proton resonances and the resulting coupling constants would also be helpful in determining whether the phosphine ligands were cis or trans to the other ligands. Various other conditions of reaction were tried in order to give soluble products, including changing the ligand X in the starting material and changing the tertiary phosphine ligand in the complex from triphenylphosphine to a more alkylated phosphine. There is evidence, however, that changing the phosphine may lead to a different mode of addition.

In most of the previous reactions (L=Ph₃, addenda H₂, D₂, HX, X₂, CH₃X, HgX₂) it was found that a 1:1 reaction product was formed containing 6 co-ordinate iridium, and that certain generalisations could be made about the I.R. spectra of such products. The initial value of 1945 cm⁻¹ for v(C-O) of the d⁸ Ir(1) complex was always increased on the formation of a d⁶ Ir(111) species. This observation is expected: the bond strength of the C-O bond will increase as the charge on the metal is increased, because of a decrease in back donation from the metal to CO. The increase in frequency was between 10 and 50 cm⁻¹, and it was postulated that the increase in frequency was a measure of the stability of the adduct with respect to dissociation. In practice, v(C-O) increased in the
order $\text{Ir(CO)Cl(PPh}_3\text{)}_2 < \text{O}_2 \text{ adduct} \approx \text{H}_2 \text{ adduct} < \text{CH}_3\text{I adduct}$. Also it was shown that in cases where the formation of Ir-H bonds was postulated, new bands appeared in the 2000-2200 cm$^{-1}$ and 300-900 cm$^{-1}$ regions; these were assigned to the stretches and bends of a hydride ligand bonded to iridium.

Work in the far I.R. region also showed that $\nu(\text{Ir-Cl})$ varied. In octahedral complexes $\nu(M-\text{Cl})$ depends on the ligand trans to Cl. This dependence may be associated with $\sigma$-electron release from the ligand to the metal, or with $\Pi$-electric effects, or with both. It should however be noted that hydride is said to have the greatest effect of the ligands in the series Cl, Br, I, PR$_3$, CH$_3$, CO, AsR$_3$, CH$_3$CO and H. This variation in $\nu(\text{Ir-Cl})$ might indicate whether rearrangement on addition was occurring or not and to test this theory a series of reactions involving $\text{IrX(CO)(PPh}_3\text{)}_2$ and HX were carried out. The reactions were studied under heterogeneous conditions since it was possible that reactions in solution were causing isomerisation of products to occur. It was found in fact that only one isomer was formed under these conditions and that a more accurate structure determination could thus be made. The reasoning on which the stereochemistry of the HX adduct was assigned was that the addition of HCl to $\text{Ir(CO)Cl(PPh}_3\text{)}_2$ could give 6 possible
isomers (See fig. 13). Of these, two (1 + 2) could be eliminated because coupling between $\nu(M-H)$ and $\nu(C-O)$ was not observed in the I.R. spectrum. Coupling of $\nu(M-H)$ and $\nu(C-O)$ occurs if these ligands are trans to one another. To determine whether it exists the hydride and analogous denteride complexes have to be prepared since the interaction manifests itself as a shift in the $\nu(C-O)$ value from the hydride to the denteride and an anomalous $\nu_{MH}/\nu_{MD}$ ratio is obtained. It is said to arise from repulsion of the $\nu_{MH}$ and $\nu_{CO}$ vibrational levels and if it is assumed that the $\nu(C-O)$ shift represents the interaction energy of the states then the energy of the 'unperturbed' state can be calculated.
Possible stereochemistry of isomers from the reaction

\[ \text{HCl with Ir(CO)Cl(PPh}_3\text{)}_2 \]
Another two (3 and 4) could also be eliminated on I.R. evidence since if H had been trans to the phosphine ligand a low value for $\nu$(Ir-H) would have been expected whereas a high value (2240 cm$^{-1}$) characteristic of H trans to Cl is in fact observed. The isomer (5) in which there are cis phosphines and cis chlorine ligands was also not favoured because of the values of $\nu$(Ir-Cl) experimentally observed and because of the overall molecular rearrangement which would have had to occur to bring about this particular configuration. Only one isomer (8) thus has an acceptable structure, implying that cis addition of HX had occurred. The results from the additions of HX(X=Cl, Br, I) to Ir(CO)X(PPh$_3$)$_2$ (X=Cl, Br, I) agreed with this postulate.

Similarly, for the H$_2$ adduct it was postulated that cis addition occurred from the observation of $\nu$(Ir-Cl) at 268 cm$^{-1}$ (characteristic of H trans to Cl). Further evidence for the stereochemistry of this adduct came from the $^1$H n.m.r. spectrum which showed two resonances at 28.4 $\tau$(H trans to Cl) and 17.3 $\tau$(H trans to CO), the assignments being made by analogy with other compounds of known stereochemistry. Each of these resonances was split into a triplet, indicating the presence of two magnetically equivalent phosphorus nuclei each cis to the hydride $J$(P$_c$-Ir-H) = 15 cps. and no trans H coupling was observed. This evidence led to the belief that the trans phosphine configuration was retained during the
reaction and that the hydride ligands were mutually cis to each other (fig. 14). The different structural environment of the hydride groups was consistent with hydride stretching bands at 2222 cm\(^{-1}\) (H trans to Cl) and 2098 cm\(^{-1}\) (H trans to CO). If the hydrides had been mutually trans a single peak at \(~1750\) cm\(^{-1}\) would have been expected. Most of the work on trans effects on values of I.R. bands has referred to platinum compounds, but the conclusions based on an extension to iridium chemistry are consistent with the n.m.r. spectra.

Addition of HD\(^{78}\) to Ir(CO)Cl(PPh\(_3\))\(_2\) resulted in the formation of three products Ir(CO)ClH\(_2\)(PPh\(_3\))\(_2\), Ir(CO)ClD\(_2\)(PPh\(_3\))\(_2\) and Ir(CO)Cl(HD)(PPh\(_3\))\(_2\) showing that some scrambling of H-D had occurred on addition. Work by Bennett and al. on the addition of X\(_2\) (X = Cl, Br, I) and CH\(_3\)I to Ir(CO)Cl(PPh\(_3\))\(_2\) in CHCl\(_3\) also led to the conclusion that these addenda give cis adducts. The ligands being studied in this case fall into the order for \(\nu\)(Ir-Cl) of Cl\(_2\) > Br\(_2\) > I\(_2\) > CH\(_3\)I and are said to fit into the general pattern for decreasing values of \(\nu\)(Ir-Cl) with trans-ligand i.e. Cl > Br > I > CO > CH\(_3\) > PR\(_3\) > AsR\(_3\) > H. The evidence for cis addition of chlorine is ambiguous since the
values of the two $\nu$(Ir-Cl) at 326 cm$^{-1}$ (Cl trans Cl) and 302 cm$^{-1}$ (Cl trans CO) could just as well arise from trans addition of Cl$_2$. The value of 311 cm$^{-1}$ for Br$_2$ addition does not exclude Cl from being trans to CO but since the values (296 cm$^{-1}$ and 292 cm$^{-1}$) observed for I$_2$ and CH$_3$I addition point to cis addition and addition of Cl$_2$ to Ir(CO)Br(PPh$_3$)$_2$ gives two $\nu$(Ir-Cl) values instead of one (Cl trans Cl) it is concluded that cis addition takes place in all cases to give products as (I) below

The absolute stereochemistry of the CH$_3$I adduct from far I.R. data is said to be (II) but there is only a very small difference between the value for $\nu$(Ir-Cl) observed in this case (292 cm$^{-1}$) assigned to Cl trans CH$_3$ and that observed for the I$_2$ addition (296 cm$^{-1}$) assigned to Cl trans I. Therefore the evidence is not absolutely definitive in this case.
<table>
<thead>
<tr>
<th>Reactants</th>
<th>$\gamma$(C-O)</th>
<th>$\gamma$(Ir-H)</th>
<th>$\delta$(Ir-H)</th>
<th>$\gamma$(Ir-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ir(CO)Cl(PPh}_3\text{)}_2$</td>
<td>1945</td>
<td>trans X</td>
<td>trans CO</td>
<td>trans others</td>
</tr>
<tr>
<td>+ Cl$_2$</td>
<td></td>
<td></td>
<td></td>
<td>317a</td>
</tr>
<tr>
<td>+ Br$_2$</td>
<td></td>
<td></td>
<td></td>
<td>318 (trans Cl)</td>
</tr>
<tr>
<td>+ I$_2$</td>
<td></td>
<td></td>
<td></td>
<td>311 (trans Br or CO)</td>
</tr>
<tr>
<td>$\text{Ir(CO)Br(PPh}_3\text{)}_2$</td>
<td>1950</td>
<td>2222</td>
<td>2093</td>
<td>326</td>
</tr>
<tr>
<td>+ Cl$_2$</td>
<td></td>
<td></td>
<td></td>
<td>302 (trans Br or CO)</td>
</tr>
<tr>
<td>$\text{Ir(CO)Cl(PPh}_3\text{)}_2$ + H$_2$</td>
<td>1970</td>
<td>2240</td>
<td>886,836</td>
<td>317a or 268</td>
</tr>
<tr>
<td>+ HCl</td>
<td>2024</td>
<td>2240</td>
<td>870,835</td>
<td>313</td>
</tr>
<tr>
<td>+ HBr</td>
<td>2022</td>
<td>2240</td>
<td>870,835</td>
<td>269</td>
</tr>
<tr>
<td>$\text{Ir(CO)Br(PPh}_3\text{)}_2$ + HCl</td>
<td>2024</td>
<td>2227</td>
<td>865,824</td>
<td>312</td>
</tr>
<tr>
<td>+ HBr</td>
<td>2024</td>
<td>2231</td>
<td>862,822</td>
<td></td>
</tr>
<tr>
<td>$\text{Ir(CO)I(PPh}_3\text{)}_2$ + HCl</td>
<td>2022</td>
<td>2200</td>
<td>835,805</td>
<td>310</td>
</tr>
<tr>
<td>+ HBr</td>
<td>2024</td>
<td>2231</td>
<td>862,822</td>
<td></td>
</tr>
<tr>
<td>$\text{Ir(CO)Cl(PPh}_3\text{)}_2$ + CH$_3$I</td>
<td>2060</td>
<td></td>
<td></td>
<td>292 (trans I or CH$_3$I)</td>
</tr>
</tbody>
</table>

*a* = CHCl$_3$ : Others recorded in solid phase as Nujol Mulls.

Some assignments in the far infrared region are slightly ambiguous.
A summary of all the results obtained for \( \nu(C-O) \), \( \nu(Ir-H) \) and \( \nu(Ir-Cl) \) as discussed above is shown in Table 1.1. and from this evidence it was concluded that cis addition of \( I_2 \), \( H_2HX \) and \( CH_3X \) to \( Ir(CO)Cl(PPh_3)_2 \) occurred with retention of the trans phosphine configuration and movement of the CO or Cl ligand out of the square plane during the addition reaction.

When methyl diphenyl phosphine ligands were substituted for triphenylphosphine ligands in Vaska's compound \( (Ir(CO)Cl(PPh_3)_2)^{73} \) kinetically controlled trans addition of \( X_2, HX, RX \) and \( RCOX \) across the square plane occurred and the resulting stereochemistry of the product was postulated from I.R. and n.m.r. spectral evidence.

These reactions were all carried out in solution and n.m.r. evidence showed that the original trans phosphine configuration was retained during all the additions. In the case of halogen addition (\( X = Cl, Br, I \)) there is no evidence to show whether it is thermodynamic or kinetic control which results in the
formation of the single isomer which is observed. For Br
and I there is no change in ν(Ir-Cl) in the product (see table 1.2.)
so it is postulated that no rearrangement occurs and that by
analogy Cl₂ also adds trans across the square plane. Various
tests were carried out to show that isomerization had not
occurred after the original addition including heating IrCl₃-
(CO)(PPh₂Me)₂ and IrBr₃(CO)(PPh₂Me)₂ in C₆H₆/MeOH under
reflux when no halogen exchange occurred.

Similarly the addition of CH₃X (in this case for L = PPh₂Me
X = Cl, Br, I) results in the formation of the product with the
trans arrangement of CH₃ and X. The fact that the addition was
CH₃-X and not CH₂X-H was shown by the presence of a resonance
line due to CH₃-Ir at ~9.64 μ (triplet J = 10 cps) and the
absence of a line due to a hydride bonded directly to a transition
metal at high μ value. Also the I.R. evidence agreed with the
absence of H directly bonded to iridium and the retention of
Cl trans to CO. For the addition, CH₃Cl to Ir(CO)Br(PPh₂Me)₂
it was shown that further isomerization of the initially formed
product occurred (B → A) (fig. 16) indicating that X trans to
CH₃ is very labile and that the initial addition is stereospecific,
trans and kinetically controlled. The ease with which (B)
isomerizes to (A) indicates the danger of concluding that the
configurations of products observed in oxidative addition
reactions are kinetically determined.
fig. 16

The additions of HX, CH₃COX and HgX₂ are slightly more complicated since although in all cases 1:1 addition products are formed, for X = Cl at least, the stereochemical course cannot be unambiguously determined (fig. 17) and for

fig. 17

X = Br either 2 isomers are formed (fig. 18) one by cis and the other by trans addition (this isomerization could have occurred after the initial addition) or intermolecular halogen exchange occurred.
Values assigned tentatively for $\nu$(Ir-Cl)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Assignment</th>
<th>Wave Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl trans Cl</td>
<td></td>
<td>330 cm$^{-1}$</td>
</tr>
<tr>
<td>Cl</td>
<td>CO</td>
<td>310</td>
</tr>
<tr>
<td>Cl</td>
<td>CH$_3$</td>
<td>250-260</td>
</tr>
<tr>
<td>Cl</td>
<td>CH$_2$CO</td>
<td>295-300</td>
</tr>
<tr>
<td>Cl</td>
<td>H</td>
<td>265</td>
</tr>
<tr>
<td>Cl</td>
<td>Br</td>
<td>310-320</td>
</tr>
<tr>
<td>Cl</td>
<td>I</td>
<td>300</td>
</tr>
<tr>
<td>Products</td>
<td>Addenda</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>Ir(CO)Cl(PPh₂Me)₂</td>
<td>--</td>
<td>1969</td>
</tr>
<tr>
<td>Br</td>
<td>--</td>
<td>1969</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Cl₂</td>
<td>2060</td>
</tr>
<tr>
<td>ClBr₂</td>
<td>Br₂</td>
<td>2060</td>
</tr>
<tr>
<td>ClI₂</td>
<td>I₂</td>
<td>2060</td>
</tr>
<tr>
<td>Cl₂CH₃</td>
<td>CH₃Cl</td>
<td>2025</td>
</tr>
<tr>
<td>ClBrCH₃(A)</td>
<td>CH₃Br</td>
<td>2025</td>
</tr>
<tr>
<td>ClBrCH₃(B)</td>
<td>CH₃Br</td>
<td>2025</td>
</tr>
<tr>
<td>Cl₂H</td>
<td>HCl</td>
<td>2050</td>
</tr>
<tr>
<td>Cl₂(CH₂CO)</td>
<td>CH₂COCl</td>
<td>2050</td>
</tr>
<tr>
<td>ClBrH</td>
<td>HBr</td>
<td>2045</td>
</tr>
<tr>
<td>ClBr(CH₂CO)</td>
<td>CH₂COBr</td>
<td>2050</td>
</tr>
<tr>
<td>ClR₂I</td>
<td>R'I'</td>
<td>2060</td>
</tr>
</tbody>
</table>

All frequencies are recorded in cm⁻¹.
Reactions involving Ir(CO)Br(PPh₂Me)₂ and HCl gave the same results showing that the configurations must be in a state of equilibrium. Despite this slightly inconclusive evidence it was claimed that by analogy the additions must be trans orientated.

A summary of the I.R. evidence on which these conclusions are based is shown in table 1.2.

From the reactions already studied it would appear that the planar d³ complex Ir(CO)XL₂(X = Cl, Br, I; L = PPh₃, PPh₂Me, PEt₃) reacts with many compounds having polar or non-polar bonds to form 1:1 adducts but that these reactions which are often reversible and are postulated to be one step processes result in the formation of adducts of varying stereochemistry. This variation (fig. 19)

\[
\text{fig. 19}
\]

seems to depend on the conditions of the reaction, the addendum and the nature of the phosphine ligands in the original complex. Products arising from cis or trans addition to 4 co-ordinate Pt (11) complexes have been observed. When the kinetics of the reactions Ir(CO)XL₂(L = PPh₂Me) and A-B were studied it was shown that they all obeyed a 2nd order rate law:
rate = \( k_2 [\text{IrX(CO)}L_2][\text{A-B}] \)

but that there were two reactivity patterns, one for the addition of hydrogen and oxygen (cis addition) and the other for the addition of \( \text{CH}_3\text{X} \) (trans addition). Both patterns were shown to exhibit large negative entropies of activation but that in the case of \( \text{D}_2 \) addition a very small kinetic isotope effect \( (k_H/k_D = 1.22) \) was observed pointing to the fact that little \( \text{H-H} \) bond breaking was occurring in the rate determining step. Therefore for cis addition it was postulated that a highly strained or ordered activated complex was involved and that concerted insertion of the iridium atom into the \( \text{H-H} \) bond occurred. A highly polar activated complex was thought to be involved in the process of trans addition; in a bimolecular \( \text{SN}_2 \) displacement reaction at the carbon atom of the alkyl group \( \text{(CH}_3\text{X)} \) the iridium atom acted as a nucleophile. This would be in agreement with the effects of changing the phosphine ligands where increased alkylation increases their \( \sigma \)-donor characteristics and thus increases the nucleophilicity of the iridium atom. Recent work\(^{100}\) has shown that a change in configuration at the carbon atom results from oxidative addition of an alkyl halide species to \( \text{Ir(CO)Cl(PR}_3)_2 \). The addendum considered was trans-1-bromo-2 fluorocyclohexane and the use of \( ^{19}\text{F} \) n.m.r. spectroscopy showed that on addition to \( \text{Ir(CO)Cl(PMe}_3)_2 \) inversion of configuration at the carbon atom occurred to give a product with cis conformation at all
temperatures.

![Chemical structure](image)

This result is further evidence for a bimolecular SN$_2$ mechanism.

The difference in the stereochemical course of these reactions with change of ligand is strange and the contrast between this course for homogeneous and heterogeneous addition reactions of HX is remarkable. However the cis addition of hydrogen under homogeneous conditions is not unexpected since this addition parallels the phenomenon of chemisorption of H$_2$ on metals and indicates the probable mechanism of homogeneous catalysis. It may be that under heterogeneous conditions HX is also acting in this way.

The reaction of Ir(CO)Cl(PPh$_3$)$_2$ with HX and other proton acids may be regarded as an acid-base reaction where the complex of iridium in a low oxidation state is acting as a base and the reaction involves the proton becoming attached to a basic metal centre causing a two unit increase in the formal oxidation state of the metal. Once co-ordinated, the 'proton' can be considered as a hydride ligand. Since mercuric halides
are Lewis acids it is not surprising that they also add readily.

Reactions with solvents can occur and a trichloride complex \( \text{Ir(CO)Cl}_3(\text{PPh}_2\text{Me})_2 \) can be formed by the reaction of \( \text{Ir(CO)Cl(} \text{PPh}_2\text{Me})_2 \) with \( \text{CCl}_4 \). The mechanism may involve a radical path and carbene-like intermediates could be formed in this way.

In comparison with the volume of work reported for reactions of \( \text{Ir(CO)Cl(PPh}_3)_2 \) and its derivatives the amount of work which has been carried out on \( \text{IrH(CO)(PPh}_3)_3 \) is very small.

This 5 co-ordinate complex of \( \text{Ir(1)} \), which exists as pale yellow, air-stable crystals and is monomeric in solution, was first prepared by the reduction of \( \text{Ir(CO)Cl(PPh}_3)_2 \) by \( \text{N}_2\text{H}_4 \):

\[
\text{Ir(CO)Cl(PPh}_3)_2 + n\text{N}_2\text{H}_4 \rightarrow \text{IrH(CO)(PPh}_3)_3 + n\text{H}_2\text{Cl} + \frac{1}{2}n\text{N}_2
\]

An X-ray study indicated that it was isostructural with the rhodium analogue and that the three phosphines occupied the equatorial plane of a trigonal bipyramid\(^{101,102}\) (fig. 21).

![fig. 21.](image-url)
Agreement for this structure came from the $^1$H n.m.r. spectrum where a quartet (at 21.2 $\gamma$ $J(P_C{-}Ir{-}H) = 42$ Hz in C$_6$H$_6$, 20.9 $\gamma$ $J = 24$ Hz in CH$_2$Cl$_2$) indicated the presence of a hydride ligand directly bonded to the iridium and (by analogy with the spectra of similar compounds) trans to CO and coupled to three magnetically equivalent phosphorus nuclei. The coupling constant $J(P_C{-}Ir{-}H)$ in C$_6$H$_6$ is much larger than is normal for such a coupling in 6 co-ordinate species where the usual value is between 10 and 20 Hz.

The discrepancy in the two literature values suggests a mistake in the former one, especially since the value determined in benzene/tetramethyl silane is 20.4 $\gamma$ $J = 21.7$ Hz.

Malatesta and co-workers report the finding of IrH(CO)(PPh$_3$)$_3$ in two different crystalline forms with different melting points and different I.R. values. From the I.R. evidence, low m.p. $\nu(Ir{-}H)$ 2120 cm$^{-1}$, $\nu$(C-O) 1920 cm$^{-1}$, $\delta$(Ir-H) 840 cm$^{-1}$; high m.p. $\nu(Ir{-}H)$ 2090 cm$^{-1}$, $\nu$(C-O) 1935 cm$^{-1}$, $\delta$(Ir-H) 780 cm$^{-1}$) they favour the idea of these two products being isomers.

One of the reactions of IrH(CO)(PPh$_3$)$_3$ studied illustrates one of the different mechanisms by which 5 co-ordinate species are thought to undergo oxidative addition reactions (see Section 1.2.). HX and DX$^{78}$ (X = Cl, Br, I) add to this complex instantly to form air stable white or pale yellow ionic adducts.
which behave as univalent electrolytes in acetone and methanol.

\[ \text{Ir(CO)H(PPh}_3)_3 + \text{HX} \rightarrow [\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^{+}\text{X}^- \]

Addition of DCl to IrH(CO)(PPh3)3 or HCl to the deuterium substituted complex results in the formation of the same ionic product \([\text{Ir(HD)(CO)(PPh}_3)_3]^{+}\text{Cl}^-\). If the reaction is carried out in the presence of excess HX, incorporation of another molecule of acid into the complex occurs to form \([\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^{+}\text{HX}_2^-\). These compounds are found to crystallize with one molecule of solvent. The stereochemistry of the cationic part is thought to be as shown in fig. 22,

![fig. 22](image)

where one hydride ligand \((\text{H}_\beta)\) is trans to CO and the other \((\text{H}_\alpha)\) is trans to a phosphine ligand. Interaction between CO and \(\text{H}_\beta\) is reflected in the I.R. bands observed; \(\gamma_\text{(C-O)}\) is found to shift from 2005 cm\(^{-1}\) for the HX adduct to 2040 cm\(^{-1}\) for the DX adduct and an anomalous \(\gamma_{\text{IrH}}/\gamma_{\text{IrD}}\) ratio is obtained.

Hydrogen also adds to the 5 co-ordinate complex but instead of giving an ionic adduct or even a 6 co-ordinate species as might have been expected, by prior dissociation of a neutral ligand, a 7 co-ordinate species \(\text{IrH}_3(\text{CO})(\text{PPh}_3)_3\) is said to be formed. \(\text{IrH}_3(\text{CO})(\text{PPh}_3)_3\) is said to be formed.
formed during the hydrogenation of olefins using \( \text{IrH(CO)(PPh}_3\text{)}_3 \) as a catalyst. \( \text{C}_2\text{H}_4 \) is also thought to form a 7 co-ordinate species by addition. \(^{76}\)

\[
\text{IrH(CO)(PPh}_3\text{)}_3 + \text{C}_2\text{H}_4 \rightarrow \text{IrH(CO)(C}_2\text{H}_4\text{)(PPh}_3\text{)}_3 \quad \text{H}_2 \rightarrow \text{Ir(CO)(C}_2\text{H}_5\text{)(PPh}_3\text{)}_2\text{H} \quad \text{IrH(CO)(PPh}_3\text{)}_3 + \text{C}_2\text{H}_6
\]

1.4. Reactions of Group IVB compounds with the complexes \( \text{Ir(CO)Cl(PPh}_3\text{)}_2 \) and \( \text{IrH(CO)(PPh}_3\text{)}_3 \).

As well as the reactions previously outlined some involving the addition of non-metal hydrides, especially those of Group IVB, to \( \text{Ir(CO)Cl(PPh}_3\text{)}_2 \) and \( \text{IrH(CO)(PPh}_3\text{)}_3 \) have been studied. All the work has been carried out with compounds of the type \( \text{R}_3\text{MH} \) (\( \text{M} = \text{Si, Ge, Sn}; \text{R} = \text{alkyl, halide, alkoxy etc.} \)) and in 1965 the system \( \text{R}_3\text{SiH} \) and \( \text{Ir(CO)Cl(PPh}_3\text{)}_2 \) was studied by Chalk and Harrod. \(^7\) Their results showed that for an electro-negatively substituted silane (\( \text{R} = \text{Cl, EtO etc.} \)) the reaction took place in a solution of the silyl compound as solvent after a period of twelve hours to give white powders as products which the weight increment showed to be 1:1 adducts.

\( \text{Ir(CO)Cl(PPh}_3\text{)}_2 + \text{SiR}_3\text{H} \rightarrow \text{Ir(CO)Cl(SiR}_3\text{)(PPh}_3\text{)}_2\text{H} \).

The frequencies of the infrared spectra of the compounds agreed with the values obtained for the same stretching frequencies \( \gamma(\text{Ir-H}) \) and \( \gamma(\text{C-O}) \) in related systems. (see table 1.3.). \(^4\)Hn.m.r.
studies were not possible because of the insolubility of the systems in common solvents but from the I.R. evidence it was thought that the reactions were forming 1:1 6 co-ordinate octahedral iridium (111)- silicon species as products. Another structure for the

TABLE 1.3.
I.R. Data from reactions of Ir(CO)Cl(PPh₃)₂ and R₃SiH.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>γ(Ir-H)</th>
<th>γ(Si-H) orig.</th>
<th>γ(C-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(CO)Cl(PPh₃)₂ + H₂</td>
<td>2190</td>
<td>2100</td>
<td>1970</td>
</tr>
<tr>
<td>+ HCl</td>
<td>2240</td>
<td>——</td>
<td>2025</td>
</tr>
<tr>
<td>+ SiHCl₃</td>
<td>2110</td>
<td>2190</td>
<td>2035,2020</td>
</tr>
<tr>
<td>+ C₂H₅Cl₂SiH</td>
<td>2145</td>
<td>2205</td>
<td>2025,2010</td>
</tr>
<tr>
<td>+ C₆H₅Cl₂SiH</td>
<td>2080</td>
<td>2195</td>
<td>1975,1970</td>
</tr>
<tr>
<td>+ (C₂H₅O)₃SiH</td>
<td>2110</td>
<td>——</td>
<td>1970</td>
</tr>
<tr>
<td>(no reaction.)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

adducts is possible where R₃SiH adds as a whole ligand through the Si atom to give penta-co-ordinate iridium and silicon atoms and this structure would in fact be an example of a very severely distorted octahedral stereochemistry. The former is more likely to be the true structure since the latter does not account for the presence of hydrogen bonded to iridium.

Thermal decomposition occurred at temperatures in excess
of 150°C and the adducts appeared to be unstable to air in solution but stable as solids.

The oxidative addition reaction appeared to be limited to electronegatively substituted silanes since no reaction was observed for R (alkyl or aryl). Obviously the reaction only occurs in the presence of an Si-H bond, since the reaction of $Q_2Si(Q = EtO, Cl)$ with Ir(CO)Cl(PPh$_3$)$_2$ did not occur.

There appears to be a rough correlation between the value of $\nu$(Si-H) in the original compound (see table 1.3) and the stability of the complex formed ($R = alkyl$ gives no reaction) which may seem strange at first sight. It was concluded that the influences which strengthen the Si-H bond must also be effective in bonding Si to Ir and that $d_{\pi}-d_{\pi}$ bonding may be responsible for this.

Considering the premise that $\nu$(C-O) is sensitive to the charge on the metal and that it should increase i.e. be strengthened as the positive charge on the metal increases then obviously from inspection of the values of $\nu$(C-O) in table 1.3 the presence of electronegatively charged substituents in $R_3SiH$ enhances the stability of the complexes containing these ligands which is as expected because they will increase the positive charge on M.

Subsequently due to work done by Glockling on the reactions of certain germanium compounds with Ir(CO)Cl(PPh$_3$)$_2$, Chalk and Harrod had to repeat their earlier experiments.
In 1969 it was shown that the reaction:

\[ \text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 + \text{R}_3\text{SiH} \rightleftharpoons \text{IrHCl}(\text{SiR}_3)(\text{CO})(\text{PPh}_3)_2 \] (I) \[ \rightleftharpoons \text{II} \]

was in fact only the first step in a reaction sequence which gave a 6 co-ordinate dihydride \( \text{IrH}_2(\text{SiR}_3)(\text{CO})(\text{PPh}_3)_2 \) as the final product by reaction with a second molecule of \( \text{R}_3\text{SiH} \).

\[ \text{I} + \text{R}_3\text{SiH} \rightleftharpoons \text{II} \]

\[ \downarrow \text{R}_3\text{SiH} \]

\[ \text{IrH}_2(\text{CO})(\text{SiR}_3)(\text{PPh}_3)_2 + \text{R}_3\text{SiCl}. \] (IV)

This product (IV) had in fact been found earlier and was formed by the reaction of the five co-ordinate hydride \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) with \( \text{SiR}_3\text{H} \). In this case the reaction was much faster, which is not unexpected since the hydride ligand is more electron releasing than the chloride one. However, as discussed in the introduction, the kinetics of the reactions of \( \text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 \) and \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) cannot be compared because of the difference in mechanism of the reactions.

Formation of (IV) by reaction of \( \text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 \) with two molecules of \( \text{R}_3\text{SiH} \) in fact also takes place for \( \text{R} \) (alkyl or aryl) if the time factor is increased e.g. by refluxing \( \text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 \) in \( \text{Et}_3\text{SiH} \) for 3 days until a clear solution of (IV) is obtained. This result is not unexpected; the reaction:

\[ \text{R}_3\text{SiH} + \text{R}_3^2\text{SiD} \rightleftharpoons \text{R}_3\text{SiD} + \text{R}_3^2\text{SiH} (\text{R} = \text{alkyl, aryl}) \]
is catalysed by \( \text{Ir(CO)Cl(PPh}_3)_2 \), showing that hydrogen-deuterium exchange must take place via an intermediate iridium complex. It was postulated that the reaction between (1) and \( R_3\text{SiH} \) (\( R = \text{alkyl} \)) had not been observed previously because the adduct, (11), which would be formed was less stable than the ones formed where \( R \) is electronegative; thus the equilibrium lay towards (1). It was only when the time of reaction was increased that the product (IV) was obtained. Since (IV) was soluble, its structure could be investigated by \( ^1\text{H} \) n.m.r. spectroscopy and the stereochemistry of the compound was elucidated from the complicated spectrum which resulted.

For \( R = \text{Et} \), the adduct was found to give resonance lines in the region 19 - 22\( \nu \), characteristic of a hydride directly bonded to an iridium atom. From these lines it could be deduced that one hydride was cis to two phosphines giving a triplet with \( J(\text{P}_{\text{cis}} - \text{Ir} - \text{H}) \approx 15\text{c/s}; \) the other was cis to one phosphine and trans to the other (doublet of doublets, large \( J(\text{P}_{\text{trans}} - \text{Ir} - \text{H}) \) and small \( J(\text{P}_{\text{cis}} - \text{Ir} - \text{H}) \). Hence the phosphines were mutually cis and that the stereochemistry was as shown below. (fig. 23)

![fig. 23.](image-url)
In view of the results obtained from the systems when 
R = alkyl, aryl the analogous reactions with R (electronegative) 
were repeated. These previously had produced insoluble 
1:1 adducts (11) but as no n.m.r. evidence was available 
for them there was a possibility that the adducts were not 
just single products but mixtures of isomers. It is likely that 
this is the case since two bands assigned to γ(C-O) were 
obtained for each compound (see table 1.3.) Therefore a 
saturated solution of (1) in benzene was treated with excess 
(\text{EtO})_3\text{SiH}, concentrated, and examined by $^1\text{H}$ n.m.r. spectroscopy. Initially a triplet at 16.1 Hz ($J = 14\text{Hz}$) was observed. 
From the low chemical shift it was postulated that this was due 
to one hydride trans to a group with a large trans effect e.g. 
$\text{Si(OEt)}_3$; the coupling constant $J(P - \text{ir} - H) = 14\text{Hz}$ indicated 
that both the phosphine ligands were cis to the hydride ligand. 
This evidence pointed towards the formation of an intermediate 
(11) in which trans addition of the addendum had occurred with 
retention of the initial trans phosphine configuration (see fig. 24) 

![Diagram](image.png)

**fig. 24.**
After 12 hours this triplet vanished. Similar results were obtained in CHCl₃ where two overlapping triplets at 17.3 \(^\text{m}\) were observed and in CH₂Cl₂ where after 3 hours a complex spectrum like that obtained previously for (IV) was found around 20\(^\text{m}\). It would seem that the solvent influences the rate of the reaction but that the formation of (IV) from (11) is faster in the case of (EtO)₃SiH than R₃SiH i.e. 3 hours compared with 12 hours. The mechanism which has been put forward involves the formation of the 1:1 adduct followed by break up of this complex to give a 4 co-ordinate intermediate IrH(CO)(PPh₃)₂(V) which subsequently adds another molecule of R₃SiH. This intermediate has been reported to have been isolated as a product from the reaction of IrH₃(PPh₃)₃ and CO and to have cis square planar configuration. No evidence for its formation during the oxidative addition reaction could be obtained but this is probably due to its ready disproportionation to

\[
\text{IrH(CO)(PPh₃)₃} \quad \text{IrH(CO)(PPh₃)₃} \quad \text{IrH(CO)(PPh₃)₃} \quad \text{IrH(CO)(PPh₃)₃}
\]

\[
\text{IrH(CO)(PPh₃)₃} \quad \text{IrH(CO)(PPh₃)₃} \quad \text{IrH(CO)(PPh₃)₃} \quad \text{IrH(CO)(PPh₃)₃}
\]
Therefore all the ideas about the sequence of the reaction between Ir(CO)Cl(PPh₃)₂ and xR₃SiH had had to be reviewed.

Shortly before the publication of the amendment, Harrod et al. had shown that the reversible reaction of the 5 co-ordinate iridium carbonyl hydride IrH(CO)(PPh₃)₃ with R₃SiH compounds gave soluble complexes from which more information about their stereochemistry could be gained because of the possibility of their being studied by ¹H n.m.r. spectroscopy. In fact as mentioned previously the two pieces of work tied in very neatly.

A rapid reaction between IrH(CO)(PPh₃)₃ and many R₃SiH compounds occurred to give stable 1:1 adducts which were shown by I.R. and n.m.r. spectroscopy to be 6 co-ordinate species of the form (IV) (fig. 25).

![Diagram](IV)

Analysis figures for some of these adducts (R = Ph, C₂H₅O, Cl) agree with the above formulation and I.R. spectra showed the usual strong and weak bands in the region ~2100 cm⁻¹ for the symmetric and asymmetric stretching frequencies of ν(Ir-H)
and in the region ~1950 cm$^{-1}$ for the $\nu$(C-O) frequency. The n.m.r. spectrum was more informative and the complicated splitting pattern observed around 20$\gamma$ was interpreted as being due to 16 lines which would be in agreement with the proposed stereochemistry of (IV). The observed n.m.r. spectrum is shown in fig. 26 and the n.m.r. data in table 1.4.

**TABLE 1.4.**

<table>
<thead>
<tr>
<th>$^1$H N.m.r. data from addition of $R_3$SiH to IrH(CO)(PPh$_3$)$_2$</th>
<th>$J(P_2-H_1)$</th>
<th>$J(P_1-H_1)$</th>
<th>$J(P_2-H_2)$</th>
<th>$J(P_1-H_2)$</th>
<th>$H_1\gamma$</th>
<th>$H_2\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(EtO)$_3$SiH</td>
<td>22</td>
<td>17</td>
<td>4</td>
<td>110.5</td>
<td>18.5</td>
<td>20.2</td>
</tr>
<tr>
<td>Ph(CH$_3$)$_2$SiH</td>
<td>23.5</td>
<td>16</td>
<td>4.5</td>
<td>113.5</td>
<td>19.5</td>
<td>20.0</td>
</tr>
<tr>
<td>Ph$_3$SiH</td>
<td>20</td>
<td>15.5</td>
<td>4.5</td>
<td>110.5</td>
<td>17</td>
<td>19.5</td>
</tr>
</tbody>
</table>

The positions of the hydride and phosphine ligands were easily determined but not that of the silyl group with respect to the carbonyl ligand. However, the insensitivity of the value of the hydride resonance to changes in substituent at the silicon atom suggests that Si$R_3$ is not trans to the hydride ligand. It was
subsequently shown by D substitution that this hypothesis is true. Reaction of (EtO)$_3$SiH with Ir(CO)D(PPh$_3$)$_3$ gives a product having two $\nu$(C-O) bands (3000 cm$^{-1}$ and 1965 cm$^{-1}$) and an n.m.r. as for the normal hydride product except for the absence of H-H coupling. Therefore, if it is assumed that the deuterium is distributed equally between positions, SiR$_3$ cannot be trans to the hydride since the value of $\nu$(C-O) would not then change on deuteration.

The compounds (V), formed by the reaction of IrH(CO)(PPh$_3$)$_3$ and SiR$_3$H, are of much greater stability than those formed by the reaction of (I) and excess SiR$_3$H. This may be due to their method of preparation. In the former case free triphenylphosphine is present in the reaction mixture and in the latter free silicon compound. The quantities of reactant R$_3$SiH needed to bring about the formation of (V) by either preparative method are comparable. For the addenda R$_3$SiH (R = Me, Et) excess R$_3$SiH is needed but for R$_3$SiH (R = Cl, OEt) only a 1:1 reaction mixture is needed to ensure completion of reaction with IrH(CO)(PPh$_3$)$_3$. The change in stability of the adducts of R$_3$SiH with respect to R (R = OEt being more stable than R = Me) is the same in both methods of preparation. The adduct of Me$_3$SiH can only be kept if stored under excess Me$_3$SiH. It is worth noting that it is the adducts that are least stable (i.e. R = alkyl) that are most effective hydrosilation catalysts.
The stability of the adducts with respect to loss of $H_2$ is great since they can be heated to charring without loss of $H_2$ or a silyl group.

As mentioned previously the theory is that oxidative addition is promoted by the presence of electron releasing ligands on the complex, hydride ligand causing an increase in the rate of reaction in comparison with chloride.

The reactions of $\text{IrH(CO)(PPh}_3\text{)}_3$ are much faster than those of $\text{Ir(CO)Cl(PPh}_3\text{)}_2$ with the same addenda. The interesting feature of these reactions is the formation of an initial complex containing cis phosphines unlike the other initial complexes from (1) which contained trans phosphines. (These of course did react further to give products containing cis phosphines). No evidence for isomerisation occurring in this reaction could be found although the spectra were run within a short time of mixing the reactants. The only other case of cis phosphines occurring in an iridium complex of this type, previously recorded, arises from the addition of allyl halides to $\text{Ir(CO)Cl(PPh}_3\text{)}_2$. This is not an unexpected result under these conditions since the mechanism of the reaction probably involves the dissociation of the original complex (111) to a 4 co-ordinate species $\text{IrH(CO)(PPh}_3\text{)}_2 \ (\text{V})$ and addition of the addendum along an axis perpendicular to the molecule i.e. cis accompanied by simultaneous phosphine migration in a direction away from the approaching addendum.
Prior dissociation of 5 co-ordinate species before oxidative addition has been postulated as one mechanism for this type of reaction (section 1.2) although it is generally thought that heating or irradiation of the reactants is necessary to bring about this dissociation. The species IrH(CO)(PPh₃)₂ had been reported to add reversibly a molecule of triphenyl phosphine to form the 5 co-ordinate hydride IrH(CO)(PPh₃)₃.

An objection to this simple scheme of a 4 co-ordinate intermediate and attack of the addendum along an axis perpendicular to the molecule resulted from deuterium substitution work where it was found that either hydride ligand in the product of the reaction Si(OEt)₃H and IrD(CO)(PPh₃)₃ could arise from the hydrogen in the addendum. Therefore, the reaction is not stereospecific.

Presumably formation of the cis phosphine complexes from the reaction of Ir(CO)Cl₂(PPh₃) and 2 SiR₃H results from rearrangement of the phosphine ligands after initial formation of the 1:1 adduct with a trans phosphine configuration.
Glockling et al have shown that the reaction of Ir(CO)Cl(PPh₃)₂ with two molecules of R₃GeH (R = Et, Me) produced 6 co-
ordinate complexes of the form Ir(CO)H₂(GeR₃)(PPh₃)₂ which were cream-coloured crystalline, air-stable solids which did
not appear to decompose in solution. This reaction was unlike those observed at the time for similar silicon and tin compounds
and the conditions of the reaction were also very different. The reactions only in fact took place if the reaction mixture was
refluxed for 12 hours or allowed to stand for several weeks at room temperature. These dihydride germyl complexes were
soluble in benzene and thus n.m.r. spectroscopic evidence was available and indicated the formation of a complex of the type (VI).

\[
\begin{array}{c}
\text{H}^a \\
\text{Ir} \\
\text{GeR}_3 \\
\text{H}^b \\
\text{P}_1 \\
\text{CO} \\
\text{P}_2 \\
\end{array}
\]

Using a 220 MHz spectrum the complicated pattern (fig. 27) due to the high field protons (Hₐ at 19.77 ppm and Hₐ at 20.86 ppm) could be
elucidated and confirmed the stereochemistry shown above. The presence of two magnetically non-equivalent phosphorus atoms
was shown by the difference in the coupling constants J(P₁-Ir-Hₐ) and J(P₂-Ir-Hₐ) although in both these cases the phosphine ligands
Diagramatic representation of the $^1$H n.m.r. spectrum from the Ir$^{111}$ resonance of the product from the reaction of Ir(CO)Cl(PPh$_3$)$_2$ with an excess of GeEt$_3$H as observed on the 220MHz n.m.r. machine.

The stereochemistry of the complex is shown in fig. (VI) on the previous page.
### TABLE 1.5.

<table>
<thead>
<tr>
<th>Addendum</th>
<th>IrH</th>
<th>γ value</th>
<th>J(P₁Ir-Hₐ)</th>
<th>J(HₐIr-Hₖ)</th>
<th>J(P₂Ir-Hₗ)</th>
<th>J(P₃Ir-Hₘ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeEt₃</td>
<td>19.77</td>
<td>20.86</td>
<td>117</td>
<td>small</td>
<td>22</td>
<td>18.5</td>
</tr>
<tr>
<td>GeMe₃</td>
<td>19.50</td>
<td>20.50</td>
<td>117</td>
<td>&quot;</td>
<td>19</td>
<td>18.0</td>
</tr>
<tr>
<td>GeMe₃⁺</td>
<td>21.31</td>
<td>21.80</td>
<td>114</td>
<td>&quot;</td>
<td>&quot;9.2</td>
<td>19.2</td>
</tr>
</tbody>
</table>

+ P=PEt₃ in initial complex. Coupling constants measured in c/s.

