

Some Reactions of Iridium and Platinum Complexes

with Hydrides of Main Group Elements

by

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To my parents  
and Anne



<u>Contents</u>	(i)
Acknowledgements	(iii)
Summary	(iv)
<u>Chapter 1: Introduction</u>	1
Nuclear Magnetic Resonance Spectroscopy (NMR)	17
References	26
<u>Chapter 2: Reactions of <math>\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2</math> with Some Silyl Compounds</u>	29
2.1 Reaction of $\text{Ir}(\text{CO})(\text{PEt}_3)_2\text{X}$ with $\text{N}(\text{SiH}_3)_3$	30
2.2 Reaction of $\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2$ with $(\text{SiH}_3)_2\text{O}$	34
2.3 Reaction of $\text{Si}_2\text{H}_6$ with $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$	41
2.4 Reaction of $\text{SiH}_n\text{F}_{4-n}$ with $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$	44
2.5 Reactions of complexes formed in this Chapter	54
References	66
<u>Chapter 3: Reactions of <math>\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2</math> with <math>\text{O}(\text{SiH}_3)_2</math> and <math>\text{N}(\text{SiH}_3)_3</math></u>	67
3.1 Reaction of $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$ with $\text{O}(\text{SiH}_3)_2$	69
3.2 Reaction of $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$ with $\text{N}(\text{SiH}_3)_3$	80
References	81
<u>Chapter 4: Reactions of <math>\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3</math> with Some Silyl Compounds</u>	82
4.1 Reaction of $\text{N}(\text{SiH}_3)_3$ with $\text{HIr}(\text{CO})(\text{PPh}_3)_3$	84
4.2 Reaction of $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$ with $\text{SiF}_3\text{H}$	95
4.3 Reaction of $\text{HIr}(\text{CO})(\text{PPh}_3)_3$ with $(\text{SiH}_3)_2\text{O}$	104
References	113



<u>Chapter 5:</u>	<u>Reactions of <math>[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-</math></u>	114
5.1	$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{HI}$	115
5.2	$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{H}_2\text{Se}$	123
5.3	$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{HCN}$	127
5.4	$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{SiH}_3\text{Cl}$	128
5.5	$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{HPF}_2\text{S}$	137
	References	141
<u>Chapter 6:</u>	<u>Experimental</u>	142
6.1	General Experimental Methods	143
6.2	Instruments	144
6.3	Preparation of Starting Materials	146
6.4	Details of Experimental Technique	150
	References	154

List of Courses Attended



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SUMMARY

This thesis describes the synthesis of some novel derivatives of iridium(III), platinum(II) and platinum(IV).

The iridium complexes were formed by oxidative addition of silyl compounds to iridium(I) compounds. With  $\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2$  ( $\text{X} = \text{Cl}, \text{I}$ ) a trans addition took place. When  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  was used there was an initial trans addition followed by rearrangement to a dihydride species with cis phosphines.  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  reacted losing a phosphine to become a species with cis phosphines, one trans to a hydride, and one trans to a silyl ligand. Some of the silyls used contained more than one  $-\text{SiH}_3$  group and bis-iridium species were observed.

The reactions of the bridged platinum complex  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  with a variety of simple molecules were investigated. Three types of reaction were observed: oxidative addition to one or both platinum, oxidative addition followed by reductive elimination of  $\text{H}_2$ , or cleavage of the  $-\text{PH}_2-$  bridge. The  $-\text{PH}_2-$  bridge was eventually broken in all cases.

Most of the new compounds prepared have been characterized by  $^{31}\text{P}$  and  $^1\text{H}$  n.m.r., and where applicable by micro-elemental analysis for C, H, and N, and by vibrational spectroscopy.



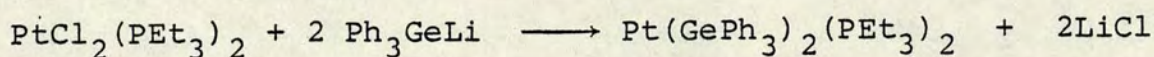
CHAPTER 1

Introduction



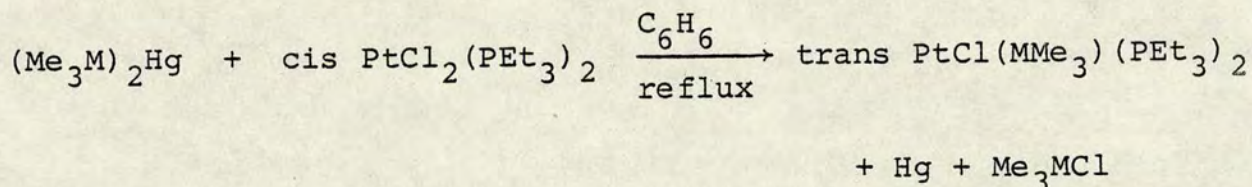
## 1. Introduction

The first Pt-M complex where M = Si, Ge was described in 1964 by Glockling<sup>1,2</sup>. He prepared it using the reaction

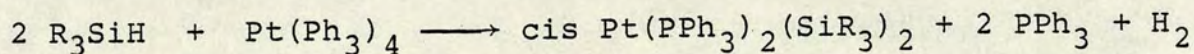
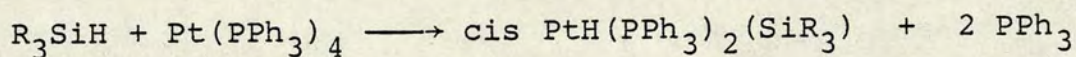


This reaction was extended to form the bis-SiMePh<sub>2</sub> and bis-SiMe<sub>2</sub>Ph complexes<sup>3</sup>. The stereochemistries of these complexes were found to be cis or trans and in solution both isomers were present.

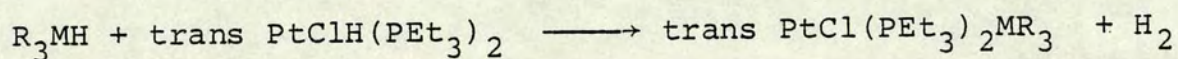
Using mercury compounds instead of the lithium salts<sup>4,5</sup> Me<sub>3</sub>M complexes were prepared.



This system gave mono- instead of bis-products. The reaction of silicon hydrides with platinum(0) compounds provides another route into silyl platinum complexes<sup>6</sup>.

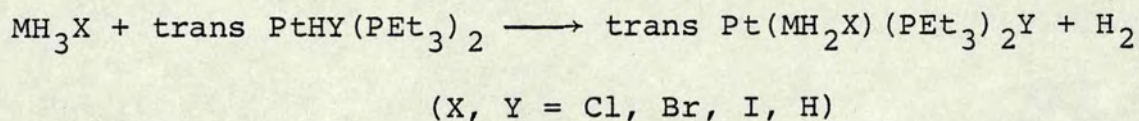


A third method by which M-Pt complexes were prepared was<sup>3,7</sup>





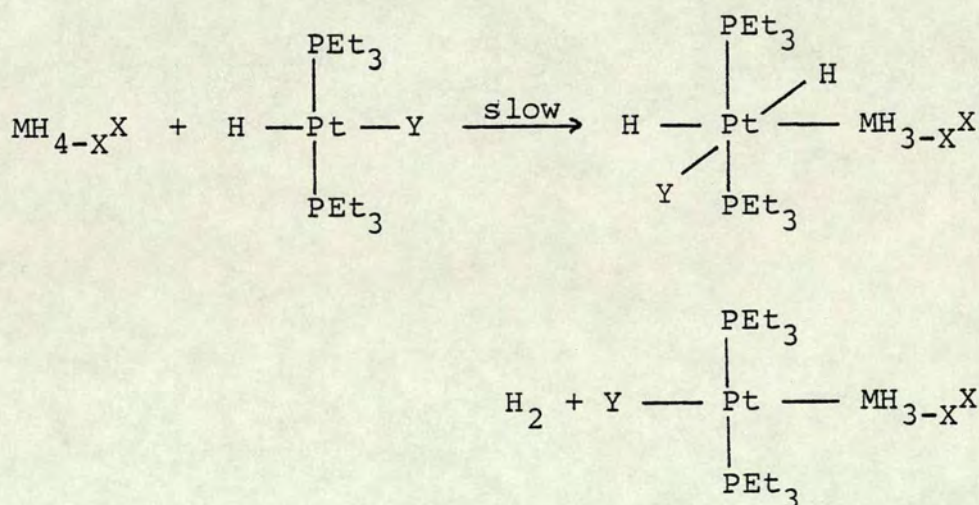
In this department Bentham has prepared a series of silyl and germyl hydride complexes of platinum<sup>8</sup>.



These systems were further studied by Anderson<sup>9</sup>. Edward<sup>10</sup> extended this work and investigated reactions of  $\text{PtH}(\text{PEt}_3)_2\text{X}$  with molecules containing more than one  $\text{SiH}_3$  group.

Reaction of  $\text{PtClH}(\text{PEt}_3)_2$  with  $(\text{SiH}_3)_2\text{O}$  gave  $\text{PtCl}(\text{PEt}_3)_2\text{SiH}_2\text{OSiH}_3$  and  $[\text{PtCl}(\text{PEt}_3)_2\text{SiH}_2]_2\text{O}$ . Reaction of  $\text{PtH}(\text{PEt}_3)_2\text{X}$  with  $\text{N}(\text{SiH}_3)_3$  only formed the mono platinum species whereas reaction with  $\text{P}(\text{SiH}_3)_3$  formed a mono- or bis- but not a tris-platinum species.

The mechanism for these silyl additions is believed to be:



Six-coordinate intermediates are observed at low temperature. Six-coordinate platinum hydrides are formed by addition of  $\text{HX}^{11,9}$  to  $\text{trans PtClH}(\text{PEt}_3)_2$ . With care  $\text{PtCl}_2\text{H}_2(\text{PEt}_3)_2$  can be isolated as a solid.

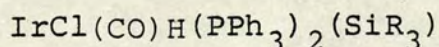


In 1959,  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ , commonly known as Vaska's compound, was first prepared from  $\text{IrCl}(\text{CO})_3$ <sup>12</sup>. This method was superseded in 1961 by Vaska's method<sup>13</sup> of reacting  $\text{IrCl}_3$  with triphenyl phosphine in refluxing dimethyl formamide.

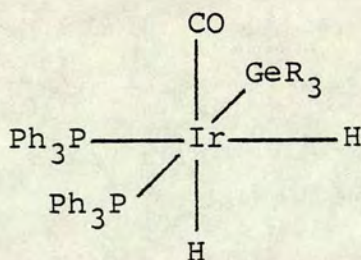
Vaska's compound was found to react with  $\text{X}_2$ , ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{H}_2$  or  $\text{D}_2$  or  $\text{HD}$ , and  $\text{HX}$  to give air-stable six-coordinate species<sup>14,15,16,17,18</sup>. It was also found to react with ethylene and reversibly with molecular oxygen<sup>19</sup>.

Work by Bennet et al<sup>20</sup> on oxidative addition of  $\text{X}_2$  and  $\text{CH}_3\text{I}$  to Vaska's compound led to the conclusion that cis adducts were formed.

In 1965 Chalk and Harrod<sup>21</sup> studied the reaction of  $\text{R}_3\text{SiH}$  with Vaska's compound ( $\text{R} = \text{Cl}, \text{EtO}$  etc.). Reaction took place using the silane as the solvent over a period of twelve hours to give 1:1 adducts.



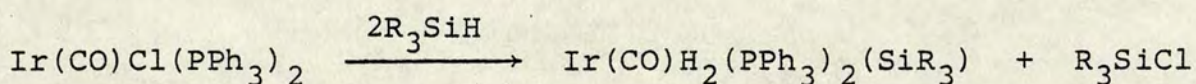
Glockling et al<sup>22</sup> showed that the reaction of  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  with two molecules of  $\text{R}_3\text{GeH}$  gave six coordinate complexes of the form





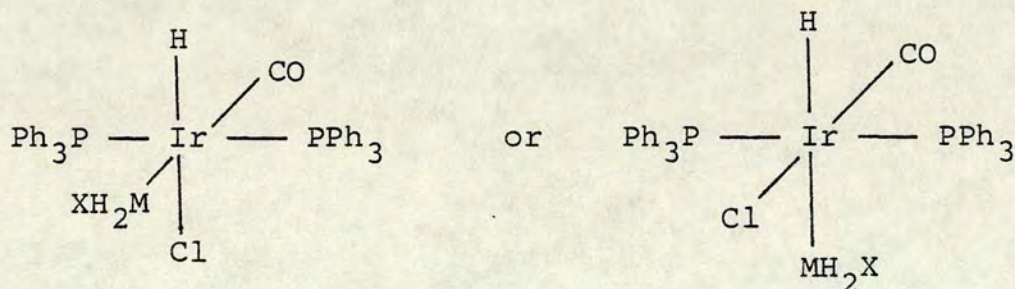
The phosphines were clearly cis and observance of couplings from the H's on R to an iridium hydride suggested the germyl group was cis to the hydrides.

Chalk and Harrod<sup>23</sup> repeated their earlier experiments, and it was shown that when Vaska's compound or its adduct with  $R_3SiH$  was allowed to stand for a long time at room temperature in the presence of an excess of silane a further reaction occurred. A silyl halide was evolved and a soluble complex of iridium was formed where there were two IrH bonds in each molecule and the  $Ph_3P$  groups were mutually cis.



Bridges<sup>24,25</sup> studied reactions of Vaska's compound with  $SiH_3X$  and  $GeH_3X$  ( $X = Cl, Br, I, H$ ). She observed formation of  $Ir(CO)ClH(PPh_3)_2(MH_2X)$  but only observed rearrangement to a dihydride species  $Ir(CO)H_2(PPh_3)_2MH_2X$  for reaction with  $SiH_3Cl$ .

Oxidative addition of  $MH_3X$  produced the isomers

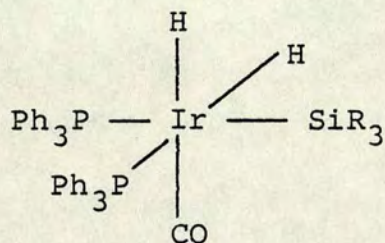


The silyl adducts were insoluble, but the germyl adducts were temporarily soluble precipitating over thirty minutes.



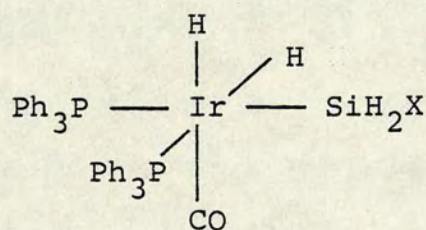
$\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  was prepared<sup>26</sup> in 1963 from Vaska's compound by reducing it with  $\text{N}_2\text{H}_4$ . It reacts with  $\text{HX}$  or  $\text{DX}$  to give<sup>17</sup>  $[\text{Ir}(\text{CO})\text{HZ}(\text{PPh}_3)_3]^+\text{X}^-$  ( $\text{Z} = \text{H}$  or  $\text{D}$  depending on reactant).  $\text{H}_2$  also reacts but gives the seven coordinate species  $\text{Ir}(\text{CO})\text{H}_3(\text{PPh}_3)_3$ <sup>15,27</sup>.

Harrod et al have shown that  $\text{SiR}_3\text{H}$  reacts reversibly with  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  giving the compound

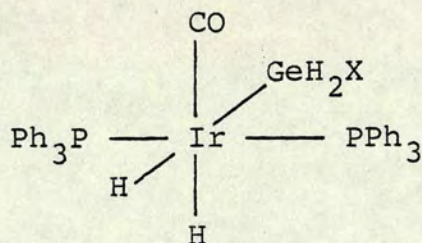


Because the compounds were soluble  $^1\text{H}$  n.m.r. spectroscopy was used to help establish their structures.

Bridges and Fraser<sup>24,30</sup> found that reactions of  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  with silyl compounds tended to give



and with germlys tended to give

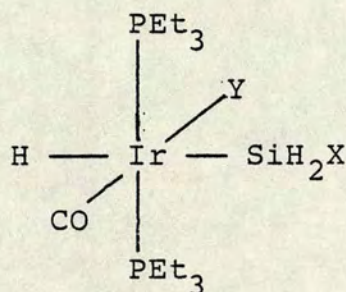


This has been confirmed by detailed n.m.r. studies<sup>29</sup>.



Fraser<sup>30,31</sup> studied reactions of the triethyl phosphine Vaska compound analogues with silyl and germyl compounds. These were found to give species of the type

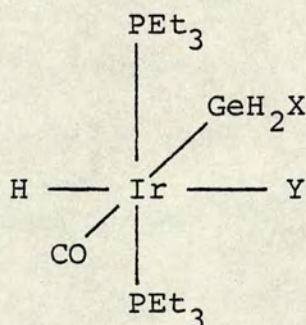
— for silyls



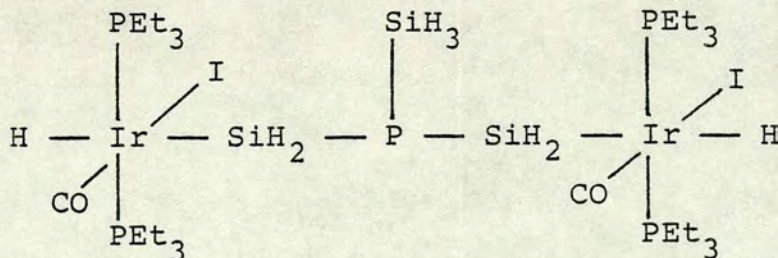
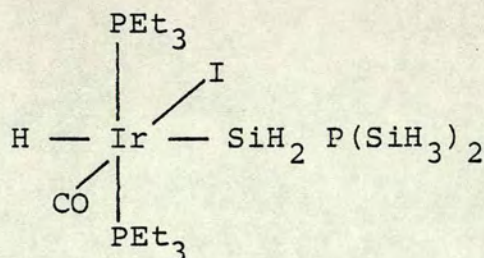
and for germyls

Y = Cl, I

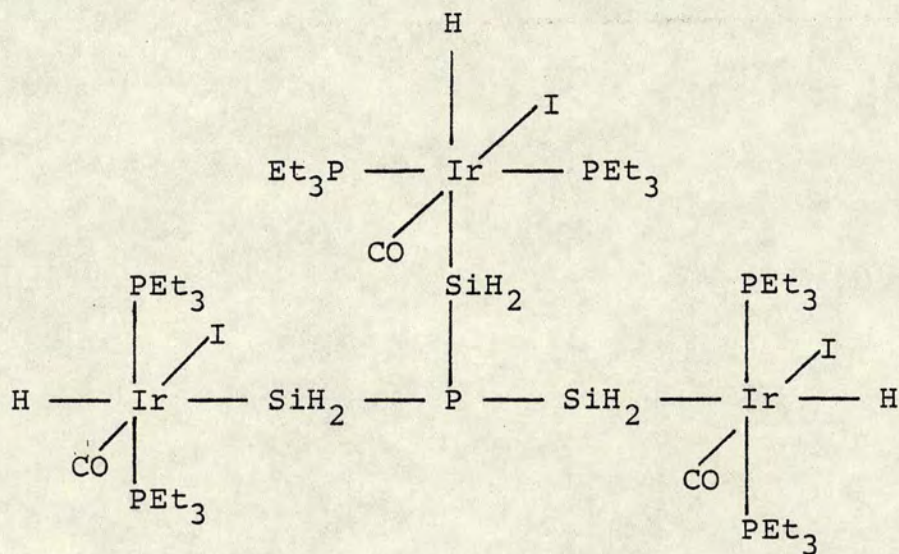
X = Cl, Br, I, H



$\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  was also reacted with compounds containing more than one  $-\text{SiH}_3$  group. These could form mono-, bis-, or tris-iridium species. e.g.  $\text{P}(\text{SiH}_3)_3$  could react to give three products dependent on the molar ratios used.