### TABLE 1.6.

<table>
<thead>
<tr>
<th>Addendum</th>
<th>γ (C-O)</th>
<th>γ (Ir-H)</th>
<th>γ (Ge-Cl)</th>
<th>γ (Ir-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeEt₃</td>
<td>1953</td>
<td>2081,2119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeMe₃</td>
<td>1956</td>
<td>2071,2123</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeCl₃</td>
<td>2055,2065,2084</td>
<td>353,372,388</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Frequencies are measured in cm⁻¹.
were cis to $H_a$ and the fact that $J(P_1-Ir-R_p)$ was so much greater than $J(P_2-Ir-H_p)$ indicated that $H_p$ was trans to $P_1$ and cis to $P_2$.

Since no long range $H-Ir-Ge-CH_2$ coupling was observed the presence of a hydride trans to the $GeR_3$ group was ruled out. This coupling is likely to be so small that it would be difficult to be sure on this evidence that $GeR_3$ is not trans to the hydride group. The relevant n.m.r. data is displayed in table 1.5.

Similarly, I.R. evidence favoured (VI) because if the $GeR_3$ group had been trans to $H$ then a low value for $\gamma(Ir-H)$ would have been observed because of the high trans effect of the $GeR_3$ group. It was shown however that $\gamma(Ir-H)$ was at 2120 cm$^{-1}$ which agreed with (VI). Also the fact that $\gamma(Ir-H)$ and $\gamma(C-O)$ are similar in the dihydride complexes arising from $Me_3Ge$ and $Et_3Ge$ addition suggests that $R_3Ge$ is cis to both these groups. The relevant I.R. data is shown in table 1.5.

It was postulated that the reaction took place via a 1:1 Cl adduct of the form $L_2(CO)H\text{Ir}GeR_3$ (11) which further reacted with another molecule of $GeR_3H$ to form $L_2(CO)H_2\text{Ir}(GeR_3)$. The addition of $Et_3N$ during the reaction had no effect which could be taken as indicating that $H$ and Cl were trans in the intermediate (11). If these ligands had been cis they might have been expected to be removed by HCl to form $Et_3NH\text{Cl}$. However, it is possible that HCl does not readily leave the intermediate even if the ligands are in a cis position. The trans postulated arrangement of
H and Cl can only arise if either there has been no rearrangement of the phosphines and cis addition of the addendum occurs with the CO ligand moving out of the plane or if rearrangement occurs and the Cl ligand moves out of the plane at the same time as cis addition occurs. The latter obviously involves much greater rearrangement within the complex prior to formation of the intermediate. Therefore, although in the final product (VI) the phosphines are cis it is possible, if not probable, that they have a trans configuration in the intermediate.

There were several interesting features of this reaction, the most notable being, in contrast to the reaction with silicon compounds, that the 1:1 adduct could never be isolated. If the reaction was carried out under 1:1 conditions the product \( \text{IrH}_2(\text{CC})\text{GeR}_3(\text{PPh}_3)_2 \) and unreacted starting material were the only products. To bring about reaction with \( \text{Ph}_3\text{GeH} \) very vigorous conditions were necessary and a 5 co-ordinate complex \( (\text{Ph}_3\text{P})(\text{CO})\text{IrH} \cdot \text{Cl(GePh}_3) \) was formed. Tris(isopropyl)germane did not react but this probably was because of steric hinderance; the reaction of \( \text{Cl}_3\text{GeH} \) was rapid and gave an insoluble white precipitate which was shown by I.R. and analysis to be of the form (VI) \( (R = \text{Cl}) \). When they tried changing the nature of the phosphine ligands they found that the whole nature of the reaction was changed as shown below:

\[
(\text{Et}_3\text{P})_2(\text{CO})\text{IrCl} + \text{Et}_3\text{GeH} \rightarrow (\text{Et}_3\text{P})_2\text{Ir(CO)H}_2\text{Cl} + \text{Me}_6\text{Ge}_2
\]
Obviously, as has been discussed in section 1.2, with reactions of other addenda, great care must be taken in interpreting the results of the reactions and it can never be assumed that changing the phosphine ligands will ensure the same reaction mechanism or type of products. Reaction of Me₃GeBr with Ir(CO)Cl(PPh₃)₂ did not occur and that of Et₃GeBr with Ir(CO)Cl(PPh₃)₂ gave GeEt₃Cl and Ir(CO)Br(PPh₃)₂ as products. The formation, therefore, of iridium-germanium complexes is dependent on the presence of a Ge-H bond in the addendum.

Cleavage of iridium-germanium bonds by HCl or C₂H₄Br₂ produces iridium hydrides and bromides respectively, but also leads to disproportionation to give Ir(1) products.

\[
\text{HCl} \rightarrow (\text{PPh}_3)_2(\text{CO})\text{IrH}_3 + \text{Me}_3\text{GeCl}
\]

\[
(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{CO})\text{GeMe}_3 + (\text{PPh}_3)_2\text{Ir}(\text{CO})\text{Cl}
\]

\[
\text{C}_2\text{H}_4\text{Br}_2 \rightarrow (\text{PPh}_3)_2(\text{CO})\text{IrBrH}_2 + \text{C}_2\text{H}_4 + \text{Me}_3\text{GeBr}
\]

\[
+ (\text{PPh}_3)_2\text{Ir}(\text{CO})\text{Br} + \text{H}_2.
\]

Reactions of Ir(CO)Cl(PPh₃)₂ with R₃SnH carried out by Lappert and Travers were in agreement with the original results from the silicon reactions; that is the formation of 1:1 adducts IrH(CO)SnR₃(PPh₃)₂ by cis or trans addition of R₃Sn and H and retention of the trans phosphine configuration. (fig. 28).
The properties of these complexes varied with R and the nature of the phosphine ligand L. Instability in air and solubility in organic solvents was least for R = Ph, L = PPh₃ and greatest for R = Me, L = PPh₂Me. The stereochemistry of the adducts, which were single isomers except in one case, was determined by I.R. and n.m.r. spectroscopy. For L = PPh₂Me, it could be shown that the phosphine ligands in all adducts were mutually trans from the observation of virtual coupling between these ligands. Addition of SnPh₃H gave an isomer of the form (VII), since γ(Ir-H) varied little with X, γ(Ir-Cl) was of the order 300 cm⁻¹ indicating that H was not trans to X, τ(Ir-H) was very low in value and no H/CO vibrational interaction was observed indicating that H was not trans to CO. This mode of addition would be in agreement with that postulated for many addenda reacting with Ir(CO)Cl(PPh₂Me)₂ as discussed in Section 1.3. However, addition of SnMe₃H gave two different isomers depending on conditions. In C₆H₆, a yellow isomer showing no variation in γ(Ir-H) with X, γ(Ir-Cl) of the order of 290 cm⁻¹, H/CO vibrational interaction and a low τ value (18.8) for the hydride
ligand was formed. It was assigned the stereochemistry (VIII).

In the absence of solvent, reaction of excess $\text{HSnMe}_3$ gave a white isomer again showing no variation in $\nu(\text{Ir-H})$ with $X$;

$\nu(\text{Ir-Cl}) \sim 300 \text{ cm}^{-1}$ no vibrational interaction of $\text{H/CO}$.

No n.m.r. evidence is available. This isomer which readily isomerised to the yellow one in CHCl$_3$ thus had the stereochemistry of (VII). These isomers were not necessarily formed by cis and trans addition respectively since isomerisation can occur after formation of the initial product. The relevant I.R. and n.m.r. data is shown in table 1.7.

In view of the results from the Sn work there does not appear to be much correlation of reaction sequence with steric bulk of $M$ in $\text{MR}_3\text{H}$ down Group IVB but there may be a dependence of reaction on the nature of $R$. Probably by analogy with the silicon reactions if $R$ was electronegative

**TABLE 1.7**

I.R. and n.m.r. data from the reaction of $\text{Ir(CO)}X(\text{PR}_3)_2$ and $\text{SnR}_3\text{H}$.

<table>
<thead>
<tr>
<th>$R^3$</th>
<th>$H$</th>
<th>$X$</th>
<th>$R$</th>
<th>Structure</th>
<th>$\nu(\text{Ir-H or D})$</th>
<th>$\nu(\text{C-O})$</th>
<th>$\nu(\text{Ir-Cl})$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}$</td>
<td>$H$</td>
<td>$\text{Cl}$</td>
<td>$\text{Ph}$</td>
<td>(VIII)</td>
<td>2080</td>
<td>1963</td>
<td>290</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>$D$</td>
<td></td>
<td></td>
<td>(VIII)</td>
<td>1508</td>
<td>1993</td>
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enough in $R_3GaH$ then the reaction sequence (1)→(11) with isolation of the intermediate (11) would occur and presumably conversion of (11)→(VI) could occur later.

Most of the six-coordinate iridium species Ir(CO)$_X$(PR$_3$)$_2$Y(MR$_3$)$_1$ appear to have the two tertiary phosphines in a trans configuration and quite often the entering groups Y and MR$_3$ are also trans. Since there are exceptions and isomerisation is known to occur in many Ir(III) compounds the structure obtained may be the most thermodynamically stable, having a ligand arrangement which prevents the highest trans effect groups lying opposite each other. Therefore, the stereochemistry of the product may not provide any information on the mode of oxidation.

Since silyl and germnyl parent hydride complexes of many different transition metals have been prepared and in view of the organo-silicon and -germanium complexes of iridium which have also been prepared it would not seem unreasonable to expect that the formation of parent hydride complexes of iridium is possible. Addenda of the form SiH$_3$X and GeH$_3$X (X = H, Cl, Br, I) would lie part way, in terms of electronegativity at least, between the systems MR$_3$H (R-alkyl, aryl) and MR$_3$H(R-halogen) which have been studied and should therefore show some relationship to these reactions. Since the reactions of Ir(CO)Cl(PPh$_3$)$_2$ and IrH(CO)(PPh$_3$)$_3$ seem to give such a
great range of products of varying stereochemistry depending on the addendum, the reaction conditions and the nature of the phosphine ligands it would be interesting to see if the products with $\text{MR}_3\text{H}$ are of the same nature as those from the $\text{MR}_3\text{H}$ systems and whether the same variation in stereochemistry is observed on changing various aspects of the reaction system.

A study of the parent hydride system also offers certain spectroscopic advantages. The infrared spectra have characteristic $\text{M} - \text{H}$ modes of vibration which are well separated from modes due to carbon-hydrogen. In the n.m.r. spectra the proton resonance of $\text{H} - \text{M}$ is more sensitive to the nature of the transition metal and its substituents than $\text{H} - \text{C} - \text{M}$ is in analogous organo-compounds. Therefore certain stereochemical speculations, only tentatively postulated in organo-compounds, should be able to be solved by the preparation of silicon and germanium hydride iridium complexes.
RESULTS AND DISCUSSION
CHAPTER TWO

PREPARATION AND SPECTROSCOPIC PROPERTIES OF SOME SIX CO-ORDINATE Ir (III) COMPLEXES, DERIVED FROM Ir(CO)Cl(PPPh3)2, CONTAINING S ILYL- AND GERMYL-LIGANDS.

Section 2:1

The Preparative Reaction.

2.1.1. Introduction.

The preparation and properties of silyl and germyl complexes of certain transition metals (Mn, Co, Fe, W, Cr, Pt, Pd) are discussed in Chapter 1. In all cases where silyl or germyl complexes of iridium have been prepared by oxidative addition, the addenda have been of the form \( R_3MH \) (M=Si or Ge); addition is of \( R_3M \) and H. On the other hand, methyl halides add as \( CH_3^- \) and X. In order to see whether the different form of addition of \( R_3M^- \) species is determined by the presence of R groups the reactions between \( MH_3X \) (X = Cl, Br, I) and Vaska's compound have been investigated. It is of interest to compare the properties and reactions of the products with those of the silyl and germyl compounds of platinum and with analogous organosilane and germane complexes of iridium.

The reaction of Vaska's compound with \( SiH_3X \) in benzene gives an insoluble product which has been shown
to be an equimolar adduct; the reaction is slow unless an initial excess of silyl halide is taken. Since all the adducts are insoluble, their structures must be inferred from vibrational spectra, and the conclusions are therefore tentative; the structure of the product formed depends upon X and upon the conditions under which the reaction is allowed to occur.

Germane also reacts with Vaska's compound to give an insoluble product; precipitation is immediate. In surprising contrast, germyl halides react rapidly with Vaska's compound, but the initial products are soluble in benzene, although precipitation occurs after a few minutes. The soluble product can be studied by n.m.r. spectroscopy prior to precipitation. The information obtained from the n.m.r. spectra, which is discussed in Section 2.5, is used in the assignment of stereochemistry to the reaction products.

In some cases there is evidence for the formation of more than one isomer. Now there are several ways in which such isomerisation might arise. First of all, isomerism might be a result of simultaneous reaction by different pathways. If MH₃X were to add either as MH₃ and X or as MH₂X and H, isomeric adducts would be formed. Assuming one mode of addition, there is the possibility that this addition might occur cis, or trans, or both; cis addition might lead to the formation
of two isomeric products, trans addition should give one, and if both mechanisms operated simultaneously three isomeric products would be expected. Finally, when the halogen in \( \text{MH}_2X \) differs from that bound to iridium, halogen exchange might lead to the formation of up to four products of the form \((\text{Ph}_3\text{P})_2\text{Ir(CO)}X\). \( \text{MH}_2Y \) for a single stereochemical arrangement.

It is probable that isomeric products are formed by all these different methods, save perhaps for that associated with addition of \( \text{MH}_3 \) and \( X \). The addition of \( \text{SiH}_3\text{Cl} \) gives rise to a mixture of isomers under different conditions. These will be discussed more fully later but probably arise from cis and trans addition of \( \text{SiH}_2\text{Cl} \) and \( H \) to the iridium complex. Silyl iodide gives a mixture of products which involve halogen exchange. The addition of germyl halides to \( \text{Ir(CO)Cl(Ph}_3\text{P)}_2 \) is preferentially cis except in the case of \( \text{GeH}_3\text{Cl} \) when a mixture of isomers arising from cis and trans modes of addition are observed. Halogen exchange may occur during the additions of \( \text{GeH}_3\text{Br} \) and \( \text{GeH}_3\text{I} \).

The nature of the reaction products as discussed in later sections is very dependent on the length of reaction time, the concentration of products, conditions of reaction and the nature of \( X \) in \( \text{MH}_3X \) (\( M = \text{Si, Ge}; X = \text{H, Cl, Br, I} \)).
Certain differences occur between the silyl and germyl complexes of iridium but analogies have been drawn when reasonable.

2.1.2. 1:1 reaction of $\text{Ir(CO)Cl(PPPh}_3\text{)}_2$ and $\text{SiH}_3X$.

($X=\text{H, Cl, Br, I}$)

When Vaska's compound was allowed to warm to room temperature in benzene with an equimolar proportion of $\text{SiH}_3X$ ($X=\text{Cl, Br, I, H}$) there was a slow reaction. The yellow colour of Vaska's compound faded, and a white precipitate formed. The reaction was complete after 1-2 days. This precipitate, which proved to be insoluble in all common solvents e.g. $\text{C}_6\text{H}_6$, THF, $\text{CH}_2\text{Cl}_2$ and hexane, is the 1:1 adduct formed by oxidative addition of $\text{SiH}_3X$ to $\text{Ir(CO)Cl(PPPh}_3\text{)}_2$. It can be isolated by evaporation of the solvent. No non-condensable gas is produced; no free silyl compound is recovered. Finally, the solids have been analysed. Thus their compositions are established.

$\text{Ir}^{\text{I}}(\text{CO})\text{Cl(PPPh}_3\text{)}_2 + \text{SiH}_3X \longrightarrow \text{Ir}^{\text{III}}(\text{CO})\text{Cl(PPPh}_3\text{)}_2 \cdot \text{SiH}_3X$

As a result of the insolubility of the complexes n.m.r. evidence regarding their composition and stereochemistry cannot be obtained but I.R. evidence provides some basis on which stereochemistry may be assigned.

It appears that two isomers are formed during the addition of $\text{SiH}_3X$ ($X=\text{Cl}$) but whether this is due to cis and
trans addition occurring to the original square planar iridium complex, the addition of SiH$_2$X and SiH$_3$ or rearrangement of the initially formed complex is not known. Similarly, for the adduct with SiH$_3$I the formation of two isomers is possible but in this case the evidence for two products is consistent with the occurrence of halogen exchange. Although the reaction products were subjected to mass spectrometry no conclusive evidence about their formulae could be obtained since the parent ion was not visible and the main part of the cracking pattern which was observed was due to the breakdown of PPh$_3$. (fig. 29). A few peaks at higher m/e value, displaying the characteristic Ir 191 40% and Ir 193 60% line ratio were observed and could be assigned tentatively to ions resulting from loss of Cl, CO or SiH$_2$X from the parent ion. This observation was made for a sample of the adduct with SiH$_3$Cl whose spectrum was run shortly after the arrival of a new mass spectrometer. Spectra run at later dates were much poorer. Obviously, since the molecular weight of the adducts will be of the order 800-1000 and there has always been great difficulty in obtaining mass spectra from other organometallic systems of similar molecular weight, it is not an unexpected result that peaks at high m/e value are not observed. However, it is disappointing since a reasonably intense cracking pattern of the region
Diagramatic representation of the mass spectrum obtained for \( {\text{H}}_{\text{Ir}}(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{SiH}_2\text{Cl} \)

fig. 29
m/3 300-1000 would have been quite indicative of the ligands attached to the central iridium atom.

The white products have a high thermal stability and only decompose at temperatures exceeding 200°C when a brown powder is obtained. Free silyl halide is recovered after pyrolysis. The solids can be kept under vacuum for long periods and even on exposure to moist air for several weeks little decomposition occurs; the I.R. spectra of the products are hardly changed after so long a period of exposure. The apparent stability to moist air is in marked contrast to the sensitivity of platinum-silyl complexes to moisture. The adduct from the addition of SiH$_3$I changes from a white powder to a yellow solid after a short time; this change is probably due to halogen exchange. Since the silyl adducts are thermodynamically unstable with respect to air and moisture, kinetic factors must be of considerable importance in determining the apparently high stability of these iridium-silyl complexes. Decomposition of the 1:1 adducts in benzene at room temperature does not occur readily.

From the evidence available the addition of SiH$_3$X is of the form SiH$_2$X and H which is in agreement with observations on the platinum-silyl systems when intermediates of the form Pt(PEt$_3$)$_2$I. H$_2$SiH$_2$I have been found. It is in direct
contrast to the addition of $\text{CH}_3X$ ($X = \text{I}$) to $\text{Ir(CO)Cl(PPh}_3\text{)}_2$ or $\text{CH}_3X$ ($X = \text{Cl, Br, I}$) to $\text{Ir(CO)Cl(PPh}_2\text{Me)}_2$ when the 1:1 adducts formed were $\text{Ir(CO)Cl}_2\text{.CH}_3\text{(PR}_3\text{)}_2$ ($R_3 = \text{Ph}_3$ or $\text{Ph}_2\text{Me}$). The reaction sequence is also in agreement with the initial work of Chalk and Harrod on the addition of $\text{SiR}_3\text{H}$ to $\text{Ir(CO)Cl(PPh}_3\text{)}_2$ when 1:1 adducts, $\text{Ir(CO)Cl}_2\text{.H.SiR}_3\text{(PPh}_3\text{)}_2$ are formed.

2.1.3. 1:1 reaction of $\text{Ir(CO)Cl(PPh}_3\text{)}_2$ and $\text{GeH}_3X$ ($X = \text{H, Cl, Br, I}$)

Germane reacts slowly in benzene with an equimolar amount of $\text{Ir(CO)Cl(PPh}_3\text{)}_2$ to form a white precipitate as for the analogous reaction with silane. No non-condensible gas was formed; no germyl compound was recovered; from these observations, from analysis and from the infrared spectrum, the compound is the 1:1 adduct.

Reaction of equimolar quantities of the germyl halides ($X = \text{Cl, Br, I}$) and Vaska's compound gives almost immediate discharge of the yellow colour in the solution due to Vaska's compound. Precipitation of a white or cream solid follows slowly, being complete within 30-60 minutes. The volatile products after the reactions are complete contain neither germyl compound nor noncondensible species; this indicates that a 1:1 adduct has been formed.
The initial products and the products resulting after precipitation can be isolated as white solids by evaporation of the solvent.

The I.R. spectra of these compounds are in agreement with the formation of the product \( \text{Ir} (\text{CC}) \text{Cl} (\text{PPh}_3)_2 \cdot \text{H} \cdot \text{GeH}_2 X \) as are the analysis data which were obtained. The analytical results obtained for these systems are not quite as close to the theoretical values as those for the analogous silyl-systems but they are still acceptable.

The most important feature of the characterization of the adducts of the germyl halides, however, is that it proved possible to obtain n.m.r. spectra for the initial products before complete precipitation occurred. Hence it was possible to make deductions about the structures of these adducts that are based on much more direct evidence than was available for the adducts of germane and the silyl halides. Because of a greater concentration of product in the n.m.r. tubes than in the reaction tubes used initially, precipitation occurred more rapidly. In order to facilitate as fast an initial reaction as possible, the iridium complex was ground to a fine powder before use since the speed of the reaction is found to depend on the state of the starting material. Presumably fine division makes Vaska's compound dissolve faster.
The addition of \( \text{GeH}_3 \text{X}(\text{X} = \text{Br}, \text{I}) \) results in each case in the formation of a single isomer, \( \text{Ir(CO)}\text{Cl(PPh}_3)_2\cdot\text{H. GeH}_2\text{X} \), as initial product, whose structure (I. fig. 30) can be almost unambiguously assigned from the n.m.r. spectrum. The n.m.r. evidence will be discussed in greater detail later; the spectra are quite consistent with addition of \( \text{GeH}_2\text{X} \) and H. Halogen exchange was observed in some tubes, the heavier halogen atom moving on to the iridium which as discussed previously is an energetically favourable reaction. The exchange may have been due to a trace of impurity in the reaction mixture, since it was not observed consistently. When the reaction of \( \text{Ir(CO)}\text{Cl(PPh}_3)_2 \) with \( \text{GeH}_3\text{Br} \) was investigated in the presence of 10\% HCl the rate of precipitation was increased, resulting in a weak n.m.r. spectrum. The spectrum, however, was identical to that obtained from the reaction of \( \text{Ir(CO)}\text{Cl(PPh}_3)_2 \) with \( \text{GeH}_3\text{Br} \) except that the resonance line at 4.84\,\delta assigned to the exchange product, was increased in intensity with respect to the line at 5.5\,\delta assigned to the normal product. From this it appears that the presence of HCl assists the halogen exchange process.

Addition of \( \text{GeH}_3\text{Cl} \) to Vaska's compound results in the formation of two isomers. One is analogous to the product observed in the reactions of \( \text{GeH}_3\text{Br} \) and \( \text{GeH}_3\text{I} \);
the other has a very different n.m.r. spectrum and its structure, (II. fig. 30) deduced from this evidence, is of the same form \( \text{Ir}(\text{CO})\text{Cl} \quad \text{H}(\text{PPh}_3)_2 \quad \text{GeH}_2\text{Cl} \) with the phosphine groups remaining mutually trans.

![Diagram](image)

There was some evidence for the presence of a third isomer present in trace amounts in some tubes.

It is possible that the precipitation which occurs after a short period may be associated with further isomerisation of the initial products but this theory of course cannot be tested by the use of n.m.r. spectroscopy. Further isomerisation could involve the rearrangement of the phosphine groups to a mutually cis configuration, resulting in a complete change of stereochemistry within the complex. A product containing cis phosphines has been obtained after the long term reaction of an excess of \( \text{SiH}_3\text{Cl} \) with Vaska's compound. The infrared spectra of the initial product and of the precipitate were not very different in character and it was difficult to determine the exact nature of the possible
isomerisation from this evidence. It is possible that isomerization occurs during the evaporation of solvent from the initial reaction system and that the two products studied by I.R. spectroscopy are in fact identical. The results are therefore rather tentative although the assignments of certain modes are in agreement with n.m.r. evidence.

Exposure of the solid products to moist air for long periods causes little change in their appearance except in the case of the adduct with germyl iodide which turns yellow-brown in colour. This change is probably due to halogen exchange rather than to decomposition since the I.R. spectra of these products show no great change from those of the original products. These observations are in agreement with those from the silyl complexes of iridium and again illustrate the dominance of kinetic factors over the inherent thermodynamic instability of the systems. The germyl complexes are less stable in benzene than the analogous silyl complexes, since after a few days standing at room temperature the mixtures, initially white solids in a colourless solvent, turn a deep yellow-brown in colour. The formation of 1:1 adducts during the reaction of Ir(CO)Cl(PPh₃)₂ with an equimolar quantity of GeH₃X is in direct contrast to Glockling’s observations on the reactions of analogous organo-germane systems. Reaction of equimolar portions
of GeR₃H and Ir(CO)Cl(PPh₃)₂ results only in the production of the soluble dihydride species IrH₂(CO)GeR₃(PPh₃)₂ and unreacted starting material.

2.1.4. 2:1 reaction of Ir(CO)Cl(PPh₃)₂ and SiH₃X

(X = H, Cl, Br, I)

Reaction of Ir(CO)Cl(PPh₃)₂ with a two-fold excess of SiH₃X (X = H, Cl, Br, I) results in the almost immediate formation of a white precipitate. The reaction reaches completion within 5-10 minutes. This result could imply that the reaction:

Ir(CO)Cl(PPh₃)₂ + xSiH₃X → Ir(CO)Cl(PPh₃)₂·H₂SiH₂X + (x-1)SiH₃X

is an equilibrium reaction. If, however, the reaction were merely an accelerated equilibrium, the 1:1 process should also go rapidly because of the insolubility of the product.

It is more likely, therefore, that the initial rate is accelerated by an excess of silyl halide and that a mechanism with a high order in SiH₃X is involved. The products of this reaction were studied under a series of conditions obtained by leaving the reactants in solution at room temperature for different periods of time. Further reaction occurs in certain systems as is discussed below.

(a) Reaction after 5-10 minutes

The initial product of the reaction of Ir(CO)Cl(PPh₃)₂ with a two fold excess of silyl compound is a white precipitate
which is the 1:1 adduct. There is a complete absence of non-condensibles in the volatiles from the reaction mixture and half the original quantity of silyl compound used is recovered. Analysis of the white powders obtained by evaporation of the solvent and removal of excess silyl halide and the I.R. spectra of these products support this conclusion. A concentrated mixture of Ir(CO)Cl(PPh₃)₂ and a two-fold excess of SiH₃Cl was investigated at the moment of reaction by n.m.r. spectroscopy. The resulting spectrum is very weak but there may have been a triplet at 18% If this is real, the phosphine ligands are remaining mutually trans, while the product is in solution. The addition of SiH₂Cl results in the formation of only one isomer, Ir(CO)Cl, H. (PPh₃)₂ SiH₂Cl, indicating that the isomerisation previously observed must be slower than the process resulting in the formation of the initial product. Addition of SiH₃Br results in the formation of one isomer, the same as the product of the 1:1 reaction, and addition of SiH₃I also gives a single isomer. Obviously in the latter case halogen exchange must be a slower process than the oxidative addition reaction.

(b) Reaction after periods of time (2-3 days)

If the initial products are left in the reaction tube at room temperature for a short time, a 1:1 adduct is formed;
this is clear since there are no non-condensible products, and the amount of silyl halide recovered corresponds with that expected. The white products obtained at this stage can be isolated by evaporation of the solvent and have been investigated by I.R. spectroscopy. There, however, the similarity in the reaction products ends. For X = Cl, an isomeric mixture of products is obtained as in the 1:1 reaction. This observation supports the idea that the isomerisation reaction is slower than the initial reaction. When X = Br, one isomer is formed (whether this results from steric hinderance to the formation of other isomers is not known) and when X = I, a mixture of products, seemingly formed by halogen exchange is found. This latter result is in agreement with evidence for halogen exchange between silyl ligands and a halogen attached to a metal atom which has been shown to occur in the platinum systems.36

(c) Reaction after long periods—fortnight.

If the reactants are allowed to react together for longer periods their behaviour is seen to vary depending on the nature of the halogen atom attached to the silicon group. For X = Cl, the white precipitate disappears after approximately 10 days, leaving a colourless solution. The nature of the product, \( \text{IrH}_2(\text{CC})\text{Cl(PPH}_3)_2\text{SiH}_2\text{Cl} \), (see fig. 31) in this solution is determined by n.m.r. spectroscopy.
This reaction appears to have followed a reaction sequence analogous to that observed for the reactions of organogermaaneses and organosilanes with the iridium complex. There is a slight trace of non-condensibles from the reaction but the main volatile products are $\text{SiH}_2\text{Cl}_2$ and small amounts of $\text{SiH}_3\text{Cl}$ and $\text{SiH}_4$. Some of the $\text{SiH}_2\text{Cl}_2$ could have arisen from disproportionation of excess $\text{SiH}_3\text{Cl}$ present in the initial reaction mixture. The main portion is thought to arise from the reaction of excess $\text{SiH}_3\text{Cl}$ with the initially formed 1:1 adduct. The dihydride complex 

$$\text{Ir(}\text{CO})\text{Cl(}\text{PPh}_3\text{)}_2\cdot\text{H. SiH}_2\text{Cl} + \text{SiH}_3\text{Cl} \rightarrow \text{Ir(}\text{CO})\text{H}_2\cdot(\text{PPh}_3)_2\cdot\text{SiH}_2\text{Cl} + \text{SiH}_2\text{Cl}_2$$

which is soluble in benzene, has been studied using both n.m.r. and I.R. spectroscopy. It can be isolated as a white solid by evaporation of the solvent and its I.R. spectrum shows significant differences from that of the 1:1 adduct 

$$\text{Ir(}\text{CO})\text{Cl(}\text{SiH}_2\text{Cl})(\text{PPh}_3)_2\cdot\text{H.}$$

These differences are consistent with the removal of the chlorine atom which was
bonded to iridium and replacement of it by a hydride ligand.

The long term reactions of SiH₃Br and SiH₃I do not produce analogous soluble dihydride complexes; SiH₄ is obtained as the volatile product from the reaction of SiH₃Br and a mixture of SiH₃Cl and SiH₃I is obtained from the SiH₃I reaction. Silane is found to be the volatile product from the SiH₃I reaction after one week's reaction time. The continual change in the nature of the volatile reaction products indicates that the reaction systems are dynamic and not static; there must be a concurrent change in the nature of the silyl complex of iridium. The white solids from these reactions can again be isolated and investigated by I.R. spectroscopy. Certain changes in these spectra compared with those for the initial and intermediate reaction products are observed. A product containing SiHBr₂ bonded to iridium probably results from the reaction of SiH₃Br with the initial 1:1 adduct, Ir(CO)Cl.H.(PPh₃)₂.SiH₂Br. Halogen exchange has occurred during the reaction of SiH₃I with Ir(CO)Cl.H.(PPh₃)₂. SiH₂I resulting in the almost complete replacement of chlorine bonded to iridium and the probable formation of the complex Ir(CO)I.H.(PPh₃)₂.SiH₂I.

It would appear, therefore, that the formation of further products of the form Ir(CO)Cl(PPh₃)₂.SiHBr₂.H and
Ir(CO)I.H.(PPh₃)₂.SiH₂I is preferential (for X = Br, I) to the formation of a dihydride complex analogous to Ir(CO)H₂(PPh₃)₂.SiH₂Cl.

The soluble dihydride complex Ir(CO)H₂(PPh₃)₂.SiH₂Cl is stable in benzene over long periods of time but the products obtained from the reactions of excess SiH₃X (X = Br, I) start to decompose after a few weeks in solution giving yellowy-brown deposits. The white solids which can be isolated in all cases are stable for a short time in moist air but their stability is much lower than that of the 1:1 adducts.

2.1.5. 2:1 reaction of Ir(CO)Cl(PPh₃)₂ and GeH₃X (X = H, Cl, Br, I)

Ir(CO)Cl(PPh₃)₂ reacts immediately with a two-fold excess of germane to form a thick white precipitate. This product is the 1:1 adduct Ir(CO)Cl.H.(PPh₃)₂.GeH₃. Half the initial quantity of germane added is recovered. The explanation of the increase in speed of this reaction in the presence of excess germane may be the same as that given for the reaction of Vaska's compound with excess silyl compounds. Namely, a mechanism involving a high order in germane occurs.

Germyl halides (X = Cl, Br, I) added in a two-fold excess immediately discharge the yellow colour due to
Ir(CC)Cl(PPh₃)₂, in benzene, in an analogous manner to the 1:1 reaction. Under these conditions the speed of reaction does not seem to differ from that using equimolar quantities. The white products are isolated by evaporation of the solvent and excess germyl compound from the reaction mixture. No non-condensible gas was formed; half the initial amount of germyl halide was recovered; from these observations, from analysis and from the I.R. and n.m.r. spectra, the products are the 1:1 adducts.

Again the reaction of GeH₃Cl with Ir(CO)Cl(PPh₃)₂ gives rise to two isomers of the same form as under 1:1 conditions and the reaction of GeH₃Br and GeH₃I gives one isomer for each product. The n.m.r. spectra are identical to those obtained under 1:1 conditions. It is possible that halogen exchange occurs during certain reactions of GeH₃X (X = Br, I). Excess GeH₃Cl is observed in the volatiles, studied both by I.R. and n.m.r. spectroscopy, from the reaction of GeH₃Cl. During the reaction of GeH₃X (X = Br, I) the peaks due to these germyl volatiles start to disappear from the n.m.r. spectrum after a short time and are replaced by peaks which can be assigned to GeH₂X₂ (X = Br, I). The same reactions gave GeH₄ as the major volatile product when the reaction products were studied under different conditions; in a larger reaction
vessel and by I.R. spectroscopy. The difference in the observation of germyl volatiles is strange since the only major difference in the reaction conditions is the size of the reaction vessel.

Precipitation occurs after a short period as in the 1:1 systems. Again it is possible that isomerisation is occurring. It would seem likely, from the change in the germyl volatiles with reaction time, that a further reaction is occurring after the initial formation of a 1:1 adduct. Halogen exchange is expected to be the preferred side reaction. The white solids which can be isolated by evaporation of the solvent are moderately stable in air. They decompose in solution in the presence of free germyl compound, after a few days, to give yellow brown products. Hydrogen and GeH₄ have been observed in the volatiles after a few days reaction. Soluble species, IrH₂(CO)(PPh₃)₂GeH₂X, analogous to those prepared by Glockling have never been isolated.

In the presence of excess GeH₃X, di- and tri- germyl species of iridium are not formed. This observation contrasts with Bentham’s findings on the reactions of trans- Pt(PEnt₃)₂HCl and excess GeH₃Cl,²⁶,⁵¹

2.1.6. Reactions of Ir(CO)Cl(PPh₃)₂ with methyl silyl chloride.

The reaction of methyl silyl chloride with Ir(CO)Cl(PPh₃)₂
results in the initial formation of the 1:1 adduct. If equimolar amounts of reactants are used, a slow reaction occurs and a mixture of isomers results. A fast reaction occurs in the presence of a two-fold excess of methyl silyl compound giving rise to predominantly one isomer. Prolonged standing of the reactants in benzene (2 weeks) produces a colourless solution and the soluble complex, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHMeCl} \). The main volatile product from this reaction is \( \text{MeSiHCl}_2 \), with traces of \( \text{MeSiH}_3 \) and \( \text{MeSiH}_2\text{Cl} \). All these results are analogous to those obtained from the reactions of \( \text{Ir(CO)Cl(PPh}_3)_2 \) and \( \text{SiH}_3\text{Cl} \) under various conditions. The different products could be isolated as white solids and were investigated by I.R. spectroscopy and analysis. The nature of the soluble complex was determined mainly from its n.m.r. spectrum. Traces of other complexes were present along with the dihydride.

Use of methylated silyl systems (\( \text{MeSiH}_2\text{X} \)) connects the study of \( \text{SiH}_3 \)-derivatives with the previous studies of complexes of organosilanes eg. \( \text{Me}_3\text{SiH} \). There seems to be a parallel between the reaction schemes observed for both systems; initial formation of a 1:1 adduct is followed by slow conversion to a dihydride species.
Section 2.2.
The reaction of Ir(CO)Cl(PPh$_3$)$_2$ and SiH$_3$Cl in chlorinated solvents.

Reaction of Ir(CO)Cl(PPh$_3$)$_2$ with a two-fold excess of silyl chloride in dichloromethane results in the immediate formation of a white precipitate. This product has exactly the same spectroscopic properties as that formed in benzene as solvent. The stoichiometry of the reaction indicates that the 1:1 adduct, Ir(CO)Cl.H$_2$.SiH$_2$.Cl. (PPh$_3$)$_2$ has again been formed. Dichloromethane can therefore be used as a reaction solvent since it does not appear to bring about decomposition of the silyl complex of iridium. Unfortunately the product is no more soluble in this solvent than it is in benzene; it was not possible to obtain an n.m.r. spectrum of the product. Furthermore, CH$_2$.Cl$_2$ has limitations as a solvent for silyl systems since a large range (4-6 ppm) of the $^1$H n.m.r. spectrum is masked by resonance lines due to the solvent.

The behaviour of CH$_2$.Cl$_2$ towards the silyl complexes of iridium contrasts with the behaviour of similar chlorinated solvents. Chloroform is said to attack metal-silicon bonds. The reaction of Ir(CO)Cl(PPh$_3$)$_2$ and a two-fold excess of silyl chloride in this solvent produces a complex mixture of products which could not be positively identified. The same reaction in CCl$_4$ also gave rise to a mixture of products.
This is not unexpected since CCl$_4$ itself is known to form an addition compound with Ir(CO)Cl(PPh$_3$)$_2$.\textsuperscript{73}

Section 2.3.

Reactions under heterogeneous conditions

The compounds which have been discussed in earlier sections have been formed under homogeneous conditions. Some reactions give rise to isomeric products. Vaska has observed, that during the addition of HX (X = Cl, Br, I) to Ir(CO)Cl(PPh$_3$)$_2$ in benzene, isomeric products are formed. Only one isomer is formed if the same reactions are carried out under heterogeneous conditions.\textsuperscript{79}

Ir(CO)Cl(PPh$_3$)$_2$ and an equimolar quantity of SiH$_3$Cl were left in a sealed tube for two weeks. No reaction was observed and the reactants were recovered unchanged after this period. It is possible that reaction might occur eventually if a large excess of silyl chloride was used. The homogeneous reaction is an equilibrium reaction and this is probably also true for the heterogeneous reaction. In the latter case the equilibrium may lie well over to the side of the reactants. It is also possible that solvent molecules are involved in the reaction mechanism and that their absence inhibits the reaction. It is impossible to determine whether it is kinetic or thermodynamic factors which are limiting the reaction.
Section 2.4.

Reactions involving Ir(CO)Y(Ph$_3$)$_2$ ($Y = Br$, I)

In an attempt to clarify the I.R. assignments for the 1:1 adducts, Ir(CO)Cl.H, SiH$_2$X (Ph$_3$)$_2$ ($X = Cl$, Br, I) the preparation of Ir(CO)Y(Ph$_3$)$_2$ ($Y = Br$, I) was attempted. It was hoped that data from the reactions of these iridium complexes with germyl halides might indicate whether halogen exchange explains the presence of extra resonance lines in the n.m.r. spectrum of Ir(CO)Cl.H, GeH$_2$X, (Ph$_3$)$_2$ ($X = Br$, I).

It was possible to obtain the bromide complex, IrBr(CO)(Ph$_3$)$_2$ pure, but the iodide complex could only be prepared as its oxygen adduct despite rigorous precautions to prevent oxygenation of the complex during preparation.

The reaction of a two-fold excess of silyl chloride and Ir(CO)Br(Ph$_3$)$_2$ gives initially a yellow solution from which a white solid rapidly precipitates. It is not known whether the initial yellow coloration is due to the bromide complex dissolving in benzene prior to a rather slower oxidative addition of silyl chloride or to a soluble silyl species of iridium. I.R. evidence and examination of the volatiles present in the reaction mixture indicates that an isomeric mixture of 1:1 adducts, Ir(CO)Br.H, SiH$_2$Cl(Ph$_3$)$_2$, is formed.
A creamy-white solid is formed immediately during the reaction of Ir(CO)Br(PPh₃)₂ and a two-fold excess of germane. Reaction of Ir(CO)Br(PPh₃)₂ and a two-fold excess of GeH₃Cl gives rise to a yellow solution initially and rapid precipitation of a white solid follows. Both reactions give rise to 1:1 adducts as products. N.m.r. investigations of the reaction products were not very successful because of the rapid precipitation and the spectra, if they could be obtained, were very weak and gave no evidence about the nature of the products. The complex, Ir(CO)Br₂H₂GeH₂Cl(PPh₃)₂ which is formed initially is less soluble in benzene than the germyl complexes which are the initial products from the reaction of Ir(CO)Cl(PPh₃)₂ and GeH₃X (X = Cl, Br, I).

### Section 2.5.

**H¹ n.m.r. spectra**

The proton resonance spectra were recorded in benzene or (in some cases) deuterobenzene using tetramethylsilane as an internal standard. Most were recorded on a Varian 100 MHz machine but for a few, where the complexes were relatively stable in solution, the Varian 220 MHz machine was used. The general features of the spectra are now discussed.

The spectrum associated with the phenyl phosphine groups
\[ \text{Fig. 32} \]

$^1H$ n.m.r. spectrum of triphenylphosphine region
is complicated and is generally masked by the strong band due to the benzene solvent. In solutions of deuterobenzene it occurs as a strong multiplet at $3.0\tau$ with a much weaker multiplet due to the protons ortho to the phosphorus atom, occurring to low field ($2.2\tau$) of the main resonance. A typical spectrum is shown in fig. 32.

Since the reaction of $\text{Ir(\text{CO})Cl(\text{FF}_{3})_{2}}$ with $\text{SiH}_{3}X (X = \text{H, Cl, Br, I})$ initially produces insoluble products, only the initial products from the reaction of this iridium complex with $\text{GeH}_{3}X (X = \text{Cl, Br, I})$ can be investigated using n.m.r. spectroscopy.