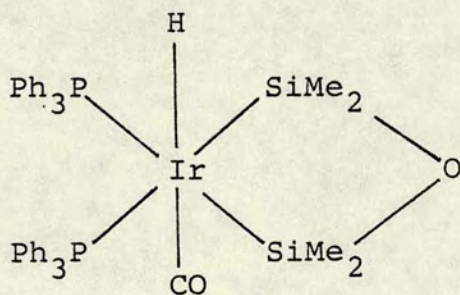






When  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  was reacted with  $(\text{SiH}_3)_2\text{O}$  a bis iridium species was observed, but evidence for a mono iridium species was inconclusive. This problem is dealt with in this thesis.

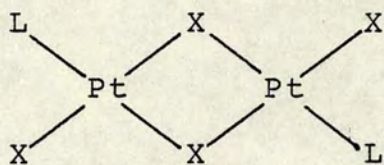
Curtis<sup>32,33,34</sup> has reported the complex



from the reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with  $(\text{HMe}_2\text{Si})_2\text{O}$  in benzene. The complex has been found to catalyse the disproportionation of 1,1,3,3-tetramethyldisiloxane into dimethylsilane and higher polysilanes.

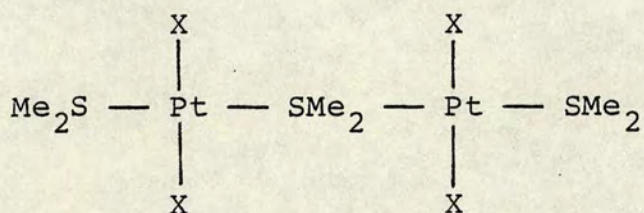
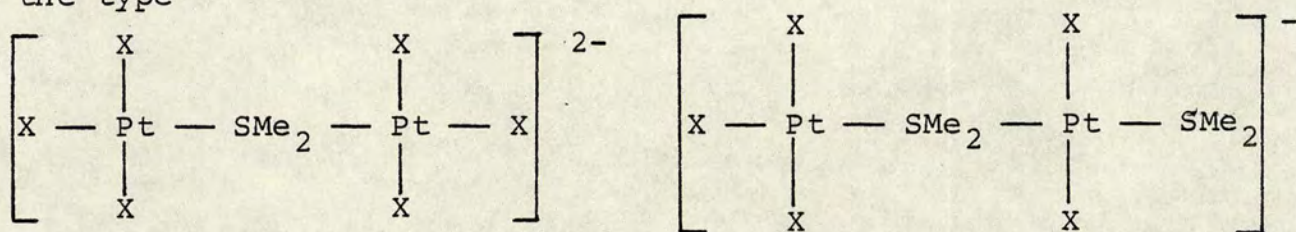


In most of the binuclear platinum complexes, known, the platinum atoms are linked by two bridging ligands. Many examples of the bridged platinum complex<sup>35</sup>

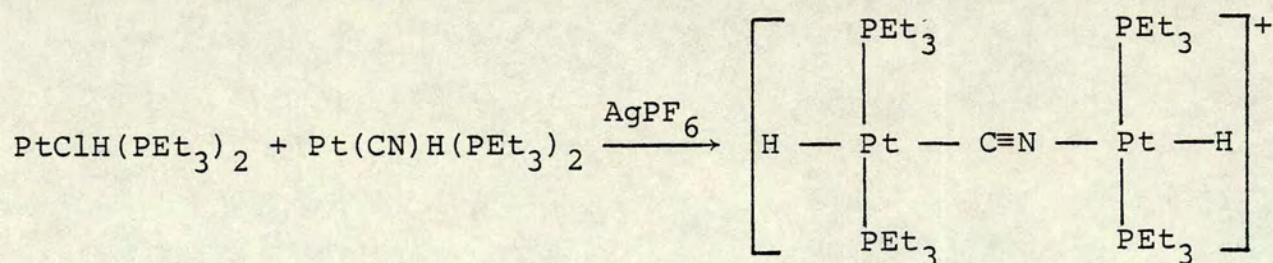


where X is an anionic ligand are known.

In 1974 examples of bridged platinum species linked by a single ligand atom were reported<sup>36</sup>. These were of the type

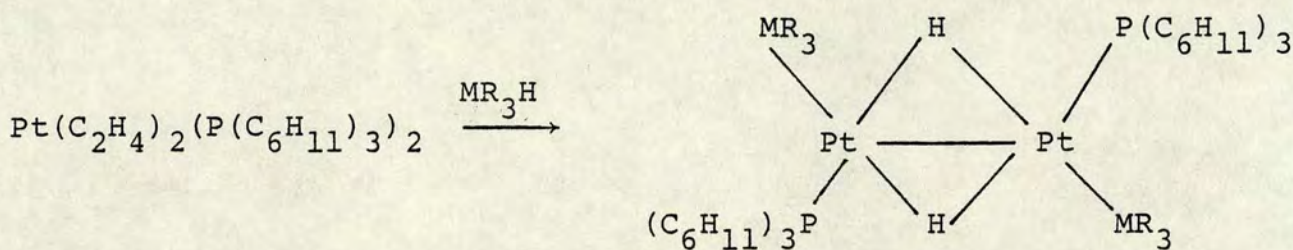


In 1976 Manzer and Parshall<sup>37</sup> reported the reaction





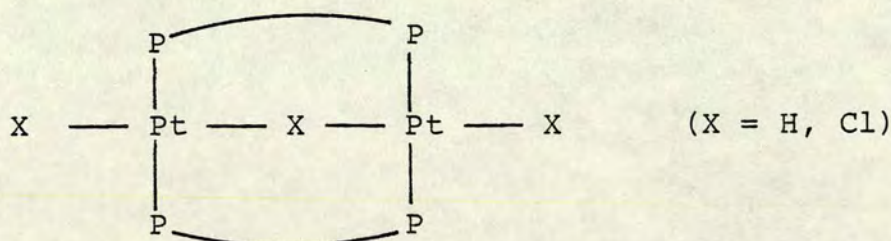
Platinum complexes containing hydride bridges have also been reported. Since 1976 several papers<sup>38,39</sup> have been published on reactions of the following series of compounds



M = Si, Ge      R = Cl, Me, Ph, CH<sub>2</sub>Ph, Et, OEt

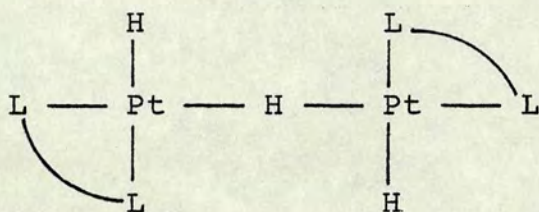
Although the bridging hydrides are not observed from the X-ray studies, the fact that they are present is confirmed from the bridge cleavage reactions they undergo. Treatment of  $\{\text{Pt}(\text{H})(\text{SiMe}_2\text{Ph})[\text{P}(\text{C}_6\text{H}_{11})_3]\}_2$  with t-butyl isocyanide, trimethylphosphine, or dimethyl-phenylarsine afforded the terminal-hydridoplatinum complexes  $\text{PtH}(\text{SiMe}_2\text{Ph})[\text{P}(\text{C}_6\text{H}_{11})_3]_2^{\text{L}}$  (L = CNBu<sup>t</sup>, PMe<sub>3</sub>, or AsMe<sub>2</sub>Ph), apparently formed by symmetrical cleavage of the Pt(H)<sub>2</sub>Pt bridges.