The $\text{GeH}$ spectrum is very characteristic: an example is shown in fig. 33. It consists of a triplet; the splitting in this peak is due to coupling of $\text{GeH}$ with the two equivalent phosphorus atoms. Therefore there are two n.m.r. parameters associated with the $\text{GeH}$ resonance of each compound: chemical shift and $J(\text{H Ge Ir})$. The reaction of $\text{GeH}_{3}\text{Cl}$ with $\text{Ir(\text{CC})Cl(\text{FF}_{3})_{2}}$ produces at least two isomeric products. One of these isomers has a $\text{GeH}$ spectrum as described but the $\text{GeH}$ spectrum of the other shows an additional doublet splitting; a third parameter $J(\text{H-Ir-Ge-\text{H}})$, as shown by decoupling, is involved. Thus, the $\text{GeH}$ spectrum is a doublet of triplets as shown in fig. 33. The parameters for the germyl complexes of iridium are recorded in table 2.1.
Diagramatic representation of the $^1$H n.m.r. spectra for GeH$_3$ and IrH$_3$ resonances in the complexes H$_2$Ir(SeCC)PPh$_3$$_2$Cl$_2$. The proposed stereochemistries of the complexes are shown above.
The chemical shift of GeH in IrH₂Cl₁(CC)GeH₂X(FF₃)₂
depends on the nature of the halogen bound to Ge. It is
in general shifted a little to low field of the value for the
parent hydride resonance in benzene, and varies with different
halogens in the same way as the value of the parent hydrides,
decreasing in the order GeH₂I > GeH₂Br > GeH₂Cl. This
order is consistent with shifts to lower field due to de-
shielding at H being caused by increasing electron withdrawal
at germanium. The coupling constant J(α-Ge-Ir-γ) remains
fairly constant for the compounds Ir(CC)Cl(GeH₂X)(F₃H)₂H₁,
showing a slight increase as X varies in the order
Cl < Br < I. The suggestion that halogen exchange occurs
in certain reactions of Ir(CC)Cl(FF₃)₂ and GeH₃Br or
GeH₃I is based on the values of γ(GeH). A triplet occurs at
the value associated with a GeH₂Cl ligand.
<table>
<thead>
<tr>
<th>Adduct</th>
<th>Structure</th>
<th>( \gamma(\text{Ge-H}) )</th>
<th>( J(\text{H-Ge-Ir-P}_c) )</th>
<th>( J(\text{H-Ge-Ir-H}_t) )</th>
<th>( \gamma(\text{IrH}) )</th>
<th>( J(\text{H-Ir-P}_o) )</th>
<th>Addendum</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ir(CO)Cl(GeH}_2\text{Cl}(\text{PPh}_3)_2\text{H}) )</td>
<td>I</td>
<td>4.75tpt</td>
<td>6c/s</td>
<td></td>
<td>27.14tpt</td>
<td>12c/s</td>
<td>( \text{GeH}_2\text{Cl} )</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>5.78dtb</td>
<td>6c/s</td>
<td>3c/s</td>
<td>17.77dtb</td>
<td>15c/s</td>
<td>( \text{GeH}_2\text{Cl} )</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>19.38mpt</td>
<td>n.o.</td>
<td>( \text{GeH}_2\text{Cl} )</td>
</tr>
<tr>
<td>( \text{Ir(CO)Cl(GeH}_2\text{Br}(\text{PPh}_3)_2\text{H}) )</td>
<td>I</td>
<td>5.40tpt</td>
<td>7c/s</td>
<td></td>
<td>27.10tpt</td>
<td>12c/s</td>
<td>( \text{GeH}_2\text{Br} )</td>
</tr>
<tr>
<td>( \text{Ir(CO)Br(GeH}_2\text{Cl}(\text{PPh}_3)_2\text{H}) )</td>
<td>I</td>
<td>4.76tpt</td>
<td>7c/s</td>
<td></td>
<td>27.03tpt</td>
<td>12c/s</td>
<td>( \text{GeH}_2\text{Cl} )</td>
</tr>
<tr>
<td>( \text{Ir(CO)Cl(GeH}_2\text{I}(\text{PPh}_3)_2\text{H}) )</td>
<td>I</td>
<td>6.52tpt</td>
<td>8c/s</td>
<td></td>
<td>26.99tpt</td>
<td>11c/s</td>
<td>( \text{GeH}_2\text{I} )</td>
</tr>
<tr>
<td>( \text{Ir(CO)I(GeH}_2\text{Cl}(\text{PPh}_3)_2\text{H}) )</td>
<td>I</td>
<td>4.79tpt</td>
<td>8c/s</td>
<td></td>
<td>26.99tpt</td>
<td>11c/s</td>
<td>( \text{GeH}_2\text{I} )</td>
</tr>
</tbody>
</table>

All products are derived from additions to \( \text{Ir(CO)Cl(PPh}_3)_2 \):

Structure refers to numbering of isomers in fig. 30:

The evidence from the Ge\textsubscript{II} spectrum is in agreement with that obtained for the products of the reaction Pt(H)X(P\textsubscript{Et\textsubscript{3}}\textsubscript{2}) and Ge\textsubscript{H}\textsubscript{2}. The relevant data is shown in table 2.2.

**TABLE 2.2.**

Parameters recorded for HGe proton resonance spectra of products from the reaction of Pt(H)X(P\textsubscript{Et\textsubscript{3}}\textsubscript{2}) and Ge\textsubscript{H}\textsubscript{2}Y.

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>(\gamma) (Ge\textsubscript{H})</th>
<th>J(HGePtP\textsubscript{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>4.95</td>
<td>7.4c/s</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>5.62</td>
<td>7.75c/s</td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td>6.51</td>
<td>8.35c/s</td>
</tr>
<tr>
<td>Cl</td>
<td>(GeHCl\textsubscript{2})</td>
<td>3.07\textsuperscript{a}</td>
<td>7.3c/s</td>
</tr>
<tr>
<td>Cl</td>
<td>H</td>
<td>7.20</td>
<td>5.8c/s</td>
</tr>
</tbody>
</table>

The parameters were measured relative to C\textsubscript{6}D\textsubscript{6} (\(\gamma\)-2.83) unless otherwise stated.

\(\textsuperscript{a}\) - observed in C\textsubscript{6}D\textsubscript{6}

The Ir\textsubscript{II} spectrum is also very characteristic. An example is shown in fig. 34. As is to be expected, for a hydride directly bonded to a transition metal, this resonance is found to high field of TMS. The spectrum consists of a triplet; the splitting is due to coupling of Ir\textsubscript{II} with the two effectively equivalent phosphorus atoms. Therefore, as for Ge\textsubscript{H}, there are two parameters associated with this resonance:
chemical shift and $J(H_c-Ir-P)$. The coupling constant is
greater than that of $J(H-Ge-Ir-P)$ as there is one less atom
between the coupling nuclei. Again the third parameter,
$J(H_t-Ir-Ge-H)$ is introduced when considering the isomeric
products from the germyl chloride reaction. The parameters
are recorded in table 2.1.

Previous work has shown that high field chemical shift
values assigned to hydride ligands attached to a central
iridium atom are determined by the nature of the ligand trans
to the hydride. These results are summarized in table 2.3
and are observed for isomers of the species $\text{IrH}_2(\text{CO})(\text{PR}_3)_2$
and other organo-silyl and germyl species of iridium. In
this assignment it appears that increasing trans effect of the
ligand trans to the hydride causes a decrease in the $\tau$ value
of $\text{IrH}$. Therefore $H$ trans to Cl would be expected to have a
large $\tau$ value and $H$ trans to $\text{GeH}_2X$ or $H$ a small $\tau$ value.
From a series drawn up by Chatt, $\text{SiH}_2X$ and $\text{GeH}_2X$ would
be expected to have high trans influences.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\tau$</th>
<th>$J(H-Ir-P_c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$ trans to Cl</td>
<td>$\sim 27$</td>
<td>$\sim 12c/s$</td>
</tr>
<tr>
<td>$H$ trans to CO )</td>
<td>$\sim 19-21$</td>
<td>$\sim 16c/s$</td>
</tr>
<tr>
<td>$H$ &quot; &quot; PR$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$ v. CO $&lt;$ Hv. PR$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$ trans Ge$_3$R$_3$</td>
<td>$\sim 17$</td>
<td>$\sim 14c/s$</td>
</tr>
<tr>
<td>$H$ &quot; SiR$_3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
By analogy the resonance lines observed at $-27 \gamma$ in the 
$\text{Ir}^H$ spectrum of the germyl species of iridium can be 
assigned to hydride trans to chlorine. The doublet of 
triplets at $-17 \gamma$ observed in the spectrum from the reaction 
of $\text{Ir(}CO)\text{Cl(PPH}_3)_2$ and $\text{GeH}_3\text{Cl}$ is assigned to hydride trans 
to a germyl ligand. Evidence for the formation of a third 
isomer in the reaction of $\text{Ir(}CO)\text{Cl(PPH}_3)_2$ and $\text{GeH}_3\text{Cl}$ came 
from the observation of a weak multiplet at $19.38 \gamma$ which 
could be assigned to a hydride trans to a CO or phosphine 
ligand.

The complete spectrum from the reaction of  
$\text{Ir(}CO)\text{Cl(PPH}_3)_2$ and $\text{GeH}_3\text{Cl}$ is shown in Fig. 35 = Plate 1. 

$\gamma(\text{Ir}^H)$ is almost independent of the halogen bound to 
germanium; the value decreases slightly. During the 
reaction of $\text{Ir(}CO)\text{Cl(PPH}_3)_2$ with $\text{GeH}_3X$ ($X = \text{Br, I}$) a weak 
triplet slightly to low field of the main resonance is assigned 
to the hydride trans to chlorine when halogen exchange has 
occurred; the isomer $\text{Ir(}CO)\text{Cl(PPH}_3)_2.H.\text{GeH}_2\text{Cl}$ is 
postulated. Resonance lines associated with the $\text{Ir}^H$ spectrum 
of the other possible isomers; $\text{Ir(}CO)\text{Br(PPH}_3)_2.H.\text{GeH}_2\text{Cl}$ 
and $\text{Ir(}CO)\text{Br(PPH}_3)_2.H.\text{GeH}_2\text{Br}$ could not be found. By 
analogy with the platinum-silyl systems studied by 
36,37 Bentham a decrease of $-100$ Hz would be expected in $\gamma(\text{Ir}^H)$ 
as the halide ligand trans to it changes from Cl to Br to I.
\[ \text{GeH region} \]

\[ \text{IrH region} \]

\[ ^1H \text{n.m.r. spectra from the reaction of Ir(CO)Cl(PPh}_3)_2 \text{ and GeH}_3\text{Cl observed at 100MHz} \]

PLATE 1
An explanation of the absence of $\nu(IrH)$ associated with these latter isomers is the greater insolubility of isomers containing bromine directly bound to iridium with respect to those containing chlorine bound to iridium.

Spin decoupling was used to differentiate between the isomers formed during the reaction of Ir(CO)Cl(PPh$_3$)$_2$ and GeH$_3$Cl. Irradiation at 17.77 GHz results in the collapse of the doublet splitting at 5.78 GHz. Thus the resonance line at 17.77 GHz can be assigned to a hydride trans to GeH$_2$Cl and $J(H_4-Ge-Ir-H)$ has been removed.

The IrH spectrum of IrH(CO)Cl$_2$((PPh$_3$)$_2$SiH$_2$Cl was investigated at the instant of warming Ir(CO)Cl(PPh$_3$)$_2$ and an excess of silyl chloride to room temperature and there is the possibility of a triplet at 17 GHz. Such a spectrum would be consistent with the phosphine ligands remaining mutually trans and the hydride being trans to a ligand of high trans effect eg. SiH$_2$Cl. However it is impossible to take this evidence as being conclusive because of the weakness of the spectrum.

The n.m.r. spectrum of the soluble dihydride species was used to determine the stereochemistry of this complex. The spectrum is very weak and complex but similar in nature to that obtained for analogous systems. Spectra have been obtained at both 100 and 220 MHz. The SiH spectrum shows a resonance at 4.54 GHz, characteristic of -SiH$_2$Cl bonded to a
transition metal. This part of the spectrum consists of a doublet of doublets and the splitting is due to coupling of \( \text{SiH}_2 \) with two non-equivalent phosphorus atoms. Some fine splitting is observed in each line but is very small. The parameters associated with this resonance are the chemical shift, \( J(P_1-\text{Ir-Si-H}) \) and \( J(P_2-\text{Ir-Si-H}) \). Thus the \( \text{SiH}_2\text{Cl} \) group is trans to one phosphine ligand and cis to the other.

The \( \text{IrH} \) spectrum (fig. 37) has two groups of peaks in the region 19-21 \( \mu \)g. Overlapping of certain resonance lines occurs when the spectrum is obtained using the 100 MHz spectrometer but this difficulty can be overcome by use of the 220 MHz machine. The first group consists of a broad triplet which would be more precisely described as a doublet of doublets of doublets; the splitting in this peak is due to coupling of \( \text{IrH}_1 \) with two non-equivalent phosphorus atoms (both cis to the hydride) and with the other hydride ligand. There are therefore four parameters associated with this resonance: chemical shift, \( J(P_1-\text{Ir-H}_1) \), \( J(P_2-\text{Ir-H}_1) \) and \( J(H_2-\text{Ir-H}_1) \). Long range coupling from the silyl protons can effectively be neglected. Spin decoupling showed that the hydride and silyl ligands were mutually cis. Irradiation at 19.53 \( \mu \text{Hz(H}_1 \) caused no change in the resonance at 4.54 \( \mu \text{Hz(SiH}_2\text{Cl}) \); thus \( J(H-\text{Si-Ir-H}) \) is not observed. The second group of peaks is also a doublet of doublets of doublets; the splitting is due to coupling of
Diagramatic representation of the $^1$H n.m.r. spectra of the SiH and IrH resonances in the complex $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Cl}.\text{SiH}_2\text{Cl}$. The proposed stereochemistry of the complex is shown above.
Ir\textsubscript{1}H\textsubscript{2} with two non-equivalent phosphorus atoms (one trans and the other cis to the hydride) and the other hydride ligand. Again there are four parameters associated with this complex; chemical shift, \(J(\text{P}_1-\text{Ir}-\text{H}_2)\), \(J(\text{P}_2-\text{Ir}-\text{H}_2)\) and \(J(\text{H}_1-\text{Ir}-\text{H}_2)\). The data from this complex is shown in table 2.4. The same dihydride complex has been prepared, as will be discussed in chapter 3, by the reaction of \(\text{IrH(CO)(PPh}_3)_3\) and \(\text{SiH}_3\text{Cl}\).

**TABLE 2.4**

Parameters from the proton resonance spectra of \(\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Cl}\).

<table>
<thead>
<tr>
<th>(\gamma(\text{SiH}))</th>
<th>(J(\text{P}_1-\text{Ir}-\text{Si}-\text{H}))</th>
<th>(J(\text{P}_2-\text{Ir}-\text{Si}-\text{H}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4.54)</td>
<td>(12\text{c/s})</td>
<td>(24\text{c/s})</td>
</tr>
<tr>
<td>(\gamma(\text{IrH}))</td>
<td>(J(\text{P}_1-\text{Ir}-\text{H})/)</td>
<td>(J(\text{H}_1-\text{Ir}-\text{H}_2)/)</td>
</tr>
<tr>
<td>(1958)</td>
<td>(16\text{c/s})</td>
<td>(4\text{c/s})</td>
</tr>
<tr>
<td>(2006)</td>
<td>(20\text{c/s})</td>
<td>(110\text{c/s})</td>
</tr>
</tbody>
</table>

The \(\text{H}^1\) n.m.r. spectrum of the soluble dihydride species formed by the reaction of \(\text{Ir(CO)Cl(PPh}_3)_2\) and a two-fold excess of methyl silyl chloride is more complex than those discussed earlier for the species \(\text{IrH}_2(\text{CO})\text{SiH}_2\text{Cl(PPh}_3)_2\). It is likely that more than one isomer is present in solution but that the predominant species is \(\text{IrH}_2(\text{CO})\text{SiHMeCl(PPh}_3)_2\). There is evidence for a weak multiplet at \(4.78\gamma\), which is assigned to \(\text{SiH}_1\), and for two complex multiplets at \(8.43\gamma\) and \(8.63\gamma\).
which are assigned to CH of the methyl group. The IrH spectrum displays the same complex overlapping of peaks but consists predominantly of a triplet at 19.7\(\gamma\)J(P-Ir-H-20c/s) and a doublet of doublets, (centre 20.2\(\gamma\), J(P-Ir-H-110c/s) J(P-Ir-H-18c/s) such a spectrum is consistent with the presence of two different hydride ligands: one mutually cis to two non-equivalent phosphorus atoms, the other trans to one phosphorus and cis to the other. By analogy with the complex, IrH\(_2\)(CO)SiH\(_2\)Cl(PPh\(_3\))\(_2\), and from the agreement in n.m.r. evidence the structure of IrH\(_2\)(CO)SiMeHCl(PPh\(_3\))\(_2\) is postulated to be as shown in fig. 38.

Because of the weakness of the SiH spectrum it is not possible to determine unambiguously the positions of CO and SiMeCl.
Section 2:6

Vibrational Spectra

The infrared spectra were recorded between 4000 and 200 cm\(^{-1}\); the compounds were generally studied as Nujol Mulls. Little success was obtained with Raman spectra. The frequencies of the various bands, together with assignments (which are in some cases tentative) are shown in Table 2.5 for the silyl compounds and in Table 2.6 for the germyl compounds. The frequencies associated with the internal vibrations of triphenylphosphine have not been included; they remain the same for all the compounds studied.

In this discussion most emphasis will be placed on the spectra from the 1:1 adducts formed from the reaction of Ir(CO)Cl(PPh\(_3\))\(_2\) and a two-fold excess of MH\(_3\)X. Thus only one isomeric form is being considered. Bands which can be assigned to vibrational modes in other isomers will be discussed when necessary.

The most useful vibrations for characterising the complexes are the modes involving the M-H, C-O and Ir-H and the M-X, Ir-M and Ir-X stretching modes. The C-O ligand is retained in all the complexes; the value of \(\nu(C-O)\) increases in all cases with respect to its value in Ir(CO)Cl(PPh\(_3\))\(_2\), as predicted by analogy with similar systems, although there is no change in band intensity. The presence of two \(\nu(C-O)\) bends is taken as
Frequencies from the infrared spectra of the iridium-silyl
in all the spectra there are bands near 2,600-3,000 cm⁻¹,
to modes of triphenylphosphine.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Phase</th>
<th>υ(Si-H)</th>
<th>υ(Ir-H)</th>
<th>υ(C-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(Cl)</td>
<td>N</td>
<td></td>
<td>1945vs</td>
<td></td>
</tr>
<tr>
<td>* V(Cl) + SiH₄</td>
<td>N</td>
<td>2105vs2095vs</td>
<td>2130m</td>
<td>1980vs</td>
</tr>
<tr>
<td>* V(Cl) + SiH₂Cl</td>
<td>N</td>
<td>2120vs2110vs</td>
<td>2130m, 2040m</td>
<td>1995 vs 1980</td>
</tr>
<tr>
<td>* V(Cl) + SiH₂Br</td>
<td>N</td>
<td>2120vs2100vs</td>
<td>2130m</td>
<td>1990vs</td>
</tr>
<tr>
<td>* V(Cl) + SiI₂</td>
<td>N</td>
<td>212021002040m</td>
<td>2170, 2040m</td>
<td>1990 vs 1980</td>
</tr>
<tr>
<td>* V(Cl) + 2SiH₄</td>
<td>N</td>
<td>2105vs2095vs</td>
<td>2130m</td>
<td>1980vs</td>
</tr>
<tr>
<td>* V(Cl) + 2SiH₂Cl</td>
<td>N</td>
<td>2120vs2100vs</td>
<td>2130m</td>
<td>1990vs</td>
</tr>
<tr>
<td>* V(Cl) + 2SiH₂Br</td>
<td>N</td>
<td>2120vs2100vs</td>
<td>2130m</td>
<td>1990vs</td>
</tr>
<tr>
<td>* V(Cl) + 2SiI₂</td>
<td>N</td>
<td>2120vs2100vs</td>
<td>2130m</td>
<td>1995vs</td>
</tr>
<tr>
<td>* V(Cl) + 2SiBr₂</td>
<td>N</td>
<td>21542s1480s</td>
<td>21583m</td>
<td>2010vs</td>
</tr>
<tr>
<td>* V(Cl) + 2SiCl₂</td>
<td>N</td>
<td>2120vs2105vs</td>
<td>2130m</td>
<td>1992vs</td>
</tr>
<tr>
<td>V(Cl) + MeSiH₂Cl</td>
<td>N</td>
<td>2082m 2065vs</td>
<td>2140, 2020m</td>
<td>1975vs</td>
</tr>
<tr>
<td>V(Cl) + 2MeSiH₂Cl</td>
<td>N</td>
<td>2073vs</td>
<td>2143m</td>
<td>1976vs</td>
</tr>
<tr>
<td>V(Br) + 2SiH₂Cl</td>
<td>N</td>
<td>2110s2100vs</td>
<td>2165, 2030m</td>
<td>1993 vs 1978</td>
</tr>
</tbody>
</table>

Adducts

<table>
<thead>
<tr>
<th>Adducts</th>
<th>Phase</th>
<th>υ(Si-H)</th>
<th>υ(Ir-H)</th>
<th>υ(C-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrH₂(CO)(CH₃)[IrBr₃]₂SiH₂Cl</td>
<td>N</td>
<td>2100vs2080vs</td>
<td>obs.</td>
<td>1990vs</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>2095sb</td>
<td>obs.</td>
<td>1980sb</td>
</tr>
<tr>
<td>IrH₂(CO)(PPh₃)₂SiHMeCl</td>
<td>N</td>
<td>2100vs2080vs</td>
<td>obs.</td>
<td>1980vs</td>
</tr>
</tbody>
</table>

V(Cl) = Ir(CO)Cl(PPh₃)₂ ; V(Br) = Ir(CO)Br(PPh₃)₂ ;
v = very ; s = strong ; m = medium ; w = weak ; b = broad ;
Phase refers to method of obtaining spectrum ;
2.5.

Compounds \( \text{H}_2\text{Ir(CO)}(\text{PF}_3)_2\text{SiH}_2 \) and \( \text{IrH}_2\text{(CO)}(\text{PF}_3)_2\text{SiH}_2 \) in cm\(^{-1}\) are given in Table 1.

<table>
<thead>
<tr>
<th>( S(\text{Si-H}) )</th>
<th>( S(\text{Ir-H}) )</th>
<th>( S(\text{C-O}) )</th>
<th>( \nu(\text{Si-X}) )</th>
<th>( \nu(\text{Ir-Si}) )</th>
<th>( \nu(\text{Ir-Cl}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>960m945s930vs</td>
<td>830m</td>
<td>605 s</td>
<td>—</td>
<td>—</td>
<td>315m</td>
</tr>
<tr>
<td>980s970m940s860s</td>
<td>850m830m</td>
<td>620 vw</td>
<td>?</td>
<td>365^	ext{v}</td>
<td>350w</td>
</tr>
<tr>
<td>975s855s</td>
<td>835m</td>
<td>618 vw</td>
<td>405s</td>
<td>340m</td>
<td>265m</td>
</tr>
<tr>
<td>980m970m940m860s</td>
<td>830m810s</td>
<td>617 vw</td>
<td>385m</td>
<td>356^	ext{v}</td>
<td>305m</td>
</tr>
<tr>
<td>960s945s930vs</td>
<td>830m</td>
<td>604 s</td>
<td>—</td>
<td>—</td>
<td>350w</td>
</tr>
<tr>
<td>980s860s</td>
<td>835m</td>
<td>618 vw</td>
<td>?</td>
<td>365w</td>
<td>265m</td>
</tr>
<tr>
<td>975s850s</td>
<td>830s</td>
<td>616 vw</td>
<td>385s</td>
<td>305m</td>
<td>260m</td>
</tr>
<tr>
<td>965s810s</td>
<td>830m</td>
<td>616 vw</td>
<td>385s</td>
<td>305m</td>
<td>260m</td>
</tr>
<tr>
<td>?640</td>
<td>7610</td>
<td>618 vw</td>
<td>401,393</td>
<td>330m</td>
<td>265m</td>
</tr>
<tr>
<td>980s860s</td>
<td>830m</td>
<td>620 vw</td>
<td>?</td>
<td>365w</td>
<td>265m</td>
</tr>
<tr>
<td>925m890w305m</td>
<td>835m</td>
<td>618 vw</td>
<td>2465</td>
<td>345w</td>
<td>255m</td>
</tr>
<tr>
<td>921m800m</td>
<td>830m</td>
<td>620 vw</td>
<td>2465</td>
<td>350w</td>
<td>255m</td>
</tr>
<tr>
<td>980m960m860sb</td>
<td>830m</td>
<td>620 vw</td>
<td>2470s</td>
<td>372w</td>
<td>—</td>
</tr>
<tr>
<td>962vs860vs</td>
<td>830s782s</td>
<td>620 vw</td>
<td>2452s</td>
<td>350w</td>
<td>—</td>
</tr>
<tr>
<td>950w850w</td>
<td>830w</td>
<td>620 vw</td>
<td>?</td>
<td>obs</td>
<td>—</td>
</tr>
<tr>
<td>905s885m</td>
<td>830s790s770m</td>
<td>618 vw</td>
<td>2445s</td>
<td>345^	ext{v}</td>
<td>325^	ext{v}</td>
</tr>
</tbody>
</table>

* = reactants postulated as giving one isomeric product;
a = prepared in CH\(_2\text{Cl}_2\); obs = region obscured;
N = Nujol Mull; B = Benzene solution
Table

Frequencies from the infrared spectra of the iridium-germyl bands near 2,600-3,000cm\(^{-1}\), 1,100-1,200cm\(^{-1}\), 650-750cm\(^{-1}\) and

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Phase</th>
<th>(\nu) (Ge-H)</th>
<th>(\nu) (Ir-H)</th>
<th>(\nu) (C-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{V(Cl)})</td>
<td>N</td>
<td></td>
<td></td>
<td>1945vs</td>
</tr>
<tr>
<td>(\text{V(Cl)} + \text{GeH}_4)</td>
<td>N</td>
<td>2010vs</td>
<td>2225w2130w</td>
<td>1970m</td>
</tr>
<tr>
<td>(\text{V(Cl)} + \text{GeH}_2\text{Cl})</td>
<td>N</td>
<td>2020vs</td>
<td>2200w2110m</td>
<td>1993vsb</td>
</tr>
<tr>
<td>(\text{V(Cl)} + \text{GeH}_2\text{Br})</td>
<td>N</td>
<td>2036s 2014w2190w2079m2109s</td>
<td></td>
<td>1996vs</td>
</tr>
<tr>
<td>(\text{V(Cl)} + \text{GeH}_2\text{I})</td>
<td>N</td>
<td>?2020v sb 2100m b</td>
<td></td>
<td>22020v sb</td>
</tr>
<tr>
<td>(\text{V(Cl)} + 2\text{GeH}_4)</td>
<td>N</td>
<td>2010vs</td>
<td>2225w2130w</td>
<td>1970s</td>
</tr>
<tr>
<td>(\text{V(Cl)} + 2\text{GeH}_2\text{Cl})</td>
<td>N</td>
<td>2020vs</td>
<td>2200w2100m</td>
<td>1990s</td>
</tr>
<tr>
<td>(\text{V(Cl)} + 2\text{GeH}_2\text{Br})</td>
<td>N</td>
<td>2017vs</td>
<td>2200m2111m</td>
<td>1997s</td>
</tr>
<tr>
<td>(\text{V(Cl)} + 2\text{GeH}_2\text{I})</td>
<td>N</td>
<td>?2020v sb 2100w</td>
<td></td>
<td>22020v sb</td>
</tr>
<tr>
<td>(\text{V(Br)} + 2\text{GeH}_4)</td>
<td>N</td>
<td>2006vs</td>
<td>2210m2110w</td>
<td>1968v sb</td>
</tr>
<tr>
<td>(\text{V(Br)} + 2\text{GeH}_2\text{Cl})</td>
<td>N</td>
<td>2017v sb 2185m2100w</td>
<td></td>
<td>1993v sb</td>
</tr>
</tbody>
</table>

\(\text{V(Cl)} = \text{Ir(Cl)Cl(PPh}_3\text{)}_2\); \(\text{V(Br)} = \text{Ir(Cl)Br(PPh}_3\text{)}_2\);

\(v=\text{very} ; s=\text{strong} ; m=\text{medium} ; w=\text{weak} ; \text{b=broa} ; \text{n.o. =not observed}\);
2.6. Compounds $H.Ir(CCl)_6Cl(PPh_3)_2GeH_2X$ in cm$^{-1}$. In all the spectra there are 430-530 cm$^{-1}$ which are assigned to modes of trichlorophosphine groups.

<table>
<thead>
<tr>
<th>$\delta$(Ge-H)</th>
<th>$\delta$(Ir-H)</th>
<th>$\delta$(C-O)</th>
<th>$\gamma$(Ge-X)</th>
<th>$\gamma$(Ir-Ge)</th>
<th>$\gamma$(Ir-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>605s</td>
<td></td>
<td>619w</td>
<td>350m</td>
<td>245vw</td>
<td>275w</td>
</tr>
<tr>
<td>890m890m327sb</td>
<td>827sb</td>
<td>840w</td>
<td>620vw</td>
<td>350m</td>
<td>265m</td>
</tr>
<tr>
<td>891m880s</td>
<td>832m790m</td>
<td>615vw</td>
<td>+345m</td>
<td>230w</td>
<td>260m</td>
</tr>
<tr>
<td>875mb</td>
<td>?830mb</td>
<td>830w</td>
<td>620vw</td>
<td>n.c.</td>
<td>280w</td>
</tr>
<tr>
<td>900m890m330vs</td>
<td>830vs</td>
<td>840m</td>
<td>615vw</td>
<td>+350m</td>
<td>230w</td>
</tr>
<tr>
<td>875m</td>
<td>830w</td>
<td>620vw</td>
<td>350s</td>
<td>n.c.</td>
<td>275m</td>
</tr>
<tr>
<td>891m870m</td>
<td>840m</td>
<td>615vw</td>
<td>+350m</td>
<td>230w</td>
<td>260m</td>
</tr>
<tr>
<td>875mb</td>
<td>?850m</td>
<td>613vw</td>
<td>+345mb</td>
<td>220240w</td>
<td>n.c.</td>
</tr>
<tr>
<td>886m837m</td>
<td>827m</td>
<td>615vw</td>
<td></td>
<td>260w</td>
<td></td>
</tr>
<tr>
<td>870mb</td>
<td>n.c.</td>
<td>615vw</td>
<td>340mb</td>
<td>n.c.</td>
<td></td>
</tr>
</tbody>
</table>

$+$=vibrational modes indicating that halogen exchange has occurred;
Phase refers to method of obtaining spectrum;
N=Nujol Mull.
indicative of an isomeric mixture. Generally, the value of \( \delta(C-O) \) also increases with respect to the original value but a distinct weakening (in most cases) in the band intensity is observed on changing from a 4-co-ordinate square planar to a 6-co-ordinate octahedral complex. It is notable that this latter effect is not observed in the unsubstituted species 
\[ \text{H.} \text{Ir(CO)} \ \text{Cl(PPh}_3\text{)}_2 \cdot \text{SiH}_3. \]

The assignment of bands to \( \nu(Si-H) \) and \( \delta(Si-H) \) in the spectrum of \( \text{H.} \text{Ir(CO)} \ \text{Cl(PPh}_3\text{)}_2 \cdot \text{SiH}_2\text{Br} \) was aided by comparison with the infrared spectrum of \( \text{D.} \text{Ir(CO)} \ \text{Cl(PPh}_3\text{)}_2 \cdot \text{SiD}_2\text{Br} \) and by analogy with the platinum species \( \text{Br.Pt(PEt}_3\text{)}_2 \cdot \text{SiH}_2\text{Br} \). The corresponding frequencies are shown in table 2.7.

<table>
<thead>
<tr>
<th></th>
<th>( \nu(Si-H) )</th>
<th>( \delta(Si-H) )</th>
<th>( \delta_2(Si-H) )</th>
<th>( \delta_3(Si-H) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H.} \text{Ir(CO)} \ \text{Cl(PPh}_3\text{)}_2 \cdot \text{SiH}_2\text{Br} )</td>
<td>2120, 2100 vs</td>
<td>975 s</td>
<td>850</td>
<td>obs.</td>
</tr>
<tr>
<td>( \text{D.} \text{Ir(CO)} \ \text{Cl(PPh}_3\text{)}_2 \cdot \text{SiD}_2\text{Br} )</td>
<td>1542, 1480 s</td>
<td>obs.</td>
<td>?640</td>
<td>obs.</td>
</tr>
<tr>
<td>( \text{Br.Pt(PEt}_3\text{)}_2 \cdot \text{SiH}_2\text{Br} )</td>
<td>2120 s</td>
<td>980 m</td>
<td>815 s</td>
<td>570 w</td>
</tr>
<tr>
<td>( \text{Cl.Pt(PEt}_3\text{)}_2 \cdot \text{SiD}_2\text{Br} )</td>
<td>1535 s</td>
<td>obs.</td>
<td>614</td>
<td>440</td>
</tr>
</tbody>
</table>

The assignment of corresponding modes in the spectra of other similar silyl and germyl compounds is made by analogy with this complex and other platinum species. It is interesting to note that the values of \( \nu(Si-H) \) in the iridium...
complexes correspond more closely to those in the 4 co-ordinate silyl species of platinum than to those in the 6 co-ordinate species, \( \text{I}_2 \text{Pt(PEt}_3)_2 \text{H}_2 \text{SiH}_2 \text{I} \). In the latter the band at \( \sim 2160 \text{cm}^{-1} \) is assigned to \( \nu(\text{Si-H}) \). Great care has to be taken in these assignments since C-O and Ir-H modes also occur in the same regions. In the germyl complexes especially there is some overlapping of bands assigned to \( \nu(\text{Ge-H}) \) and \( \nu(\text{C-O}) \). The band at higher wavenumber is assigned to \( \nu(\text{Ge-H}) \) in all cases since the decrease observed from the value in the parent hydride is comparable to the decrease occurring in the analogous silyl species. All assignments must therefore remain to some extent tentative.

Two M-H stretching modes are expected: the antisymmetric and the symmetric stretch. Two bands in close proximity are observed in the spectrum (nujol mull) in the region assigned to \( \nu(\text{M-H}) \) and could be due to these two stretching modes (when the vibrations must have similar energies) or to solid state splitting effects. The existence of the latter effect could not be determined since solution spectra cannot be obtained. There are four possible modes of deformation for \( \text{MH}_2 X \): 'scissors', 'wagging', 'twisting', and 'rocking' vibrations. They will all
be infrared active since the maximum symmetry at \( M \) is \( C_s \). By analogy with related compounds, the energy of deformations is expected to be in the order in which they are listed above. Hence, \( \delta_1(MH) \) is the 'scissors' mode and \( \delta_2(MH) \) is the 'wagging' mode. In nearly all cases (\( M=Si \) \( \delta_3(MH) \), the 'twisting' mode and \( \delta_4(MH) \), the 'rocking' mode lie in regions obscured by bands of triphenylphosphine.

As far as effects of co-ordination of the silyl ligand to a transition metal are concerned there should not be much change observed in the value of the Si-H bend but the Si-H wag is more sensitive to changes at silicon and should decrease in value. As \( X \) changes from Cl to I, the deformation modes shift to lower frequencies. A similar shift in related compounds has been attributed partly to the increase in reduced mass, and partly to electronegative effects. In the germyl complexes only one deformation mode can be assigned since the other modes are probably obscured by bands of triphenylphosphine.

In the spectra of the unsubstituted species \( H.Ir(CO)Cl(PPPh_3)_2.MH_3 \) the three stretching frequencies expected, again coincide. The same effect of possible solid state splitting observed in the substituted species is seen here. The isolated -MH group which has \( C_{3v} \) symmetry has three
modes of deformation: an antisymmetric bend(e), a symmetric (bend(a1)) and a rock(e). For the H.Ir(CO)Cl(PPh3)2.MH3 species the symmetry at M is lower and the degenerate modes may be split; the observed bands may be assigned as shown below in table 2.8.

<table>
<thead>
<tr>
<th></th>
<th>antisym. bend</th>
<th>symm. bend</th>
<th>rock bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>H.Ir(CO)Cl(PPh3)2.SiH3</td>
<td>960,945 cm⁻¹</td>
<td>930 cm⁻¹</td>
<td>?</td>
</tr>
<tr>
<td>H.Ir(CO)Cl(PPh3)2.GeH3</td>
<td>900, 890 cm⁻¹</td>
<td>830 cm⁻¹</td>
<td>?</td>
</tr>
<tr>
<td>Cl Pt (PEt3)2.SiH3</td>
<td>970, 945 cm⁻¹</td>
<td>915 cm⁻¹</td>
<td>n.o.</td>
</tr>
<tr>
<td>Cl Pt (PEt3)2.GeH3</td>
<td>905, 885 cm⁻¹</td>
<td>830 cm⁻¹</td>
<td>570 cm⁻¹</td>
</tr>
</tbody>
</table>

n.o. = not observed

The values assigned to these modes are very similar to those observed in the system trans XPt(PEt3)2MH3. Both these species and the silylcobaltcarbonyl and silylmanganesecarbonyl species, discussed in the introduction, have similar spectra in the ν(Si-H) and S(Si-H) regions. The bands observed for the iridium compounds have been assigned in a similar manner. In these different complexes the change in co-ordination number at the metal has very little effect on the modes of M-H. Observations on the spectra of the unsubstituted species have been useful in
assigning the band at 830 cm\(^{-1}\) to \(\delta(\text{Ir-H})\). This band remains fairly constant in position as \(X\) and \(M\) vary. Such an observation could be expected if the hydride ligand is not trans to \(M\)\(_2\)\(X\). Bands of medium intensity in the same region as the bands assigned to \(\delta(M-H)\) are assigned to \(\gamma(\text{Ir-H})\). The position of the band \(\sim 2180 \text{ cm}^{-1}\) indicates that the hydride ligand is trans to a ligand of low trans influence, such as a halide. Other bands at lower energy occur in the spectra of isomeric mixtures. These values assigned to \(\gamma(\text{Ir-H})\) are consistent with the hydride being trans to a ligand of high trans influence such as a silyl or germym group or to a ligand such as a carbonyl or a phosphine.

The \(MX\) and \(IrX\) stretching frequencies come in characteristic regions, though the former are lower in the spectra of the solid compounds than in the vapour phase spectra of the parent halides. The relatively low values of \(\gamma(\text{Ir-X})\) are consistent with the high trans influences of silicon and germanium\(^{114}\) as well as that of hydrogen. On the basis of a list made by Chatt\(^{119}\) it appears that \(-\text{SiH}_2\)\(X\) and \(-\text{GeH}_2\)\(X\) may have very high trans influences. Thus they probably have at least the same effect as the hydride ligand. Evidence from the platinum species \(\text{trans-} \text{Pt}\left(\text{PET}_3\right)_2\text{MH}_2\)\(X\)\(Y\) where \(\gamma(\text{Pt-Cl})\) is
270 cm\(^{-1}\) (\(M=\text{Si}, X=\text{Cl}, Y=\text{Cl}\)) or 282 cm\(^{-1}\) (\(M=\text{Ge}, X=\text{Cl}, Y=\text{Cl}\)) is consistent with this suggestion. The 'normal' range for \(\nu(\text{Ir-Cl})\) is 260-270 cm\(^{-1}\) when Cl is trans to a hydride ligand. The Ir-Cl stretching frequency may not be a true indication of the trans influence however, for it may be coupled with an Ir-M stretching vibration.

Assignment of bands in the far infrared is difficult because of the possibility of coupling between different skeletal modes of the same symmetry. It is a general feature that the coupling of the vibrations \(\nu(\text{Ir-M})\) and \(\nu(M-X)\) in Ir-M-X will be quite large if two heavy atoms surround a light one and the vibrations are of similar frequency. One will shift up and the other down and the shifts will be quite large from the original values. Thus some of the above and the following assignments are tentative and the frequencies of the assigned bands may not represent the true values for uncoupled vibrations. A band, varying in position from 305-365 cm\(^{-1}\) is assigned to \(\nu(\text{Ir-Si})\). This is in reasonable agreement with a band assigned to \(\nu(\text{Pt-Si})\) which varies from 328-344 cm\(^{-1}\).

The position of this band is sensitive to the nature of X in \(\text{SiH}_2\text{X}\) and the existence of two bands in close proximity is thought to arise from the presence of two isomers or products arising from halogen exchange. The Ge-Ir
stretching mode is tentatively assigned as 230 cm\(^{-1}\) in
fair agreement with that calculated roughly, using a
reduced mass equation, from the value assigned to
\(\nu(\text{Ir-Si})\). However, it must be remembered that such a
calculation makes no provision for coupling between this and
other vibrations and it is hard to know what to take for the
reduced mass.

The stereochemistry of the iridium silyl complexes
has had to be assigned from infrared information alone.
Some comparison with analogous systems of organosilane
complexes, germyl complexes and some platinum species has
been made. However, without confirmatory evidence as to
the arrangement of the phosphine groups the assignment of
the stereochemistry can only be tentative.

The available evidence suggests that in the complex the
chlorine ligand is trans to a group with a high trans
influence. Either hydride, silyl or germyl could give rise
to the low \(\nu(\text{Ir-Cl})\) value observed. In view of this,
chlorine is unlikely to be trans to either phosphorus or CO.
It appears that rearrangement has taken place within the
complex during oxidative addition. Six stereochemistries
for the 1:1 adduct, \(\text{H}_2\text{Ir(CO)Cl(PPH}_3)_2\text{SiH}_2X\) are thus
possible and are shown in fig. 39. Three involve retention
of the trans phosphine configuration and the other three
involve rearrangement of the phosphines to a cis configuration. It has been noted in the introduction that only a few iridium complexes formed by oxidative addition of an addendum to Ir(CO)Cl(PPh$_3$)$_2$ have been proved to contain mutually cis phosphine ligands. The fact that $\nu$(Ir-Cl) remains fairly constant as $X$ varies suggests that -SiH$_2$X is not in fact trans to chlorine, favouring structures II, III, V & VI. $\nu$(Ir-Cl) is not however, likely to be very sensitive to changes in $X$. The low value of (Ir-Cl) suggests that the chloride ligand is no longer trans to carbonyl thus eliminating VI. The high value assigned to $\nu$(Ir-H), (2180 cm$^{-1}$) by analogy with other systems, suggests that the hydride is trans to a ligand with a very low trans influence, again favouring II and III. It is possible, however, that coupling with $\nu$(CO) raises $\nu$(Ir-H) for structure I. Hydride trans to phosphine or carbonyl usually has a value in the region 2100 cm$^{-1}$. Evidence from the deuterated species D$_2$Ir(CO)Cl(PPh$_3$)$_2$.SiD$_2$Br shows that the value of $\nu$(C-O) increases with respect to that in the analogous undeuterated compound. Previously this increase in $\nu$(C-O) has been taken to indicate coupling between the vibrations of Ir-H and C-O, and would thus only favour structure I. Structures III, IV and VI can be reasonably safely eliminated since if CO were trans to a phosphine ligand effects from deuteration should not be observed.
However, it is possible that if CO is trans to a deuterated ligand -SiD$_2$Br (as in II) that the same effect will be observed but that the shift in $\nu$(C-O) could be smaller.

Previously recorded increases in $\nu$(C-O) on deuteration of the hydride ligand in the complexes studied have been of the order 30-35 cm$^{-1}$ whereas the shift in this case is 20 cm$^{-1}$.

Thus a structure involving mutually trans phosphines is favoured; the evidence for and against the two possible isomers I and II is conflicting. By analogy with the structures determined by n.m.r. spectroscopy for the germyl complexes, structure II is favoured. Such a structure is not in agreement with those postulated for analogous silicon and tin complexes of iridium by other workers. In the complex, H$\cdot$Ir(CO)Cl(PPh$_3$)$_2$(SiCl$_3$)$_2$, the hydride ligand is said to be trans to the silicon group and in the complex, H$\cdot$Ir(CO)Cl(PPh$_3$)$_2$(SnMe$_3$)$_2$, isomers are known in which the hydride can either be trans to the tin or the carbonyl ligand. There is, however a general agreement in all complexes of the form H$\cdot$Ir(CO)Cl(PPh$_3$)$_2$MR$_3$ (M=Si, Sn), that the phosphine ligands have a mutually trans configuration.

By analogy with the isomeric mixture obtained during the reaction of Ir(CO)Cl(PPh$_3$)$_2$ and GeH$_3$Cl, the isomeric products obtained from the reaction of equimolar portions of...
Vaska's compound and SiH₃Cl probably are of the same form. One of these isomers has already been discussed (Structure II); the I.R. evidence available, low value of γ(Ir-H), for the other is consistent with a complex containing hydride trans to SiH₂Cl as in structures V or VI. However, infrared assignments are so tentative that no accurate determination of the structures of the different products resulting from this reaction can be made. It is interesting to note that the same ratio of products is obtained on all occasions indicating that the isomers are probably in equilibrium. (fig. 40).

I.R. evidence for the products resulting from the reaction of Ir(CO)Cl(PPh₃)₂ and SiH₃I is consistent with halogen exchange occurring since the band assigned to γ(Ir-Cl) decreases in intensity with respect to the value for the initial product H₂Ir(CO)Cl(PPh₃)₂SiH₂I. The complexity of
the spectrum in the regions assigned to $\nu$(Ir-H), $\nu$(C-O),
$\delta$(Si-H), $\delta$(Ir-H) and $\nu$(Ir-Si) can also be explained by the
occurrence of halogen exchange. It is possible that some
isomerisation is also occurring. Again no definite
conclusion can be drawn about the structure of these isomers.

I.R. evidence from the reaction of Ir(CO)Br(PPh$_3$)$_2$
and a two fold excess of silyl chloride indicates that an
isomeric mixture of products is formed. The presence of
two bands which can be assigned to $\nu$(Ir-H) and two to $\nu$(C-O),
together with the complexity of the region associated with
$\delta$(Si-H) and $\delta$(Ir-H) is in agreement with this postulate. This
observation is in contrast to that from the reaction of
Ir(CO)Cl(PPh$_3$)$_2$ and 2SiH$_3$Cl or 2SiH$_3$Br. As is to be
expected there is no evidence for $\nu$(Ir-Cl) since halogen
exchange in this system is energetically unfavourable. It is
likely, by analogy, that the isomers have structures II and V.
The infrared spectra from the products of the long term
reaction of Ir(CO)Cl(PPh$_3$)$_2$ and a two fold excess of
SiH$_3$Cl or MeSiH$_2$Cl differ markedly from those due to the
1:1 adducts. The values assigned to the various modes are
shown in table 2.5. The most notable feature in each case
is the disappearance of the bands at $\sim$2180cm$^{-1}$ (assigned
to a hydride trans to chloride) and at $\sim$260cm$^{-1}$ (assigned
to a chloride trans to a hydride). It is likely that the bands
due to \( \nu(Ir-H) \) are now obscured by the strong band at 2100 cm\(^{-1} \) assigned to \( \nu(Si-H) \). Placement of the hydride band in this region would be in agreement with n.m.r. evidence which indicates that the hydride ligands are trans to phosphine and carbonyl respectively. The spectrum due to the dihydride complex containing an \(-\text{MeSiHCl}\) ligand is slightly more complex than that containing \(-\text{SiH}_2\text{Cl}\) and this observation is in agreement with observations from the n.m.r. spectrum of the former species. In this case it is postulated that other products are formed in small amounts.

As mentioned previously assignments to vibrational modes of the germyl complexes \( \text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{GeH}_2\text{X} \) must be very tentative. Overlapping of bands in the region assigned to \( \nu(Ir-H) \), \( \nu(Ge-H) \) and \( \nu(C-O) \) as well as obscuring of \( \Sigma(Ge-H) \) modes by triphenylphosphine bands occurs. The infrared spectra however give evidence for the structure of these complexes which is in agreement with that obtained from the n.m.r. spectra. Because of the occurrence of isomerisation during the reaction of \( \text{Ir(CO)Cl(PPh}_3\text{)}_2 \) with \( \text{GeH}_3\text{Cl} \) and halogen exchange during the reaction of the iridium complex with \( \text{GeH}_3\text{Br} \) and \( \text{GeH}_3\text{I} \), the spectra are rather complex. The appearance of a band at \( \sim 350 \text{ cm}^{-1} \) which is assigned to \( \nu(\text{Ge-Cl}) \) is thought to be indicative of halogen exchange during the reactions of
Ir(CO)Cl(PPh$_3$)$_2$ with GeH$_3$Br and GeH$_3$I.

Many infrared spectra have been obtained for the products arising from the reactions of Ir(CO)Cl(PPh$_3$)$_2$ with varying proportions of MH$_3$X (M=Si, Ge; X=H, Cl, Br, I) over different periods of time. Most of these are very complex and are difficult to analyse satisfactorily. Since no definite conclusions about the nature of these products can be drawn from these spectra they have not been included in this discussion.

N.m.r. spectroscopy is preferred for identification of compounds although much information is available from infrared spectra. Since the sample can be prepared for the n.m.r. spectrometer under vacuum there is less likelihood of decomposition. The stereochemistry of a compound can be determined easily from n.m.r. data whereas infrared assignments are always tentative and require further confirmation. As can be seen from the evidence discussed in this section mixtures of isomers are difficult to identify by infrared. Their n.m.r. spectra however are usually well separated and the different isomers can be readily identified.

Section 2.7

The mechanism of the preparative reaction

The iridium -M bond is probably formed by the oxidative
addition of an M-H bond to the four co-ordinate Ir(I) species giving rise to a six co-ordinate Ir(III) species. Such a species has been postulated as an intermediate in the reactions of trans \( \text{Pt.H.Cl(PEt}_3)\) and \( \text{MH}_3\text{X} \). The formation of the platinum species is generally followed by rapid elimination of \( \text{H}_2 \) to form a 4-co-ordinate Pt(II) species but it should be noted that these species which eliminate \( \text{H}_2 \) fast have two hydrogens on platinum. In the reactions of \( \text{Ir(CO)Cl(PPh}_3)\), the initially formed six co-ordinate species is very stable and similarly the adduct of \( \text{SiH}_3\text{X} \) with \( \text{(Et}_3\text{P)}_2\text{PtI}_2 \), having only one hydrogen on platinum is fairly stable.

![Diagram](https://example.com/diagram.png)

**fig. 41**

The resulting products can be said to arise by cis or trans addition of silyl or germyl halides to the square planar Ir(I) complex. see **fig. 41**. This addition can occur with retention or rearrangement of the original trans phosphine configuration. It is dangerous to be specific about the nature (cis or trans) of the addition since the products
isolated may be the most thermodynamically stable ones rather than those initially formed (kinetically stable products). Products containing the entering ligands, from the addendum, in a cis orientation are favoured. As discussed in Chapter 1, different modes of addition are postulated under varying conditions for addition of HX, CH₃X etc. to Ir(CO)Cl(PR₃)₂, (R=Ph, Ph₂Me).

The possible number of stereochemistries which can result by varying the orientation of the phosphine ligands and varying the mode of addition is quite large and the infrared and n.m.r. evidence has been used to elucidate the correct structure of the adducts Ir(CO)Cl₂H₂SiH₂X(PPh₃)₂. The evidence available suggests that the initially formed adducts retain the trans phosphine configuration. From evidence presented in Chapter 111 it is unwise to assume that the stereochemistry of analogous silicon and germanium systems will be the same.

Formation of the soluble complex, IrH₂(CO)SiH₂X(PPh₃)₂ probably occurs by elimination of the SiH₂Cl₂ from the 1:1 adduct and subsequent attack by SiH₃Cl on the 4-coordinate intermediate, IrH(CO)(PPh₃)₂, which is formed. A similar hydride complex has been prepared previously and such a mechanism has been put forward to explain the reaction of analogous systems. Since the initial
1:1 adduct has phosphine ligands in a mutually trans configuration and the dihydride complex has phosphine ligands which are mutually cis then rearrangement of the phosphines must occur at some stage in the reaction. This rearrangement may occur at the start of the reaction scheme, (a 1:1 adduct with cis phosphines may exist) in the middle, (conversion of the species IrH(CO)(PPh₃)₂ containing trans phosphines to the same species with cis phosphines), or at the end (a dihydride species with trans phosphines may exist at some time). (see fig. 42). Since the stereochemical assignment of the 1:1 silyl adduct is tentative but the stereochemistry of the dihydride is much more certain it is possible that rearrangement does not need to occur and that the phosphines are cis orientated at all times.

(favoured)
Discussion of Results.

There are several general features of the reactions of MH₃X (M = Si, Ge; X = H, Cl, Br, I) with Ir(CO)Cl(PPh₃)₂ which need careful consideration. It is noticeable that the rate of reaction of an equimolar portion of the silyl compounds SiH₃X (X = H, Cl, Br, I) and of GeH₄ with Vaska's compound is much slower than that of an equimolar portion of GeH₃X (X = Cl, Br, I) with this iridium complex. It is interesting that germane should differ from the other germaly compounds in this respect and in others which will be discussed later. The reaction rate of SiH₃X or of GeH₄ is increased by taking an initial excess, but increasing the initial quantity of GeH₃X had no apparent effect on the reaction rate. It would be interesting to know whether these results indicate that an equilibrium reaction is involved. In both cases the reactions are faster than those observed for the analogous systems studied by Chalk and Harrod⁷,¹⁰⁹ and Glockling.¹⁰⁸

The apparent difference in solubility between the initially formed complexes H₂Ir(CO)Cl(PPh₃)₂MH₂X (M = Si; X = H, Cl, Br, I; M = Ge; X = H) and the complexes H₂Ir(CO)Cl(PPh₃)₂GeH₂X (X = Cl, Br, I) is also of interest. It is possible that these observations may be due to a difference in mechanism or to rapid isomerisation of one form of the complexes.

The formation of a soluble dihydride species,
IrH₂(CO)(PPh₃)₂SiH₂Cl, as a result of the long term reaction of SiH₃Cl with Vaska's compound is analogous to the results obtained by Chalk for the long term reactions of R₃SiH and Vaska's compound. An analogous reaction sequence involving the initial formation of an insoluble species, H Ir(CO)Cl(PPh₃)₂SiH₂Cl is postulated. However, none of the other silyl compounds forms a soluble dihydride species during their reactions with Vaska's compound. Glockling has obtained soluble dihydride species, IrH₂(CO)(PPh₃)₂GeR₃ as the products of the reaction of R₃GeH with Vaska's compound. In contrast the reaction of the germyl compounds GeH₃X (X = H, Cl, Br, I) produces only monohydride complexes. The variation in results from the reactions of the silyl and germyl compounds with Vaska's compound and with those obtained previously is notable. It is necessary to consider why these differences should arise. Since, however, previous work has shown that a slight change in either the ligands at Ir or the substituents at M can cause great changes in the nature of the products from the reaction of Ir(CO)Cl(PR₃)₂ with MR₃H (M = Si, Ge) great care must be taken when comparing results from different reaction systems. It is possible that the differences could be attributed to either kinetic or thermodynamic factors and these will be discussed below.

A final general feature of these reactions is that the mode of addition of MH₃X to Ir(CO)Cl(PPh₃)₂ is always of the form
MH_{2}X and H whereas Heck has shown that the addition of CH_{3}X to Vaska’s compound is of the form CH_{3} and X.

Each of the novel features of the reaction of MH_{3}X with Ir(CO)Cl(PPh_{3})_{2}, namely a) the difference in the rate of reaction of equimolar portions of SiH_{3}X and GeH_{3}X with Vaska’s compound,b) the difference in the solubility of the silyl and germyl complexes initially formed during the reaction of MH_{3}X with Ir(CO)Cl(PPh_{3})_{2},c) the difference in the products of the long term reaction of an excess of MH_{3}X with Vaska’s compound and d) the difference in the mode of addition of CH_{3}X and MH_{3}X (M = Si, Ge) to Vaska’s compound, will be considered in turn.

There may be two different mechanisms of formation of the complexes H. Ir(CO)Cl(PPh_{3})_{2}MH_{2}X, one pertaining to the reaction of SiH_{3}X and GeH_{4} with Vaska’s compound and the other to the reaction of GeH_{3}X with Vaska’s compound which explain the difference in the rate of reaction. A mechanism involving a high order in SiH_{3}X or GeH_{4} might explain the slowness of the reaction between equimolar portions of these compounds and Ir(CO)Cl(PPh_{3})_{2} and its acceleration in the presence of excess silyl halide or gemmane. It is doubtful whether the reaction: Ir(CO)Cl(PPh_{3})_{2} + xSiH_{3}X \rightarrow H \rightarrow Ir(CO)Cl(PPh_{3})_{2}SiH_{2}X + (x-1)SiH_{3}X is an equilibrium reaction since if the reaction were merely an accelerated equilibrium, the 1:1 process should also go rapidly because of the insolubility of the product. Thus a mechanism
Involving a high order in $\text{SiH}_3X$ seems a plausible proposition. Then a mechanism involving a low order of $\text{GeH}_3X$ would explain why the reaction of Vaska's compound and $\text{GeH}_3X$ proceeds rapidly whatever the concentration of $\text{GeH}_3X$. It is interesting that $\text{GeH}_4$ should differ so markedly from $\text{GeH}_3X$ in speed of reaction with $\text{Ir(CO)Cl(PPh}_3)_2$. However, if the rate determining step of the reaction is electrophilic attack by germanium or hydrogen at iridium, then electron withdrawal from germanium would enhance this attack. A difference in rate of attack of $\text{SiH}_4$ and $\text{GeH}_4$, as compared with $\text{GeH}_3\text{Cl}$ and $\text{SiH}_3\text{Cl}$, on $\text{XPt(PEt}_3)_2\text{H}$ has been explained in this way by Bentham. However, it is notable that there was no marked difference in the rate of reaction of $\text{SiH}_4$ and $\text{SiH}_3\text{Cl}$ with Vaska's compound.

It is not surprising that the silyl and germyl halides react at a faster rate with Vaska's compound than the alkyl silanes and germanes. Bentham has shown that the reaction of $\text{SiH}_3X$ with $\text{H Pt(PEt}_3)_2\text{X}$ occurs rapidly whereas the reaction of $\text{R}_3\text{SiH}$ ($\text{R} = \text{aryl}$) with this platinum complex only occurs on heating the reactants to 80 - 90°C and the reaction of $\text{R}_3\text{SiH}$ ($\text{R} = \text{alkyl}$) does not occur at all. The presence of electron withdrawing groups on the silicon appears to assist the reaction since the reaction of $\text{HSiCl}_3$ with $\text{HPt(PEt}_3)_2\text{X}$ proceeds rapidly.

During the oxidative addition of $\text{MH}_3X$ to Vaska's compound,
kinetic factors may determine the difference in solubility of the initial products. If it is assumed that all the compounds MH₃X, add initially in the same manner, i.e. cis or trans to the square planar iridium complex then the insoluble complexes which are formed are probably the thermodynamically stable products formed by isomerisation of the initially formed species, whose structures are determined by the mechanism of the reaction. Thus the immediate precipitation of an insoluble product from the reaction of SiH₃X (X = H, Cl, Br, I) or GeH₄ with Vaska's compound would be the result of rapid isomerisation of the initial product, formation of a soluble product followed by slow precipitation in the reaction of GeH₃X (X = Cl, Br, I) with Vaska's compound would reflect slower isomerisation of the initial products to the more thermodynamically stable and insoluble form, see fig. 43. There is no obvious reason, however, why rearrangement of the germyl compounds should be so much slower.

Another possibility is that there may be a difference in the mode of addition of silyl and germyl halides to Vaska's compound. The silyl halides and germane may add in one sense to the iridium complex to form insoluble complexes (thermodynamic product) and the germyl halides may add in another sense (possibly cis since the n.m.r. spectra of the initially formed germyl species indicate that H and GeH₂X are in general cis orientated) to give a soluble species
(thermodynamically unstable product) which then isomerizes to give an insoluble species (thermodynamic stable). (See fig. 43). The reasons why the silyl and germyl halides should add in a different manner and why germane should differ from the other germyl compounds are not known. It is doubtful, however, whether either of these simple theories is satisfactory, since more than one isomeric product is formed during the reactions of both the silyl and germyl compounds with Ir(CO)Cl(PPh₃)₂ indicating that at least for the chlorides the reactions are not stereospecific. Thus no definite conclusions can be drawn about the reasons for the difference in solubility of the complexes.

Thermodynamic factors may influence the difference in the products of the long term reaction of the silyl halides with Vaska’s compound. It is possible that the soluble product IrH₂(CO)(PPh₃)₂SiH₂Cl and the products H₃.Ir(CO)Cl(PPh₃)₂SiHBr₂ and H₃.Ir(CO)I(PPh₃)₂SiH₂I are the thermodynamically most stable products of the reaction of a two-fold excess of silyl halide with Ir(CO)Cl(PPh₃)₂. Other reasons why only SiH₃Cl should form a soluble dihydride complex are not apparent. The solubility of the dihydride complex seems to depend either on the replacement of X directly attached to iridium by a hydride ligand or on rearrangement of the phosphine ligands from a mutually trans configuration (in the initial monohydride complex) to a cis configuration, or on both. As discussed in Chapter III it is likely that removal of X is the more important factor.
Perhaps decomposition of the soluble monohydride complexes, H.Ir(CO)Cl(PPh₃)₂GeH₂X, occurs before they can react further with excess of GeH₃X to form the dihydride species, IrH₂(CO)(PPh₃)₂GeH₂X. This decomposition could explain why species analogous to those observed by Glockling during the reaction of Vaska’s compound with a 2-fold excess of alkyl germanes are not observed.

In summation, the various novel features of the reactions of silyl and germyl compounds with Vaska’s compound can be interpreted in various different ways, but at the present it is not possible to decide between the different possible explanations.
Preparation and Spectroscopic Properties of Some Six-
Co-ordinate Ir(III) Complexes, Derived from IrH(CO)(PPh$_3$)$_3$
Containing Silyl- and Germyl- Ligands

SECTION 3:1
The Preparative Reaction

3.1.1. Introduction

The preparation and properties of silyl and germyl complexes of iridium derived from Ir(CO)Cl(PPh$_3$)$_2$, are described in Chapter 2; it has been shown that the mode of addition of MH$_3$X (M=Si, Ge; X=H, Cl, Br, I) is of the form MH$_2$X and H, to give a six co-ordinate Ir(III) hydride species. These products have been compared and contrasted with analogous organo-silane and germane complexes of iridium and with those from the reactions of Pt(PEt$_3$)$_2$HX with MH$_3$X. In order to extend the knowledge of iridium-silyl and germyl chemistry and to determine what influence the stereochemistry and the nature of the ligands in the initial iridium complex, have on the nature of the reaction with MH$_3$X, another iridium complex, IrH(CO)(PPh$_3$)$_3$, differing both in stereochemistry and ligands present, was chosen for study. It is interesting to compare the reactions of this complex with those of Ir(CO)Cl(PPh$_3$)$_2$ and also the products of the reaction with those from analogous organo-silane reactions, where the mode of addition was MR$_3$ and H. The germyl complexes formed from this complex are the first known products from the reaction of a germane with IrH(CO)(PPh$_3$)$_3$. 
The reaction of this hydride of five co-ordinated iridium with an equimolar proportion of SiH₃X or GeH₃X in benzene is rapid at room temperature and gives a soluble product. The structures of the products have been deduced from n.m.r. spectra with some confirmation from vibrational spectra; the detailed evidence is discussed in sections 3.2 and 3.3. The structure of the product formed depends on M and to a certain extent on the nature of X. It has been shown that the complexes formed are of the form IrH₂(CO)(PPh₃)₂MH₂X with six-coordinated iridium. A mechanism for their formation similar to that proposed for the reaction of IrH(CO)(PPh₃)₃ and SiR₃H, is proposed and discussed in Section 3.4. Addition of MH₅X is in the sense MH₂X and H. It is interesting to note the difference between the reactions of IrH(CO)(PPh₃) and Ir(CO)Cl(PPh₃)₂ with MH₃X. The formation of stable, soluble products with the former is in marked contrast to the formation with the latter of products which are either insoluble (addenda SiH₃X) or only transiently soluble (addenda GeH₃X). The solubility of the adducts of the hydride is of course of great value in facilitating the study by n.m.r. spectroscopy of the complexes and their structures are postulated with much more certainty than those of the adducts of Vaska’s compound.

In some cases there is evidence for the formation of more than one isomer, although one isomer predominates, and the possible ways in which such an isomerization might occur are almost the same as those which have been discussed in Section 2.1. relating to the reactions of Ir(CO)Cl(PPh₃)₂ and MH₃X. The
possibility of halogen exchange is, of course, excluded owing to
the absence of an halogen atom in the initial iridium complex but
a halogen atom could replace one of the hydride ligands attached to
iridium. It is probable that the isomeric products are formed by
the cis, and/or trans addition of MH₃X to the complex. The mode
of addition has been investigated using a deuterium substituted
compound, SiD₃Br, as is described in Section 3.2.

The addition of SiH₃X results in the formation of
dihydride complexes having cis phosphines. Silyl iodide gives a
complex mixture of reaction products. In contrast to the silyl-
products, the addition of GeH₃X gives dihydride complexes having
trans phosphines. The nature of the reaction products as discussed
in later sections is independent of the length of reaction time and the
concentration of the reactants, but is highly dependent on the
nature of the M and X in MH₃X. The products from the reaction of
SiH₃X and GeH₃X with IrH(CO)(PPh₃)₃ will be considered separately
in the following sections but will be compared and contrasted when
necessary and correlations drawn when reasonable.

3.1.2. 1:1 reaction of IrH(CO)(PPh₃)₃ and MH₃X (M=Si, Ge;
X=H, Cl, Br, I)

When IrH(CO)(PPh₃)₃ was allowed to warm to room
temperature in benzene with an equimolar proportion of MH₃X
(M=Si, Ge; X=H, Cl, Br, I ) there was an immediate reaction. The
yellow colour of the solution faded, and a clear solution, colourless
in the case of SiH₃X and yellowish with GeH₃X, was formed. The
reaction was complete within a few minutes. The greater speed of the reaction of SiH₃X with an equimolar proportion of IrH(CO)(PPh₃)₃ in comparison with the rate of the analogous reaction with Vaska’s compound is very noticeable. Such an increase has been previously observed for analogous reactions where the chlorine atom in the iridium complexes has been replaced by a hydrogen atom which has a greater electron releasing power.¹¹¹

There is of course a considerable difference in the stereochemistry of the two complexes and this may be the dominating factor in determining the rate of reaction. There is almost certainly a difference in reaction mechanism. Occasionally a white precipitate forms as the reaction proceeds but disappears on agitation of the solution and only the soluble product obtained at completion of the reaction has been identified. This soluble product which can be studied extensively by n.m.r. spectroscopy, is a dihydride of six co-ordinate Ir(III) IrH₂(CO)(PPh₃)₂MH₂X, formed by the oxidative addition of MH₃X to IrH(CO)(PPh₃)₃.

\[
\text{Ir}^1\text{H(CO)(PPh}_3\text{)}_3 + \text{MH}_3\text{X} \rightarrow \text{Ir}^{\text{III}}\text{H}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_2\text{X} + \text{PPh}_3
\]

No non-condensible gas is formed; only a trace of silyl or germyl compounds is recovered. These observations are in agreement with the formulation of the product as IrH₂(CO)(PPh₃)₂MH₂X. This can be isolated, in an impure form, by evaporation of the solvent and exists as a white solid or jelly-like material in the case of IrH₂(CO)(PPh₃)₂SiH₂X and as a yellowish solid or gum for the products IrH₂(CO)(PPh₃)₂GeH₂X. Analysis of these products is difficult because of contamination from triphenylphosphine which is
produced during the reaction and which is also isolated during solvent evaporation. Because of handling difficulties it has not proved possible to separate the products from triphenylphosphine. Their compositions are established on the basis of the volatile products recovered and are in agreement with those deduced from n.m.r. spectra. The products have been studied by I.R. spectroscopy both in the solution and in the solid state and this spectral evidence has confirmed that obtained by n.m.r. spectroscopy. No satisfactory mass spectra could be obtained. The I.R. and n.m.r. spectra show that the addition of $\text{MH}_3\text{X}$ has occurred as $\text{MH}_2\text{X}$ and H; this is as found in the iridium-silyl systems, $\text{IrH(CO)Cl(PPh}_3)_2\text{MH}_2\text{X}$ previously studied, and in the analogous platinum-silyl systems.\(^\text{36, 37}\)

The stability of the soluble products in benzene solution varies; precipitation or formation of a brown solution after a few days or weeks may occur and is dependent on the nature of M and X and the concentration of the reactants in the reaction tube. Use of a certain concentration of $\text{SiH}_3\text{Br}$ and $\text{IrH(CO)(PPh}_3)_3$, for instance, results in the formation of a colourless, soluble product which is stable in solution for many weeks whereas the use of a slightly higher concentration of reactants can result in the almost immediate formation of a white precipitate which does not redissolve. The infrared spectra indicate that there is no difference in the structure of the two compounds formed. The germyl complexes generally decompose to give yellow - brown solutions after a few weeks. One adduct of germyl iodide for instance, gives a brown solution and
bright green crystals after two weeks. An I.R. spectroscopic study of these crystals showed them to be an iridium-hydride carbonyl complex probably anionic system, [c.f. other green derivatives of Ir(III)] but the material was not identified further.

Neither type of product obtained by evaporation of the solvent is particularly stable for long periods of time either under vacuum or nitrogen or in air. The complexes IrH₂(CO)(PPh₃)₂SiH₂I and IrH₂(CO)(PPh₃)₂GeH₃, for instance, initially a white gum and a cream solid, respectively, decompose to brown gelatinous masses after 12 hours exposure to nitrogen in a glove bag. Decomposition is faster in air and slower under vacuum. This trend in decomposition of the products is the same as that observed for the long term reaction product from the reaction of Vaska's compound with a two-fold excess of silyl chloride.

The stability of the dihydride complexes to air and moisture is very different to that of the complexes IrH(CO)Cl(PPh₃)₂MH₂X which have been discussed in Chapter 2, but is still greater than that of the platinum-silyl complexes³⁶,³⁷ PtY(PEt₃)₂SiH₂X. Since all are thermodynamically unstable with respect to air and moisture, the kinetic stability of the dihydride complexes must be much less than that of the monohydride species. Prior to their decomposition at room temperature which has been described, the products are stable to loss of hydrogen or MH₃X up to ~200°C when they decompose to give brown tarry products.

The reaction sequence which has been observed for both the
addition of SiH₃X and GeH₃X to IrH(CO)(PPh₃)₃ is in agreement with that determined by Harrod and co-workers during their work on the addition of SiR₃H to IrH(CO)(PPh₃)₃, when the complexes IrH₂(CO)(PPh₃)₂SiR₃ were formed. It involves the rearrangement of the trigonal bipyramidal structure, with loss of a triphenylphosphine ligand, to an octahedral structure. As will be described in Section 3.2., the n.m.r. spectra obtained for the products IrH₂(CO)(PPh₃)₂SiH₂X are very similar to those obtained by Chalk and Harrod for the products IrH₂(CO)(PPh₃)₂SiR₃ (prepared by the reaction of both Ir(Cc)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ with SiR₃H and by Glockling for the products IrH₂(CO)(PPh₃)₂GeR₃ (prepared by the reaction of Ir(CO)Cl(PPh₃)₂ with GeR₃H). It will be seen that the spectra of the germyl complexes IrH₂(CO)(PPh₃)₂GeH₂X differ markedly from those of all the afore-mentioned complexes indicating an inherent difference in structure of the germyl complexes.

The recovery of a trace of volatile silyl or germyl compound at the end of the reaction indicates that the reaction probably does not go to completion. During the reaction of SiH₃I and GeH₃I with IrH(CO)(PPh₃)₃ these volatiles take the form of SiH₄ and GeH₄ indicating that the iodine atom may replace one of the hydrogen atoms bound to iridium. This exchange does not appear to occur to any great extent, since spectroscopic evidence indicates the presence of IrH₂(CO)(PPh₃)₂MH₂I as the predominant species.

The addition of SiH₄ results in the formation of one isomer IrH₂(CO)(PPh₃)₂SiH₃ whose structure (I fig. 44) is almost unambiguously
assigned from the n.m.r. spectrum and which has mutually cis phosphines. Addition of SiH₃X (X=Cl, Br), however, results in the formation of a different isomer (II fig. 44) whose structure has again been assigned from its n.m.r. spectrum and which differs only in the relative position of the silyl group with respect to the other ligands. Silyl iodide adds to give two isomers. One is analogous to the product from the addition of SiH₃Cl and SiH₃Br, and the other has a different n.m.r. spectrum and its structure (III fig. 44) with the phosphine groups mutually trans, is more like one of the germyl complexes which will be discussed later. There is some evidence that reactions with SiH₃Cl and SiH₃Br also produce a second isomer which has the same phosphine configuration as that already mentioned but varies in the position of the silyl group. The structure is thought to be the same as that of the product from the reaction with SiH₄ (I fig. 44). Of the two proton resonances observed in the region 4-6 'H that at lower 'H, a broad hump, has been assigned to this second complex and the peak at higher 'H value to the main isomer.

![Figure 44](image-url)
In conclusion it should be noted that in these iridium-silyl complexes the phosphines are generally cis, with one of the hydride ligands present trans to a phosphine ligand and the other trans to a carbonyl or silyl group. The characteristic IrH spectrum is in complete agreement with this structure and further n.m.r. evidence indicates the relative position of the other ligands.

There is a marked difference in the stereochemistry of the iridium-germyl complexes. The addition of GeH₃X (X=H, Cl, Br, I) to IrH(CO)(PPh₃)₃ results in the formation of one isomer IrH₂(CO)(PPh₃)₂GeH₂X whose structure (I fig. 45) is almost unambiguously assigned from the n.m.r. spectrum and in which the phosphine ligands are mutually trans. In this case the hydride ligands are trans to a carbonyl ligand and a germyl ligand and the characteristic n.m.r. spectrum displayed by these ligands is the primary indication of the stereochemistry of the complexes. The suggestions are confirmed by homonuclear spin decoupling using double irradiation in the ¹H n.m.r. spectra of these complexes. An anomaly was observed in the n.m.r. spectrum of one sample of the product from the reaction of GeH₃Cl and IrH(CO)(PPh₃)₃; transiently an IrH spectrum characteristic of a species containing mutually cis phosphines was observed, implying that the stereochemistry of the complex initially present was like those of the iridium-silyl complexes previously described (II fig. 45). A similar observation has been made during the reaction of GeH₄ with IrH(CO)(PPh₃)₃.
Therefore, although the general trend is for iridium-silyl complexes to contain mutually cis phosphines and the germyl-iridium complexes to contain mutually trans phosphines this is not always true. It is doubtful whether the reactions are stereospecific. Perhaps the germyl complex with mutually cis phosphines is an intermediate which is formed prior to the formation of the possibly more stable form containing trans phosphines. This would imply either that the silyl compounds were more stable thermodynamically in the cis configuration, or that there was a substantial barrier to rearrangement in the silyl complexes but not for their germyl analogues.

3.1.3. 2:1 reaction of IrH(CO)(PPh₃)₃ and MH₃X (M=Si, X=Cl; M=Ge, X=H)

In order to investigate the effect of reactant concentration on the mode of the reaction and reaction products, the addition of a two-fold excess of GeH₄ to IrH(CO)(PPh₃)₃ was studied. The reaction proceeded at the same rate as for the 1:1 reaction mixture and a yellowish solution was formed after a few minutes. There was a complete absence of non-condensibles at the end of the reaction and half the initial quantity of germane was recovered. Therefore there
is no change in the speed of the reaction and the 1:1 reaction product, IrH$_2$(CO)(PPh$_3$)$_2$GeH$_3$, is formed. The n.m.r. spectrum of this yellow solution confirmed this, since it was identical to that obtained previously for the 1:1 adduct. No six co-ordinate iridium species containing two germyl ligands was formed by the reaction of an excess of germyl compound with IrH(CO)(PPh$_3$)$_3$. There was no apparent change in the reaction products after a long reaction time (two weeks) except for decomposition as previously observed. This apparent unwillingness to form bis-germyl species of six co-ordinate iridium by either iridium complex (Vaska's compound or the five co-ordinate complex) is in direct contrast to the results obtained by Bentham for the reaction of Pt. H. Cl(PEt$_3$)$_2$ with an excess of GeH$_3$Cl. In this case the formation of bis- and tri- germyl species of platinum was explained by the strength of the bond between germanium and platinum which is formed and was thought to be an energetically favourable reaction. Since, in the platinum reactions the loss of H$_2$, from the initially formed six co-ordinate complexes, has been shown to occur readily, thus facilitating the addition of further germyl molecules, it is probable that it is the lack of ease of H$_2$ removal from the complexes IrH$_2$(CO)(PPh$_3$)$_2$GeH$_2$Cl which prevents the formation of bis- and tri- germyl species of iridium. Similar results were obtained from the addition of a two-fold excess of silyl chloride to IrH(CO)(PPh$_3$)$_3$. In this case the results are in agreement with those from the addition of SiH$_3$Cl to the platinum species.
3.1.4. 1:1 reaction of IrH(CO)(PPh₃)₃ and silyl- and germyl-
species containing two halogen atoms (SiH₂Cl₂ and GeH₂Br₂)

The yellow colour of the IrH(CO)(PPh₃)₃ was discharged relatively slowly (~1/2 hour) by an equimolar quantity of SiH₂Cl₂ when the two reactants were allowed to warm to room temperature in benzene. A colourless solution was formed but precipitation of a thick white solid followed. This solid, which would not redissolve in the benzene, was isolated by solvent evaporation and identified by I.R. spectroscopy. Its I.R. spectrum was similar to that of the products, IrH₂(CO)(PPh₃)₂SiH₂X and it is thought to be the complex IrH₂(CO)(PPh₃)₂SiHCl₂. The solid is stable for long periods when kept under nitrogen in a glove bag. This stability is in contrast to that of the other products from the reaction of IrH(CO)(PPh₃)₃ and SiH₃X. Similarly, when an equimolar mixture of IrH(CO)(PPh₃)₃ and GeH₂Br₂ was allowed to warm up to room temperature in benzene an immediate reaction occurred and a deep yellow oil was formed in the bottom of the reaction tube with a clear solution above. An I.R. analysis of this oil indicated that it was probably the complex, IrH₂(CO)(PPh₃)₂GeHBr₂. This oil is also stable for long periods under nitrogen. The clear solution was benzene, probably with some triphenylphosphine dissolved in it, which had been formed during the reaction. In neither reaction system was any non-condensable gas formed, nor was there any free silyl or germyl compound recovered. These observations indicate that a 1:1 reaction has occurred and are
in agreement with the formation of the products, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MHX}_2$.

Unfortunately in neither case could a strong n.m.r. spectrum be obtained and thus structural assignments for these products are based on i.r. evidence alone.

Thus, introduction of a second halogen atom into the species $\text{MH}_3\text{X}$ ($\text{M}=$Si, Ge; $\text{X}=$Cl, Br) during their reaction with $\text{IrH(CO)(PPh}_3)_3$, results in the formation of complexes analogous to $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_2\text{X}$ but these differ in solubility and stability under nitrogen. These reactions contrast with those of Bentham$^{36, 37}$ on the addition of $\text{MH}_2\text{X}_2$ to $\text{PtHY(PEt}_3)_2$. In the latter the rate of reaction of the dihalides with the platinum complex was much slower than that of the monohalides. A noticeable difference in reaction rate is not observed here.

3.1.5. Reaction of $\text{IrH(CO)(PPh}_3)_3$ with methyl silyl chloride

An equimolar mixture of $\text{IrH(CO)(PPh}_3)_3$ and $\text{MeSiH}_2\text{Cl}$ which is allowed to warm up to room temperature in benzene almost immediately reacts to form a colourless solution. The reaction is complete within a few minutes. This soluble product which can be studied using n.m.r. spectroscopy is the six co-ordinate Ir(III) species, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHMeCl}$, which has been identified previously as the long term reaction product from the reaction of Vaska’s compound with a two-fold excess of methyl silyl chloride. Again no non-condensible gas is formed; only a trace of silyl compound is
recovered. This evidence is in agreement with the postulate of the formation of $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHMeCl}$. The n.m.r. spectrum is identical with that obtained earlier for the Vaska's reaction and indicates that the product has cis phosphines. The product can be isolated as a colourless jelly-like material which is only stable at room temperature for a few hours. Its I.R. spectrum is in agreement with previous evidence. Therefore, again, as discussed in Section 3.1.4, by changing one of the substituents at silicon in $\text{SiH}_3\text{X}$, in this case replacing a hydride ligand by a methyl group, a reaction sequence occurs analogous to that observed previously, resulting in the formation of a six co-ordinate dihydride species. In contrast to replacing the hydride ligand with a halogen atom, replacement with a methyl group has no marked effect on the solubility of the system.

Section 3.2

$^1\text{H}$ n.m.r. spectra

Many of the comments made in Section 2.5. about the proton n.m.r. spectra of the species $\text{HfIr(} \text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{X}$ are relevant here. The spectra were recorded in benzene, or in many cases deuterobenzene, using tetramethyl silane as internal standard and were obtained on the Varian 100 and 220 MHz n.m.r. machines. The latter proved most useful since spectra from it showed as separate
certain peaks which overlap at 100 MHz. A comparison of spectra of the same complex observed on both the 100 and 220 MHz n.m.r. machines is made in plate 2. Since, the reactions of both SiH$_3$X and GeH$_3$X with IrH(CO)(PPh$_3$)$_3$ produce soluble products, all the iridium complexes can be investigated by n.m.r. spectroscopy. The exact positions of both the silyl and germyl groups, with respect to the other ligands present, is much easier to determine for these systems than for those resulting from the reaction of IrH(CO)(PPh$_3$)$_3$ with SiR$_3$H or Ir(CO)Cl(PPh$_3$)$_2$ with SiR$_3$H and GeR$_3$H. Since two less bonds separate the hydrogen atoms in the silyl and germyl ligands from the other ligands, coupling with both the phosphorus and the hydrogen atoms directly attached to iridium, $^3$J(H-Si-Ir-P) and $^3$J(H-Si-Ir-H) can be observed. Thus n.m.r. spectroscopic evidence is very useful in the determination of the structure of these complexes. As with the spectra of the complexes, HIrCl(CO)(PPh$_3$)$_2$GeHX$_2$ the region associated with the phenyl phosphine protons is complicated and observable, in deuterobenzene, as a complex multiplet centred around 3.0%. A typical spectrum is shown in fig. 32.

Both the SiH and GeH spectra are very characteristic but differ according to the position of the silyl and germyl groups with respect to the other ligands in the complex: examples are shown in fig. 46.
Comparison of $^1$H n.m.r. spectra of the iridium-silyl complex, IrH$_2$(CO)(PPh$_3$)$_2$ SiH$_2$Br, obtained at 100 and 220 MHz.

PLATE 2
The reaction of SiH₄ with IrH(CO)(PPh₃)₃ produces one isomer. The SiH spectrum consists of a doublet of triplets, (see fig. 46 (III); the splitting in this peak is due to coupling of SiH with two almost equivalent phosphorus atoms and also with a single proton. Therefore there are four n.m.r. parameters associated with this resonance: chemical shift, $^3J(H-Si-Ir-P_1)$, $^3J(H-Si-Ir-P_2)$ and $^3J(H-Ir-Si-H)$. This final parameter is shown to be involved by homonuclear spin decoupling; irradiation at 19.80° causes collapse of the doublet splitting in the peak associated with SiH at 6.43°.

The reaction of the silyl halides with IrH(CO)(PPh₃)₃ usually produces at least two isomeric products in each case. Silyl chloride and silyl bromide give similar isomers. The structure of one of these, the minor product, is thought to be the same as that of the adduct of SiH₄; the SiH resonances of these products are observed at 4.0° and 4.4°, respectively. The SiH spectrum of the major product consists of a doublet of doublets [see fig. 46 (I)]; the splitting is assigned to coupling of SiH with two non-equivalent phosphorus atoms. Thus there
are three parameters associated with this resonance for each compound: chemical shift, $^3J(H-Si-Ir-P_t)$ and $^3J(H-Si-Ir-P_c)$. Long-range coupling of the $SiH$ resonance with the cis protons produces further very small splitting. Homonuclear decoupling shows that neither of the resolved doublet splittings is due to coupling $^3J(H-Si-Ir-H)$; irradiation at the $IrH$ resonance 19.68 $\gamma$ and 19.66 $\gamma$) does not affect the main $SiH$ resonance in either case. We deduce that $SiH_2X$ (X=Cl or Br) is trans to P, not to H, in this isomeric form. Silyl iodide produces two isomeric products, one of which, the major isomer, is thought to be similar to the major isomer from the $SiH_3Cl$ and $SiH_3Br$ reactions. The peak at 6.6 $\gamma$ in the $SiH$ spectrum is assigned to the $SiH$ resonance of this isomer. The $SiH$ resonance of the other product differs from all those previously described, and consists of a finely split doublet of triplets; the splitting in this peak is assigned to coupling of $SiH$ with two effectively-equivalent phosphorus atoms and a proton. Evidence discussed later indicates that these particular phosphorus atoms are in mutually trans phosphine groups. The parameters for all these silyl complexes of iridium are recorded in table 3.1. The reaction of $GeH_3X$ (X=H, Cl, Br, I) with $IrH(CO)(PPh_3)_3$ generally results in the formation of a single isomer. The $GeH$ spectrum consists of a doublet of triplets [see fig. 46 (II)]; the splitting in the peak is due to coupling of the $GeH$ resonances with two equivalent phosphorus atoms and a proton. The doublet splitting is shown by homonuclear decoupling to be due to
coupling of GeH with a trans hydride ligand. Irradiation at the
IrH resonance frequency (20.46 γ, 20.01 γ, 20.28 γ and 20.54 γ
respectively, for the products from GeH₄, GeH₃Cl, GeH₃Br and
GeH₃I) causes the collapse of the doublet splitting in the GeH
resonances (at 7.72 γ, 5.05 γ, 5.60 γ and 6.76 γ). Using field sweep
on the 220 MHz n.m.r. machine it was shown that the collapse of
the peak at 5.05 γ to a triplet by irradiation at 20.01 γ took place over
a range of 16 c/s around the region of 20.01 γ; this is in keeping with
the very broad IrH resonance. The GeH resonance associated with
the product from the reaction of GeH₃I with IrH(CO)(PPh₃)₃ has
another observable splitting, and is a doublet of doublets of triplets;
the additional splitting is assigned to coupling of the resonance with the
cis hydride ligand, and irradiation at 19.99 γ causes the collapse of
this coupling. In the other products this coupling is very small and is
barely visible even on an expanded spectrum. The breadth of the
resonances, which has been mentioned above, has been demonstrated
further by a study of the effects of irradiating at 20.45 γ on the
resonance at 5.05 γ in the GeH spectrum of IrH₂(CO)(PPh₃)₂GeH₂Cl.
The GeH spectrum was observed at a 250 Hz (4-fold) expansion and
it was shown that irradiation over a range of values around 20.45 γ
cause different parts of the peak at 5.05 γ (which is a doublet of
doublets of triplets) to collapse. The inner peaks collapse to singlets
at differences of 1147 and 1186 c/s between resonances and the outer
peaks at a difference of 1168 c/s. The breadth of the resonance at
20.45 γ makes it almost impossible to irradiate at one point and collapse
Parameters from the $^1$H n.m.r. spectra of the iridium-silyl are resonance lines $\sim 3 \gamma$ which can be assigned to the aromatic benzene or deuterobenzene as solvent and TMS as internal standard.

<table>
<thead>
<tr>
<th>Product</th>
<th>$\gamma$SiH</th>
<th>$J(H-Si-P_1)$</th>
<th>$J(H-Si-P_2)$</th>
<th>$J(H-Ir-Si-H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Br}$ (I)</td>
<td>6.43</td>
<td>5c/s</td>
<td>2c/s</td>
<td>2c/s</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Cl}$ (II)</td>
<td>4.65</td>
<td>12c/s</td>
<td>26c/s</td>
<td>v. small</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Br}$ (II)</td>
<td>4.0</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Br}$ (II)</td>
<td>5.2</td>
<td>12c/s</td>
<td>24c/s</td>
<td>v. small</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Br}$ (II)</td>
<td>4.4</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{I}$ (III)</td>
<td>6.6</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{I}$ (III)</td>
<td>5.3</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>$\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Br}$ (II)</td>
<td>4.78</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

*dbt=doublet; tpt=triplet; qut=quartet; mpt=multiplet;*

The roman numerals I,II and III in the table above refer to the diagrams opposite which represent the various possible stereocchemistries for the complexes $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{X}$.

![Diagram](image)
3.1. Complexes IrH₂(CO)(PPh₃)₂SiH₂X. In all the spectra there are protons of triphenylphosphine. The spectra are recorded in standard on the Varian 100 or 220MHz n.m.r. spectrometers.

<table>
<thead>
<tr>
<th>Hₐ</th>
<th>IrH</th>
<th>Hₜ</th>
<th>J(Hₐ-Ir-P₁)</th>
<th>J(Hₐ-Ir-P₂)</th>
<th>J(Hₜ-Ir-P₁)</th>
<th>J(Hₐ-Ir-P₂)</th>
<th>J(Hₜ-Ir-Hₜ)</th>
<th>J(Hₜ-Ir-Hₜ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.50 20.12</td>
<td>20c/s</td>
<td>16c/s</td>
<td>112c/s</td>
<td>20c/s</td>
<td>5c/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.55 20.15</td>
<td>20c/s</td>
<td>18c/s</td>
<td>114c/s</td>
<td>20c/s</td>
<td>5c/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.30 20.13</td>
<td>19c/s</td>
<td>19c/s</td>
<td>19c/s</td>
<td>small</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.67 20.15</td>
<td>20c/s</td>
<td>15.5c/s</td>
<td>112c/s</td>
<td>18.5c/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.7 20.2</td>
<td>20c/s</td>
<td>18c/s</td>
<td>110c/s</td>
<td>18c/s</td>
<td>small</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b=basic; com=complex; ?=peak too weak or complex to make an accurate assessment of the coupling constant value.