Another bridged compound observed as an intermediate in the reaction of  $\text{PtCl}_2(\text{dppm})$ <sup>40</sup> (dppm = bis(diphenylphosphino)methane) with NaBPh<sub>4</sub> followed by HCl in boiling benzene was



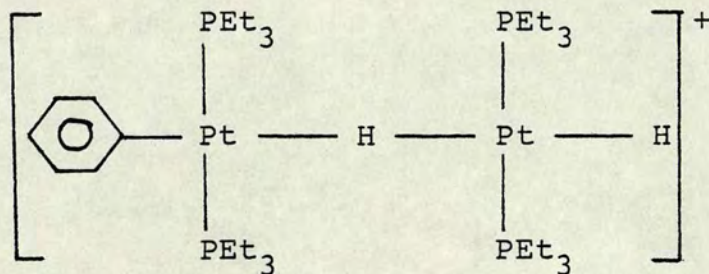


Another example where a single hydride bridge is postulated is <sup>41</sup>



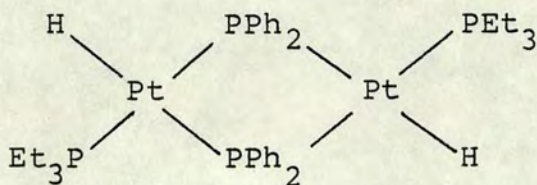
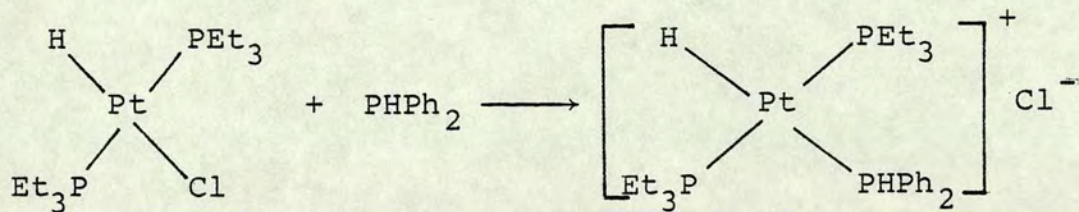
There is fast exchange between the bridging hydride and the terminal hydride, and even at  $-100^{\circ}\text{C}$  only one signal is observed. Terminal P-H stretches are observed in the infrared spectrum.

A complex isolated from the reaction of  $\text{trans}[\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2] + \text{NaBPh}_4$  <sup>42</sup> was found to be



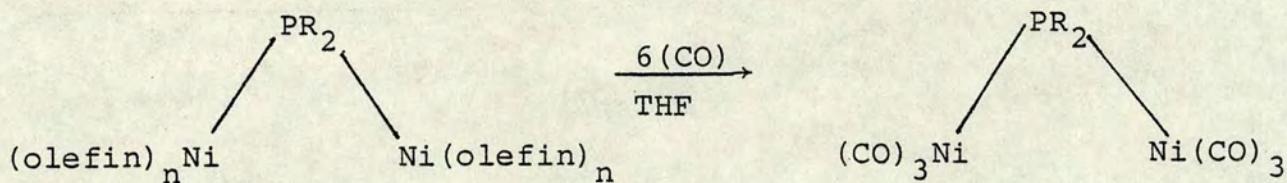
The structure has been proved by X-ray analysis.

Phosphine bridges have been known for some time. Chatt and Davidson <sup>43</sup> state that they are the strongest bridging group known in platinum complexes and report the following.

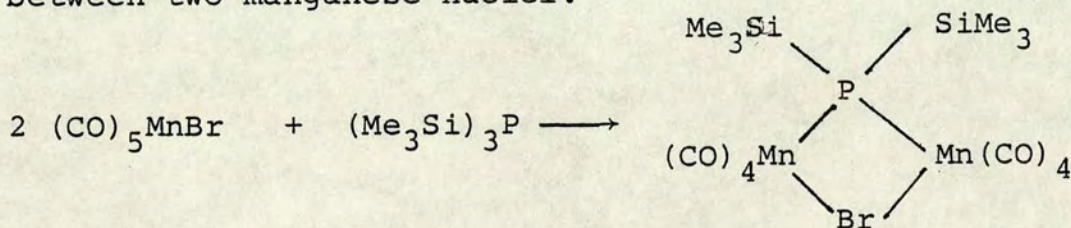




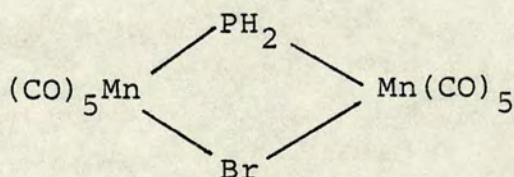
In one reported nickel complex<sup>44</sup> the phosphine bridge appears to be stable to ligand exchange.



Schafer<sup>45</sup> has reported formation of a PH<sub>2</sub> bridge between two manganese nuclei.

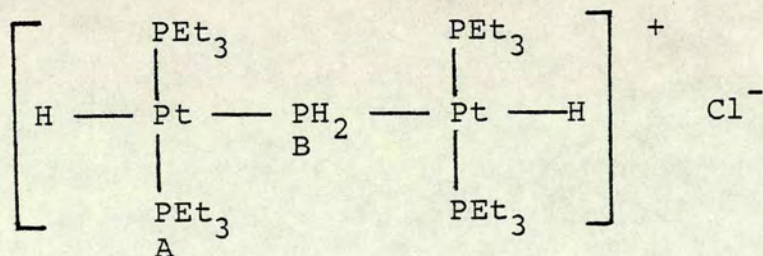


Reaction of this with methanol produced



Other major advances in synthesizing novel monobridged binuclear platinum complexes have come from work carried out in this department<sup>46,47</sup>.

Edward<sup>10</sup> found that reaction of H<sub>2</sub>PSiH<sub>3</sub> with PtClH(PET<sub>3</sub>)<sub>2</sub> yielded as one of the products

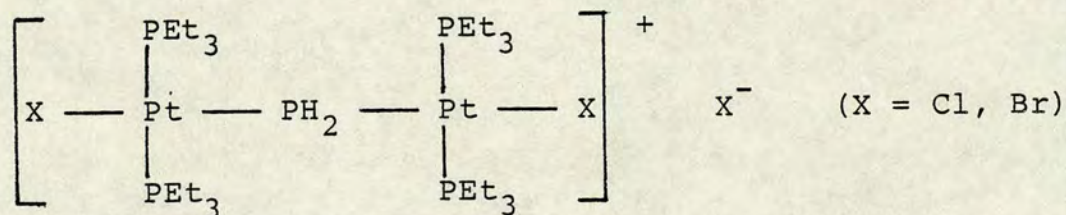




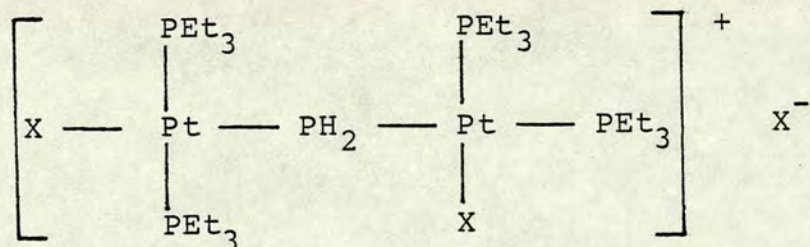
The product was clearly defined by its  $^{31}\text{P}$  n.m.r. spectrum. The resonance in the  $\underline{\text{P}}\text{Et}_3$  region appeared as a doublet with  $^{195}\text{Pt}$  satellites. The resonance in the  $\underline{\text{P}}\text{H}_2$  region appeared as a pseudo quintet of quintets. The pseudo quintet was of intensity 1:8:18:8:1 which arises from the probabilities of being bonded to two, one, or no  $^{195}\text{Pt}$  nuclei. This is characteristic of the group Pt-P-Pt. The quintet coupling was of the same magnitude as the doublet coupling and assigned as arising from  $^2J_{\text{P}^2\text{PtP}}$ .

The reaction was not clean because  $\text{SiH}_3\text{Cl}$  formed in the reaction reacted with Pt(II) species present. It was found that  $[\text{PtH}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  could be synthesized cleanly by reacting  $\text{PtClH}(\text{PEt}_3)_2$  with  $\text{H}_2\text{PSiMe}_3$  in toluene where the cation precipitated out of solution. There were no oxidative addition side reactions.

Henner extended this work to reactions of  $\text{X}_2\text{Pt}(\text{PEt}_3)_2$  with  $\text{H}_2\text{PSiMe}_3$ . This gave