[Diagrams of (II) and (III)]
Table

Parameters from the $^1$H n.m.r. spectra of the iridium-germanium resonance lines near $\delta \chi$ which can be assigned to the aromatic benzene or deuterobenzene as solvent with TMS as internal.

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>$^1$H</th>
<th>$J(Ir-Ir-Ge-H)$</th>
<th>$J(H-Ir-Ge-H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrH$_2$(CO)(PPh$_3$)$_2$GeH$_3$</td>
<td>I</td>
<td>7.72 $\delta$</td>
<td>4c/s</td>
<td>2c/s</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>7.01 tpt</td>
<td>8c/s</td>
<td>v. small</td>
</tr>
<tr>
<td>IrH$_2$(CO)(PPh$_3$)$_2$GeH$_2$Cl</td>
<td>I</td>
<td>5.05 dbt/tpts</td>
<td>5c/s</td>
<td>5c/s</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>5.00 dbt/dbts</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>IrH$_2$(CO)(PPh$_3$)$_2$GeH$_2$Br</td>
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<td>5.60 dbt/tpts</td>
<td>5c/s</td>
<td>7c/s</td>
</tr>
<tr>
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<td>I</td>
<td>6.76 dbt/dbt tpts</td>
<td>5.5c/s</td>
<td>5.5c/s</td>
</tr>
</tbody>
</table>

$dbt = doublets; tpt = triplet; com. = complex;$

$I$ and $II$ are the proposed stereochemistries for the
3.2.

complexes $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X$ in cm$^{-1}$. In all the spectra there are protons of triphenylphosphine groups. The spectra are recorded in standard on the Varian 100 or 220MHz n.m.r. spectrometers.

<table>
<thead>
<tr>
<th>$H_a$</th>
<th>IrH</th>
<th>$H_b$</th>
<th>$J(2-\text{Ir}-H_a)$</th>
<th>$J(2-\text{Ir}-H_b)$</th>
<th>$J(H_a-\text{Ir}-H_b)$</th>
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<tr>
<td>19.28</td>
<td>20.46</td>
<td>tpt/tpt</td>
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<td>16c/s</td>
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<tr>
<td>19.99</td>
<td>20.80</td>
<td>com.tpt/dbc/dbt</td>
<td>17c/s</td>
<td>120c/s</td>
<td>21c/s</td>
</tr>
<tr>
<td>20.47</td>
<td>20.01</td>
<td>dbt/tpt/dbc/dbt</td>
<td>17.5c/s</td>
<td>16c/s</td>
<td>4c/s</td>
</tr>
<tr>
<td>16.48</td>
<td>20.08</td>
<td>tpt/dbc/dbt</td>
<td>16c/s</td>
<td>115c/s</td>
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<tr>
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<tr>
<td>19.99</td>
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<td>tpt/com.tpt</td>
<td>16.5c/s</td>
<td>15.5c/s</td>
<td>4c/s</td>
</tr>
</tbody>
</table>

![diagram](image)

iridium-germyl complexes $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X$. 

the coupling $J(H_c-Ir-Ge-H)$, thus complicated decoupling effects are observed. In this case coupling with the cis hydride ligand is concerned and again collapse has been shown to occur within the GeH resonance over a range of $\sim 20c/s$. This phenomenon is shown in fig. 47. The reactions of GeH$_4$ and GeH$_3$Cl with IrH(CO)(PPh$_3$)$_3$ have been shown, on certain occasions, to produce a minor isomer together with the major product. The GeH resonance associated with these minor isomers is again basically a doublet of triplets; the splitting is due to coupling with two almost equivalent phosphorus atoms and a single proton. In both cases the coupling with the hydride ligand is smaller than that observed for the more abundant isomers previously considered. On the basis of evidence discussed later the phosphorus atoms appear, this time, to be mutually cis. The parameters for all the germly complexes are presented in table 3.2.

The chemical shift values of both SiH and GeH in the complexes, IrH$_2$(CO)(PPh$_3$)$_2$MH$_2$X, show the same trends as those for GeH in H$_2$Ir(CO)(PPh$_3$)$_2$GeH$_2$X (see Section 2.5). The GeH chemical shifts are comparable, those of the Ir (III) dihydride species being slightly higher ($\sim 20c/s$) than those of the monohydride species. Values for the coupling constants $^3J(H-Ge-Ir-P)$ are fairly constant and increase slightly as X varies in the order H < Cl < Br < I, the same order as found in the complexes H$_2$Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$X, though the values in the dihydride complexes are smaller. The coupling constants $^3J(H-Ge-Ir-H)$ are also fairly constant and increase in the order of
Effects of irradiation over a range of values around 20.45° on the resonance at 5.05° in the GeH spectrum of \( \text{IrH}_2(\text{CO})(\text{PF}_{3})_2\text{GeH}_2\text{Cl} \). The spectrum was observed at a 250Hz(4-fold) expansion. The values in c/s denote the differences between resonances.

fig. 47
halogens defined above. The coupling constants $^{3}J(P_{1}-Ir-Si-H)$ and $^{3}J(P_{2}-Ir-Si-H)$ in the complexes IrH$_{2}$(CO)(PPh$_{3}$)$_{2}$SiH$_{2}$X (X=Cl, Br, I) are very different in magnitude from any previously discussed. The relatively large value ($J(P_{1}-Ir-Si-H)$ 24c/s) is not unexpected but this is accompanied by an increase in $J(P_{c}-Ir-Si-H)$ to 12c/s.

The SiH and GeH spectra are generally like those obtained by Bentham for the products Pt(PEt$_{3}$)$_{2}$X, MH$_{2}$X, 36, 37 Some of the relevant data is shown in table 2.3.

The IrH spectra of both the silyl- and germyl- dihydride complexes are again very characteristic and examples are shown in fig. 48 and plates 2&3. The pattern is a good indication of the structure of the isomer concerned.

This resonance is found to high field of TMS and in a similar position to that of the monohydride complexes. The chemical shift depends on the nature of the ligand trans to hydride. A discussion of this dependence and of the assignment of the experimental values to hydride ligands in a particular environment is given later. The IrH
$^1$H n.m.r. Spectrum at 220 MHz

(expansion to 250 Hz)

IrH region of $^1$H n.m.r. spectrum of the iridium-germyl complex, IrH$_2$(CO)(PPh$_3$)$_2$ GeH$_2$I

PLATE 3
spectrum of all save one of the silyl complexes, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{X} \) \((\text{X}=\text{Cl, Br, I})\), consists of two sets of peaks, [see fig. 48]. One is widely spaced doublet of doublets of doublets; the splitting is due to coupling of \( \text{IrH} \) with two non-equivalent phosphorus atoms (one trans and the other cis to the hydride) and with the other hydride ligand. The other set of peaks appears as a complex triplet, which is analysed as an overlapping doublet of doublet of doublets; the splitting again is due to coupling of \( \text{IrH} \) with two almost equivalent phosphorus atoms (both cis to this hydride) and the other hydride ligand. For the complex, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_3 \), this second peak is coupled with \( \text{SiH}_3 \), thus the already complicated \( \text{IrH} \) shows an additional quartet splitting, \( J(\text{H-Si-Ir-H}) \). The existence of this coupling is shown by spin decoupling. The \( \text{IrH} \) spectra are in agreement with those obtained from products of the reaction of \( \text{Ir(CO)Cl(PPh}_3)_2 \) and \( \text{IrH(CO)(PPh}_3)_3 \) with alkyl silanes,\(^{109,110}\) which indicate the presence of two hydride ligands, one trans to the one phosphine ligand and cis to the other, and the other cis to both phosphine ligands. The n.m.r. parameters for the \( \text{SiH}_3^- \) and \( \text{SiH}_2\text{X}^- \) products are presented in table 3.1.

The \( \text{IrH} \) spectra of the germyl complexes, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{X} \) \((\text{X}=\text{H, Cl, Br, I})\), also consist of two sets of peaks, [see fig. 48]. One is a doublet of triplets; the splitting is due to coupling of \( \text{IrH} \) with the two effectively equivalent phosphorus atoms and with the other hydride. The other peak is a triplet or quartet of doublets of triplets; the splitting is due to coupling of
IrH with the two effectively equivalent phosphorus atoms, the other hydride ligand and with GeH. Coupling of GeH with IrH has been shown by spin decoupling as discussed earlier. The complex triplets at 20.46, 20.01, 20.28 & 20.54° can be persuaded by irradiation in the GeH region to collapse to doublets of triplets. The GeH spectra of the germyl complexes indicate that both the hydride ligands are mutually cis to the two phosphine ligands. The parameters are recorded in table 3.2. Evidence for the formation of different isomers during the reaction of IrH(CO)(PPh₃)₃ with GeH₃Cl and SiH₃I came from evidence from the IrH spectra of these complexes. In the addition of SiH₃I to IrH(CO)(PPh₃)₃ resonance peaks associated with a species containing mutually trans phosphines were observed in the IrH spectrum. Similarly, during the addition of GeH₃Cl, peaks associated with a complex containing mutually cis phosphines were observed. In Section 2.5 a discussion is given of the chemical shift values assigned to hydride ligands attached to a central iridium atom and how these values are determined by the nature of the ligand trans to the hydride. Based on this information, which is summarized in table 2.4., the peaks observed in the 19-21° region for the complexes, IrH₂(CO)(PPh₃)₂MH₂X can be assigned to hydrides trans to phosphine, carbonyl, silyl or germyl ligands. The actual chemical shift values, therefore, do not give much indication of the stereochemistry of the complexes. The coupling constants and the results of spin decoupling are of much greater value in determining the stereochemistry and, a discussion of these shows how use of general
trends in chemical shift values can be misleading in assigning trans positions to hydride ligands. Thus great care must be taken in using such values. For instance, the data in table 2.3. indicates that the $\gamma$ value for H trans to a silyl or germyl group ($\sim 17\gamma$) is lower than that for H trans to either a phosphine or carbonyl ligand ($\sim 19-21\gamma$). Assignment of the resonance at $\sim 17\gamma$ in the $\text{IrH}$ spectrum of $\text{Ir(CO)Cl(PPh}_3)_2\text{GeH}_2\text{Cl}$ to a hydride trans to a germyl ligand was in agreement with this generalization. However, (see table 3.2) consider three complexes $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{X}(\text{X}=\text{Cl, Br, I})$ of identical stereochemistry. The chemical shift for hydride trans to carbonyl is to high field of H trans to GeH$_2$X when X=Cl (20.47$\gamma$ vs. 20.01$\gamma$), is almost the same field value when X=Br (both at $\sim 20.30\gamma$), and is to low field of H trans to GeH$_2$X when X=I (19.99$\gamma$ vs. 20.54$\gamma$). A diagramatic representation of this is shown in fig. 49 and plate 4.

Therefore the previously noted trend would have led to wrong assignments in some of these complexes. The relative values of the chemical shift for H trans to carbonyl and germyl ligands in $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_3$ are also inconsistent with the generalization previously made. If $\gamma(\text{IrH})$ reflects the trans
Comparison of $^1$H NMR spectra for three complexes, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X$ (X = Cl, Br, I) of identical stereochemistry. The relationship between the chemical shift values for H trans to CO and H trans to GeH$_2X$ as $X$ varies is shown.
Influence of the trans ligand the trans influences of silyl and germyl groups in these systems depend on the other atoms or groups bound to Ge or Si. Indeed, in the complexes, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X$, the halogen atom at germanium affects the chemical shift of the hydride ligand cis to the germyl as well as that of the trans hydride. The effects are opposed, a slight increase for H trans to GeH$_2X$ and a slight decrease for H trans to CO as X varies in the order Cl $\rightarrow$ Br $\rightarrow$ I. The chemical shifts for the hydrides trans to the silyl and phosphine ligands are in agreement with these observations, but a change in halogen atom at silicon in $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2X$, has very little effect on the chemical shift of either hydride; the chemical shift decreases slightly for hydride trans to carbonyl and remains constant for hydride trans to phosphine. The coupling constants $J(\text{P}_c-\text{Ir}-\text{H})$, $J(\text{P}_c-\text{Ir}-\text{H})$ and $J(\text{H}-\text{Ir}-\text{H})$ are fairly constant as X varies in MH$_3X$ (M=Si, Ge; X=H, Cl, Br, I). As might be expected, they are much larger than those for the SiH and GeH resonances as there is one less atom between the coupling nuclei. Both these and the coupling constant $J(\text{H}-\text{Ge}-\text{Ir}-\text{H})$ are substantially larger than the comparable coupling constants for the complexes, $\text{H.Ir(CO)Cl(PPh}_3)_2\text{GeH}_2X$. The coupling constant $J(\text{P}_c-\text{Ir}-\text{Ge}-\text{H})$ is however smaller.

Spin decoupling was used to determine the stereochemical relationship between the hydride ligands and the silyl and germyl ligands in the iridium (III) complexes. By analogy with Bentham's platinum complexes, it is likely that in almost all cases long range
coupling $(J_{\text{H}_2-\text{Ir-M-H}})$ can be ignored. Collapse of the doublet splitting at 5.05 $\tau$ in the complex, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{Cl}$, results from irradiation at 20.01 $\tau$; thus a trans relationship between the legands associated with these resonances is postulated. In this way, the germyl ligands are shown to be trans to hydride in all the germyl complexes, and $\text{SiH}_3^-$ is shown to be trans to the hydride in the complex, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_3^-$. Long range cis coupling $3J(\text{H-Si-Ir-H}_2)$ is very small but can be detected, as has been shown by spin decoupling. Irradiation, for instance, at 20.47 $\tau$ caused a distinct sharpening of the doublet of triplets at 5.05 $\tau$ for the complex, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{Cl}$. Observations on this system have been described earlier in this section.

It was hoped that heteronuclear spin decoupling by irradiation at phosphorus would show the homonuclear coupling between the protons on silicon or germanium and those on iridium in the simplified proton spectra. Irradiation of phosphorus and observation of the MH and IrH spectra could have shown this coupling if collapse of the coupling between phosphorus and the protons had been achieved. The spin decoupling experiments attempted did not prove successful partly because the concentration of solution, in the n.m.r. tube, necessary for these experiments was such that precipitation of the iridium complexes occurred rapidly. In view of the excellent results obtained during experiments on analogous platinum systems it is felt that if the heteronuclear spin decoupling facilities had been available earlier and if more time could have been
spent on the iridium systems that there might have been greater success with the latter. Observation of the \( \text{IrH} \) and \( \text{MH} \) spectra, alone, indicates almost conclusively that both homonuclear (\( \text{MH} \) and \( \text{IrH} \)) and heteronuclear (\( \text{MH} \), \( \text{IrH} \) and \( \text{IrP} \)) coupling does exist.

The \( ^1\text{H n.m.r.} \) spectrum of the soluble dihydride species formed during the reaction of \( \text{MeSiH}_2\text{Cl} \) with \( \text{IrH(CO)(PPh}_3)_3 \) is similar in character to that already described for the complex \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Cl} \). It is also the same as that obtained previously for the compound presumably \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHMeCl} \), produced during the long term reaction of an excess of methyl silyl chloride with Vaska's compound. There is a doublet of doublets at 4.78 \( \tau \) which is assigned to \( \text{SiH} \) and a complex multiplet at \( \sim 8.57 \tau \) which is assigned to \( \text{CH} \). The \( \text{IrH} \) spectrum, with two sets of peaks centred at 19.77 and 20.2 \( \tau \), indicates that the orientation of the hydrides to the other ligands is as in the silyl chloride complex.

The parameters are presented in table 3.1. Thus a structure as shown in fig. 50 is postulated.

![fig. 50](image)

The addition of \( \text{SiD}_3\text{Br} \) to \( \text{IrH(CO)(PPh}_3)_3 \) provided evidence both for the non-stereospecific nature of the addition reaction and
for the basic nature of the IrH spectrum. There was no SiH spectrum; thus exchange of H and D does not occur during the reaction. The IrH spectrum showed two similar sets of peaks, as observed for the IrH spectrum of the complex, IrH₂(CO)(PPh₃)₂SiH₂Br. They were, however, much simpler. Both were doublets of doublets. In one set, where the lines overlap, the splitting was due to coupling of IrH with two phosphorus atoms, both cis to the hydride but non-equivalent; in the other set the splitting is assigned to coupling of IrH with two non-equivalent phosphorus atoms (one trans and the other cis to the hydride). The coupling constants, J(H-Ir-Hc) and J(H-Ir-Si-H), as expected, are missing. The parameters involved are recorded in table 3.1. For this complex it is easy to determine the exact values of the coupling constants, ²J(H-Ir-Pc), ²J(H-Ir-Pc₁) and ²J(H-Ir-Pc₂) and to show the difference between the latter two. The structures assigned to the products from this reaction are shown in fig. 51.

Use of the 220 n.m.r. machine made it much easier to analyse the IrH spectra obtained for the complexes IrH₂(CO)(PPh₃)₂MH₂X. The spectra were much stronger than those obtained at 100 MHz.
Phase refers to method of obtaining spectrum;

v=very; s=strong; m=medium; w=weak; b=broad; sh=shoulder;

?=very tentative assignment;

<table>
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<th>Product</th>
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<th>( \nu (\text{Ir-H}) )</th>
<th>( \nu (\text{C-C}) )</th>
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</thead>
<tbody>
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<td>N</td>
<td></td>
<td>2110m</td>
<td>1915vs</td>
</tr>
<tr>
<td>&quot;</td>
<td>B</td>
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<td>2058m</td>
<td>1920vs</td>
</tr>
<tr>
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<td>obs.</td>
<td>1965vs</td>
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<td>2022w</td>
<td>1988vs</td>
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<td>B</td>
<td>2100vs</td>
<td>obs.</td>
<td>1980vs</td>
</tr>
<tr>
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<td>2095vs2080vs</td>
<td>obs.</td>
<td>1982vs</td>
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<td>2020w</td>
<td>1980s</td>
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<td>2055m</td>
<td>2005s 1978s</td>
</tr>
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<td>obs.</td>
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<td>&quot;</td>
<td>B</td>
<td>2080sb</td>
<td>2035m</td>
<td>1960sb</td>
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<tr>
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<td>N</td>
<td>2120vs</td>
<td>?2080sh</td>
<td>2000vs</td>
</tr>
</tbody>
</table>
3.3. 

compounds IrH$_2$(CO)(PPh$_3$)$_2$SiH$_2$X and others in cm$^{-1}$. In all the spectra 430-530 cm$^{-1}$ which are assigned to modes of triphenylphosphine groups.

<table>
<thead>
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<th>δ (Si-H)</th>
<th>δ(Ir-H)</th>
<th>δ(C-C)</th>
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<td>—</td>
<td>822m</td>
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<td>—</td>
<td>—</td>
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<td>n.o.</td>
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<td>obs.</td>
<td>348w</td>
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N=Nujol mull; B=benzene solution; 
obs.=region obscured; n.o.=not observed; 
*=product formed by the reaction of IrH(CO)(PPh$_3$)$_3$ and 2SiH$_2$Cl
Table

Frequencies from the infrared spectra of the iridium-germyl are bands near 2,600-3,000 cm\(^{-1}\), 1,000-1,200 cm\(^{-1}\), 650-750 cm\(^{-1}\) and The spectra are recorded as nujol mulls, benzene solutions.

<table>
<thead>
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<th>(\nu) (Ir-H)</th>
<th>(\nu) (C-O)</th>
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</thead>
<tbody>
<tr>
<td>IrH(CO)(PPh(_2))(_3)</td>
<td>N</td>
<td>---</td>
<td>2110m</td>
<td>1915vs</td>
</tr>
<tr>
<td>Ir(_2)(CO)(PPh(_2))(_2)Ge(_3)</td>
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<td>1960v sb</td>
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<tr>
<td>&quot; &quot;</td>
<td>B</td>
<td>1970v sb</td>
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<td>1970v sb</td>
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<tr>
<td>Ir(_2)(CO)(PPh(_2))(_2)Ge(_2)Br</td>
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<td>1980v sb</td>
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<td>1985v sb</td>
<td>2005s</td>
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<tr>
<td>Ir(_2)(CO)(PPh(_2))(_2)GeBr(_2)</td>
<td>L</td>
<td>2105vs</td>
<td>22150s</td>
<td>2005v s</td>
</tr>
</tbody>
</table>

Phase refers to method of obtaining the spectrum:

v=very; s=strong; m=medium; w=weak; b=broad;
n.s.=region not studied; ?=tentative assignment.
4 compounds, \( \text{Ir}_2(C)(PPh_3)_2\text{GeR}_x \) in cm\(^{-1}\). In all the spectra there are modes of triphenylphosphine groups or liquid films.

<table>
<thead>
<tr>
<th>( \delta(\text{Ge-H}) )</th>
<th>( \delta(\text{Ir-H}) )</th>
<th>( \delta(\text{C-O}) )</th>
<th>( \gamma(\text{Ge-X}) )</th>
<th>( \gamma(\text{Ir-Ge}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>822m</td>
<td>610w</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>890w</td>
<td>828s</td>
<td>616vw</td>
<td>—</td>
<td>n.o.</td>
</tr>
<tr>
<td>875m</td>
<td>830w</td>
<td>615vw</td>
<td>325m</td>
<td>275w</td>
</tr>
<tr>
<td>875m</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>875m</td>
<td>825w780w</td>
<td>615vw</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>870s</td>
<td>840m</td>
<td>618vw</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>875m</td>
<td>840w785w</td>
<td>n.o.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>845vsh</td>
<td>825sh</td>
<td>618w</td>
<td>n.s.</td>
<td>210w236w</td>
</tr>
</tbody>
</table>

N=Nujol mull; B=benzena solution; L=liquid film;
sh.=shoulder; n.o.=not observed;
Furthermore, the increase in operating frequency led to a considerable simplification, partly by increasing the separation in Hz between resonances differing in chemical shift and partly by reducing second order effects. Some of the 220 Hz n.m.r. spectra are illustrated in plates 2,3, & 4.

The proton n.m.r. spectra have, therefore, proved to be invaluable in assigning stereochemistries to the products of the reaction of IrH(CO)(PPh$_3$)$_3$ and MH$_3$X.

Section 3.3.

Vibrational Spectra

The infrared spectra were recorded between 4000 and 200 cm$^{-1}$; the complexes were studied both as Nujol Mulls and as benzene solutions. In common with results from the monohydride complexes, H$_2$Ir(CO)Cl(PPh$_3$)$_2$MH$_2$X (M=Si, Ge; X=H, Cl, Br, I) there was little success with Raman spectra. The frequencies of the various bands, together with assignments (which are tentative in some cases) are shown in tables 3.3 (for the silyl compounds) and 3.4 (for the germyl compounds). There has been no inclusion of the frequencies associated with the internal vibrations of triphenylphosphine since they remain the same for all compounds studied. As noted in Section 3.2. many of the comments on the spectra of the products from the reaction of Vaska's compound with silyl and germyl halides are relevant to the spectra of the dihydride complexes.
The modes involving M-H, C-O and Ir-H, and M-X and Ir-M stretching modes are the most useful vibrations for characterising the complexes. The same characteristics are shown in these spectra as in those discussed in Section 2.6. The CO ligand is retained in all the complexes and a strong band varying in position from 1960 - 2000 cm\(^{-1}\) is assigned to this vibrational mode. The value of \(\nu(C-O)\) increases in all cases with respect to its value in \(\text{IrH(CO)(PPh}_3\text{)}_3\), as predicted by analogy with similar systems on changing from Ir(I) to Ir(III) and in keeping with the increase in \(\nu(CO)\) from Vaska's compound to any of the complexes, \(\text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{MH}_2\text{X}\).

Again \(\delta(C-O)\) occurs as a weak band at \(\sim 620\) cm\(^{-1}\).

Great care has to be taken in assignment of specific frequencies to the C-O, Ir-H and M-H stretching modes since all occur in the same region. In the silyl complexes, there is overlapping of the bands assigned to \(\nu(Si-H)\) and \(\nu(Ir-H)\) and in the germyl complexes there is some overlapping of bands assigned to \(\nu(Ge-H)\) and \(\nu(Cl-O)\). This latter effect had been observed in the spectra of the species, \(\text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{GeH}_2\text{X}\), and as for those complexes all the I.R. assignments made must remain tentative to some extent. The assignment of bands to \(\nu(Si-H)\) and \(\delta(Si-H)\) in the spectrum of \(\text{IrH}_2(CO)(PPh}_3\text{)}_2\text{SiH}_2\text{Br}\) was aided by comparison with the infrared spectrum of \(\text{IrHD(CO)(PPh}_3\text{)}_2\text{SiD}_2\text{Br}\) and by analogy with the spectra of the species \(\text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{SiH}_2\text{Br}\) and \(\text{Dlr(CO)Cl(PPh}_3\text{)}_2\text{SiD}_2\text{Br}\). The frequencies associated with these latter complexes have been discussed in Section 2.6. and are presented in table 3.5. With this
TABLE 3.5

<table>
<thead>
<tr>
<th></th>
<th>(\nu(\text{Si-H}))</th>
<th>(\delta_1(\text{Si-H}))</th>
<th>(\delta_2(\text{Si-H}))</th>
<th>(\delta_3(\text{Si-H}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{Ir(CO)Cl(PPh}_3\text{)_2SiH}_2\text{Br})</td>
<td>2120, 2100 vs</td>
<td>975 s</td>
<td>850 s</td>
<td>obs.</td>
</tr>
<tr>
<td>(\text{D}_2\text{Ir(CO)Cl(PPh}_3\text{)_2SiH}_2\text{Br})</td>
<td>1542, 1480 s</td>
<td>obs</td>
<td>7640 s</td>
<td>obs.</td>
</tr>
<tr>
<td>(\text{IrH}_2\text{(CO)(PPh}_3\text{)_2SiH}_2\text{Br})</td>
<td>2090</td>
<td>955</td>
<td>820 s</td>
<td>obs.</td>
</tr>
<tr>
<td>(\text{IrHD(CO)(PPh}_3\text{)_2SiD}_2\text{Br})</td>
<td>1580, 1520</td>
<td>obs?</td>
<td>600 s</td>
<td>obs.</td>
</tr>
</tbody>
</table>

information the bands at \(~2080\) cm\(^{-1}\) and \(955\) and \(820\) cm\(^{-1}\) have been assigned to \(\nu(\text{Si-H})\) and \(\delta(\text{Si-H})\), respectively. The band at \(1970\) cm\(^{-1}\) is assigned to \(\nu(\text{C-O})\) by comparison of the spectra of \(\text{IrH}_2\text{(CO)SiH}_2\text{Br(PPh}_3\text{)_2}\) and its deuterated analogue. In the spectrum of the latter compound a second band at \(2000\) cm\(^{-1}\) also assignable to \(\nu(\text{C-O})\), appears, together with that at \(1970\) cm\(^{-1}\). The n.m.r. spectrum of the products from this reaction indicates that two isomers are formed by the non-stereospecific addition of \(\text{SiD}_3\text{Br}\) to \(\text{IrH(CO)(PPh}_3\text{)_3}\). Therefore, two bands assignable to \(\nu(\text{C-O})\) might be expected if it is presumed that coupling occurs between vibrations of mutually trans \(\text{Ir-H}\) and \(\text{C-O}\); one is assigned to the vibration of the \(\text{CO}\) ligand trans to the deuteride ligand in one isomer and the other is assigned to the vibration of the \(\text{CO}\) ligand trans to the hydride ligand in the other isomer. Conflicting evidence discussed in Section 2.5 has shown that the observation of shifting of a band assignable to a carbonyl stretch in a deuterated silyl species of iridium can probably occur when the carbonyl ligand is trans to a deuterated silyl ligand.
In this case, however, unambiguous n.m.r. evidence has already established that the hydride and deuteride ligands, are trans to a phosphine and a carbonyl ligand.

In the infrared spectrum of the product of the addition of \((\text{EtO})_3\text{SiH}\) to \(\text{IrD(CO)(PPh}_3\text{)}_3\) when scrambling occurs two bands, at 2000 cm\(^{-1}\) and 1965 cm\(^{-1}\), assignable to \(\nu(\text{C-O})\) in two different isomers are also observed, just as found here. The assignment of corresponding modes in the spectra of the other silyl and germyl compounds is made by analogy with this complex and the previous iridium complexes which have been analysed. It can be seen that the values assigned to \(\nu(\text{Si-H}), \nu(\text{Ge-H}), \delta(\text{Si-H}), \delta(\text{Ge-H}),\) and \(\nu(\text{C-O})\) in both the monohydride and dihydride complexes of Ir(III) are almost the same. This observation is not unexpected since the vibrational modes being considered should not be greatly affected by so slight a change in the nature of the iridium complex as replacement of a chlorine by a hydride ligand. Owing to the breadth, in Nujol mulls and benzene solutions, of both the \(\nu(\text{Si-H})\) and \(\nu(\text{Ge-H})\) peaks, because of overlapping with \(\nu(\text{Ir-H})\) and \(\nu(\text{C-O})\), respectively, it is impossible to distinguish whether the symmetric and antisymmetric stretching modes of \(\text{M-H}\) coincide or not. The nature of these modes and the stretching modes of the unsubstituted species \(\text{H}_2\text{Ir(CO)Cl(PPh}_3\text{)}_2\text{MH}_3\) have been discussed in Section 2.5. as have the four possible modes of deformation of \(\text{MH}_2\text{X}\): 'scissors', 'wagging', 'twisting' and 'rocking' vibrations, and the three possible
modes for MH$_3$: symmetric bend local symmetry class (a$_1$), antisymmetric bend (e) and rock (e). By analogy with vibrational frequencies for similar complexes of platinum and iridium, the observed bands for the complexes IrH$_2$(CO)(PPh$_3$)$_2$MH$_2$X and IrH$_2$(CO)(PPh$_3$)$_2$MH$_3$ are assigned as shown in tables 3.5. and 3.6. Again in the germyl complexes only one GeH deformation can be assigned since the other modes are probably obscured by bands of triphenylphosphine.

**TABLE 3.6**

<table>
<thead>
<tr>
<th></th>
<th>antisym.</th>
<th>symm.</th>
<th>rock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bends</td>
<td>bend</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S$_1$(MH)</td>
<td>S$_2$(MH)</td>
<td>S$_3$(MH)</td>
</tr>
<tr>
<td>H. Ir(CO)Cl(PPh$_3$)$_2$SiH$_3$</td>
<td>960, 945 cm$^{-1}$</td>
<td>930</td>
<td>?</td>
</tr>
<tr>
<td>H. Ir(CO)Cl(PPh$_3$)$_2$GeH$_3$</td>
<td>900, 890</td>
<td>830</td>
<td>?</td>
</tr>
<tr>
<td>IrH$_2$(CO)(PPh$_3$)$_2$SiH$_3$</td>
<td>950, 935</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>IrH$_2$(CO)(PPh$_3$)$_2$GeH$_3$</td>
<td>? 890 w</td>
<td>828</td>
<td>?</td>
</tr>
</tbody>
</table>

Two bands assignable to the symmetric and asymmetric stretching modes of Ir–H are to be expected. The frequencies of these will depend on the trans ligand. If the two hydride ligands are mutually trans then only one band should be observed. This band, which generally lies in the region of $\sim$1785 cm$^{-1}$, has not been observed in these particular iridium complexes. The n.m.r. spectra imply that the hydrides are trans to phosphine, carbonyl or silyl or germyl ligands. All these ligands have relatively high trans influences and thus the values for the hydrides would be
expected to be around 2000 cm\(^{-1}\). In the I.R. spectra of the silyl complexes, \(\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{X}\), the band assigned to \(\nu(\text{Si-H})\) obscures the region around 2100 cm\(^{-1}\) and similarly in the spectra of the germyl complexes the band assigned to \(\nu(\text{Ge-H})\) obscures 2000 cm\(^{-1}\). However, the spectra of the germyl complexes show one band near 2100 cm\(^{-1}\) and the spectra of the silyl complexes show another near 2020 cm\(^{-1}\). Evidence from the spectrum of the deuterium substituted species, \(\text{IrHD}(\text{CO})(\text{PPh}_3)_2\text{SiD}_2\text{Br}\), supports the assignment of these bands to \(\nu(\text{Ir-H})\). These values are in agreement with those obtained by Vaska for the addition of \(\text{H}_2\) to \(\text{Ir(CO)Cl(PPh}_3)_2\) (H trans to CO - 2098 cm\(^{-1}\)), by Chalk and Harrod for the addition of excess \((\text{C}_2\text{H}_5\text{O})_3\text{SiH}\) to \(\text{Ir(CO)Cl(PPh}_3)_2\) (H trans to \((\text{C}_2\text{H}_5\text{O})_3\text{Si}\) - 2080 cm\(^{-1}\), H trans to \(\text{PPh}_3\) ~ 2100 cm\(^{-1}\)) and by Glockling for the addition of excess GeR\(_3\text{H}\) to \(\text{Ir(CO)Cl(PPh}_3)_2\) (H trans to \(\text{PPh}_3\) and CO - 2081 and 2119 cm\(^{-1}\), R=Et; H trans to \(\text{PPh}_3\) and 2065 and 2084 cm\(^{-1}\), R=Cl). It is probable that the lower value assigned to \(\nu(\text{Ir-H})\) is due to the hydride trans to -\(\text{MH}_2\text{X}\) since \(\text{MH}_2\text{X}\) will have a higher trans effect than either phosphine or carbonyl.

The presence of different bands assignable to \(\nu(\text{Ir-H})\) could also be explained by the formation of various isomers during the reaction of \(\text{IrH(CO)(PPh}_3)_3\) and \(\text{MH}_3\text{X}\). Not unexpectedly there is no band at ~2180 cm\(^{-1}\), which would imply H trans to Cl, (as observed in the complexes H.\(\text{Ir(CO)Cl(PPh}_3)_2\text{MH}_2\text{X}\)), since the hydride cannot be trans to a halide ligand unless exchange between a halogen on -\(\text{MH}_2\text{X}\) and one of the hydride ligands has occurred.
The spectra of the unsubstituted species, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_3$, and the deuterated species, $\text{IrHD}(\text{CO})(\text{PPh}_3)_2\text{SiD}_2\text{Br}$, are useful in assigning the band at $\sim 830 \text{ cm}^{-1}$ to $\delta(\text{Ir-H})$. The position of this band is similar to that of $\delta(\text{Ir-H})$ in $\text{H.Ir(CO)Cl(PPh}_3)_2\text{MH}_2\text{X}$ and in the initial complex, $\text{IrH(CO)(PPh}_3)_3$. A second weak band at $\sim 780 \text{ cm}^{-1}$ can be tentatively assigned to the second Ir-H deformation mode although this mode may be obscured by bands due to $\zeta(\text{M-H})$. Both the bands assigned to $\gamma(\text{Ir-H})$ and $\delta(\text{Ir-H})$ remain fairly constant in frequency as $\text{X}$ and $\text{M}$ vary. This is true not only for complexes where n. m. r. spectra show that $\text{H}$ is cis to $\text{MH}_2\text{X}$, but also for those in which $\text{MH}_2\text{X}$ is trans to $\text{H}$ (i.e. $\text{M}=\text{Ge}$). The former is not unexpected but the latter is. Thus the effect of changes at germanium on the trans hydride ligand must be small in terms of changes in properties which determine I. R. frequencies.

The $\text{MX}$ stretching frequency comes in a characteristic region and the values tentatively assigned to $\gamma(\text{Si-X})$ and $\gamma(\text{Ge-X})$ are in agreement with those observed for the monohydride complexes. A weak band, varying in position from 320 - 350 cm$^{-1}$, is assigned to $\gamma(\text{Ir-Si})$ and again this is in reasonable agreement with the frequency of the band assigned to $\gamma(\text{Ir-Si})$ in the products from the reaction of silyl halides with Vaska's compound. The Ge-Ir stretching mode is tentatively assigned to a weak band varying from 210 - 275 cm$^{-1}$. By analogy with the monohydride complexes the possibility of coupling between different skeletal modes whose vibrational frequencies occur in the far infrared, makes the
assignment of observed frequencies to particular stretching modes very tentative.

The stereochemistry of the silyl and germyl complexes has already been assigned on the basis of the n.m.r. spectra. The I.R. evidence available is consistent with these assignments.

Section 3.4.

The mechanism of the preparative reaction.

The outstanding feature of the formation of the soluble six co-ordinate iridium complexes, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_2\text{X} \,(\text{M}=\text{Si, Ge})$, during the reaction of $\text{IrH( CO)(PPh}_3)_3$ with $\text{MH}_3\text{X}$, is that the stereochemistry of the germyl complexes differs significantly from that of the silyl complexes. (Notably these germyl complexes also differ significantly in stereochemistry from all previously prepared complexes of the type $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MR}_3 \,(\text{M}=\text{Si, Ge}; \, \text{R}=\text{alkyl, aryl, alkoxy, halide})$.) It is necessary to consider why these differences should arise. It is possible that they could be attributed to either kinetic or thermodynamic factors. If thermodynamic factors alone influence the formation of the complexes, i.e. the different stereochemistries observed are in fact those of the thermodynamically stable products, it is difficult to find reasons for this occurrence. Thermodynamic factors controlling the ligand arrangement, such as those preventing the highest trans effect groups from lying opposite to each other, would be expected to be the same
in both types of complexes. Arguments in terms of the bulk of ligands do not explain these observations, since ligands are no more crowded in one isomeric form of either the silyl or germyl complexes than they would be in any other. Also germanium and silicon do not differ appreciably in size and thus steric effects at certain positions in the germyl complexes should not be very different from steric effects at the same positions in the analogous silyl complexes. It is possible that the difference in polarity of Si-H and Ge-H may be of significance. The bond between germanium and a transition metal is thought to be stronger than that between silicon and a transition metal, and the GeH bond energy is less than that of the SiH bond. Bentham has postulated that the formation of bis- and tris germyl species of platinum can be attributed to such thermodynamic factors since the addition of a Ge-H bond to Pt will be energetically more favourable than the addition of an Si-H bond. Bis- and tris silyl analogues of these platinum species have not been prepared. However, in the formation of the iridium complexes which contain only one silyl or germyl ligand the relative bond energies are unlikely to affect the stereochemistry of the resulting products.

The difference in stereochemistry of the silyl and germyl complexes could be accounted for either by a basic difference in the mechanisms by which the silyl and germyl complexes are formed or by the fact that they are formed by the same mechanism but a) a difference in orientation of the addendum occurs during the addition reaction or b) that rearrangement of the initially formed complexes occurs in one
case only (either silyl or germyl) to give the thermodynamically stable products. Thus kinetic factors may be of great significance in determining the observed stereochemistry of the complexes since the stereochemistry of the germyl complexes may be that of the thermodynamically stable products whereas that of the silyl complexes could be assigned to that of the kinetically stable products or vice versa. It is possible to propose several mechanisms by which the complexes may be formed.

Formation of the soluble complexes, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_2\text{X} \), during the reaction of \( \text{MH}_3\text{X} \) with \( \text{IrH(\text{CO})(PPh}_3)_3 \), probably occurs by elimination of a triphenylphosphine ligand from the \( \text{Ir(I)} \) species to form the 4 co-ordinate intermediate, \( \text{IrH(\text{CO})(PPh}_3)_2 \), followed by attack by \( \text{MH}_3\text{X} \) on this intermediate, as shown in fig. 52. In this way the iridium -M bond is formed by oxidative addition of \( \text{MH}_3\text{X} \) to an iridium (I) species. Such a mechanism has been proposed previously to explain the reaction of \( \text{Ir(H(\text{CO})(PPh}_3)_3 \) with \( \text{SiR}_3\text{H} \). Harrod proposed that the addendum \( \text{SiR}_3\text{H} \) adds along an axis perpendicular to the molecule i.e. cis, accompanied by simultaneous phosphine migration in a direction away from the approaching addendum. The postulated 4 co-ordinate intermediate has also been prepared previously and is said to contain cis phosphines. The possibility of addition of \( \text{MH}_3\text{X} \) to \( \text{IrH(\text{CO})(PPh}_3)_3 \) to form an intermediate 7 co-ordinate \( \text{Ir(III)} \) species cannot be completely excluded since previous work has shown that formation of such a species by the addition of \( \text{H}_2 \) or \( \text{C}_2\text{H}_4 \) to \( \text{IrH(\text{CO})(PPh}_3)_3 \) can occur.
Subsequent elimination of a phosphine ligand would then follow. The formation of such a sterically crowded intermediate, for either or both the silyl and germyl complexes, however, is thought to be highly unlikely.

Thus, since a mechanism involving a 4 co-ordinate intermediate is thought to be most likely for the formation of both the six co-ordinate silyl and germyl complexes, then in order to account for the differences in their structures it is necessary to consider the different possible modes of attack of $\text{MH}_3X$ on this 4 co-ordinate intermediate which might give rise to these variations. The 4 co-ordinate intermediate may occur in two different forms, one containing mutually cis phosphines (A) and the other mutually trans phosphines (B) (see fig. 52). Then cis or trans addition of $\text{SiH}_3X$ to (A) would give rise to the products, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2X$ containing cis phosphines. Cis or trans addition of $\text{GeH}_3X$ to (B) would give rise to the products, $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X$ containing mutually trans phosphines. Thus isomerization between different forms of the 4 co-ordinate intermediate would explain the variation in stereochemistry of the products. Why one form of the intermediate should be preferentially attacked by $\text{SiH}_3X$ rather than by $\text{GeH}_3X$ cannot be satisfactorily explained.

However, possibly, only one form of the 4 co-ordinate intermediate exists, either (A) or (B), to which both $\text{SiH}_3X$ and $\text{GeH}_3X$ add in a cis or trans manner. Isomerization of one form of the initial products, either silyl or germyl, could occur later to
fig. 52
give the final products whose stereochemistry is determined by n.m.r. spectroscopy. The observation of a transient species which was thought to contain mutually cis phosphine ligands, during the reaction of GeH₃Cl with IrH(CO)(PPh₃)₃, is possible evidence for the theory of rearrangement of the initially formed products. Similarly, observation of a trace of a silyl complex containing mutually trans phosphines during the reaction of SiH₃I with IrH(CO)(PPh₃)₃ indicates that some form of rearrangement may occur during these reactions. Even if one presumes that only one form of the intermediate exists it is not possible to predict which form (A) or (B) is preferred since modes of addition of MH₃X (M=Si, Ge) involving either one or the other can be postulated. Cis or trans addition of SiH₃X to (A) would give the observed silyl products and the final germyl complexes could be obtained by cis or trans addition of GeH₃X to (A) followed by rearrangement of the initial products. Thus kinetic factors, namely the fast rearrangement of the germyl complexes and apparent kinetic blocking of the silyl complexes, would determine the difference in stereochemistry if an intermediate (A) was postulated. However, cis addition of SiH₃X and GeH₃X to (B) accompanied by phosphine migration (as postulated for the addition of R₂SiH to IrH(CO)(PPh₃)₃ followed by rearrangement of the initial germyl products or trans addition of SiH₃X and GeH₃X to (B) followed by rearrangement of the initial silyl products would also give the observed final products.
Thus the rapid rearrangement of either the initial silyl or germyl complexes would again explain the differences in stereochemistry if an intermediate (B) is postulated. In the former case the silyl complexes would be kinetically blocked to rearrangement and in the latter it would be the germyl complexes which were blocked.

The existence of the transient germyl species, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{Cl} \) or the silyl species \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{I} \) containing mutually trans phosphines, could, however, be accounted for just as satisfactorily by the mechanistic theory involving two forms of the intermediate in co-existence. Two forms of the intermediate may co-exist and the addition of \( \text{MH}_3\text{X} \) may not be as specific as initially thought. Under certain conditions, for instance, \( \text{GeH}_3\text{Cl} \) could attack (A) instead of (B) to give an initial product containing mutually cis phosphines which then isomerizes to the more stable product containing trans phosphines. Similarly \( \text{SiH}_3\text{I} \) could attack (B) instead of (A) to give a product containing mutually trans phosphines. Thus there are several possible postulates which can account for the formation of the complexes \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_2\text{X} \), of varying stereochemistry by means of a reaction mechanism based on the formation of a 4 co-ordinate species, \( \text{IrH}(\text{CO})(\text{PPh}_3)_2 \) by dissociation of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \). It is impossible to determine the mode (cis or trans) of addition of \( \text{MH}_3\text{X} \) to \( \text{IrH}(\text{CO})(\text{PPh}_3)_2 \) since the final products of this reaction contain two indistinguishable hydride ligands. Also determination
of the mode of addition of \( \text{MH}_3X \) is precluded by the possibility that the final products are the most thermodynamically stable and isomerization of the initially formed species may have occurred. The impossibility of this determination is confirmed by evidence from the addition of \( \text{SiD}_2 \) to \( \text{IrH(CO)}(\text{PPh}_3)_3 \), when scrambling occurs during the reaction to give two isomeric products. Addition of \( (\text{EtO})_3\text{SiH} \) to \( \text{IrD(CO)}(\text{PPh}_3)_3 \) had given similar results. Also the observation of silyl complexes having slight differences in stereochemistry, (although all have mutually cis phosphines), during the reactions of \( \text{SiH}_3X \) (\( X=\text{H}, \text{Cl}, \text{Br}, \text{I} \)) with \( \text{IrH(CO)}(\text{PPh}_3)_3 \), indicates that the reactions are not stereospecific. Generally the silyl group is trans to one of the phosphine ligands but on certain occasions it may be trans to one of the hydride ligands. Such differences could be accounted for by cis addition occurring in one instance and trans in another or by rearrangement after initial complex formation.

Thus the reactions are not stereospecific, objections arise to the simple reaction mechanism, described earlier by Harrod,\textsuperscript{110} to explain the addition of \( R_3\text{SiH} \) to \( \text{IrH(CO)}(\text{PPh}_3)_3 \) and no definite conclusions can be drawn about the reaction mechanism for the formation of the complexes \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MH}_2X \) by the addition of \( \text{MH}_3X \) to \( \text{IrH(CO)}(\text{PPh}_3)_3 \). It is, however, thought more likely that it involves the dissociation of \( \text{IrH(CO)}(\text{PPh}_3)_3 \) to a 4 co-ordinate intermediate and attack of \( \text{MH}_3X \) on this intermediate, than any other type of mechanism.
The difference in stereochemistry of the germyl complexes \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X \) from those prepared by Glockling, during the reaction of an excess of \( \text{GeR}_3\text{H} \) with Vaska's compound, cannot be satisfactorily explained. However since one type is derived from the reaction of germyl compounds with a square planar iridium (I) species and the other type by the reaction of germyl compounds with a five co-ordinate iridium (I) species the differences in reaction mechanism probably account for the differences in stereochemistry. It should be remembered that the reactions of \( \text{GeH}_3\text{X} \) with \( \text{Ir(}CO\text{)Cl(}P\text{Ph}_3\text{)}_2 \) as described in Chapter II were not the same as those of \( \text{R}_3\text{GeH} \) with \( \text{Ir(}CO\text{)Cl(}P\text{Ph}_3\text{)}_2 \) so that significant differences occurring in products from the reactions of \( \text{GeH}_3\text{X} \) with \( \text{IrH(}CO\text{)}(\text{PPh}_3)_3 \) and \( \text{GeR}_3\text{H} \) with \( \text{Ir(}CO\text{)Cl(}P\text{Ph}_3\text{)}_2 \) are not unexpected. In view of the results from the addition of \( \text{SiR}_3\text{H} \) and \( \text{SiH}_3\text{X} \) to \( \text{IrH(}CO\text{)(}P\text{Ph}_3\text{)}_3 \), where the stereochemistries of the resultant dihydride species are the same, it would be interesting to compare the stereochemistry of the products from the reaction of \( \text{R}_3\text{GeH} \) with \( \text{IrH(}CO\text{)(}P\text{Ph}_3\text{)}_3 \) with those of the dihydrides \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeR}_3 \). If the products, presuming them to be dihydrides of the form \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeR}_3 \), were to differ in stereochemistry from those of the dihydrides, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2X \) it would be extremely difficult to find any valid reasons for this difference.
CHAPTER FOUR

Some Novel Reactions of Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃

Section 4:1 Introduction

4.1.1. Scope of the Reactions

The reactions of Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ with the simple mono-silyl and germyl complexes, MH₃X (X = H, Cl, Br, I; M = Si, Ge), have been described in Chapters 2 and 3. It has been shown that complexes of six co-ordinate Ir(111) are formed by oxidative addition of MH₃X to the initial iridium complexes. In order to consider whether such reactions are limited to the addition of these simple silyl and germyl complexes or whether they can be extended to the addition of other silyl and germyl species, further studies on the reactions of the Ir(1) complexes have been carried out. The reactions of Vaska's compound and of IrH(CO)(PPh₃)₃ with disilane, trisilane, trimethyl-silyl silane, digermane and silyl- and germyl- cyclopentadiene have been investigated and will be described in separate sections of this chapter. These reactions will show whether the addition breaks Si-Si or Si-H bonds and also whether the SiH₃C₅H₅ and GeH₃C₅H₅ molecules are still fluxional when bonded to a transition metal. The conditions of reaction were like those used to study the reactions between the iridium complexes and the mono-silyl and germyl species. In general the reactions of Vaska's compound and of the 5 co-ordinate iridium hydride with di- and tri- silyl and germanyl species
follow reaction sequences similar to those described in chapters 2 and 3: Vaska's compound reacts with the silicon compounds to form white insoluble species and with the germanium compounds to form transiently soluble species; \(\text{IrH(CO)(PPh}_3\text{)}_3\) reacts with both silicon and germanium compounds to produce soluble species. There are certain exceptions to this generality: the reaction of Vaska's compound with trisilane, for instance, produces a soluble species as the initial product. I.R. and n.m.r. spectroscopy were used to determine the nature of the reaction products and their stereochemistries. In the adducts of silicon compounds the phosphines are mutually cis, and in all but one of the adducts of the germyl derivatives they are mutually trans. The one exception to this is the product of the reaction of \(\text{IrH(CO)(PPh}_3\text{)}_3\) and \(\text{GeH}_3\text{C}_5\text{H}_5\), in which the phosphines are mutually cis. The vibrational modes and n.m.r. parameters which have been used in this structural analysis have been discussed thoroughly in chapters 2 and 3 and will only be referred to briefly, when necessary, in this chapter. Although the reactions of Vaska's compound and of \(\text{IrH(CO)(PPh}_3\text{)}_3\) with the complex silanyl and germanyl species will be discussed separately in different sections of this chapter the frequencies of various I.R. bands, together with assignments, and values of n.m.r. parameters will be tabulated collectively in tables 4.1., 4.2., 4.3., and 4.4. for comparative purposes.
4.1.2. Previous work on reactions of silaryl and germanyl species with platinum complexes

Disilane was characterised by Stock in 1916 and digermane by Dennis et al. in 1924 but neither the reactions of these compounds nor of other disilanyl, trisilanyl or digermanyl species with transition metal complexes have been studied in much detail. Bentham and other workers have shown that disilanyl and digermanyl derivatives of platinum compounds can be prepared:

\[
\begin{align*}
1) & \quad \text{Si}_2\text{H}_6 + \text{trans-}{\text{I}}\text{Pt(PEt}_3\text{)}_2\text{H} \rightarrow \text{trans-}{\text{I}}\text{Pt(PEt}_3\text{)}_2\text{Si}_2\text{H}_5 + \text{H}_2 \\
2) & \quad \text{Ge}_2\text{H}_6 + \text{trans-Cl Pt(PEt}_3\text{)}_2\text{H} \rightarrow \text{trans-Cl Pt(PEt}_3\text{)}_2\text{Ge}_2\text{H}_5 + \text{H}_2 \\
3) & \quad \text{Si}_2\text{H}_5\text{Cl} + \text{trans-}{\text{I}}\text{Pt(PEt}_3\text{)}_2\text{H} \rightarrow \text{trans-}{\text{I}}\text{Pt(PEt}_3\text{)}_2\text{SiClSiH}_3 + \text{H}_2 \\
4) & \quad \text{SiH}_3\text{SiHCl}_2 + " \quad " \quad \rightarrow \quad " \quad " \quad \text{SiH}_2\text{SiHCl}_2 + \text{H}_2 \\
5) & \quad \text{SiH}_3\text{SiMe}_3 + " \quad " \quad \rightarrow \quad " \quad " \quad \text{SiH}_2\text{SiMe}_3 + \text{H}_2 \\
\end{align*}
\]

In contrast to the first reaction the reaction of \(\text{Si}_2\text{H}_6\) or \(\text{Si}_2\text{H}_5\text{Cl}\) with \(\text{trans-Cl Pt(PEt}_3\text{)}_2\text{H}\) resulted in the immediate separation of the reaction mixture into two phases whose nature is not understood. \(\text{Si}_2\text{H}_5\text{Pt(PEt}_3\text{)}_2\text{I}\) has moderate stability in benzene solution at room temperature, whereas \(\text{trans-}{\text{I}}\text{Pt(PEt}_3\text{)}_2\text{SiClSiH}_3\) and \(\text{trans-ClPt(PEt}_3\text{)}_2\text{Ge}_2\text{H}_5\) decomposed rapidly at room temperature.

The reaction of \(\text{SiH}_3\text{SiMe}_3\) with \(\text{trans-ClPt(PEt}_3\text{)}_2\text{H}\) is slower than the analogous reaction with the iodide complex but the amount of \(\text{H}_2\) evolved and the n.m.r. spectrum of the product indicate that a similar species \(\text{trans-ClPt(PEt}_3\text{)}_2\text{PtSiH}_2\text{SiMe}_3\) has been formed,
It has also been shown that trisilanyl, silyl- and germyl-cyclopentadiene derivatives of platinum can be prepared. The complexes from the reactions of trans-ClPt(PET₃)H and Si₃H₈, SiH₅C₅H₅ and GeH₅C₅H₅ were not very stable and the reactions gave a mixture of products. The reactions of trans-I Pt(PET₃)₂H were more informative:

\[
\begin{align*}
\text{Si}_3\text{H}_8 + \text{trans-I Pt(PET₃)}_2\text{H} & \xrightarrow{0^\circ\text{C}} \text{trans-I Pt(PET₃)}_2\text{Si}_3\text{H}_7 \text{ (2 pdts) + H}_2 \\
\text{SiH}_3\text{C}_5\text{H}_5 + "" & \xrightarrow{0^\circ\text{C}} \text{trans-I Pt(PET₃)}_2\text{SiH}_2\text{C}_5\text{H}_5 \text{ + H}_2 \\
\text{GeH}_3\text{C}_5\text{H}_5 + "" & \xrightarrow{0^\circ\text{C}} \text{trans-I Pt(PET₃)}_2\text{GeH}_2\text{C}_5\text{H}_5 \text{ + H}_2
\end{align*}
\]

The reactions were carried out at 0°C to prevent rapid decomposition of the products. Anderson has shown that trisilane probably reacts to form two mono-substituted species, ¹²⁵

\[
\begin{align*}
\text{PEt₃} & \quad \text{SiH}_3 \\
\text{I} \underset{\text{Pt}}{\text{---SiH}} \quad \text{SiH}_2 \quad \text{SiH}_3 \\
\text{PEt₃} & \quad \text{and} \\
\text{PEt₃} & \quad \text{SiH}_3 \\
\text{I} \underset{\text{Pt}}{\text{---SiH}} \\
\text{PEt₃} & \quad \text{SiH}_3
\end{align*}
\]

which have been characterised on the basis of n.m.r. evidence and hydrogen evolution (1 mole H₂/mole Si₃H₈.) The spectrum was very complex and only peaks due to the SiH₃ protons of the preferred iso species have been definitely identified (6.29 \( \tau \) \( ^3J(\text{Pt-Si-Si-}) = 40\text{Hz} \); \( ^3J(\text{H-Si-Si-H}) = 4.0\text{Hz} \)). With excess of platinum complex there is more effervescence; the solution darkens and the n.m.r. simplifies to two complex multiplets, at \( \sim 6.4 \tau \) and 6.9 \( \tau \). The amount of H₂ evolved (0.30 moles H₂/0.13 moles Si₃H₈) indicated that at
least some Si$_3$H$_8$ was trisubstituted with Platinum and that there was a fair proportion of diplatinated product. Owing to the number of possible products and the complexity of the spectrum, Anderson has been unable to analyze the n.m.r. spectrum of these complexes satisfactorily even using spin decoupling. In all these reactions with compounds containing Si-Si or Ge-Ge bonds, however, it appears that the addition is in the sense H and Si/Ge, and that the thermodynamically weak Si-Si or Ge-Ge bonds are not broken.

Silyl cyclopentadiene reacted rapidly with trans-I Pt(PEt$_3$)$_2$H, to give trans-I Pt(PEt$_3$)$_2$SiH$_2$C$_5$H$_5$ as the main product of an incomplete reaction. The n.m.r. spectrum of the product indicated that the product was fluxional (see fig. 53). At room temperature the SiH resonance showed a doublet of triplets at 7.07  $	au$  

$^2$J(Pt-Si-H) = 78.4 Hz; $^3$J(P-Pt-Si-H) = 9.2 Hz] and the CH resonance was a broad hump at ~ 3.8  $	au$. Cooling to -40°C froze the conformation on the n.m.r. time scale; the resonance of the proton bound to the saturated carbon atom was a complex multiplet (triplet of triplets) at 6.65  $	au$ [$^3$J(H-C-Si-H) = 2.9 Hz; $^3$J(H-C=C-H) = 4.5 Hz] and the other CH resonance was a complex multiplet at 3.54  $	au$. The SiH resonance broadened out at -40°C.

It was thought some exchange of triethylphosphine ligands might be occurring. The reaction of GeH$_3$C$_5$H$_5$ with the platinum iodide complex was faster than that of SiH$_3$C$_5$H$_5$ but was also incomplete.
after 1 hour. The GeH resonance of the product showed a doublet of triplets at 7.06 \( \tau \) \( ^2J(Pt-Ge-H) = 144.0 \text{ Hz} \) and \( ^3J(P-Pt-Ge-H) = 8.0 \text{ Hz} \). The CH resonance was a sharp peak at 4.11 \( \tau \) indicating that the cyclopentadiene ring was moving faster in the fluxional germyl complex at room temperature than in the silyl analogue (see fig. 53). On cooling, this peak initially broadened out and then sharpened up about -70 to -80°C giving a sharp peak at 3.57 \( \tau \) (due to the four CH protons). The CH resonance of the proton cis to the germanium atom was hidden under the peak due to unreacted starting material. The GeH resonance also broadened out at -70 to -80°C.

![Figure 53](https://via.placeholder.com/150)

'Frozen' structures of I Pt\((\text{PET}_3)_2\text{MH}_2\text{C}_5\text{H}_5\) at -40 to -80°C

It will be of interest to compare and contrast the products of these reactions with those from the reactions of Vaska's compound and \(\text{IrH(CO)}(\text{PPh}_3)_3\) with the same silyl and germyl species.
Section 4.2. Reactions of disilane

4.2.1. Reactions with Ir(CO)Cl(PPh₃)₂

When a portion of Vaska's compound was allowed to warm to room temperature with an equimolar quantity of disilane an immediate reaction occurred, the yellow colour of Vaska's compound was discharged, and an insoluble white precipitate resulted. The reaction appeared to be complete within 30 minutes. The formation of this precipitate is not unexpected by analogy with the results obtained from the addition of monosilyl compounds to Vaska's compound; this reaction, however, was much faster. Approximately 50% of the initial disilane was recovered at the end of the reaction. No non-condensible gas was formed. The I.R. spectrum of the white product, which was isolated by solvent evaporation, did not give any conclusive evidence about its nature. This evidence is consistent with partial disilanylation, (e.g. H. Ir(CO)Cl(PPh₃)₂Si₂H₅) with formation of a bridged bis iridium species, (e.g. HCl(CO)(PPh₃)₂Ir₂H₄Ir(PPh₃)₂(CO)Cl). With addition of Si₂H₆ as SiH₃ and SiH₃ to give (SiH₃)₂Ir(CO)Cl(PPh₃)₂. The I.R. spectrum of the product did not give any conclusive evidence about its nature but a band at 2120 cm⁻¹ assignable to ν(Ir-H) and a band at 260 cm⁻¹ assignable to ν(Ir-Cl) are observed. It is probable, therefore, that H. Ir(CO)Cl(PPh₃)₂Si₂H₅ is one of the products. The frequencies of the various bands, together with assignments (which are tentative in some cases)
are shown in table 4.3. N.m.r. evidence was impossible to obtain and efforts to procure a mass spectrum also failed, the most prominent m/e value being that of 262-triphenylphosphine. This failure was not unexpected in view of experiences with the products from the addition of SiH₃X to Vaska's compound. The white product is stable for long periods under solvent, in vacuum under nitrogen, or in air; these observations are analogous to those made for the products H. Ir(CO)Cl(PPh₃)₂SiH₂X. It decomposes on pyrolysis above 200°C to give a brown product and free disilane. The recovery of disilane after pyrolysis indicated that the iridium complex probably contained Si-Si bonds. Evidence from the reaction of Vaska's compound with a two-fold excess of disilane was no more conclusive in determining the nature of the reaction product than was that from the equimolar reaction. The reaction rate was apparently the same, an insoluble white precipitate was formed with a trace of non-condensible gas and more than half the initial quantity of disilane was recovered at the end of the reaction. A soluble species was not obtained as the long-term product of this reaction. Analysis of the white solids did not establish their exact composition since the results obtained were not conclusive for any of the possible products. Indeed, there was nothing to show that the materials were homogeneous. Thus no definite conclusions about the nature of the products from the reaction of Si₂H₆ with Vaska's compound can be drawn.
4.2.2. Reactions with IrH(CO)(PPh₃)₃

When the 5 co-ordinate iridium hydride, IrH(CO)(PPh₃)₃, was allowed to warm to room temperature in benzene with an equimolar quantity of disilane an immediate reaction occurred and the yellow colour of the starting material was discharged. A colourless solution was formed and the reaction was complete within a few minutes. There was a trace of non-condensibles and a trace of disilane was recovered at the end of the reaction. I.R. and n.m.r. spectra could be obtained and confirmed that the product was IrH₂(CO)(PPh₃)₂Si₂H₅. The stereochemistry of the complex (see fig. 54) has been assigned from this evidence and is the same as that assigned to the products IrH₂(CO)(PPh₃)₂SiH₂X (X = Cl, Br, I). From the evidence available the addition of Si₂H₆ is in the sense Si₂H₅ and H.

![Diagram](image)

fig. 54

The SiH resonance of the product shows a doublet of triplets at 6.05 ᵇ [^4J(H-Si-Si-P₂) = 3 c/s and ^3J(H-Si-Si-H) = 3 c/s] and a complex multiplet at 6.56 ᵗ. The former is assigned to SiH₃ of Si₂H₅ and the latter to SiH₂ of Si₂H₅. Irradiation at 6.56 ᵗ
caused the peak at 6.05 \( \gamma \) to collapse to a broad singlet (theoretically a doublet) but the effect on the peak at 6.56 \( \gamma \) of irradiation at 6.05 \( \gamma \) could not be observed because of the presence of a beat in the spectrum. Thus no simplification of the complex multiplet at 6.56 \( \gamma \) could be achieved but it has been shown that coupling occurs between the peaks at 6.05 \( \gamma \) and 6.56 \( \gamma \). It is interesting that the peak at higher \( \gamma \) value should be assigned to SiH\(_2\) and that at lower \( \gamma \) value to SiH\(_3\); Bentham has observed the same phenomenon in the n.m.r. spectrum of the product trans-IrPt(P\( \equiv \)t\(_3\))\(_2\)Si\(_2\)H\(_5\).\(^{36,37}\) The IrH resonance is a doublet of doublets of doublets at 19.73 \( \gamma \) \([\,2J(H_a-Ir-P) = 20 \text{ c/s}; \, 2J(H_a-Ir-P) = 17 \text{ c/s} \text{ and } 2J(H_a-Ir-H_b) = 3.5 \text{ c/s}\] and a doublet of doublets of doublets at 20.59 \( \gamma \) \([\,2J(H_b-Ir-P) = 115 \text{ c/s}; \, 2J(H_b-Ir-P) = 19 \text{ c/s} \text{ and } 2J(H_a-Ir-P) = 3.5 \text{ c/s}\]. Irradiation at 19.73 \( \gamma \) and 20.59 \( \gamma \) has no observable effect on the peaks at 6.05 or 6.56 \( \gamma \) indicating that coupling between SiH and IrH is probably small and thus supporting the postulated cis relationship between the silyl and hydride ligands. The n.m.r. parameters are presented in table 4.1. and the I.R. frequencies in table 4.3. It has not been possible to assign a frequency to the Si-Si stretching mode. This compound is stable for a long time in benzene but when isolated as a white gelatinous product by evaporation of the solvent it is only stable for a short time either under vacuum or nitrogen.
Section 4:3 Reactions of digermane

4.3.1. Reactions with Ir(CO)Cl(PPh$_3$)$_2$

An immediate reaction occurs when a portion of Vaska's compound is warmed to room temperature in benzene with an equimolar portion of digermane. The reaction is complete within 5 minutes and a pale yellow solution results which persists for 30 minutes when an insoluble white precipitate is formed. Thus a transiently soluble species is the initial product of the reaction of Vaska's compound with digermane. This observation is in agreement with those made on the reactions of Vaska's compound and germyl halides but contrasts the reaction of Vaska's compound with germane when an insoluble species, formed after a slow reaction (1 day), is the initial product. The possible reasons for the differences in the reactions of Vaska's compound with germyl halides and with germane have been discussed in Section 2.8. No non-condensable gas was formed during the reaction and only a trace of GeH$_4$ or Ge$_2$H$_6$ was recovered at the end of the reaction. The transiently soluble species has been investigated by n.m.r. spectroscopy and its stereochemistry (fig. 55) has been assigned from this evidence. It is the same as that found for the products of the reaction of Vaska's compound with GeH$_3$X.

![Figure 55](image-url)
The GeH resonance of the product showed a triplet at 6.86 \( \tau \) 
\[ ^3J(\text{H-Ge-Ge-H}) = 4 \text{ c/s} \] and a weak complex multiplet at \( \sim 7.96 \tau \) 
(in fact a triplet of quartets) \[ ^3J(\text{H-Ge-Ge-H}) = 4 \text{ c/s and} \]
\[ ^3J(\text{P-Ir-Ge-H}) = 6 \text{ c/s} \]. The former is assigned to GeE3 of Ge2H5 and the latter to GeE2. Spin decoupling was difficult because of the close proximity of the peaks and the resultant spectra were complicated because of beats but irradiation at 6.86 \( \tau \) caused the peak at 7.96 \( \tau \) to collapse partially to a broad triplet. Thus coupling occurs between the peaks at 6.86 and 7.96 \( \tau \).

The IrH resonance is a triplet at 27.6 \( \tau \) 
\[ ^2J(\text{H-Ir-P}) = 12 \text{ c/s} \]. By analogy with previous results104 this chemical shift value indicates that the hydride ligand is probably trans to chlorine. Irradiation at 27.6 \( \tau \) had no observable effect on the peak at 7.96 \( \tau \) indicating that \( ^3J(\text{H-Ir-Ge-H}) \) is, as expected, very small.

The I.R. spectrum of the white insoluble species isolated by evaporation of solvent from the solution confirms the formation of the 1:1 adduct and the frequencies of the various bands together with assignments are presented in table 4.4. The product was analysed and the results were in accord with its formulation as H.Ir(CO)Cl(PPh3)2Ge2H5. It is stable for fairly long periods of time under nitrogen and in air, finally decomposing to a brown solid after a few weeks. In benzene a brown product is formed after 10 days.
4.3.2. Reactions with \( \text{IrH(CO)(PPh}_3\text{)}_3 \)

The yellow colour of \( \text{IrH(CO)(PPh}_3\text{)}_3 \) is discharged immediately in the usual manner during the equimolar reaction of this iridium hydride with digermane. The reaction is complete within 5 minutes and a colourless solution is formed. No non-condensable gas was recovered and only a trace of germane was detected at the end of the reaction. The solution is stable for a few days at room temperature, eventually turning a deep brown in colour. I.R. and n.m.r. spectra were obtained and confirmed that the product was \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Ge}_2\text{H}_5 \) although it is possible that 2 stereoisomers of this complex are present. The possible stereochemistries of the products are shown in fig. 56.

\[
\begin{align*}
\text{Ir} & \quad \text{CO} \\
\text{PPh}_3 & \quad \text{GeH}_2\text{GeH}_3
\end{align*}
\]

\( \text{H}_a \quad \text{H}_b \)

\( \text{H}_a \quad \text{H}_b \)

\( \text{(I)} \)

\( \text{(II)} \quad \text{P}_1=\text{P}_2=\text{PPh}_3 \)

\begin{align*}
\text{The } \text{GeH}_\text{res} & \text{onance of the major product (I fig. 56) shows a} \\
& \text{triplet at } 6.72 \tau [^{3}\text{J(H-Ge-Ge-H)} = 4 \text{ c/s}] \text{ and a weak complex} \\
& \text{multiplet (doublet of triplets of quartets) at } 7.71 \tau. \text{ The former is} \\
& \text{assigned to GeH}_3 \text{ of Ge}_2\text{H}_5 \text{ and the latter to GeH}_2 \text{ of Ge}_2\text{H}_5.}
\end{align*}

\begin{align*}
\text{Again spin decoupling is difficult because of the close proximity} \\
& \text{of the peaks but irradiation at } 7.71 \tau \text{ causes the peak at } 6.72 \tau
\end{align*}
to collapse to a singlet and the reverse operation causes a slight simplification in the peak at $7.71 \text{ } \tau$. Here again, as for $\text{H. Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{Ge}_2\text{H}_5$ the chemical shift of $\text{GeH}_3$ in $\text{GeH}_2\text{GeH}_3$ is substantially to low field of that of $\text{GeH}_3$ in the product $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_3$ but that the chemical shift of $\text{GeH}_2$ in the digermanyl products is of comparable value to that of $\text{GeH}_3$ in the germyl species. Bentham has observed the same phenomenon in the n. m. r. spectrum of trans-I Pt(PEt$_3$)$_2\text{Ge}_2\text{H}_5$. The IrH resonance shows a triplet at $19.65 \text{ } \tau$ [$^2J(\text{P-Ir-H}_b) = 18 \text{ c/s}$] and a triplet at $20.18 \text{ } \tau$ [$^2J(\text{P-Ir-H}_a) = 18 \text{ c/s}$]. The former is assigned to $\text{H}_b$ and the latter to $\text{H}_a$ (see fig. 56). Triple irradiation at $20.18 \text{ } \tau$ and $6.72 \text{ } \tau$ causes the peak at $7.71 \text{ } \tau$ to collapse to a broad triplet indicating that the $\text{GeH}_2$ protons are coupled to both IrH and GeH$_3$.

It is possible that a small amount of a second product is formed during the reaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with Ge$_2$H$_6$. A weak quartet or overlapping doublet of triplets is observed at $6.2 \text{ } \tau$ which would tentatively be assigned to GeH$_3$ of Ge$_2$H$_5$, with a weak triplet at $19.86 \text{ } \tau$ [consistent with $\text{H}_a$ if $^3J(\text{P-Ir-H}_a) = 18 \text{ c/s}$] and a doublet of doublets at $20.95 \text{ } \tau$ [which could be assigned to $\text{H}_b$ if $^2J(\text{P}_1-\text{Ir-H}_b) = 120 \text{ c/s}$ and $^2J(\text{P}_2-\text{Ir-H}_b) = 18 \text{ c/s}$]. The postulated stereochemistry of this species is shown in fig. 56 II. It differs basically from that of the major product in the relative configuration of the phosphine ligands. A mixture of products has been observed previously during the reaction of GeH$_3$Cl and IrH(CO)(PPh$_3$)$_3$ and indicates that the reactions are not stereospecific.
Section 4.4. Reactions of trisilane

4.4.1. Reactions with Ir(CO)Cl(PPh$_3$)$_2$

The yellow colour of Vaska's compound was rapidly discharged and a colourless solution formed when a portion of Vaska's compound was warmed to room temperature in benzene with an equimolar portion of trisilane. The reaction was complete within 10 minutes. No noncondensible gas was recovered and only a trace of Si$_3$H$_8$ remained at the end of the reaction. The colourless solution was stable at room temperature for several days turning yellowish eventually but no precipitate was formed. After 2 weeks some hydrogen had been evolved (0.3 m moles /m mole Si$_3$H$_8$ added) and a small amount of SiH$_4$ was recovered. The initial product of this reaction is outstanding for its solubility and stability. No other product from the addition of SiH$_3$X or Si$_2$H$_6$ to Vaska's compound has been soluble under these reaction conditions. Also the product is much more stable at room temperature in benzene than was that formed during the reaction of Si$_3$H$_8$ with trans-XPt(P$_{Et_3}$)$_2$H (X=Cl, I) which decomposed after a few hours. I.R. and n.m.r. spectra were obtained and indicate that more than one species had probably been formed.

The features of the n.m.r. spectrum are: four peaks in the SiH$_3$ region of the spectrum, a triplet at 6.54 $\tau$, a complex multiplet at 6.12 $\tau$, a triplet at 5.12 $\tau$ and a weaker triplet at 5.04 $\tau$, and several peaks in the IrH$_3$ region of the spectrum, a complex triplet at 19.63 $\tau$, a doublet of doublets of doublets at 20.60 $\tau$ and other
weak complex multiplets in the 19-20 \text{\textmu} region. The main features indicate that a six co-ordinate dihydride species, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Si}_3\text{H}_6\text{Cl} \) is the major product. The probable stereochemistry of this complex which is shown in fig. 57, has been assigned from n. m. r. evidence but must remain to some extent tentative.

![Diagram](image)

**fig. 57**

The triplet in the \( \text{SiH} \) resonance at 6.54 \( \text{\textmu} \) [\( ^3J(\text{H-Si-Si-H}) = 4 \text{ c/s} \)] is assigned to \( \text{SiH}_3 \) of \(-\text{SiHCl. SiH}_2. \text{SiH}_3\) and the complex multiplet at 6.12 \( \text{\textmu} \) is assigned to \( \text{SiH}_2 \) of \(-\text{SiHCl. SiH}_2. \text{SiH}_3\). Irradiation at 6.12 \( \text{\textmu} \) caused the peak at 6.54 \( \text{\textmu} \) to collapse to a singlet thus indicating that these two resonances are coupled. The effect on the peak at 6.12 \( \text{\textmu} \) of irradiation at 6.54 \( \text{\textmu} \) could not be observed because of the presence of a beat in the spectrum. No resonance which could be categorically assigned to \( \text{SiHCl} \) is observed. This resonance should be a doublet of doublets of triplets, perhaps further split as a consequence of local molecular asymmetry, and although it will be weaker than the other resonances some observation of its existence should be possible. By analogy with Bentham's values\textsuperscript{36} for the chemical shift of \( \text{SiHCl} \) in trans-\( \text{IPt(PEt}_3)_2\text{SiHCl. SiH}_3 \) (4.86 \( \text{\textmu} \)) one might expect to see this resonance around 5 \( \text{\textmu} \). It is possible that it is hidden under one of
the other peaks in the SiH resonance at 5.04 \text{\textgreek{\textmu}} or 5.12 \text{\textgreek{\textmu}}. Irradiation at these points did not have any observable effect on the peak at 6.12 \text{\textgreek{\textmu}}. The IrH resonance shows a complex triplet at 19.63 \text{\textgreek{\textmu}} \text{[}^{2}\text{J(P-Ir-Ha)} = 20 \text{c/s}] \text{, assigned to Ha, and a doublet of doublets at 20.60 \text{\textgreek{\textmu}} \text{[}^{2}\text{J(P}}_{\text{1}}\text{-Ir-H}_{\text{B}} = 120 \text{c/s and} \text{^{2}\text{J(P}}_{\text{2}}\text{-Ir-H}_{\text{B}} = 20 \text{c/s}] \text{assigned to H}_{\text{B}}. The nature of the spectrum indicates that the complex contains mutually cis phosphines and is thus of the same basic stereochemistry as the other silyl derivatives of the 6 co-ordinate dihydride species. The position of the substituted trisilanyl ligand is ambiguous (trans either to a phosphine or hydride ligand) but by analogy with the disilanyl and silyl halide dihydride species it is tentatively given trans relationship with the phosphine (see fig. 57). I.R. evidence agrees with the formation of a dihydride species (absence of \nu(Ir-Cl) and relative positions of \nu(Ir-H) and \nu(Si-H) - one strong, broad band at 2080 cm^{-1}). The other peaks in the SiH region of the n.m.r. spectrum, a triplet at 5.12 \text{\textgreek{\textmu}} (J = 3.5 \text{c/s}) and a weaker triplet at 5.04 \text{\textgreek{\textmu}} (J = 3.5 \text{c/s}) could be assigned to SiH_{2}Cl in an SiH_{2}.SiH_{2}.SiH_{2}Cl ligand of another complex of 6 co-ordinate iridium (111). The chemical shift values are in agreement with those of Bentham for SiHCl in the complex trans-Ir\text{\textgreek{\textmu}}(\text{PET}_{3})_{2}SiHCl.SiH_{3}. No further evidence for the resonances associated with the other silyl protons in this ligand could be obtained. The weak complex multiplets in the IrH region of the spectrum could be assigned to the hydride ligands of this complex. At any rate it appears that
at least two different species are formed during this reaction. Only the major product has been identified or is discussed in any great detail.

During the reaction of Si₃H₈ with Vaska's compound a silicon atom bound to chlorine appears to become attached to iridium (at least in the major product IrH₂(CO)(PPh₃)₂SiHClSiH₂SiH₃). This is consistent with the results obtained by Bentham for the addition of Si₂H₅Cl to trans-I Pt(Pェ₃)₂H when the product trans-I Pt(Pェ₃)₂SiHClSiH₃ is formed. Its formation implies that electrophilic attack at iridium is an important feature of the reaction. In view of the possible existence of a product containing the ligand SiH₂SiH₂SiH₂Cl such electrophilic attack may not be the overriding feature of the reaction, unless chlorination at silicon takes place after addition.

The formation of the dihydride species may take place by oxidative addition of MH to Vaska's compound, as shown in fig. 58, followed by elimination of SiH₂ClSiH₂SiH₃ and subsequent attack of this entity on the 4 co-ordinate intermediate IrH(CO)(PPh₃)₂.
A similar mechanism has been used to explain the formation of the dihydride species, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiR}_3 \). It is interesting that trisilane should be the only silyl hydride, with the exception of silyl chloride, to form such a dihydride species and that disilane is not chlorinated by \( \text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 \) in a similar way. However, it is notable that the trisilyl derivative is formed during the reaction of equimolar quantities of Vaska's compound and trisilane whereas the other dihydride species, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MR}_3 ~(M=\text{Si, Ge}) \) have always resulted from the reaction of an excess of the alkyl silane, alkyl germane or silyl chloride with Vaska's compound. Thus this chlorination reaction may be specific to a co-ordinated trisilyl ligand. The rate of this reaction is also much faster. Reaction of Vaska's compound with excess of trisilane gives the same product as the equimolar reaction. The intermediate 1:1 adduct \( \text{H.Ir(CO)Cl(PPPh}_3)_2\text{Si}_3\text{H}_7 \) has not been observed. The reasons for these differences are not known. It is possible that the bulk of the trisilyl ligand renders the 1:1 adduct sterically unstable whereas the ligands may not be so crowded in the dihydride \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHCl, SiH}_2, \text{SiH}_3 \). It is also possible that electronic effects control the stereochemistry and nature of the ligands in the complex. The dihydride species does, however, appear to be the most thermodynamically stable complex in this particular reaction system.
4.4.2. Reactions with IrH(CO)(PPh₃)₃

An immediate reaction occurred when a portion of IrH(CO)(PPh₃)₃ was warmed to room temperature with an equimolar portion of trisilane. The yellow colour of the mixture was discharged to give a colourless solution. The reaction was complete within ½ hour. The product is stable in solution for several days but when isolated as a white, gelatinous substance by evaporation of the solvent it rapidly decomposes under vacuum or nitrogen.

The I.R. and n.m.r. spectra indicate that the major product is IrH₂(CO)(PPh₃)₂Si₃H₇ although it is possible that two stereoisomeric forms may be present. The stereochemistry of the products has been assigned from this evidence (see fig. 59).

The n.m.r. of the major product is consistent with the trisilanyl ligand being bound to iridium via one of the terminal silicon atoms rather than through the central silicon atom. This contrasts with Anderson's observations on the species trans Pt(PEt₃)₂Si₃H₇ where the preferred product has platinum bound to the central silicon atom of the trisilanyl ligand— the platinum derivative is much less
stable at room temperature in benzene than is the iridium species.

In the $^1$H n.m.r. spectrum of the iridium complex, the SiH resonance was observed as a multiplet at 6.14 ppm [$^3J(\text{H-Si-Si-H}) = 4 \text{ c/s}$] and a triplet at 6.58 ppm [$^3J(\text{H-Si-Si-H}) = 4 \text{ c/s}$]. The former is assigned to $^b$SiH$_2$ of $^a$SiH$_2$ $^b$SiH$_2$ SiH$_3$ and the latter to SiH$_3$. Irradiation at 6.14 ppm causes the peak at 6.58 ppm to collapse to a broad singlet. Thus these 2 peaks are coupled. It is possible that a very weak multiplet at $\sim$ 6.80 ppm (observed only at 220 MHz) or another at 6.02 ppm could be assigned to a SiH$_2$ but no conclusive evidence for coupling between either of these multiplets and the peak at 6.14 ppm could be obtained. It is more likely that the multiplet at $\sim$ 6.80 ppm is due to $^a$SiH$_2$ since in the complexes, IrH$_2$(CO)(PPh$_3$)$_2$M$_2$H$_5$ (M = Si, Ge) and trans-X Pt(PEt$_3$)$_2$M$_2$H$_5$ (M = Si, Ge), it has been noted that the chemical shift of the protons on M directly attached to Ir or Pt, i.e. MH$_2$ of MH$_2$. MH$_3$ is to high field of that of the protons of MH$_3$. Thus the order of increasing chemical shift values for SiH resonances of the protons in $^a$SiH$_2$ $^b$SiH$_2$ SiH$_3$ is probably $^b$SiH$_2$, $^c$SiH$_3$ and $^a$SiH$_2$.

A comparable trend was observed for SiH$_2$ and SiH$_3$ of SiHClSiH$_2$SiH$_3$ in IrH$_2$(CO)(PPh$_3$)$_2$ SiHClSiH$_2$SiH$_3$ where the peak at 6.12 ppm is assigned to SiH$_2$ and that at 6.54 ppm to SiH$_3$. The IrH resonance shows a complex triplet at 19.78 ppm [$^2J(P_{-}\text{Ir-Ha}) = 16.5 \text{ c/s}$ and $^2J(H_b-\text{Ir-Ha}) = 4.5 \text{ c/s}$] and a doublet of doublets of doublets at 20.67 ppm [$^2J(P_{1-}\text{Ir-Hb}) = 113.5 \text{ c/s}$ $^2J(P_{2-}\text{Ir-Hb}) = 19 \text{ c/s}$ and $^2J(H_{a-}\text{Ir-Hb}) = 4 \text{ c/s}$]. Thus the phosphines are
mutually cis in this complex as in all other silyl derivatives of 6 co-ordinate Iridium (111). Irradiation at 19.78 \( \gamma \) and 20.67 \( \gamma \) has no observable effect on any of the peaks in the region 6-7 \( \gamma \) but this is not surprising since the coupling between the hydride ligands and \( \text{SiH}_2 \) and \( \text{SiH}_3 \) will be small and the effect of decoupling on the weak multiplet due to \( \text{SiH}_2 \) would be hardly noticeable even if one of the hydride ligands and the trisilanyl ligand are mutually trans. The position of the trisilanyl ligand is not determined but by analogy with the other silyl complexes it is probably trans to the phosphine ligand. Evidence for the formation of a second product comes from the n.m.r. spectrum. The \( \text{SiH} \) resonance also shows a multiplet at 5.85 \( \gamma \) and a doublet of triplets at 6.02 \( \gamma \) and the \( \text{IrH} \) resonance shows a doublet of doublets at 20.80 \( \gamma \) \( \left[ ^2J(P_{\text{Ir}-H_b^1}) = 115 \text{ c/s}; \ ^2J(P_{\text{Ir}-H_b^1}) = 19 \text{ c/s and } ^2J(H_{\text{Ir}-H_b^1}) = 4 \text{ c/s} \right] \). The other part of the \( \text{IrH} \) resonance may be hidden under the complex triplet at 19.78 \( \gamma \). The peak at 6.02 \( \gamma \) could reasonably be assigned to \( \text{SiH}_3 \) and the multiplet at 5.85 \( \gamma \) to \( \text{SiH} \) of \( \text{SiH}_3\text{SiHSiH}_3 \). The presence of an iso-trisilanyl ligand in the other product is not unlikely by analogy with Anderson’s results.\(^{125}\) The basic stereochemistry round iridium of the minor product is thus the same as that of the major product and explains the very slight change in chemical shift values for the \( \text{IrH} \) resonances which is observed. It is interesting that the preferred orientation of the trisilanyl ligand in the iridium and
platinum complexes should be different. A possible reason for this difference is steric crowding in the iso-substituted species $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}(\text{SiH}_3)_2$.

Section 4.5. Reactions of the cyclopentadiene derivatives $\text{SiH}_3\text{C}_5\text{H}_5$ and $\text{GeH}_3\text{C}_5\text{H}_5$

4.5.1. Reactions with $\text{IrH(CO)(PPh}_3)_3$

A colourless solution was formed after 1 hour when a portion of $\text{IrH(CO)(PPh}_3)_3$ was warmed to room temperature with an equimolar quantity of $\text{MH}_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Si, Ge}$) in benzene or deuteriobenzene. No non-condensibles were formed and only a trace of $\text{MH}_3\text{C}_5\text{H}_5$ was recovered at the end of the reaction. This solution is stable for several days at room temperature before turning yellowish-brown. The I.R. and n.m.r. spectra are in agreement with the formulation of this complex as a fluxional molecule whose possible stereochemistry is shown in fig. 60.