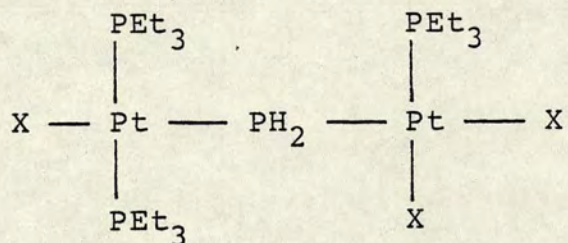


This species slowly isomerised to

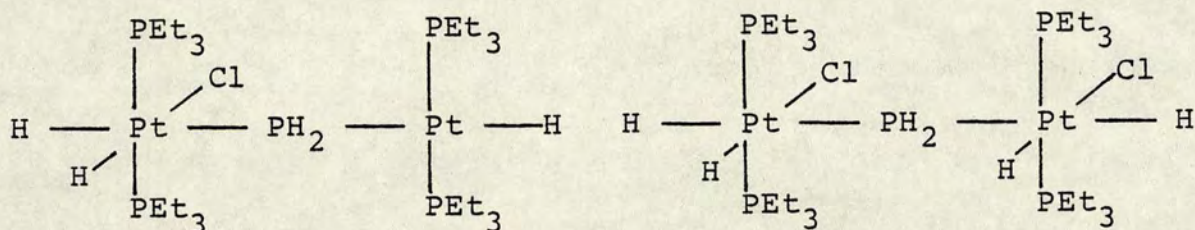




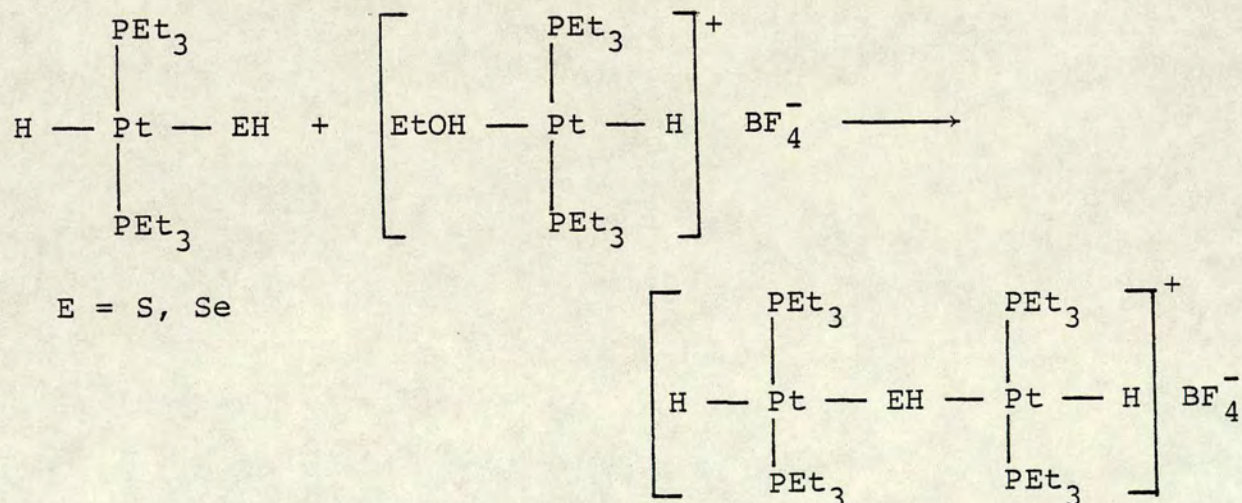
which then disproportionated to



$[\text{PtH}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  was allowed to react with HCl<sup>47,48</sup> to produce two species at  $-60^\circ\text{C}$  depending on the concentration of HCl used.

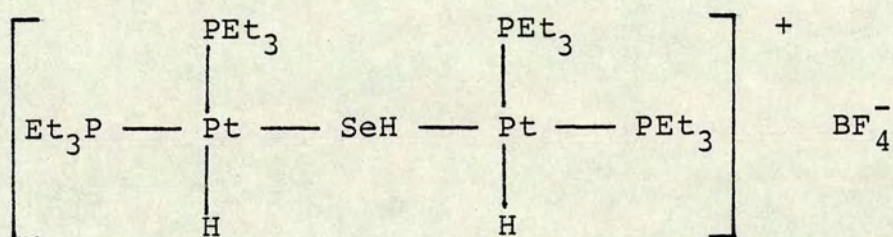


Robertson<sup>47</sup> synthesized complexes having SH and SeH bridging groups. Here the bridged compounds were formed from direct reaction of two platinum substrates.



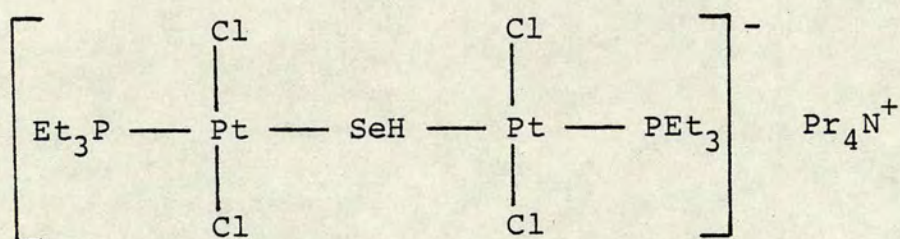
The Se system isomerized in solution to give



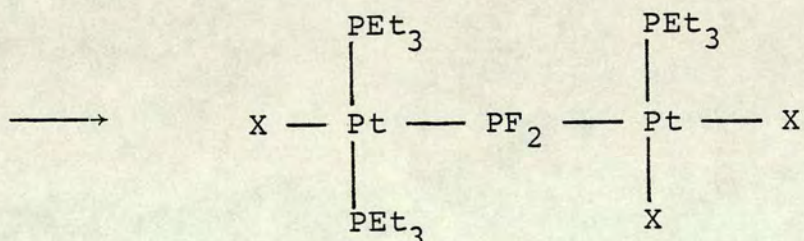
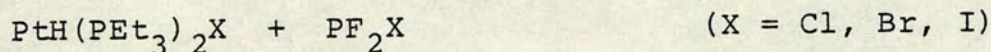


Attempts were made to carry out oxidative additions to these complexes but bridge cleavage appeared to be the initial reaction<sup>49</sup>. With HCl cis, cis, trans-[H<sub>2</sub>Pt(Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] was the major product. Attempts to deprotonate the bridge with bases failed.

Henderson<sup>50</sup> has studied the reaction of Pr<sub>4</sub>N<sup>+</sup>-[Cl<sub>3</sub>Pt(PEt<sub>3</sub>)]<sup>-</sup> + H<sub>2</sub>Se to give at -40°C,



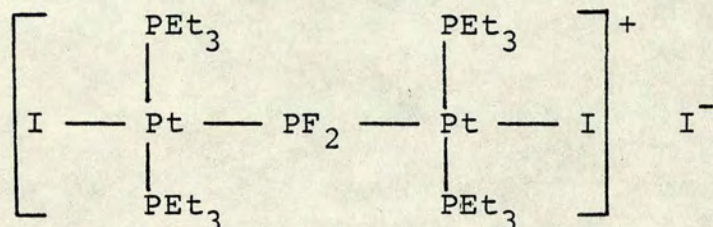
The other type of bridge synthesized in this group by Whitelock<sup>47,51,52</sup> has a PF<sub>2</sub> bridging ligand.



It has been found that the bromide and iodide are better synthesized by a metathesis of the chloride.



Whitelock<sup>53</sup> has very recently observed the low temperature intermediate for  $[\text{PtI}(\text{PEt}_3)_3]^+\text{BPh}_4^-$  with a four-fold excess of  $\text{PF}_2\text{I}$ .



In this thesis there are reported some more reactions of  $[\text{PtH}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$ .



## Nuclear Magnetic Resonance Spectroscopy (n.m.r.)

N.m.r. spectra may be obtained in two ways. The first is called the continuous wave method (C.W.). The area of the n.m.r. in which the observed nucleus resonates is scanned by varying the magnetic field and holding the radio frequency constant, or by varying the radio frequency and holding the magnetic field constant. The latter method is used when carrying out decoupling experiments.

The other method is the pulsed or Fourier Transform (F.T.) method. The region of the n.m.r. where the nuclei resonate is pulsed with a single frequency. The free induction decay (F.I.D.) of the observed nuclei is recorded, and by means of a Fourier Transform from the time domain into the frequency domain, the n.m.r. is produced in a usable form.

The C.W. method is only used now for observation of  $^1\text{H}$  and is now being superseded even for it by F.T. methods.

The two parameters obtained from the spectrum recorded are the chemical shift ( $\delta$ ) measured in p.p.m. from some standard, and the spin spin coupling ( $J$ ) measured in Hz. These both can give a great deal of information on the molecule being observed.

The phenomenon of the chemical shift arises because of the shielding of the nuclei from the external magnetic field by the surrounding electrons. Hydrogens bonded to a transition metal resonate at low frequency because the



hydride is shielded by electrons in  $d_{xy}$ ,  $d_{xz}$  or  $d_{yz}$  orbitals on the metal. An electron withdrawing group trans to the hydride will tend to make it resonate at higher frequency, whereas an electron releasing group will tend to make it resonate at lower frequency. A hydride trans to CO on Ir(III) resonates at higher frequency (-9 to -11 ppm) than a hydride trans to a halogen (-15 to -20 ppm). Carbonyls are very electron withdrawing.

Trends like this are observed for nuclei other than  $^1\text{H}$ . For  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$   $\delta\text{p} = 12$  ppm, whereas for  $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$   $\delta\text{p} = 22$  ppm. Cl is more electron withdrawing than I and hence deshields the phosphorous more than I.

The chemical shift of  $\underline{\text{PEt}}_3$  bound to Ir(I) comes above 10 ppm, but  $\underline{\text{PEt}}_3$  bound to Ir(III) resonates at less than 0 ppm a difference that may be an effect of changing electron density.

Spin spin coupling also provides information on the stereochemistry within a molecule. The size of the coupling constant between trans ligands is in general greater than that for cis ligands. Couplings are transmitted by electrons in bonds and trans ligands share more common s, p, and d orbitals than do cis ligands. e.g.  $^2\text{J}_{\text{H Ir P}(t)} \sim 120$  Hz whereas  $^2\text{J}_{\text{H Ir P}(c)} \sim 20$  Hz.

It has been put forward that the coupling constants are related to the s character shown by the ligands<sup>54</sup>.



Pople and Santry<sup>55</sup> give the approximate expression for the coupling constant ( $J_{PtP}$ ) as

$$J_{PtP} \propto \gamma_{Pt} \gamma_P \Delta E^{-1} \alpha_{Pt}^2 \alpha_P^2 |\psi_{Pt}(6s)(0)|^2 |\psi_P(3s)(0)|^2$$

$\gamma$  - gyromagnetic ratio

$\Delta E$  - mean excitation energy

$\alpha_X^2$  - s character of the hybrid used by X in the PtP bond.

$|\psi(0)|^2$  - electron density of indicated orbitals evaluated at parent nuclei.

Reeves<sup>56</sup> and co-workers showed that  $\Delta E^{-1}$  can be regarded as constant within a series of similar compounds.  $\gamma_{Pt} \gamma_P \Delta E^{-1}$  can be regarded as constant.