![Diagram](image)

At room temperature the $\text{SiH}$ resonance of $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{C}_5\text{H}_5$ shows a multiplet at $\sim 6.0 \tau$ and the $\text{CH}$ resonance is a broad hump.
at \( \sim 3.3 \) \( \gamma \). The IrH resonance is a doublet of doublets of triplets at 19.78 \( \gamma \) \[ 2J(P_1-Ir-Ha) \text{ and } 3J(H-Ge-Ir-Ha) = 4.5 \text{ c/s} \] and a doublet of doublets of doublets at 20.66 \( \gamma \) \[ 2J(P_1-Ir-Hb) = 115 \text{ c/s} \text{ and } 2J(Ha-Ir-Hb) = 118 \text{ c/s} \text{ and } 2J(Ha-Ir-Hb) = 4.5 \text{ c/s} \]. At room temperature the GeH resonance of IrH2(CO)(PPh3)2GeH2C5H5 shows a doublet of triplets at 6.38 \( \gamma \) \( (J = 5 \text{ c/s and } 45 \text{ c/s}) \) and the CH resonance is a broad hump at 3.8 \( \gamma \). It is interesting that in both the iridium complexes the CH resonance is a broad hump indicating that the cyclopentadiene ring is moving at almost the same rate in both these complexes whereas it moved at a faster rate in the germyl species trans-X Pt(PEt3)2GeH2C5H5. The IrH resonance is a doublet of doublets of triplets at 20.02 \( \gamma \) \[ 2J(P_1-Ir-Ha) \text{ and } 2J(P_2-Ir-Ha) = 21 \text{ c/s and } 15.5 \text{ c/s} \text{ and } 3J(H-Ge-Ir-Ha) = 4.5 \text{ c/s} \] and a doublet of doublets of doublets at 20.98 \( \gamma \) \[ 2J(P_1-Ir-Hb) = 118 \text{ c/s} \text{ and } 2J(P_2-Ir-Hb) = 118 \text{ c/s} \text{ and } 2J(Ha-Ir-Hb) = 4 \text{ c/s} \]. The high field n.m.r. spectra of IrH2(CO)(PPh3)2GeH2C5H5 is shown diagramatically in fig. 61 and in plate. 5. The theoretical and observed IrH spectra are compared. The results for the IrH spectra of IrH2(CO)(PPh3)2SiH2C5H5 are identical in form. It is noticeable that in the IrH resonance one coupling J(Hb-Ir-Ha) is apparently missing in the observed spectrum in the peaks at 19.78 \( \gamma \) and 20.02 \( \gamma \) assigned to Ha, in IrH_aH_b (CO) (PPh3)2SiH2C5H5 and IrH_aH_b (CO)(PPh3)2GeH2C5H5 respectively. In all other IrH spectra of the species
Theoretical \(^1H\) n.m.r. spectrum for IrH resonance of \(\text{IrH}_2(\text{CO})(\text{Ph}_3)_2\text{GeH}_2\text{C}_5\text{H}_5\) (stereochemistry as shown in fig. 59)

Observed \(^1H\) n.m.r. spectrum for IrH resonance of \(\text{IrH}_2(\text{CO})(\text{Ph}_3)_2\text{GeH}_2\text{C}_5\text{H}_5\)

fig. 51
$^1$H n.m.r. Spectrum of IrH$_2$(CO)(PPh$_3$)$_2$GeH$_2$C$_5$H$_5$

Increasing $\tau$

20.02 $\tau$       20.98 $\tau$

Observed high field (~20 $\tau$) $^1$H n.m.r. spectrum of IrH$_2$(CO)(PPh$_3$)$_2$GeH$_2$C$_5$H$_5$

PLATE 5
IrH₂(CO)(PPh₃)₂MH₂X the observed spectra have agreed very well with the predicted spectra. All couplings that might be expected in such systems are observed. The reasons for the absence of $J_{(H a-I r-H b)}$ are not known; it is possible that second order effects may account for the anomalous spectrum although we do not know how. Certainly the $I r H$ spectrum of $H_b$ in IrH₂(CO)(PPh₃)₂GeH₂C₅H₅ shows certain second order effects (see plate 5) even when observed at 220 MHz. The intensity of the outer peaks of this doublet of doublets of doublets is less than that of the inner peaks. The spectra may be deceptively simple thus allowing apparent values to be assigned to all the other couplings, though these apparent values may not in fact be correct. It is also possible that there is some interaction between the cis hydride ligand $H_b$ and the cyclopentadiene ring which may account for these differences.

Attempts to slow down the exchange and study the n.m.r. spectra of the products at lower temperatures (-40 to -80°C) were thwarted by the insolubility of the products in Arcton 11 even at room temperature. When an equimolar portion of IrH(CO)(PPh₃)₃ was warmed to room temperature in CCl₃F with MH₃C₅H₅ (M = Si, Ge) a very slow reaction occurred (possibly because of the insolubility of the starting material in Arcton 11) and after 1 day cream coloured crystals were obtained. The L.R. spectrum of these crystals was the same as that of the product isolated by solvent
evaporation from the colourless solution formed during the reaction in benzene. Therefore it did not prove possible to study the products at low temperature in this solvent. No observable change in the spectrum was noted when the benzene solution was cooled to 0°C. Spin decoupling studies were partially successful.

Irradiation at 19.78 °C sharpened up the peaks in the multiplet at \( \sim 6.0 \) °C assigned to SIH although triple irradiation at 19.78 °C and \( \sim 3.3 \) °C did not have any marked effect on this peak.

Thus it is possible that at room temperature both the silyl- and germylcyclopentadiene derivatives of iridium have the same stereochemistry (containing mutually cis phosphines) and are fluxional molecules. Only the reaction of germylcyclopentadiene and IrH(CO)(PPh₃)₃ appears to give as major product a dihydride species of this stereochemistry. Also in contrast to most of the other reactions of IrH(CO)(PPh₃)₃ with silyl derivatives the product appears to have the SiH₂C₅H₅ ligand in a position trans to a hydride rather than trans to a phosphine ligand. Thus the presence of a cyclopentadiene ring in a substituted silyl or germyl compound seems to have a marked effect on the stereochemistry of the product of its reaction with IrH(CO)(PPh₃)₃. However, owing to the anomaly in the IrH spectrum of both the silyl- and germylcyclopentadiene derivatives their stereochemistry cannot be assigned with certainty.
Table

Parameters from the \(^7\)H n.m.r. spectra of the iridium-silyl
are resonance lines which can be assigned to the aromatic
benzene or deuterobenzene as solvent and TM3 as internal

<table>
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<th>Product</th>
<th>(\gamma_{\text{SiH}})</th>
<th>(J(\text{P-Ir-Si-H}))</th>
<th>(J(\text{H-Si-Si-H}))</th>
<th>(J(\text{H-Si-Si-Ir-H}))</th>
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<td>(\text{IrH}_2(\text{CC})(\text{PPh}_3)_2\text{Si}_2\text{H}_5)</td>
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<td>6.12</td>
<td>4c/s</td>
<td>4c/s</td>
<td>3c/s</td>
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<tr>
<td>(\text{IrH}_2(\text{CC})(\text{PPh}_3)_2\text{Si}_3\text{H}_7)</td>
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<td>4c/s</td>
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<tr>
<td>(\text{IrH}_2(\text{CC})(\text{PPh}_3)_2\text{Si}_2\text{H}_5\text{C}_5\text{H}_5)</td>
<td>6.02</td>
<td>4c/s</td>
<td>3c/s</td>
<td>3c/s</td>
</tr>
</tbody>
</table>

The reference numbers in column 1 refer to the number of figures which are to be found in the text. These figures show the tentative stereochemistry which has been assigned to the complexes.

\(\text{CH}_2\) for \(\text{IrH}_2(\text{CC})(\text{PPh}_3)_2\text{Si}_2\text{H}_5\text{C}_5\text{H}_5\) is to be found at \(\sim 3.3 \gamma\).
4.1. complexes $\text{Ir}^+\text{Ir}^+ (\text{PtPh}_3)_2 \text{SiH}_2 \text{X}$. In all the spectra there
protons of tritylphenylphosphine. The spectra are recorded in
standard on the Varian 100 or 220 MHz n.m.r. spectrometers.

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<th>$\tau_{\text{Ir}^+}$</th>
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<th>$J(E_{\text{Ir}-1})$</th>
<th>$J(E_{\text{Ir}-2})$</th>
<th>$J(E_{\text{Ir}-1})$</th>
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<td>?</td>
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<tr>
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<td>?</td>
<td>115c/s</td>
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<td>120c/s</td>
<td>?</td>
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<tr>
<td>19.30 20.50</td>
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<td>120c/s</td>
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<td>?</td>
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<tr>
<td>19.78 20.66</td>
<td>20.5c/s and 15.5c/s</td>
<td>115c/s</td>
<td>18c/s</td>
<td>4.5c/s</td>
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<tr>
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<td>dbts</td>
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dbt=doublet; tpt=triplet; mpt=multiplet; w=weak; com.=complex;
?=peak too weak or complex to make an accurate assessment
of the coupling constant or chemical shift value
The reference numbers in column 1 refer to the number of a figure which is to be found in the text. These figures show the tentative stereochemistry which has been assigned to the complexes.

CH for Ir\(_2\)(CO)(PPhi\(_3\))\(_2\)GeH\(_2\)C\(_2\)H\(_5\) is to be found at ~3.8 ppm.
complexes $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SeH}_2X$. In all the spectra there protons of triphenylphosphine. The spectra are recorded in standard on the Varian 100 or 220MHz n.m.r. spectrometers.

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<tr>
<th>$\text{H}_a$</th>
<th>$\text{H}_b$</th>
<th>$J(\text{H}_a-\text{Ir}-\text{P}_1)$</th>
<th>$J(\text{H}_a-\text{Ir}-\text{P}_2)$</th>
<th>$J(\text{H}_b-\text{Ir}-\text{P}_1)$</th>
<th>$J(\text{H}_b-\text{Ir}-\text{P}_2)$</th>
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<td>19.86</td>
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<td>18c/s</td>
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<td>120c/s</td>
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dbt=doublet; tpt=triplet; mpt=multiplet; b.=basic; w.=weak; *=peak too weak or complex to make an accurate assessment of the coupling constant
Table

Frequencies from the infrared spectra of the iridium-silyl
tribenzyl phosphine groups. The spectra are recorded

<table>
<thead>
<tr>
<th>Product</th>
<th>Phase</th>
<th>$\nu$(Si-H)</th>
<th>$\nu$(Ir-H)</th>
<th>$\nu$(C-C)</th>
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<tbody>
<tr>
<td>IrH$_2$(CC)(PPh$_3$)$_2$SiH$_2$</td>
<td>B</td>
<td>2100vsb</td>
<td>2100vsb</td>
<td>1975vsb</td>
</tr>
<tr>
<td>H$_2$Ir(CC)Cl(PPh$_3$)$_2$SiH$_2$</td>
<td>B</td>
<td>2100vsb</td>
<td>2100vsb</td>
<td>1975vsb</td>
</tr>
<tr>
<td>Cl(CC)(PPh$_3$)$_2$Ir$_2$SiH$_2$</td>
<td>B</td>
<td>2120m, 2070m</td>
<td>2120m</td>
<td>1980vsb</td>
</tr>
<tr>
<td>Cl(CC)(PPh$_3$)$_2$Ir$_2$SiH$_2$</td>
<td>N</td>
<td>2075vsb</td>
<td>2075vsb</td>
<td>1975vsb</td>
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<tr>
<td>IrH$_2$(CC)(PPh$_3$)$_2$SiH$_2$Cl</td>
<td>N</td>
<td>2070vsb</td>
<td>2070vsb</td>
<td>1970vsb</td>
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<tr>
<td>IrH$_2$(CC)(PPh$_3$)$_2$SiH$_2$SiPh$_2$</td>
<td>N</td>
<td>2100s, 2080vs</td>
<td>2040s</td>
<td>1970vsb</td>
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<tr>
<td>IrH$_2$(CC)(PPh$_3$)$_2$SiH$_2$SiPh$_2$</td>
<td>N</td>
<td>2100m</td>
<td>2040w</td>
<td>1965m</td>
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v=very; s=strong; m=medium; w=weak; b=broad; sh=shoulder;
n.o. = not observed; n.s. = region not studied;
4.3 compounds, IrH₆(CC)(PPh₃)₂SiHₓ and IrH(CC)(PPh₃)₂Cl₃SiHₓ in cm⁻¹. 1,000-1,200cm⁻¹, 650-750cm⁻¹ and 430-530cm⁻¹ which are assigned to as Nujol mulls or benzene solutions.

<table>
<thead>
<tr>
<th>δ(Si-H)</th>
<th>δ(Ir-H)</th>
<th>δ(C-C)</th>
<th>v(Si-Si)</th>
<th>v(Ir-Cl)</th>
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<tr>
<td>950m</td>
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<td>n.e.</td>
<td>n.e.</td>
<td>n.s.</td>
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<tr>
<td>960m940w</td>
<td>890m 830w</td>
<td>614w</td>
<td>n.e.</td>
<td>265m</td>
<td>310vw</td>
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<tr>
<td>940mb</td>
<td>865mb830m</td>
<td>615w</td>
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<tr>
<td>930mb</td>
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</tr>
<tr>
<td>n.e.</td>
<td>n.e.</td>
<td>n.e.</td>
<td>n.e.</td>
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<tr>
<td>960s945vs930s835s820s</td>
<td>620w</td>
<td>n.e.</td>
<td>—</td>
<td>350m</td>
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</tr>
</tbody>
</table>

Phase refers to method of obtaining spectrum;
N=Nujol mull; B=benzene solution;
Section 4:6 Reaction of trimethylsilyl silane

4.6.1. Reaction with IrH(CO)(PPh$_3$)$_3$

The reaction between equimolar portions of IrH(CO)(PPh$_3$)$_3$ and SiH$_3$SiMe$_3$ proceeded slowly and after 4 hours a pale yellow solution was formed. There were no non-condensibles. The product is thought to be IrH$_2$(CO)(PPh$_3$)$_2$SiH$_2$SiMe$_3$ formed by oxidative addition of SiH$_3$SiMe$_3$ to IrH(CO)(PPh$_3$)$_3$. This assignment is based on n.m.r. evidence. The n.m.r. spectrum is very weak because of the small amount of SiH$_3$SiMe$_3$ available but shows a multiplet at 6.96 ppm (assigned to SiH) and a broad complex triplet at 19.3 ppm and a doublet of doublets at 20.50 ppm (assigned to IrH). The solution is stable at RT for several days. Thus SiH$_3$SiMe$_3$ forms a complex with an iridium species in the same way as with a Pt species by the addition of SiH$_2$SiMe$_3$ and H.

Section 4:7 Conclusions

In this chapter it has been shown that the formation of "silyl" and "germyl" derivatives of iridium (111) is not limited to simple mono-silyl and germyl species but can be extended to unsubstituted and substituted disilanyl species, digermanyl species, trisilanyl species and cyclopentadiene derivatives of silane and germane. Comparison of the nature of these products and their stereochemistry with those formed during the reactions of MH$_3$X (M = Si, Ge; X = H, Cl, Br, I) with Vaska's compound and IrH(CO)(PPh$_3$)$_3$ has shown that they are very similar both in nature.
and stereochemistry and that in all cases reaction occurs to form stable six-coordinate derivatives of Ir(111).

The apparent failure of disilane to add as SiH₃ and SiH₃ rather than Si₂H₅ and H is of interest as are the reactions of all the compounds containing Si-Si and Ge-Ge bonds since it appears in all cases that the addition to Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ is in the sense H and Si or Ge. Thus the thermodynamically weak Si-Si or Ge-Ge bonds are not broken under these reaction conditions. Preservation of these weak bonds has also been observed during the reactions of Si₂H₆, Si₃H₈, Ge₂H₆ and SiH₂ClSiH₃ with trans-I Pt(PEt₃)₂H.¹²⁵

Differences which have been observed have been discussed and reasons for the differences in behaviour have been postulated. These postulates can only be tentative since in these reactions as in all other oxidative addition reactions of Ir(1) species so many factors influence the reaction mechanism and the nature of the reaction products that it is difficult to decide which is of greatest importance. However it appears that the oxidative addition of silyl and germyl species to the complexes Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ is a common reaction.
CHAPTER FIVE
SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

In chapters 2, 3 and 4 it has been shown that the oxidative addition of SiH₃X (X = H, Cl, Br, I, SiH₃, Si₂H₅, SiMe₃ and C₅H₅) and GeH₃X (X = H, Cl, Br, I, GeH₃ and C₅H₅) to the Ir(I) complexes, Ir(CO)Cl(PPh₃)₂ and IrH(CO)(PPh₃)₃ occurs readily and that stable derivatives of 6 co-ordinate Ir(111) are formed. Two types have been identified: H. Ir(CO)Cl(PPh₃)₂MH₂X and IrH₂(CO)(PPh₃)₂MH₂X. All are far more stable at room temperature than analogous 6 co-ordinate Pt(IV) complexes which have been postulated as intermediates during the reaction of SiH₃X and GeH₃X with trans-XPt(P₃Et)₂H but of which only some have been isolated. It must, however, be remembered that triphenylphosphine ligands generally impart greater stability to transition metal complexes, than triethylphosphine ligands. Neither do they react further at any time to form 4 co-ordinate silyl and germyl derivatives of Ir(1). The reasons why H. Ir(CO)Cl(PPh₃)₂MH₃X does not form 4 co-ordinate products have been discussed. IrH₂(CO)(PPh₃)₂MH₂X could eliminate H₂ but does not do so readily. Thus 6 co-ordinate derivatives of Ir(111) are seemingly more stable than similar 4 co-ordinate derivatives of Ir(1). The formation of the 6 co-ordinate iridium (111) species does support the interpretation of Bentham's reactions in terms of intermediates containing 6 co-ordinate
platinum. The reactions also confirm the results obtained by Bentham and other workers$^{36,37,125}$ on the modes of addition of silyl and germyl species to transition metal complexes and the nature of the products of these reactions.

The stability of these Ir(111) species possibly indicates why iridium complexes are not widely used in homogeneous catalysis. In contrast Pt complexes which form relatively unstable products are widely used.

The reactions of the iridium (111) complexes, $\text{H} \cdot \text{Ir(CO)}\text{Cl(PPh}_3\text{)}_2\text{MH}_2\text{X}$ and $\text{IrH}_2\text{(CO)(PPh}_3\text{)}_2\text{MH}_2\text{X}$ with air, water, $\text{MeOH}$, acid, alkali, $\text{HX}$ or $\text{MH}_3\text{X}$ either under homogeneous or heterogeneous conditions are very slow and the spectra of the products which are eventually formed are so complex in nature and difficult to interpret that no attempt has been made to describe these reactions in this thesis. Such lack of reactivity merely suffices to emphasize the stability of these species. The difference in reactivity between silyl or germyl complexes of 6-co-ordinated iridium species and 4 co-ordinate silyl and germyl derivatives of platinum is not surprising; the latter can readily react to form 6 co-ordinate species (as intermediates), whereas it is unlikely that the formation of 7 or 8 co-ordinate intermediates of iridium would occur so readily. A more detailed study of the reactions of the Ir(111) species might yield some useful information about the mechanism of such reactions.
It would be interesting to extend the study of iridium substituted disilanyl, digermanyl and trisilanyl compounds to the addition of Ge$_2$H$_5$Cl, SiHCl$_2$SiH$_3$, SiH$_3$GeH$_3$ and other substituted silanyl and germayl species to Ir(CO)Cl(PPh$_3$)$_2$ and IrH(CO)(PPh$_3$)$_3$. Each of these reactions would contribute further to an understanding of the modes of addition of silyl and germayl species to transition metal compounds and to the influence of various substituents on this mode of addition. The latter reaction with SiH$_3$GeH$_3$ in particular would indicate the preferential addition of a silyl or germayl group to iridium.

The main problem in elucidating the stereochemistry of the products, H. Ir(CO)Cl(PPh$_3$)$_2$SiH$_2$X was their insolubility in all known solvents. Preliminary studies have shown that the products of the reaction of Ir(CO)Cl(PPh$_2$Me)$_2$ and SiH$_3$Cl are slightly more soluble in benzene although the n.m.r. spectra are still very weak. Further investigations using tertiary alkyl phosphine analogues of Vaska's compound may prove successful in giving soluble products whose stereochemistry can be determined. However these results might differ from those postulated for Vaska's compound since it has been shown$^{73,108}$ that a slight change in the nature of the ligands in an iridium complex during oxidative addition reactions may have a marked effect on the mechanism and products of these reactions.

The suggestions for future work, which have been
mentioned above, are some examples of points arising from work described in this thesis. There are other reactions with different systems which could be investigated, including reactions of silyl acetylenes and silyl azides with Vaska's compound and IrH(CO)(PPh3)3. There are also several other iridium complexes, in particular iridium hydrides, such as IrHCl2(PR3)3 and IrH2Cl(PR3)3 whose reactions with silyl and germlyl species could be investigated. Preliminary studies on certain systems of this type have been carried out. It is probable that substitution of hydride by a silyl ligand occurs during the reaction of IrHCl2(PR3)3 (R3 = PhEt2) and IrH2Cl(PR3)3 (R3 = Ph3 or PhEt2) with equimolar or excess quantities of SiH3Cl. Hydrogen is evolved and the I.R. and n.m.r. spectra indicate that the products are probably IrCl2(PPh3)3SiH2Cl and IrHCl2(PR3)3SiH2Cl. The reactions are rather slow and have not been investigated in any detail. Halogen exchange, followed by a slower substitution reaction, may occur during the reaction of IrCl3(PR3)3 (R3 = Ph3 or PhEt2) with SiH3Br. Thus there appears to be some potential in studying the reactions of silyl and germlyl species with other iridium complexes.

It may be possible to extend the studies of the reactions of transition metal complexes with MH3X to other transition metals such as rhodium. A small amount of work has been carried out on the reactions of trans-ClPd(PEt3)2Cl with SiH3X. Preliminary studies on the reactions of Rh(CO)Cl(PPh3)2 with
SiH₃Cl have been carried out. However, attempts to prepare silyl derivatives of Rh(111) by this reaction under the usual reaction conditions have proved unsuccessful. Hydrogen was evolved and the I.R. and n.m.r. spectra of the brown solution which were obtained were so broad and complex that they precluded any satisfactory analysis of this reaction system. It is possible that an ionic species is formed. Similar studies on the reactions of alkyl silanes with Rh(1) species have also proved to be very difficult. The reluctance of Rh complexes to undergo oxidative addition has been attributed to the greater instability of Rh in the higher oxidation state. However, it is possible that if the reactions of Rh(CO)Cl(PPh₃)₂ and RhH(CO)(PPh₃)₃ with MH₃X are studied at low temperature or under different reaction conditions that useful information about these systems might be obtained.

One of the conclusions which may be drawn from this thesis is that a study of hydride derivatives of silicon and germanium complements the study of organo-derivatives and may provide additional information relevant to the understanding of the chemistry of silicon and germanium complexes of transition metals.
Section 6.1. Experimental Methods

Volatile compounds were manipulated in a conventional Pyrex glass vacuum system. Quantities of condensible materials were measured in a calibrated volume using a glass spiral gauge to measure pressures. Involatile air sensitive solids were handled under dry nitrogen in an evacuable glove-box or polythene bag and reactions were normally carried out in all glass break-seal ampoules.

Infrared spectra were recorded using a Perkin-Elmer 457 spectrometer. For high resolution spectra or for low frequency spectra down to 200 cm\(^{-1}\) a Perkin-Elmer 225 spectrometer was used. Vapour phase and solution spectra were recorded in the normal manner. Nujol mull spectra were recorded using CsI plates held in a sealed container using nujol which had been carefully dried over sodium wire. Samples for Raman spectroscopy were run on a Cary 81 laser Raman spectrometer, using finely powdered solid samples. Proton n.m.r. spectra were recorded either on a Varian Associates H.A.100 spectrometer in this Department or on a Varian Associates H.R.220 spectrometer at I.C.I.'s Petrochemicals and Polymer Laboratory in Runcorn. The former was used preferentially for analysis of resonances to low-field of the lock (T.M.S.@ 10°C) and for spin-decoupling investigations and the latter for the study of resonances to high field of the lock. A Muirhead oscillator was attached to the H.A.100 spectrometer for spin decoupling.

In the normal field or frequency sweep H.A. modes of operation the range of the H.A.100 spectrometer is limited by the range of the manual oscillator (1,500-3,500 Hz) and the range of the swept oscillator
(2,500-3,500 Hz) to 10° (1,000 Hz) to high-field of the lock and to 20° (2,000 Hz) to low-field of the lock. Thus transition metal hydride resonances with a chemical shift above 20° are beyond the range of normal operation of the instrument because the internal standard having the highest practical chemical shift is T.M.S. (10°). The high-field range of the spectrometer was extended by using the frequency sweep mode while locking on the first lower side-band of the T.M.S. main resonance. The recorded spectrum was then upside-down and back to front, and the high field limit was 30°, 2,000 Hz, above the lock. It was found that the exciting power could be increased by 10 dB without saturation, thus improving the sensitivity for detection of high-field resonances although the phase was difficult to adjust. Despite this increase in sensitivity the spectra of the high-field resonances studied using the H.A.100 spectrometer were very weak and complicated and more satisfactory spectra of these resonances were obtained using the H.R.-220 spectrometer. This spectrometer, which has a superconducting solenoid magnet, gives spectra with reduced complicating second order effects and increased sensitivity. These advantages, which arise from (a) effects of increasing the ratio of the chemical shift terms to the spin-spin coupling terms in the matrix equation (δ/J effects), and (b) increased signal-to-noise ratio, were of considerable importance in analysing the nature of the high-field resonances of the iridium complexes. The sensitivity increases with B (magnetic flux density) because the small excess population in the lower energy spin state (N1-N2) increases with B 2 owing to the appearance of B in the Boltzmann equation: N1/N2 = e δB/2kT.

The spectra of the low-field resonances were not as satisfactory on the H.R.-220 machine as on the H.A.100 machine and spin decoupling effects could not be studied owing to the lack of necessary attachments for the H.R.-220 spectrometer.
Mass spectra were recorded on the A.E.I. MS 902 spectrometer at a range of temperatures. Analysis for C and H only was carried out using a Perkin-Elmer 240 Elemental Analyser in this Department.

Section 6.2.
Starting Materials

<table>
<thead>
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<th>Compound</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
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<td>SiH₄</td>
<td>SiCl₄ + LiAlH₄</td>
<td>126</td>
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<td>SiD₄</td>
<td>SiCl₄ + LiAlD₄</td>
<td>126</td>
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<tr>
<td>Si₂H₆</td>
<td>Si₂Cl₆ + LiAlH₄</td>
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<tr>
<td>SiH₃Br</td>
<td>PhSiCl₃ + LiAlH₄ then HBr</td>
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<tr>
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<td>GeH₃I</td>
<td>GeH₃Cl + H I</td>
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<td>Ir(CO)Cl(PPh₃)₂</td>
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<tr>
<td>IrH(CO)(PPh₃)₃</td>
<td>Ir(CO)Cl(PPh₃)₂ + nN₂H₄ in ethanol</td>
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</tbody>
</table>
The following materials were also prepared either using a modified method or a new method. SiH₃Mg₂, Si₂H₆, M₃C₅H₅ were prepared in conjunction with J.E.Bentham, Miss H.E.Wilson and Miss S.Smith.

IrBr(CO)(PPh₃)₂

Ir(CO)Cl(PPh₃)₂ (0.4976 gms) was weighed into a glass reaction ampoule fitted with a greaseless tap together with LiBr (5 gms). The ampoule was evacuated on the vacuum line and pure dried degassed THF (50 mls) was added to the solids mixture. The ampoule was shaken at R.T. for 1 hour until the solids had completely dissolved and a yellow solution was formed. The reaction mixture was left for 2½ hours at R.T. and then the solvent was slowly pumped off under vacuum. A yellow solid was recovered. Water (~50 mls) was added to this product to dissolve excess LiBr and then LiCl and the mixture was filtered in air and dried to give a yellow solid. It was recrystallised from C₆H₆ under N₂. (Yield = 0.4 gms). The infrared spectrum of the product showed Ir(CO)Br(PPh₃)₂.

Attempted preparation of IrI(CO)(PPh₃)₂

(1) Sodium iodide (2.3 gms) dissolved in acetone (100 mls) was added to Ir(CO)Cl(PPh₃)₂ (0.9186 gms) dissolved in C₆H₆ (30 mls) under N₂ and the mixture was refluxed for 16 hours under N₂. The nitrogen was dried by passing through H₂SO₄ and the O₂ removed by
passing through Na dithionate. MeOH (50 mls) was added under N₂ to the hot yellow solution which was then left to cool. Brown crystals separated slowly (~2 days) from the solution and the I.R. spectrum of the product showed IrI(0₂)(CO)(PPh₃)₂.

(2) Ir(CO)Cl(PPh₃)₂ (1.87 gms) was dissolved in C₆H₆ (40 mls) by refluxing under N₂ and LiI (22 gms) in hot EtOH (30 mls) was added under N₂. More EtOH (~20 mls) was added until a clear solution was obtained. The mixture was refluxed under N₂ for 3 hours, until a deep golden yellow solution resulted. Methanol (~200 mls) was added to this solution after cooling. A mixture of brown and yellow crystals was precipitated which was filtered off. The I.R. spectrum of the product showed IrI(CO)(O₂)(PPh₃)₂ mixed with IrI(CO)(PPh₃)₂.

Efforts to separate these products by recrystallization in C₆H₆ under N₂ resulted in complete oxygenation of the complexes to give brown crystals of IrI(O₂)(CO)(PPh₃)₂ as final product. Boiling in DMF did not remove the oxygen.

Kinetic studies on the addition of oxygen to Vaska's compound and its analogues have shown that the rate of addition is directly proportional to temperature and that the ease of addition increases in the order Cl < Br < I. Thus it is not surprising that it is difficult to prepare uncontaminated Ir(CO)I(PPh₃)₂ if there is the least trace of oxygen in the reaction system.

Ir(CO)Cl(PPh₂Me)₂

Ir(CO)Cl(PPh₃)₂ (1.0013 grams) was dissolved in C₆H₆ (35 mls) and PPh₂Me (0.7 mls) was added. The solution was heated under reflux (10 mins) and the solvent was removed under vacuum. A bright orange oil resulted. N-hexane (40 mls) was added and the mixture was heated under reflux for 2 hours and then cooled. An orange-yellow solid
precipitated. The I.R. spectrum of the product showed a mixture of
Ir(CO)Cl(PPh₂Me)₂, Ir(CO)Cl(PPh₃)₂ and a trace of an iridium hydride
which proved to be inseparable or convertible to pure Ir(CO)Cl(PPh₂Me)₂.
Trial experiments were carried out using this mixture and are reported
in Chapter 5.

\[
\text{SiH₃SiMe₃}
\]

\[(\text{SiMe₃})₂\text{Hg (1.9 m.moles)}\text{ and } 2 \text{ m.moles SiH₃Br in benzene (5 mls)}\]
were warmed to room temperature in a greaseless tap ampoule and left
for 2 days. Since no reaction had occurred after this time the tube
was exposed to a low intensity ultraviolet lamp for several hours.
A greyish white precipitate formed initially, presumably HgBr₂, and
then mercury was deposited. The volatile product was fractionated
through a -90°C bath to remove solvent impurities and trapped at 112°C.
The infrared spectrum of the product showed it to be SiH₃SiMe₃.

\[
\text{Si₃H₆, SiH₃C₅H₅ and GeH₃C₅H₅}
\]

These compounds were supplied by J.E. Bentham. Trisilane was
prepared by the reduction, using LiAlH₄, of a fraction of chlorinated
silanes, predominantly Si₃Cl₈, prepared during a study of the base
catalysed disproportionation of Si₂Cl₃. Silyl- and germicyclo-
pentadienes were prepared by the reaction of SiH₃Br and GeH₃Br,
respectively, with the potassium salt of cyclopentadiene, K⁺C₅H₅⁻,
under heterogeneous conditions.

Other compounds were commercially available. The purity of the
starting materials was checked spectroscopically and by measurement
of vapour pressure for volatile compounds, boiling point for involatile
liquids and melting point for solids.

Solvents were purified as follows:
(For H.Ir(CO)Cl(PPh$_3$)$_2$SiH$_2$Cl, found C, 52.9; H, 3.9%).

C$_{37}$H$_{33}$Cl$_p$OIrSi requires C, 52.5; H, 3.9%), and the structures by spectroscopy (see Chapter 2).

H.Ir(CO)Cl(PPh$_3$)$_2$SiH$_2$ found C, 54.9; H, 4.1%.

C$_{37}$H$_{34}$Cl$_p$OIrSi requires C, 54.7; H, 4.2%;

H.Ir(CO)Cl(PPh$_3$)$_2$.SiH$_2$Br, found C, 49.9; H, 3.7%.

C$_{37}$H$_{33}$ClBr$_p$OIrSi requires C, 49.7; H, 3.7%).

The products are stable in solution and under vacuum, nitrogen and air for a few weeks. No change in the I.R. spectrum was observed after this time.

6:3:2. 1:1 reaction of Ir(CO)Cl(PPh$_3$)$_2$ and GeH$_2$

Experiment 2.5.  H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$

This compound was prepared as a white solid as in experiments 1.1-1.4, and was identified by mass-balance, I.R. spectroscopy and analysis.

(For H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$, found C, 50.1; H, 3.9%. C$_{37}$H$_{34}$Cl$_p$OIrGe requires C, 51.9; H, 4.0%). The product is stable in solution or under vacuum, nitrogen or air for a few days. No change in the I.R. spectrum was observed.

6:3:3: 1:1 reaction of Ir(CO)Cl(PPh$_3$)$_2$ and GeH$_2$X

Experiment 2.6-2.8

H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Cl.

H.Ir(CO)Cl(PPh$_3$)$_2$Ge$_2$Br, H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$I

Treatment of finely divided Ir.(CO)Cl(PPh$_3$)$_2$ (0.1 m.mole) with GeH$_2$X (0.1 m.mole) at R.T. in benzene solution for a few minutes gave a colourless solution and after 30-60 minutes a white precipitate was formed. The initial soluble product, H.Ir(CO)Cl(PPh$_3$)$_2$Ge$_2$X was identified by its n.m.r. spectrum and the insoluble products isolated
by evaporation of the solvent by its I.R. spectrum and by analysis.
For H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Cl, found C, 49.2; H, 3.6%.

$0.37H_33Cl_2P_4OIrGe$ requires C, 49.9; H, 3.7%; H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Br,
found C, 47.1; H, 3.3%; $0.37H_33ClBr.P_4OIrGe$ requires C, 47.5; H, 3.5%;
H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$I, found, C, 44.9; H, 3.2%. $0.37H_33ClIP_4OIrGe$
requires C, 45.2; H, 3.4%. The products are stable in solution and
under vacuum, nitrogen or air for a few days. No change was observed
in the I.R. spectrum after this time.

6:3:4. 1:1 reaction of Ir(CO)Cl(PPh$_3$)$_2$ with GeH$_2$Br in presence HCl

Experiment 2.9.

H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Br/H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Cl

Germyl bromide (0.06 m.moles) was allowed to react at room
temperature with Ir(CO)Cl(PPh$_3$)$_2$ (0.06 m.moles) in benzene in the
presence of HCl (0.006 m.moles 10%). The soluble product which was
formed, a mixture of H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Br/H.Ir(CO)Cl(PPh$_3$)$_2$GeH$_2$Cl,
was identified by its n.m.r. spectrum; the white solid which rapidly
precipitated from this solution, appeared from its I.R. spectrum to
be the same mixture of substances.

6:3:5. 2:1 reaction of Ir(CO)Cl(PPh$_3$)$_2$ with SiH$_3$X

Experiment 2.10-2.13. H.Ir(CO)Cl(PPh$_3$)$_2$SiH$_3$,

H.Ir(CO)Cl(PPh$_3$)$_2$SiH$_2$Cl,

H.Ir(CO)Cl(PPh$_3$)$_2$SiH$_2$Br,

H.Ir(CO)Cl(PPh$_3$)$_2$SiH$_2$I.

Treatment of Ir(CO)Cl(PPh$_3$)$_2$ (0.1 m.moles) with SiH$_3$X (0.2 m.
moles) at R.T. in benzene solution (~1 ml) for 5-10 minutes resulted
in the formation of a white precipitate and SiH$_3$X (0.1 m.moles) was
recovered. The product was identified by mass-balance, I.R.
spectroscopy and analysis as \( \text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{SiH}_2\text{X} \). For
\( \text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{SiH}_2\text{Cl} \), found C, 52.9; H, 3.9%; \( \text{C}_{37}\text{H}_{33}\text{Cl}_2\text{OIrSi} \) requires C, 52.5; H, 3.9%. \( \text{H.Ir(CO)Cl(PPh}_3\text{)}_2\text{Br} \), found C, 49.9; H, 3.7%. \( \text{C}_{37}\text{H}_{33}\text{ClBrP}_4\text{OIrSi} \) requires C, 49.9; H, 3.7%.

**Experiment 2.14-2.17**

Complex halogen exchange products of H.Ir(CO)Cl(PPh\(_3\))\(_2\)SiH\(_2\)X

Treatment of Ir(CO)Cl(PPh\(_3\))\(_2\) (0.1 m.moles) with SiH\(_3\)X (0.2 m.moles) at R.T. in benzene (~1 ml) for 2-3 days resulted in the formation of a white precipitate. The products were identified by mass-balance evidence and I.R. spectroscopy. SiH\(_3\)X (0.1 m.moles) was recovered.

**Experiment 2.18.** Ir\(_2\)(CO)(PPh\(_3\))\(_2\)SiH\(_2\)Cl

Silyl chloride (0.2 m.moles) was allowed to react with Ir(CO)Cl(PPh\(_3\))\(_2\) (0.1 m.mole) for 10 days in benzene at R.T. SiH\(_2\)Cl\(_2\) (0.1 m.mole) was recovered and a colourless solution resulted. The soluble product Ir\(_2\)(CO)(PPh\(_3\))\(_2\)SiH\(_2\)Cl\(_2\) was identified by its n.m.r. spectrum and was stable in solution for several weeks. The product, isolated as a colourless, gelatinous solid, decomposed in a few hours.

**Experiment 2.19.** H.Ir(CO)Cl(PPh\(_3\))\(_2\)SiH\(_2\)Br\(_2\)

Silyl bromide (0.2 m.moles) was allowed to react with Ir(Cl) (0.1 m.mole) for 2 weeks in benzene at R.T. A mixture of SiH\(_3\)Cl and a trace of SiH\(_3\)I (~0.1 m.mole) were recovered and a white solid, H.Ir(CO)I(PPh\(_3\))\(_2\)SiH\(_2\)I, identified by its I.R. spectrum was obtained. The product decomposed after a few weeks in solution to give a yellow-brown deposit.
2:1 reaction of Ir(CO)Cl(PPh_3)_2 with GeH_4

**Experiment 2.21. H.Ir(CO)Cl(PPh_3)_2 GeH_3**

Treatment of Ir(CO)Cl(PPh_3)_2 (0.1 m.mole) with germane (0.2 m.moles) in benzene at R.T. for 5 minutes gave GeH_4 (0.1 m.mole) and a white insoluble product, H.Ir(CO)Cl(PPh_3)_2, which was identified by mass-balance, I.R. spectroscopy and analysis. (For H.Ir(CO)Cl(PPh_3)_2GeH_3, found, O, 51.5; H, 3.7%. C_{37}H_{33}ClP_4OIrGe requires O, 51.9; H, 4.0%). The product was stable in solution and under nitrogen or in air for a few days. No change in the I.R. spectrum was observed after this time.

2:1 reaction of Ir(CO)Cl(PPh_3)_2 and GeH_3X

**Experiment 2.22-2.24.**

- H.Ir(CO)Cl(PPh_3)_2GeH_2Cl, H.Ir(CO)Cl(PPh_3)_2GeH_2Br,
- H.Ir(CO)Cl(PPh_3)_2GeH_2I

Vaska's compound (0.1 m.mole) was allowed to react with GeH_3X (0.2 m.moles) for 5 minutes in benzene at room temperature. GeH_3X (0.1 m.mole) was recovered and a colourless solution resulted. The soluble product, H.Ir(CO)Cl(PPh_3)_2GeH_2X, was identified by its n.m.r. spectrum and by I.R. spectroscopy and analysis. (For H.Ir(CO)Cl(PPh_3)_2GeH_2Cl found, O, 49.7; H, 4.1%. C_{37}H_{33}Cl_2P_4OIrGe requires, O, 49.9; H, 3.7%. H.Ir(CO)Cl(PPh_3)_2GeH_2Br found, O, 45.2; H, 3.5%.

C_{37}H_{33}ClP_4OIrGe requires, O, 45.2; H, 3.4%).

In the presence of excess of GeH_3X these products decompose in solution after a few days to give yellow-brown products. The solid products are stable for a few hours under nitrogen or in air. No change is observed in the I.R. spectrum after this time.
6:3:8. 1:1 reaction of Ir(CO)Cl(PPh₃)₂ and MeSiH₂Cl

Experiment 2.25. HIr(CO)Cl(PPh₃)₂SiMeHCl

This compound was prepared as a mixture of isomers as in experiments 1.1-1.4, and was identified by mass-balance, I.R. spectroscopy and analysis. (For HIr(CO)Cl(PPh₃)₂SiMeHCl found, C, 52.5; H, 3.9%. C₃₈H₃₅Cl₂P₀IrSi requires C, 53.0; H, 4.1%).

6:3:9. 2:1 reaction of Ir(CO)Cl(PPh₃)₂ and MeSiH₂Cl

Experiment 2.26-2.27.

H'Ir(CO)Cl(PPh₃)₂SiHMMeCl and IrH₂(CO)(PPh₃)₂SiHMMeCl

Treatment of Vaska's compound (0.1 m.moles) with MeSiH₂Cl (0.2 m.moles) in benzene at R.T. for 5 minutes gave MeSiH₂Cl (0.1 m.moles) and H'Ir(CO)Cl(PPh₃)₂SiHMMeCl as a white precipitate. This product was identified by mass-balance, I.R. spectroscopy and analysis. (For H'Ir(CO)Cl(PPh₃)₂SiMeHCl, found, C, 53.2; H, 4.0%. C₃₈H₃₅Cl₂P₀IrSi requires C, 53.0; H, 4.1%. If these reactants are allowed to react together for 2 weeks, a colourless solution results and MeSiHCl₂ (~ 0.03 m.moles) is recovered, together with a trace of MeSiH₃ and MeSiH₂Cl. The soluble product, IrH₂(CO)Cl(PPh₃)₂SiHMMeCl, was identified by its n.m.r. spectrum, and is stable for several weeks in benzene solution. No change in the n.m.r. spectrum was observed. When isolated as a white gelatinous solid it decomposes in a few hours.

6:3:10. 2:1 reaction of Ir(CO)Cl(PPh₃)₂ with SiH₃Cl in CH₂Cl₂

Experiment 2.28. H'Ir(CO)Cl(PPh₃)₂SiH₂Cl

Silyl chloride (0.2 m.moles) reacted in CH₂Cl₂ (~ 1 ml) for 5 mins with Ir(CO)Cl(PPh₃)₂ to give SiH₃Cl (0.1 m.mole) and
H\textsubscript{2}Ir(CO)Cl(PPh\textsubscript{3})\textsubscript{2}SiH\textsubscript{2}Cl as a white insoluble product. (Found. C, 52.3; H, 3.8%. \textsubscript{C}\textsubscript{57}\textsubscript{H}_{\textsubscript{113}}\textsubscript{Cl}_2\textsubscript{P}_4\textsubscript{O}IrSi requires C, 52.5; H, 3.9%).

63121. 2:1 reaction of Ir(CO)Cl(PPh\textsubscript{3})\textsubscript{2} with SiH\textsubscript{3}Cl in CHCl\textsubscript{3} & CCl\textsubscript{4}

Experiment 2.29-2.30.

Treatment of Vaska's compound (0.1 m.moles) with SiH\textsubscript{3}Cl (0.2 m.moles) in CHCl\textsubscript{3} or CCl\textsubscript{4} (∼1 ml) at R.T. for 5-10 mins resulted in the precipitation of a white solid. This solid was a complex mixture of products which could not be positively identified. Attempts at incorporating a sinter in the reaction apparatus to filter off the white solid "in situ" and obtain an n.m.r. spectrum of the solution failed; the solution was too weak.

63122. 1:1 reaction of Ir(CO)Cl(PPh\textsubscript{3})\textsubscript{2} and SiH\textsubscript{3}Cl under heterogeneous conditions

Experiment 2.31.

Vaska's compound and an equimolar portion of SiH\textsubscript{3}Cl (0.1 m.mole) were left together in a sealed tube for 2 weeks. The reactants were recovered unchanged after this time.

63123. 2:1 reaction of Ir(CO)Br(PPh\textsubscript{3})\textsubscript{2} and SiH\textsubscript{3}Cl

Experiment 2.32. H\textsubscript{2}Ir(CO)Br(PPh\textsubscript{3})\textsubscript{2}SiH\textsubscript{2}Cl

Treatment of Ir(CO)Br(PPh\textsubscript{3})\textsubscript{2} (0.1 m.mole) with SiH\textsubscript{3}Cl (0.2 m.mole) in benzene at R.T. for 5 mins, gave initially a yellow solution from which a white solid rapidly precipitated. Silyl chloride (0.1 m.mole) was recovered. The product which was a mixture of isomers of H\textsubscript{2}Ir(CO)Br(PPh\textsubscript{3})\textsubscript{2}SiH\textsubscript{2}Cl was identified by its I.R. spectrum.