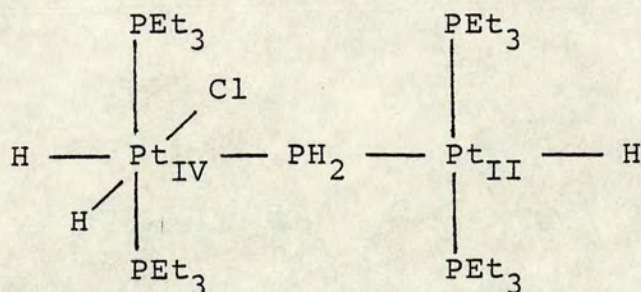
The s character of the hybrid used by a given atom X,  $\alpha_X^2$  in the X-Y bond appears to have a larger effect than the corresponding  $|\psi_X(0)|^2$  term in determining the value of the nuclear spin coupling constant  $J_{XY}$ .

For a square planar Pt(II) complex the bonding is  $dsp^2$  hybridized; the s orbital is shared between four ligands. For octahedral Pt(IV) complexes the bonding is  $d^2sp^3$  hybridized; the s orbital is shared between six ligands. The theoretical ratio of the s character of Pt(II) and Pt(IV) complexes is  $J_{PPtII}/J_{PPtIV} = 4/6 = 0.67$ .

This seems to work well.



e.g. for <sup>49</sup>



	$J_{P \text{ Pt IV}}$	$J_{P \text{ Pt II}}$	$J_{P \text{ Pt IV}}/J_{P \text{ Pt II}}$
<u>PH</u> <sub>2</sub> signal	830	1275	0.65
<u>PEt</u> <sub>3</sub> signal	1697	2494	0.68

Techniques of Nuclear Magnetic Double Resonance<sup>57</sup> can give useful information on the system being examined.

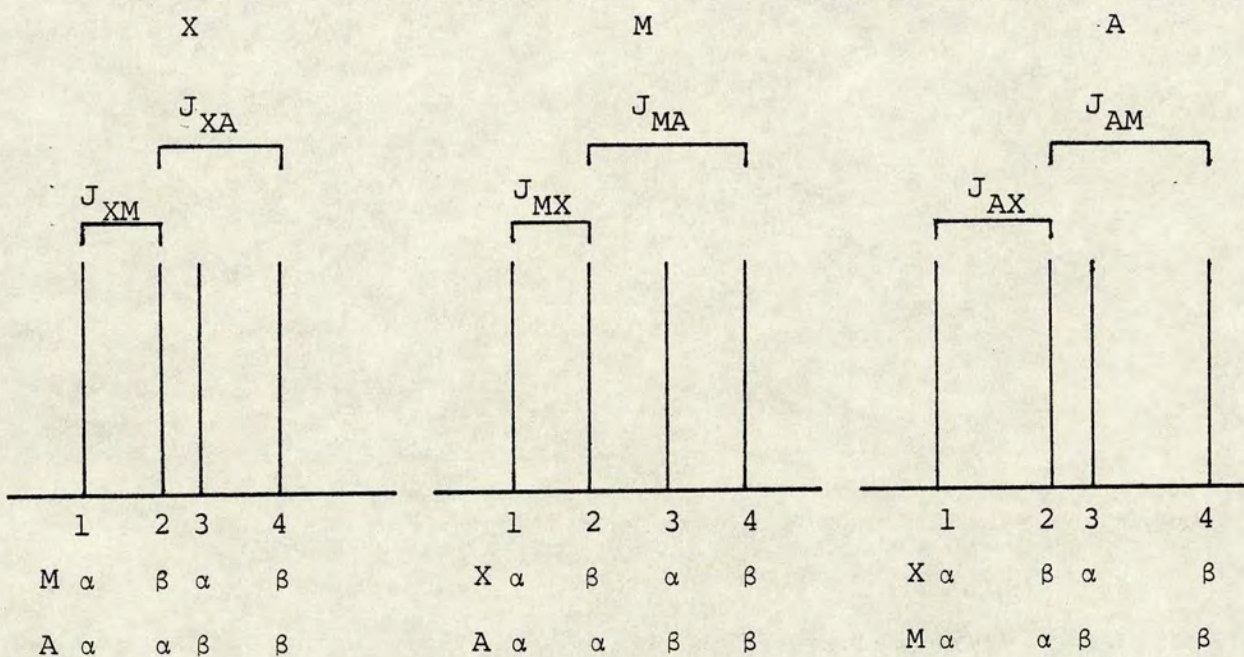
In the <sup>31</sup>P n.m.r. studies in this thesis a lot of use has been made of broad band proton decoupling. This effectively removes all <sup>1</sup>H couplings by using a wide spread radio frequency in the <sup>1</sup>H region. If this is not used the resonances from PEt<sub>3</sub> or PPh<sub>3</sub> ligands appear as broad, and additional narrow couplings are not observed.

High power spin decoupling at one frequency removes the coupling associated with the nucleus resonating at this frequency. This is a powerful tool in helping elucidate what certain couplings are and also in simplifying spectra. This can take the form of heteronuclear or homonuclear spin decoupling.



Selective spin decoupling uses much lower power irradiation and is used to irradiate particular lines in a multiplet while observing the effect on another multiplet. This type of experiment can give information on the relative signs of coupling constants.

If the A.M.X. spin system is considered, the spin states can be assigned as



This assumes that all couplings have the same sign.

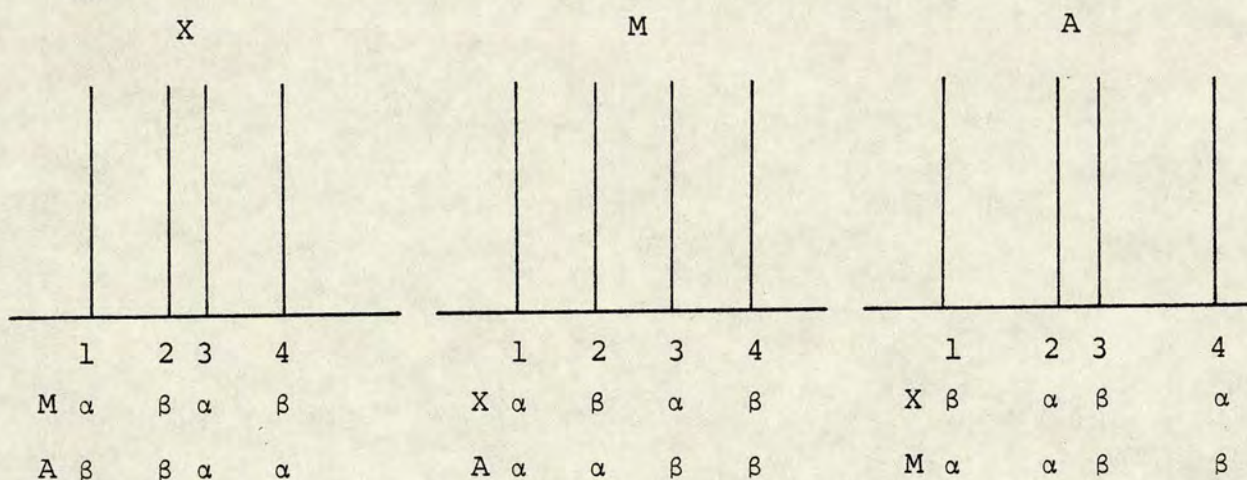
If X is observed while  $M_4$  is irradiated, the  $\beta$  spin of A is affected and hence lines  $X_3$  and  $X_4$  will be affected. If the power used is moderately low they will split into doublets. This is called spin tickling. If slightly more power is used they will converge, i.e. the doublet will be collapsed.



If X is observed while  $M_1$  is irradiated the  $\alpha$  spin of A is affected and hence lines  $X_1$  and  $X_2$  will be affected.

In this example because irradiating the high frequency part of the M spectrum affects the high frequency part of the X spectrum, and irradiation of the low frequency part of the M spectrum affects the low frequency part of the X spectrum, the relative signs of the coupling constants  $J_{MA}$  and  $J_{XA}$  are the same. In such an experiment the couplings compared are to the nucleus that is neither observed or irradiated.

If the sign of  $J_{AX}$  were opposite to those of  $J_{MX}$  and  $J_{AM}$ , the spin states would be assigned as:-



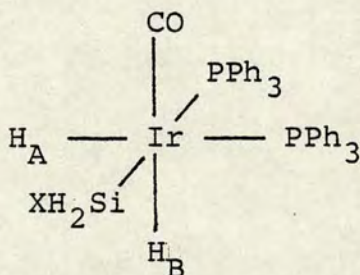
If X is observed while  $M_4$  is irradiated, the  $\beta$  spin of A is affected and hence lines  $X_1$  and  $X_2$  are affected. If X is observed while  $M_1$  is irradiated the  $\alpha$  spin of A is affected and hence  $X_3$  and  $X_4$  are affected.

In this example because irradiation of the high frequency part of the M spectrum affects the low frequency part of the X spectrum, and irradiation of the low frequency part of the M spectrum affects the high frequency part of



the X spectrum, the relative signs of the coupling constants  $J_{MA}$  and  $J_{XA}$  are opposite.

When the difference in chemical shift between similar nuclei becomes close to the magnitude of the coupling constants, second order effects arise. This can lead to difficulty in the interpretation and analysis of n.m.r. spectra. Use of larger magnetic fields can overcome this because they increase the difference in chemical shifts. Bridges made use of a CW220 MHz  $^1\text{H}$  n.m.r. spectrometer in her studies on



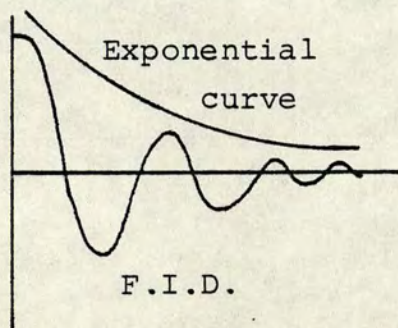
where  $\text{H}_A$  and  $\text{H}_B$  were showing second order effects.