Experiment 2.33. H\textsubscript{2}Ir(CO)Br(PPh\textsubscript{3})\textsubscript{2}GeH\textsubscript{2}

The reaction of Ir(CO)Br(PPh\textsubscript{3})\textsubscript{2} (0.1 m.moles) with GeH\textsubscript{4} (0.2 m.moles) in benzene at R.T. for 10 mins, gave a creamy white solid.
and GeH₄ (0.1 m.mole) was recovered. The product, H.Ir(CO)Br(PPh₃)₂
GeH₃ was identified by its I.R. spectrum.

Experiment 2.34. H.Ir(CO)Br(PPh₃)₂GeH₂Cl.

Treatment of Ir(CO)Br(PPh₃)₂ (0.1 m.moles) with GeH₃Cl (0.2 m.
moles) in benzene at R.T. for 5 mins, gave initially a yellow solution
in which rapid precipitation of a white solid, identified as
H.Ir(CO)Br(PPh₃)₂GeH₂Cl by its I.R. spectrum, occurred.
GeH₃Cl (0.1 m.moles) was recovered.

6.3.14. 1:1 reaction of IrH(CO)(PPh₃)₂ and Mi₂X

Expts. 3.1-3.8. IrH₂(CO)(PPh₃)₂Mi₂X (M = Si, Ge; X = H, Cl, Br, I)

IrH(CO)(PPh₃)₃ (0.1 m.mole) was treated with Mi₂X (M = Si, Ge;
X = H, Cl, Br, I) (0.1 m.moles) in benzene at R.T. for 5 mins, until
a clear solution, colourless for SiH₃X and yellowish for GeH₃X,
resulted. The soluble product, IrH₂(CO)(PPh₃)₂Mi₂X, was identified
by its n.m.r. spectrum and by mass-balance and, when isolated as a
gelatinous solid by evaporation of the benzene, by its I.R. spectrum.
The products decomposed when left in solution for several weeks, the
gemyl complexes giving yellow-brown solutions. The product,
IrH₂(CO)(PPh₃)₂GeH₂I, gave a brown solution and bright green
crystals after two weeks. The solid products decomposed to brown
gelatinous masses after 12 hours under N₂ or more rapidly in air.

Experiment 3.9. IrH(D)(CO)(PPh₃)₂SiD₂Br.

This compound was prepared as a mixture of isomers as in
experiments 3.1-3.8, and was identified by mass balance and by its
n.m.r. and I.R. spectra.
Experiment 3.10. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Cl} \)

This product was prepared as in experiments 3.1-3.8, and identified by mass-balance and by its n.m.r. and I.R. spectra. When isolated as a colourless jelly-like material it decomposed at R.T. either under vacuum or nitrogen for a few hours.

Experiment 3.11. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHCl}_2 \)

Treatment of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) (0.1 m.mole) with \( \text{SiH}_2\text{Cl}_2 \) (0.1 m.mole) in benzene at R.T. for 1/2 hour gave a colourless solution in which a thick white solid rapidly precipitated. This product, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHCl}_2 \) when isolated, was identified by mass-balance and by its I.R. spectrum. It is stable for long periods under vacuum or nitrogen or in air. No change was observed in the I.R. spectrum.

Experiment 3.12. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeHBr}_2 \)

The reaction of equimolar portions of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) and \( \text{GeH}_2\text{Br}_2 \) (0.1 m.mole) in benzene at R.T. gave a colourless solution and a deep yellow oil in the bottom of the reaction tube. This oil when isolated was identified as the product, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeHBr}_2 \), by mass-balance and by I.R. spectroscopy. It is stable for long periods under nitrogen. No change in the I.R. spectrum was observed.

6:13:15. 2:1 reaction of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) and \( \text{MH}_2\text{X} \)

Experiments 3.13-3.14. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Cl} \), \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_3 \)

Treatment of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) (0.1 m.mole) with \( \text{SiH}_2\text{Cl} \) or \( \text{GeH}_4 \) (0.2 m.moles) in benzene at R.T. for 5 mins, gave \( \text{SiH}_2\text{Cl} \) or \( \text{GeH}_4 \) (0.1 m.moles) and a clear solution, yellowish in the reaction with \( \text{GeH}_4 \) and colourless in the case of \( \text{SiH}_2\text{Cl} \). The soluble products, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{Cl} \) and \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_3 \), which were identified
by their n.m.r. spectra, were identical to those formed during the equimolar reaction of IrH(CO)(PPh₃)₃ and SiH₃Cl or GeH₄. The products were stable in solution for two weeks after which brownish solutions were formed. When isolated as gelatinous solids they showed the same decomposition characteristics as observed previously.

6:3:16. 1:1 and 2:1 reaction of Ir(CO)Cl(PPh₃)₂ with Si₂H₆

**Experiments 4.1-4.2.**

- H·Ir(CO)Cl(PPh₃)₂Si₂H₅/Ir(CO)Cl(PPh₃)₂(SiH₃)₂
- or H·Ir(CO)Cl(PPh₃)₂₂Si₂H₄

Treatment of Ir(CO)Cl(PPh₃)₂ (0.1 m.moles) with disilane (0.1 m.moles) in benzene at R.T. for 30 mins, gave an insoluble white precipitate and Si₂H₆ (0.05 m.moles). This precipitate was investigated by I.R. spectroscopy and by analysis, and could have been any one or any mixture of three products: (i) H·Ir(CO)Cl(PPh₃)₂Si₂H₅, (ii) Ir(CO)Cl(PPh₃)₂(SiH₃)₂ or (iii) [H·Ir(CO)Cl(PPh₃)]₂₂Si₂H₄. (Found: C, 55.7; H, 4.0%. (i) and (ii) require C, 52.7; H, 4.3%, (iii) requires C, 58.4; H, 4.3%). The white product is stable for long periods in solution, under vacuum or nitrogen, or in air. No change in the I.R. spectrum was observed.

Treatment of Vaska's compound (0.1 m.moles) with Si₂H₆ (0.2 m.moles) in benzene at R.T. for 20 minutes gave an insoluble white precipitate and Si₂H₆ (≈ 0.13 m.moles). Investigation of this product by I.R. spectroscopy and by analysis gave no conclusive evidence about its nature. No further reaction in solution was observed.
Experiment 4.3. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Si}_2\text{H}_5 \)

Treatment of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) (0.1 m.mole) with \( \text{Si}_2\text{H}_6 \) (0.1 m.mole) in benzene (or deuteriobenzene) at R.T. for 5 mins, gave a trace of \( \text{H}_2 \), a trace of \( \text{Si}_2\text{H}_6 \) and a colourless solution. The soluble product, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Si}_2\text{H}_5 \) has been identified by its n.m.r. spectrum and by I.R. spectroscopy. The product is stable in solution for several weeks but decomposes as a solid after a few hours.

Experiment 4.4. \( \text{HIr}(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{Ge}_2\text{H}_5 \)

Reaction of equimolar portions of Vaska's compound and \( \text{Ge}_2\text{H}_6 \) (0.1 m.moles) in benzene at R.T. for 5 mins, gave a pale yellow solution in which a white solid precipitated after 30 mins. The soluble product, \( \text{HIr}(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{Ge}_2\text{H}_5 \), has been identified by its n.m.r. spectrum and also when isolated as a solid by I.R. spectroscopy and analysis. (Found, C, 47.8; H, 4.1%. \( \text{C}_{37}\text{H}_{36}\text{ClP}_4\text{OIrGe}_2 \) requires, C, 47.6; H, 3.9%). The product forms a brown solution in benzene after 10 days and decomposes as a solid after a few weeks.

Experiment 4.5. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Ge}_2\text{H}_5 \)

Treatment of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) (0.1 m.mole) with \( \text{Ge}_2\text{H}_6 \) (0.1 m.mole) in \( \text{C}_6\text{H}_6 \) or \( \text{C}_6\text{D}_6 \) at R.T. gave a colourless solution after 5 minutes, and a trace of germane (\( \sim 0.01 \) m.mole). The product, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Ge}_2\text{H}_5 \), was identified by its n.m.r. and I.R. spectra. It is stable in solution for a few days at R.T., then giving a brown solution. It decomposes after isolation as a gelatinous solid under vacuum or nitrogen after a few hours.
Experiment 4.6. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHClSiH}_2\text{SiH}_3 \)

Vaska's compound (0.1 mmole) was reacted with trisilane (0.1 mmole) in benzene at R.T. for 5 mins, until a colourless solution was formed. A trace of \( \text{Si}_2\text{H}_6 \) was recovered. The soluble product, probably \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiHClSiH}_2\text{SiH}_3 \), was identified by its n.m.r. and I.R. spectra. It is stable in solution for several days when a yellowish solution is formed. Hydrogen (0.03 mmole) and \( \text{SiH}_4 \) (a trace) were recovered after 2 weeks. The product is isolated by solvent evaporation as a white solid which is stable for several days under nitrogen.


Experiment 4.7. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{Si}_3\text{H}_7, \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SIH(SiH}_3)_2 \)

Treatment of \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_3 \) (0.1 mmole) with \( \text{Si}_3\text{H}_8 \) (0.1 mmole) in benzene at R.T. for 30 mins, gave a colourless solution and a trace of trisilane. The soluble products, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{SiH}_2\text{SiH}_3 \) and \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SIH(SiH}_3)_2 \), were identified by n.m.r. spectroscopy, and were stable in solution for several days. They were isolated as white, gelatinous solids which decompose rapidly under vacuum or in nitrogen.

6:3:22.

Experiment 4.8-4.9. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{C}_5\text{H}_5, \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_2\text{C}_5\text{H}_5 \)

\( \text{IrH}_2(\text{CO})(\text{PPh}_3)_3 \) (0.1 mmole) was reacted with \( \text{M}_3\text{C}_5\text{H}_5 \) (\( \text{M} = \text{Si}, \text{Ge} \)) (0.1 mmole) in benzene or deuteriobenzene for 1 hour at R.T., until a colourless solution was formed. A trace of \( \text{M}_3\text{C}_5\text{H}_5 \) was recovered. The solution turned yellowish-brown after a few days. The soluble products, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{M}_2\text{C}_5\text{H}_5 \), were identified by n.m.r. and I.R.
spectroscopy. The products were isolated by solvent evaporation as white gelatinous solids which were stable for a few hours under vacuum or nitrogen.

6:3:23.

Experiments 4.10-4.11. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_3\text{C}_5\text{H}_5 \), \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{GeH}_3\text{C}_5\text{H}_5 \)

Treatment of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) (0.1 m.mole) with \( \text{MCl}_3\text{H}_5 \) (M = Si, Ge) (0.1 m.mole) in \( \text{OCl}_3\text{F} \) (Aroton II) at R.T. for 1 day, gave cream coloured crystals and a trace of \( \text{MCl}_3\text{H}_5 \). The products, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{MCl}_3\text{H}_5 \) (M = Si, Ge) were identified by I.R. spectroscopy and the I.R. spectra were identical to those of the products prepared in experiments 4.8-4.9. The products were stable in solution for several days (no change was observed in the I.R. spectrum), but decomposed in air after a few hours.


Experiment 4.12. \( \text{IrH}_2(\text{CO})(\text{PPh}_3)_2\text{SiH}_2\text{SiMe}_3 \)

Equimolar quantities of \( \text{IrH}(\text{CO})(\text{PPh}_3)_3 \) and \( \text{SiH}_2\text{SiMe}_3 \) (0.05 m.mole) were reacted together in benzene at R.T. for 4 hours, until a pale yellow solution was formed. The product, \( \text{IrH}_2(\text{CO})(\text{PPh}_3)\text{SiH}_2\text{SiMe}_3 \), was identified by its n.m.r. spectrum and is stable in solution for several days. No change was observed in the n.m.r. spectrum after this time.

6:3:25.

Experiment 5.1.

Treatment of \( \text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2 \) (0.1 m.mole) with \( \text{SiH}_3\text{Cl} \) (0.2 m.mole) in benzene at R.T. for \( \frac{1}{2} \) hour, gave a yellow solution, hydrogen (0.06 m.mole) and \( \text{SiH}_3\text{Cl} \) (0.08 m.mole). After 2 hours the solution was brown. The product was investigated by n.m.r. and I.R. spectroscopy.
Experiments 5.2-5.3.

IrH₂Cl₄(PR₃)₃ (R₃ = Ph₃ or PhEt₂) (0.1 mole) was reacted with SiH₂Cl (0.1 m.mole) in benzene (~ 1 ml) at R.T. Effervescence occurred and hydrogen (~ 0.05 m.mole) was recovered. A yellow solution together with a black deposit resulted. The product was investigated by I.R. and n.m.r. spectroscopy.

Experiment 5.4.

IrHCl₂(PPhEt₂) (0.5 m.moles) was reacted with SiH₂Cl (0.6 m.moles) in benzene at R.T. Effervescence occurred and hydrogen (0.34 m.moles) was evolved. A yellow solution and a slight black deposit were formed. The product was investigated by I.R. and n.m.r. spectroscopy.

Experiment 5.5-5.6.

Equimolar quantities of IrCl₃(PR₃)₃ (R₃ = Ph₃, PhEt₂) (0.1 m.mole) and SiH₂Br were reacted at R.T. in benzene, and the path of the reaction was followed by n.m.r. spectroscopy. Effervescence occurred initially and a yellow solution was formed which darkened in colour after a few hours. The products of the reaction volatiles and solid were studied by I.R. spectroscopy. The yellow solid which was isolated by solvent evaporation turned brown rapidly under nitrogen or in air.

Section 6.4
Reactions
Experiments 2.1-2.8

H.Ir(00)Cl(PPh₃)₂SiH₂Cl prepared as described in experiments 2.10-2.13 was isolated as a white solid and used in various experiments to test the reactions of iridium-silyl complexes. The reactions of equimolar quantities of this complex and MeOH, water,
HX (X = Cl, Br), SiH₂X (X = Br, I) and GeH₂X (X = Cl, Br) (0.1 m. moles) were studied in benzene at R.T. and the products, volatile and solid, were investigated by I.R. spectroscopy in the solid and gaseous phase. The reactions were very slow in all cases and complex mixtures of products were obtained.

Experiment 4.13.

Vaska's compound (0.1 m.mole) was reacted with Si₂H₆ (0.1 m. mole) in benzene at R.T. for 5 mins, until the white precipitate prepared in experiments 4.1-4.2 was formed. The excess Si₂H₆ and solvent were removed and the dry white solid was slowly heated in an evacuated tube until it charred. The gaseous products were analysed by I.R. spectroscopy, and shown to be a mixture of Si₂H₆, SiH₄ and C₆H₆.

Errata: - for condensible read condensable
for deuterobenzene read deuteriobenzene.
APPENDIX

THE MOLECULAR STRUCTURE OF NITROSYL-TRIS(TRIFLUOROPHOSPHINE)-
RHODIUM IN THE GAS PHASE, DETERMINED BY ELECTRON DIFFRACTION

Introduction

Although well over a hundred transition metal complexes of trifluorophosphine have been characterised, very little structural work on them has been reported. Crystallographic studies, except at low temperatures are difficult, because the complexes generally have low melting points. However, structure determination by electron diffraction is possible since many of the compounds have fairly high volatilities. Certain tetrahedrally co-ordinated derivatives of first and third series transition metals, tetrakis(trifluorophosphine)nickel and tetrakis(trifluorophosphine)platinum have been studied. Frenz and Ibers have studied hydrido-tetrakis(trifluorophosphine)cobalt and Rankin et al have investigated the structure of the octahedral complex pentacarbonyl(trifluorophosphine)molybdenum which is the only structure of a trifluorophosphine complex of a second series transition metal to have been studied.

Considerable interest has been shown in the changes of properties of trifluorophosphine on co-ordination. Very little change is observed in the angles between the phosphorus-fluorine bonds in the co-ordinated compounds compared with trifluorophosphine, but the bonds are shorter, much more so in the platinum complex than in the nickel one. The most striking feature of these results concerns the metal-phosphorus bond lengths. In the nickel and cobalt complexes, these bonds are about 0.12Å shorter than in most phosphine complexes of these metals.
The molybdenum complex shows a similar shortening of about 0.10\% but the platinum complex has metal-phosphorus bonds of a length that would be expected for a tetrahedral complex. It appears therefore that replacement of alkyl or aryl groups on phosphines by fluorine greatly increases the π acceptor properties of the ligand and results in a shortening of the metal-phosphorus bonds.

It was considered to be of interest to investigate the structure of another second series transition metal and to determine whether the same metal-phosphorus bond shortening was observed. The tetrahedrally co-ordinated rhodium complex, nitrosyl-tris(trifluorophosphine)rhodium, Rh(NO)(PF₃)₃ has been studied¹⁴⁹ and the results of this study are reported here.

The molecular intensity functions derived from photographically recorded sectorcd diffraction patterns were fitted by full-matrix least-squares refinements of a molecular model. The principal parameters of the molecule, assuming that it has a 3-fold axis of symmetry, have been determined and it has been shown that the trifluorophosphine groups are twisted by about 10⁰ from the configuration in which each PF₃ group is eclipsed with respect to the RhP₂N group. The complex, which is an orange volatile liquid, was prepared and supplied by Dr.J.F.Nixon. It is prepared by shaking tetrakis(trifluorophosphine)dichlorodirhodium with copper, trifluorophosphine and nitric oxide¹⁹⁰ or by displacement of the π-allyl group in π-allyltris(trifluorophosphine) rhodium with nitric oxide.¹⁵¹ The gas phase infrared spectrum of this complex has been studied above 650 cm⁻¹. The band at 1820 cm⁻¹ is assigned to ν(N-O) and the bands at 925, 898, 885, 865 and 858 cm⁻¹ are assigned to the P-F stretching modes. An analysis has been made¹⁵² of the ¹⁹F n.m.r. spectrum, which is very
complex, as an $[X_3A]_3$ nuclear spin system, which suggests that the molecule has $3_m$ ($C_{3v}$) symmetry.

**Results and Discussion**

**Results**

Electron diffraction data was obtained for camera heights, i.e. nozzle to plate distances of 25, 50 and 100 cm., using the Balzers' KD.G2 gas diffraction apparatus at the University of Manchester Institute of Science and Technology. The data reduction and least-squares refinement programmes and modifications to factors and expressions used in these programmes are described in the experimental section. The molecular intensity curves, obtained after preliminary reduction of the data and drawing of background (see experimental section), and final weighted difference curves are shown in fig.A.1; the weighting functions are given in table A.1.

**Table A.1**

<table>
<thead>
<tr>
<th>Camera Height</th>
<th>$s$</th>
<th>$s_{\text{min}}$</th>
<th>$s_1$</th>
<th>$s_2$</th>
<th>$s_{\text{max}}$</th>
<th>$p/h$</th>
<th>Scale Factor</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 mm</td>
<td>0.4</td>
<td>6.0</td>
<td>9.0</td>
<td>22.0</td>
<td>26.8</td>
<td>0.4410</td>
<td>1.196±0.031</td>
<td>0.05665 Å</td>
</tr>
<tr>
<td>500 mm</td>
<td>0.2</td>
<td>3.0</td>
<td>5.0</td>
<td>12.5</td>
<td>15.0</td>
<td>0.4922</td>
<td>0.978±0.024</td>
<td>0.05665 Å</td>
</tr>
<tr>
<td>1000 mm</td>
<td>0.1</td>
<td>1.3</td>
<td>2.5</td>
<td>5.6</td>
<td>7.4</td>
<td>0.4993</td>
<td>0.753±0.043</td>
<td>0.05665 Å</td>
</tr>
</tbody>
</table>

The molecular model used for the full-matrix least-squares refinements was based on the assumption that the molecule has a three-fold rotation symmetry axis, with a linear Rh-N-O group and and local three-fold symmetry for each Rh-PF$_3$ group. Seven independent geometrical parameters were used to define the model. These were chosen as the four different bonded inter-atomic
Observed and final weighted difference molecular intensities for data sets obtained with nozzle-to-plate distances of
a) 250 mm, b) 500 mm and c) 1000 mm.

fig. 1A
distances (N-O, P-F, Rh-P, Rh-N) and three angles (PPhP, FPF and a twist angle). The PF₃ groups were allowed to have a twist. If the fluorine atoms attached to one phosphorus atom are labelled F(1), F(2) and (F3), and zero twist is defined for F(1) eclipsing the nitrosyl group, then a positive twist θ involves rotation of the PF₃ group about the Rh-P bond, atom F(1) moving towards the site of F(2), etc. The other fluorine atoms, F(1'), F(2'), F(3'), F(1''), F(2'') and F(3''), are similarly rotated about their respective Rh-P' and Rh-P'' bonds by θ, in the same sense, thus preserving the three-fold axis. The molecular point group is therefore 3(C₃), and for twist angles of 0 or 60° it is 3m (C₃v).

The radial distribution curve, and the difference between the experimental and calculated curves are shown in Fig.2a. Most of the principal features of this curve may be assigned to the four types of atom pairs involving rhodium, and to the strong phosphorus-fluorine peak at 1.56 Å. These five distances define all the geometrical parameters except for the PPhP and twist angles. These depend on the complex series of overlapping peaks extending from 3.3 to 6.2 Å. After several trial refinements with the twist angle fixed at various values between 0 and 60°, both these additional angles refined satisfactorily.

Due to the complexity of the series of overlapping peaks, it was impossible to refine all the amplitudes of vibration, and so a number of constraints were applied. Thus, for example, the amplitudes for the N-F(2) and N-F(3) distances were assumed to be equal, and moreover, to be 0.8 times as great as the O-F(2) and O-F(3) amplitudes. All such constraints that were applied are noted in the table of parameters, Table A.2. The quoted error for the first named amplitude of each such group applies in fact to the whole
Fig. 2A. Radial distribution curve, $P(r)/r$, and final deviations between experimental and calculated curves for Rh(NO)(PF$_3$)$_3$. Before Fourier inversion the data were multiplied by $s \exp(-0.0015r^2)/(z_{\text{Rh}}-f_{\text{Rh}})(z_{\text{P}}-f_{\text{P}})$. 

$\text{Rh(NO)(PF}_3)_3$ $P(r)/r$
<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>Refinement A</th>
<th>Distance (Å)</th>
<th>Refinement B</th>
<th>Shrinkage correction (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r 1 P-F</td>
<td>1.558 ± 0.009</td>
<td>1.558 ± 0.003</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>r 2 Rh-P</td>
<td>2.246 ± 0.024</td>
<td>2.245 ± 0.005</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>r 3 Rh-N</td>
<td>1.343 ± 0.065 (fixed)</td>
<td>1.358 ± 0.018</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>r 4 N-O</td>
<td>1.147 ± 0.037 (fixed)</td>
<td>1.149 ± 0.019</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>d 5 Rh-F</td>
<td>3.274 ± 0.011 O.010</td>
<td>3.273 ± 0.011 O.010</td>
<td>- O.O10</td>
<td></td>
</tr>
<tr>
<td>d 6 Rh-O</td>
<td>2.995 ± 0.091 (fixed)</td>
<td>2.975 ± 0.065 (fixed)</td>
<td>- O.O65</td>
<td></td>
</tr>
<tr>
<td>d 7 P-N</td>
<td>3.346 ± 0.019 (fixed)</td>
<td>3.331 ± 0.017 (fixed)</td>
<td>- O.O17</td>
<td></td>
</tr>
<tr>
<td>d 8 P-O</td>
<td>4.296 ± 0.012 (fixed)</td>
<td>4.269 ± 0.021 (fixed)</td>
<td>- O.O21</td>
<td></td>
</tr>
<tr>
<td>d 9 P-F</td>
<td>3.683 ± 0.053 (fixed)</td>
<td>3.681 ± 0.017 (fixed)</td>
<td>- O.O17</td>
<td></td>
</tr>
<tr>
<td>d 10 F(1)-F(2)</td>
<td>2.396 ± 0.075 (fixed)</td>
<td>2.389 ± 0.075 (fixed)</td>
<td>- O.O75</td>
<td></td>
</tr>
<tr>
<td>d 11 P-F(1')</td>
<td>4.901 ± 0.016 (fixed)</td>
<td>4.887 ± 0.013 (fixed)</td>
<td>- O.O13</td>
<td></td>
</tr>
<tr>
<td>d 12 P-F(2')</td>
<td>4.731 ± 0.020 (t-u11)</td>
<td>4.730 ± 0.025 (t-u11)</td>
<td>- O.O25</td>
<td></td>
</tr>
<tr>
<td>d 13 P-F(3')</td>
<td>3.811 ± 0.014 (t-u11)</td>
<td>3.812 ± 0.025 (t-u11)</td>
<td>- O.O25</td>
<td></td>
</tr>
<tr>
<td>d 14 P-F(1)</td>
<td>4.722 ± 0.016 (t-u11)</td>
<td>4.707 ± 0.022 (t-u11)</td>
<td>- O.O22</td>
<td></td>
</tr>
<tr>
<td>d 15 P-F(2)</td>
<td>3.814 ± 0.015 (t-u13)</td>
<td>3.819 ± 0.024 (t-u13)</td>
<td>- O.O24</td>
<td></td>
</tr>
<tr>
<td>d 16 F'F(3)</td>
<td>4.906±0.013</td>
<td>0.203 (t-u11)</td>
<td>4.905±0.022</td>
<td>0.286 (t-u11)</td>
</tr>
<tr>
<td>d 17 F(1)-F(1')</td>
<td>5.624±0.019</td>
<td>0.169±0.031</td>
<td>5.619±0.017</td>
<td>0.152±0.027</td>
</tr>
<tr>
<td>d 18 F(1)-F(2')</td>
<td>5.998±0.023</td>
<td>0.169 (t-u17)</td>
<td>5.985±0.027</td>
<td>0.152 (t-u17)</td>
</tr>
<tr>
<td>d 19 F(1)-F(3')</td>
<td>4.719±0.022</td>
<td>0.213 (fixed)</td>
<td>4.711±0.026</td>
<td>0.213 (fixed)</td>
</tr>
<tr>
<td>d 20 F(2)-F(1')</td>
<td>5.099±0.015</td>
<td>0.213 (fixed)</td>
<td>5.097±0.025</td>
<td>0.213 (fixed)</td>
</tr>
<tr>
<td>d 21 F(2)-F(2')</td>
<td>4.728±0.029</td>
<td>0.213 (fixed)</td>
<td>4.736±0.026</td>
<td>0.213 (fixed)</td>
</tr>
<tr>
<td>d 22 F(2)-F(3')</td>
<td>3.320±0.017</td>
<td>0.213 (fixed)</td>
<td>3.335±0.030</td>
<td>0.213 (fixed)</td>
</tr>
<tr>
<td>d 23 F(3)-F(1')</td>
<td>6.244±0.017</td>
<td>0.169 (t-u17)</td>
<td>6.232±0.018</td>
<td>0.152 (t-u17)</td>
</tr>
<tr>
<td>d 24 F(3)-F(2')</td>
<td>5.663±0.025</td>
<td>0.169 (t-u17)</td>
<td>5.672±0.029</td>
<td>0.152 (t-u17)</td>
</tr>
<tr>
<td>d 25 F(3)-F(3')</td>
<td>5.103±0.023</td>
<td>0.213 (fixed)</td>
<td>5.107±0.021</td>
<td>0.213 (fixed)</td>
</tr>
<tr>
<td>d 26 N-F(1)</td>
<td>3.590±0.013</td>
<td>0.123±0.040</td>
<td>3.565±0.017</td>
<td>0.157±0.054</td>
</tr>
<tr>
<td>d 27 N-F(2)</td>
<td>4.562±0.020</td>
<td>0.110±0.033</td>
<td>4.543±0.022</td>
<td>0.104±0.032</td>
</tr>
<tr>
<td>d 28 N-F(3)</td>
<td>4.404±0.021</td>
<td>0.110 (t-u27)</td>
<td>4.383±0.021</td>
<td>0.104 (t-u27)</td>
</tr>
<tr>
<td>d 29 O-F(1)</td>
<td>4.217±0.017</td>
<td>0.154 (t-u26)</td>
<td>4.183±0.021</td>
<td>0.197 (t-u26)</td>
</tr>
<tr>
<td>d 30 O-F(2)</td>
<td>5.523±0.023</td>
<td>0.138 (t-u27)</td>
<td>5.496±0.026</td>
<td>0.130 (t-u27)</td>
</tr>
<tr>
<td>d 31 O-F(3)</td>
<td>5.313±0.026</td>
<td>0.138 (t-u27)</td>
<td>5.283±0.029</td>
<td>0.130 (t-u27)</td>
</tr>
</tbody>
</table>

**Angles**

| < 1 PRhP | 109.8±0.6 | 110.4±0.5 |
| < 2 FPF | 110.5±0.5 | 110.1±0.7 |
| < 3 Twist | 9.7±0.5 | 9.8±0.6 |

**Note:** (t-u17) after an amplitude means that the amplitude is tied to amplitude number 17.
group. Even with these restrictions, attempts to refine all four groups involving phosphorus and fluorine atoms in different PF$_3$ units led to instability, and so these values were refined independently in sequence until a mutually consistent solution was obtained.

It has usually been found that tabulated phase angles ($\eta$) are inadequate for calculations involving molecules that include atom pairs with widely differing atomic numbers. Thus it is necessary to use cubic functions derived from tabulated values given by Cox and Bonham,$^{153}$ the phase shift term for the i-$j$ atom pair being

$$\eta_i - \eta_j = a_i - a_j + (b_i - b_j)s + (c_i - c_j)s^2 + (d_i - d_j)s^3.$$ 

This may be rewritten as

$$\Delta \eta = \Delta a'(s - s_c) + \Delta c'(s - s_c)^2 + \Delta d'(s - s_c)^3,$$

with initial values of $s_c$ for the atom pairs calculated so that $\Delta \eta = \pi/2$ when $s = s_c$.

The initial values, calculated from the tabulated phases, for Rh-P, Rh-F, Rh-O and Rh-N were 39.5, 26.6, 26.1 and 24.6 Å$^{-1}$. The values for Rh-P and Rh-F were allowed to refine, optimum values of 37.2 and 24.8 Å$^{-1}$ being obtained. The Rh-O and Rh-N cut-off points were then reduced to 24.3 and 22.8 Å$^{-1}$ respectively, and all four values were subsequently fixed.

The molecular parameters at this stage, before application of shrinkage corrections, are listed in Table 1.2 as refinement A.

In the absence of any vibrational analysis of nitrosyl-tris(trifluorophosphine)rhodium, the shrinkage corrections had to be estimated, on the basis of published values for various carbonyl complexes$^{154,155,156}$ and for trifluorophosphine.

Cox and Brittain$^{157}$ have noted that $\pi$-cyclopentadienyl (nitrosyl)nickel appears to be a symmetric top molecule when studied
by microwave spectroscopy, but an electron diffraction study\textsuperscript{158} indicates that the NiNO angle is 160°. The large amplitude bending motion of the Ni-N-O group, the frequency of vibration being 153 cm\textsuperscript{-1}\textsuperscript{159} causes this large shrinkage effect. The possibility of a similar effect in the rhodium-nitrosyl complex was therefore studied, and an apparent RhNO angle of 163° was found. This result implies that a shrinkage correction for the Rh-O distance of 0.0285 Å is necessary, assuming that in the average structure the Rh-N-O group is linear.

After use of the corrections which have been described the final R factors were 0.15 (\(R_g\)) and 0.12 (\(R_p\)). The results of the best refinement including the shrinkage corrections are listed as refinement B in Table A.2, together with values of all the corrections. It should be noted that in estimating the corrections no account was taken of the effects of torsional oscillations about the rhodium-phosphorus bonds. It is quite possible, therefore, that the observed twist angle of 9.8° does not represent the mean position of the trifluorophosphine groups, which may be oscillating about the fully eclipsed position, with the molecular point group being 3\(m\), as is suggested by n.m.r. spectroscopy.

The errors quoted in Table A.2 are estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. The use of an off-diagonal weight matrix ensures that the least-squares derived errors are realistic.

The final least-squares correlation matrix is given in Table A.3. Views of nitrosyl-tris(trifluorophosphine)rhodium a) along the three-fold axis and b) along one phosphorus-rhodium bond are shown in fig. 3A.
Views of nitrosyl-tris(trifluorophosphine)rhodium

a) along the three-fold axis        b) along one phosphorus-rhodium bond

fig. 3A.
| R 1 | R 2 | R 3 | R 4 | < 1 | < 2 | < 3 | U 1 | U 2 | U 5 | U 8 | U 9 | U 17 | U 26 | U 27 | K 1 | K 2 | K 3 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1000 | -37 | 396 | -63 | 221 | -314 | -83 | 87 | 85 | 9 | -60 | -30 | 45 | 34 | -134 | 54 | 22 | -12 |
| 396 | -16 | 1000 | -390 | 250 | -143 | -284 | 208 | 54 | -262 | -184 | -128 | 125 | -97 | -140 | 124 | -74 | -167 |
| 221 | -459 | 250 | 341 | 1000 | -628 | -246 | 193 | 438 | 190 | 145 | -174 | 127 | 202 | -331 | 179 | 110 | -6 |
| -314 | 320 | -143 | -240 | 1000 | -504 | -504 | 1000 | -37 | 128 | -48 | -68 | 60 | -45 | 15 | 272 | -9 | -24 | 1 |
| -83 | -73 | -284 | 9 | -246 | -504 | 1000 | -37 | 128 | -48 | -68 | 60 | -45 | 15 | 272 | -9 | -24 | 1 |
| 87 | -317 | 208 | -48 | 193 | -100 | -37 | 1000 | 252 | 122 | -9 | -44 | 88 | 36 | -47 | 674 | 235 | 3 |
| 85 | -228 | 54 | 141 | 438 | -572 | 128 | 252 | 1000 | 158 | 98 | -36 | 17 | 59 | -150 | 285 | 187 | 61 |
| 9 | -231 | -262 | 305 | 190 | -68 | -48 | 122 | 158 | 1000 | -158 | 456 | 66 | 572 | 35 | 175 | 347 | 239 |
| -30 | 18 | -128 | 163 | -174 | 75 | 60 | -44 | -36 | 456 | -270 | 1000 | 4 | 26 | -1 | -49 | 7 | 86 |
| 45 | -60 | 125 | 268 | 127 | -60 | -45 | 88 | 17 | 66 | 90 | 4 | 1000 | 26 | 289 | 113 | 15 | -53 |
| 34 | -151 | -97 | 34 | 202 | -108 | 15 | 36 | 59 | 572 | -354 | 26 | 20 | 1000 | 77 | 37 | 221 | 180 |
| -134 | 96 | -140 | 214 | -331 | 107 | 272 | -47 | -150 | 35 | 203 | -1 | 289 | 77 | 1000 | -19 | -43 | -23 |
| 54 | -385 | 124 | 2 | 179 | -62 | -9 | 674 | 285 | 175 | 22 | -49 | 113 | 37 | -19 | 1000 | 246 | 14 |
| -12 | -38 | -167 | -35 | -6 | 15 | 1 | 3 | 61 | 239 | -53 | 86 | -53 | 180 | -23 | 14 | 114 | 1000 |
Discussion

The geometrical parameters for the trifluorophosphine ligands found in the present study fit in well with the trends that have been noted for other co-ordinated trifluorophosphine ligands, with shorter phosphorus-fluorine bonds (1.558 Å) and wider FPF angles (100.5°) than in the free ligand. These changes are small (∼ 0.10 Å for the P-F bond and ∼ 2.5° for FPF), but do agree with the general trends which could be confirmed by further studies.

The value of the rhodium-phosphorus bond length (2.246 Å) in nitrosyl-tris(trifluorophosphine)rhodium lies between the values reported for trimethyl-phosphite complexes of rhodium (∼ 2.19 Å) and those reported for aryl- or alkyl-phosphine derivatives (about 2.31 to 2.40 Å) of rhodium. Table A.4 lists some values (all crystallographic) that have been reported for tetrahedral, square planar, square pyramidal, trigonal bipyramidal and octahedral rhodium phosphine complexes. These values indicate that the nature of the phosphorus substituents rather than the oxidation state or co-ordination pattern of the rhodium atom determine the slight variation in the rhodium-phosphorus bond lengths. Since the values for the trimethyl-phosphite and trifluorophosphine complexes are less than those for the aryl- or alkyl-phosphine complexes, it is likely that the electron withdrawing properties of the fluorine atoms or methoxy groups attached to phosphorus enhance the π-acceptor properties of the phosphine group as a ligand. It is possible that the shortness of Rh-P in the trimethyl-phosphite rhodium complexes could be caused by the other ligands present in the particular complexes that have been studied.

The linear Rh-N=O grouping is consistent with the idea of the complexing ligand being NO⁺, rather than a neutral group.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Rhodium coordination polyhedron</th>
<th>Bond lengths (e.s.d. in brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{RhCl}_3(\text{PBu}^n)_2\text{P(OMe)}_3 )</td>
<td>octahedral</td>
<td>2.400(5)  2.379(5)  2.199(5)</td>
</tr>
<tr>
<td>( \text{Rh(CO)(PPh}_3)_3 )</td>
<td>trigonal bipyramidal</td>
<td>2.315(8)  2.316(9)  2.336(8)</td>
</tr>
<tr>
<td>( \text{Rh(P(OMe)}_3\text{)}_2\text{BPh}_4 )</td>
<td>(one phenyl group bonded)</td>
<td>2.18(1)  2.18(1)</td>
</tr>
<tr>
<td>( \text{RhI}_2\text{Me(PPh}_3\text{)}_2\text{C}_6\text{H}_6 )</td>
<td>square pyramidal</td>
<td>2.35</td>
</tr>
<tr>
<td>( \text{RhCl(CO)}(\text{SO}_2)(\text{PPh}_3)_2 )</td>
<td>distorted square pyramidal</td>
<td>2.371(2) 2.367(2)</td>
</tr>
<tr>
<td>( \text{RhHCl(SiCl}_3\text{)(PPh}_3\text{)}_2\times\text{SiHCl}_3 )</td>
<td>distorted trigonal bipyramidal</td>
<td>2.344(4) 2.332(4)</td>
</tr>
<tr>
<td>( \text{RhCl(CS)(PPh}_3\text{)}_2 )</td>
<td>square planar</td>
<td>2.335(2) 2.337(2)</td>
</tr>
<tr>
<td>( \text{RhCl(PPh}_3\text{)}_3 )</td>
<td>distorted tetrahedral</td>
<td>2.218(8) 2.315(8)  2.327(8)</td>
</tr>
<tr>
<td>( \text{RhCl(C}_2\text{F}_4\text{)(PPh}_3\text{)}_2 )</td>
<td>distorted square planar</td>
<td>2.374(8) 2.370(8)</td>
</tr>
<tr>
<td>( \text{RhH(PPh}_3\text{)}_4\text{C}_6\text{H}_6 )</td>
<td>tetrahedral</td>
<td>2.34(5)  2.39(3)</td>
</tr>
<tr>
<td>( \text{RhCl(PPh}_3\text{)}(\text{Et}_2\text{NPF}_2\text{)}_2 )</td>
<td>square planar</td>
<td>2.352(3) 2.215(3)  2.136(3)</td>
</tr>
<tr>
<td>( \text{Rh(NO)(PF}_3\text{)}_3 )</td>
<td>tetrahedral</td>
<td>2.245(5)</td>
</tr>
</tbody>
</table>
A similar situation has been reported for tetracarbonyl(nitrosyl) manganese, which has a nitrogen-oxygen bond length of $1.152 \pm 0.015$ Å. In other nitrosyl complexes angles at nitrogen close to $120^\circ$ have been reported, and in these cases the complexing ligand is thought to be NO$^-$.

It is possible that intermediate cases may occur.

The difference between the experimental rhodium-phosphorus and rhodium-nitrogen distances is $0.398$ Å, compared with a difference of $0.386$ Å between the carbon-phosphorus and carbon-nitrogen length in trimethylphosphine and trimethylamine. This suggests that the bond orders of the two types of rhodium bonds are similar. In the molybdenum carbonyl complex which has been studied, this type of relationship has been noted for metal-phosphorus and metal-carbon bonds.
Experimental Procedure

Electron diffraction patterns were recorded photographically on Ilford N60 plates using a Balzers KD.62 gas diffraction instrument. The electron wavelength, obtained both by direct measurement of the accelerating voltage and from the diffraction pattern of powdered thallous chloride, was $0.05665 \pm 0.00003 \AA$. The sample and inlet nozzle were maintained at 295°K and 328°K respectively during the exposures. Data from the three plates, exposed with nozzle-to-plate distances of 250, 500 and 1000 mm were used, giving a range of 1.3 to 26.8 Å⁻¹ in the scattering variables. Photographic intensities were reduced to digital form using a fully automated Joyce-Loebl microdensitometer. Normally eight diameters of each plate are traced by the microdensitometer.

Electron diffraction programmes and calculations

All calculations were carried out using an IBM 360/50 computer at the Edinburgh Regional Computing Centre, and data reduction and least-squares refinement programmes that have been developed at an earlier date. The data reduction programme centres the microdensitometer traces, applies corrections for emulsion response, plate planarity and sector shape and interpolates the data in even s intervals. The individual traces are then combined and averaged, and the calculated coherent atomic scattering is subtracted. Subtraction of some of the extraneous scattering is achieved by fitting a cubic function to the data by a least squares procedure. At this stage, a smooth background is drawn through the molecular scattering and subtracted. This makes allowance for incoherent atomic scattering. The complex scattering factors of Cox and Bonham were used, with the phase
shift factors modified as described earlier.

In the full-matrix least-squares refinement programme, the expression used to calculate the theoretical molecular scattering is

\[ I_{\text{calc}}(s) = k_m \sum_{m} G_{ij} \sin \left[ s(r_{ij} - K_{ij} s^2) \right] \exp(-u_{ij} s^2/2) s r_{ij} \]

where \( k_m \) is the refinable scale factor for the data set \( m \), \( G_{ij} \) is the term calculated from the scattering amplitudes and phase shift parameters for the \( i-j \) atom pair, and \( r_{ij}, u_{ij} \) and \( K_{ij} \) are the interatomic distance \( r_{ij}(1) \), amplitude of vibration and anharmonicity for the atom pair.

The latter values were calculated using the relation

\[ K_{ij} = a_{ij} u_{ij}^2 / 6 \]

where \( a_{ij} \) is an asymmetry parameter, set at 2\( \AA^{-1} \) for all bonded distances and zero for non-bonded distances.

The refinement programme uses an off-diagonal weight matrix to allow for the correlation between adjacent data points. For a data set \( m \), extending from \( s_{\text{min}} \) to \( s_{\text{max}} \), two weighting points \( s_1 \) and \( s_2 \) are chosen by inspection. The weight matrix elements are then

\[
\begin{align*}
&w_{ii} = \frac{(s_i - s_{\text{min}})}{(s_1 - s_{\text{min}})} & s_{\text{min}} < s_i < s_1 \\
&w_{ii} = 1 & s_1 < s_i < s_2 \\
&w_{ii} = \frac{(s_{\text{max}} - s_i)}{(s_{\max} - s_2)} & s_2 < s_i < s_{\text{max}} \\
&w_{ij} = 0 & i \neq j \pm 1 \\
&w_{ij} = -0.5 \left( w_{ii} + w_{jj} \right) \left( p/h \right)_m & i = j \pm 1
\end{align*}
\]

The values of the weighting points used, together with the correlation parameters, \( p/h \) and the scale factors, are given in Table A.1.

If this weight matrix \( W \), and \( I \) and \( U \) represent the vectors of observed intensities \( (I_{\text{obs}}) \) and differences \( (I_{\text{obs}} - I_{\text{calc}}) \)
respectively, then the quantity minimised in the refinements is $U'WU/\bar{I}'WI$. The square root of this quantity is the 'generalised' R factor $R_g$. A 'diagonal' R factor $R_D$ is defined by

$$R_D = \sqrt{\frac{\sum_{i} w_{i} I_{i}^2}{\sum_{i} w_{i} I_{i}}}$$

The radial distribution curves, $P(r)/r$ and $P(r)$ are calculated and plotted by Fourier inversion of the intensity curves. Since the distances calculated in the refinement are $r_g$ they correspond to the centres of gravity of the peaks in the $P(r)/r$ curve.
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Appendix