A multinuclear F.T. spectrometer operating at a field strength of 360 MHz has been acquired by this department, and its use has made study of these complexes much simpler.

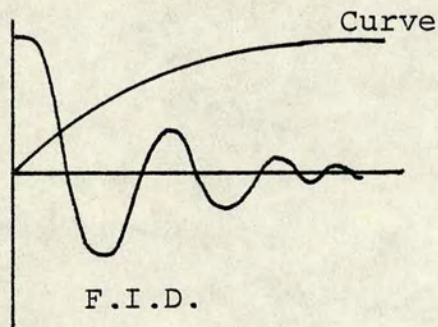
Use of line narrowing programmes to transform the F.I.D.s has been made to help improve the spectra obtained in the study of some complexes in this thesis.

Before transforming the F.I.D. to the frequency domain it is common practice to multiply the F.I.D. curve by some exponential curve.





Most information is in the first part of the F.I.D. and mostly noise is in the latter part. This multiplication reduces noise in the transformed spectrum. However, the latter part of the F.I.D. does contain structural detail, and if the F.I.D. is multiplied by a curve increasing asymptotically towards some fixed positive value, this detail is observed in the transformed spectrum.

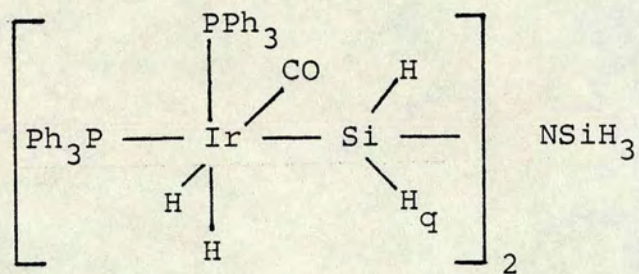


Where a lot of pulses have been accumulated detailed spectra with narrow lines are obtained. Couplings not resolved by the ordinary transform can be observed when the line narrowing programme is used.

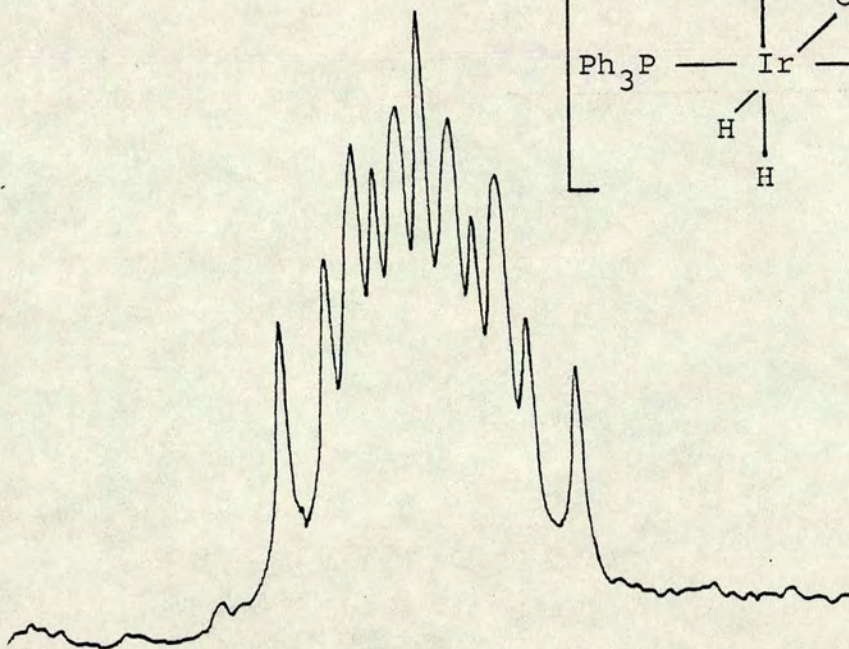


Figure 1.1

$^1\text{H}_q$  n.m.r. resonance of:

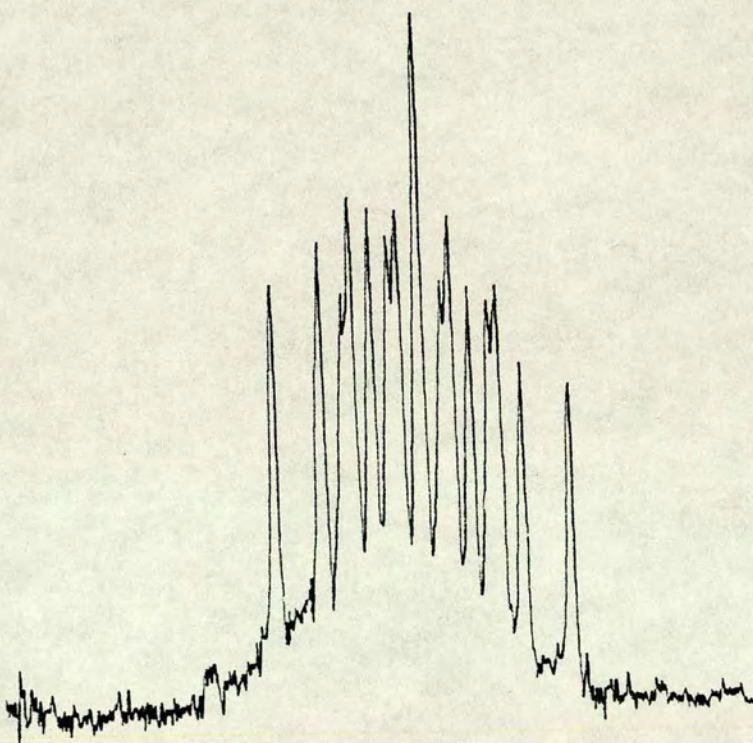


at 360 MHz



Normal Spectrum

1 cm = 5Hz



Line Narrowed Spectrum



Throughout this thesis all chemical shifts are measured in p.p.m., and all coupling constants in Hz.  $^1\text{H}$  chemical shifts are positive to high frequency of  $\text{SiMe}_4$ .  $^{19}\text{F}$  chemical shifts are positive to high frequency of  $\text{CCl}_3\text{F}$ .  $^{15}\text{N}$  chemical shifts are positive to high frequency of  $\text{Me}_4\text{N}^+\text{I}^-$ .  $^{31}\text{P}$  chemical shifts are positive to high frequency of  $\text{H}_3\text{PO}_4$ .  $^{29}\text{Si}$  chemical shifts are positive to high frequency of  $\text{SiMe}_4$ .



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CHAPTER 2

Reactions of  $\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2$

with some silyl compounds

(X = Cl, I)



2.1 Reaction of  $\text{Ir}(\text{CO})(\text{PET}_3)_2\text{X} + \text{N}(\text{SiH}_3)_3$  ( $\text{X} = \text{Cl}, \text{I}$ )

Previous research in this group<sup>1</sup> has shown that reaction of  $(\text{SiH}_3)_3\text{P}$  with  $\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2$  yields three compounds, dependant on the molecular ratio used, these having one, two or three iridium groups bound to silicon, while preserving the  $\text{Si}_3\text{P}$  skeleton. The complex  $\text{Pt HI}(\text{PET}_3)_2$  was found to react with  $(\text{SiH}_3)_3\text{P}$  where two platinum groups could be bonded to silicon, and  $(\text{SiH}_3)_3\text{N}$  where only one platinum group could be bonded to silicon<sup>2</sup>.

2.1.1  $\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2 + \text{N}(\text{SiH}_3)_3$  (excess)

$\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2$  was reacted with a three-fold excess of  $\text{N}(\text{SiH}_3)_3$  in benzene. Reaction took place as soon as the solvent thawed but in the  $^1\text{H}$  n.m.r. spectrum peaks due to several species were observed at first, but after several hours at room temperature only one species was present.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectra showed a singlet in the region associated with triethyl phosphine bound to six-coordinated iridium(III). This singlet appeared as a very narrow doublet when the reaction was carried out using trisilylamine containing 95%  $^{15}\text{N}$ . On selectively decoupling the ethyl and silyl proton frequencies, a doublet was obtained due to one hydride bound to iridium.

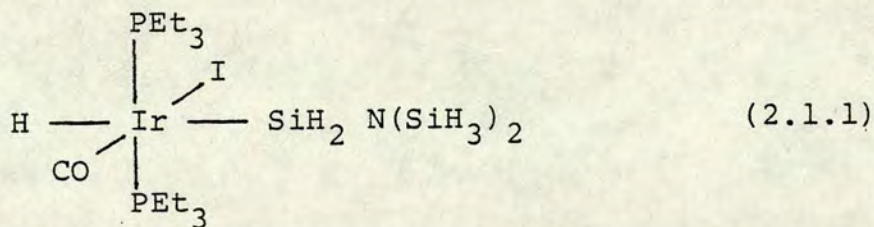
The  $^1\text{H}$  n.m.r. spectra showed resonances in the silyl region, the triethyl phosphine region, and the iridium hydride region.



There were two signals in the silyl region, a strong singlet and a weaker triplet of doublets. The triplet coupling was collapsed by irradiating at the frequency of the  $^{31}\text{P}$  resonance. The doublet coupling was assigned to  $^3J_{\text{HSiIrH}}$ . The intensity of the singlet was three times that of the multiplet. When the reaction was carried out using trisilylamine containing 95%  $^{15}\text{N}$  the singlet appeared as a doublet and the triplet of doublets as a pseudo-quartet of doublets. The extra doublet coupling on both resonances could be collapsed by irradiation at the same  $^{15}\text{N}$  frequency.

The hydride resonance appeared as a triplet of triplets, the large triplet coupling being collapsed by irradiation at the frequency of the  $^{31}\text{P}$  resonance, and the small triplet coupling by irradiation at the proton frequency which gave the multiplet in the silyl region. The hydride signal came in the region associated with H trans to carbonyl or silicon and because of the size of  $^3J_{\text{HSiIrH}}$  the trans ligand was taken to be  $-\text{SiH}_2-$ . The signal appeared as a triplet of pseudo-quartets in the  $^{15}\text{N}$  enriched complex. The pseudo quartet arose from two overlapping triplets due to the additional  $^3J_{\text{HIrSi}}^{15}\text{N}$  coupling.

This information gives the following structure:



Parameters are detailed in Table (2.1).



The compound was isolated as a white solid which gave carbon, hydrogen and nitrogen analysis in agreement with the above formulation. The infrared spectrum was recorded, showing characteristic absorptions for  $\nu_{\text{IrH}}$ ,  $\nu_{\text{SiH}}$  and  $\nu_{\text{CO}}$ .

2.1.2  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  excess +  $\text{N}(\text{SiH}_3)_3$ .

This reaction was carried out in benzene in two stages: first forming the mono species as in the last section, and then treating it when isolated with a two fold excess of  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$ .

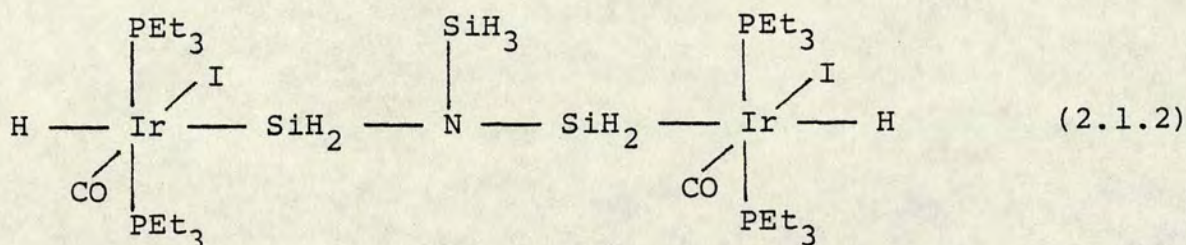
The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectra showed two singlets. The singlet at higher frequency was due to the excess of  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$ . The singlet at lower frequency appears in the region associated with triethylphosphine bound to six-coordinate iridium(III). On selectively decoupling the ethyl and silyl proton frequencies a doublet was obtained due to coupling between P and one hydride bound to iridium.

The  $^1\text{H}$  n.m.r. spectrum of the silyl region was similar to that for complex (2.1.1) already described, except that the peak due to the free  $\text{SiH}_3$  groups was of three-quarters the intensity of the multiplet.

The signal from the hydride was much less well resolved but could be seen as a broad triplet of triplets. On making the  $^{15}\text{N}$  enriched complex only a large broad triplet was observed.



This information is in harmony with the following structure for the complex:



Parameters are detailed in Table (2.1)

The compound was eventually isolated as a white solid though the separation from excess of  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  was difficult. Analysis for carbon, hydrogen and nitrogen fitted the above formulation.

The infra-red spectrum was recorded and showed characteristic absorptions for  $\nu_{\text{IrH}}$ ,  $\nu_{\text{SiH}}$  and  $\nu_{\text{CO}}$ .

### 2.1.3 Reaction of $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$ with $\text{N}(\text{SiH}_3)_3$

The reaction of  $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$  with  $\text{N}(\text{SiH}_3)_3$  gave similar products to reaction with the iodide, showing the same type of n.m.r. spectra. Parameters are detailed in Table (2.1).

### 2.1.4 Discussion of reactions with $\text{N}(\text{SiH}_3)_3$

Even on reacting  $(\text{SiH}_3)_3\text{N}$  with a large excess of  $\text{Ir}(\text{CO})(\text{PEt}_3)_2\text{X}$  only a bis species could be formed. This can be contrasted with the reaction of  $\text{N}(\text{SiH}_3)_3$  with  $\text{PtHI}(\text{PEt}_3)_2$



where only a mono species can be detected. As the final product of the latter reaction contains four-coordinated platinum, steric considerations make it somewhat surprising that more six-coordinated iridium centres than analogous four-coordinated platinum ones can be accommodated round the molecule of trisilylamine. The explanation could be that the iridium(III) oxidation state is very much more stable than platinum(IV) through which the platinum must go.

The reaction with  $N(SiH_3)_3$  can also be contrasted with the reactions of  $P(SiH_3)_3$  where a tris species can be formed with  $Ir(CO)I(PEt_3)_2$  and a bis species with  $PtHI(PEt_3)_2$ . Presumably the difference arises from steric factors.

It is interesting to note that if the bis species is left with excess of  $N(SiH_3)_3$  it will equilibrate after six hours to form the mono species as the sole Ir-Si species.

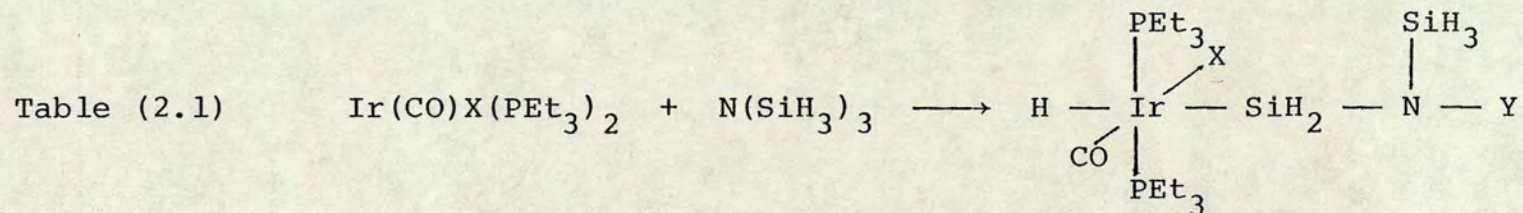
## 2.2 Reaction of $Ir(CO)(PEt_3)_2X$ with $(SiH_3)_2O$ ( $X = Cl, I$ )

Although this reaction had been studied before<sup>1</sup>, the evidence for a mono added species was inconclusive.

### 2.2.1 $Ir(CO)I(PEt_3)_2 + (SiH_3)_2O$

Under conditions using either a two-fold excess of disiloxane or an excess of iridium in benzene the same product was obtained.





	$\delta^{15}\text{N}$	$\delta\text{P}$	$\delta\text{SiH}_2$	$\delta\text{SiH}_3$	$\delta\text{IrH}$	$^2\text{J}_{\text{HP}}$	$^3\text{J}_{\text{HP}}$	$^3\text{J}_{\text{HH}}$	$^2\text{J}_{\text{H}_2\text{Si}^{15}\text{N}}$	$^2\text{J}_{\text{H}_3\text{Si}^{15}\text{N}}$	$^3\text{J}_{^{15}\text{NP}}$	$^3\text{J}_{\text{H}^1\text{IrSi}^{15}\text{N}}$
A	-6.5	-16.9	5.32	4.74	-9.82	15.2	6.9	2.3	4.9	4.3	0.2	1.9
B	-5.2	-16.7	4.85	5.47	-9.75	15.5	7.1	2.5	4.9	4.1	nm	nr
C		-6.6	5.12	4.73	-7.72	16.0(4)	6.0(4)	3.0(4)				
D		-6.9	5.28	4.79	-7.53	16.0(4)	6.0(4)	1.0(4)				

N.m.r. parameters obtained at room temperature using  $\text{C}_6\text{D}_6$  as solvent.

A      X = I      Y =  $\text{SiH}_3$   
 B      X = I      Y =  $\text{SiH}_2\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2\text{H}$   
 C      X = Cl      Y =  $\text{SiH}_3$   
 D      X = Cl      Y =  $\text{SiH}_2\text{Ir}(\text{CO})\text{Cl}(\text{PET}_3)_2\text{H}$

nm = not measured

nr = not resolved



The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum appeared as a singlet in the region associated with triethylphosphine bound to six-coordinate iridium(III). On selectively decoupling the ethyl and silyl proton frequencies the signal was split into a doublet indicating one hydride bound to iridium.

The  $^1\text{H}$  n.m.r. spectra (see Figure 2.1) showed resonances in the silyl region, the triethylphosphine region, and the iridium hydride region.

The silyl resonance appeared as a triplet of doublets, the triplet being collapsed by irradiation of the frequency of the  $^{31}\text{P}$  resonance. The doublet was assigned as due to  $^3\text{J}_{\text{HSiIrH}}$ .

The iridium hydride resonance appeared as a triplet of triplets in the region associated with H trans to carbonyl or silicon, and, because of the magnitude of  $^3\text{J}_{\text{HSiIrH}}$ , the trans-ligand atom was supposed to be silicon. The wide triplet could be collapsed by irradiation of the  $^{31}\text{P}$  frequency and the small triplet had the same coupling constant as that already assigned as  $^3\text{J}_{\text{HlrSiH}}$ .

The  $^{29}\text{Si}$  n.m.r. spectrum appeared as a very wide triplet of pseudo-quartets, the quartets arising from overlapping doublets of triplets. Broad band decoupling of the protons collapsed this to a narrow triplet due to coupling with triethyl phosphine. The wide triplet was due to coupling with the two protons bound to silicon and the small doublet to coupling with the hydride.



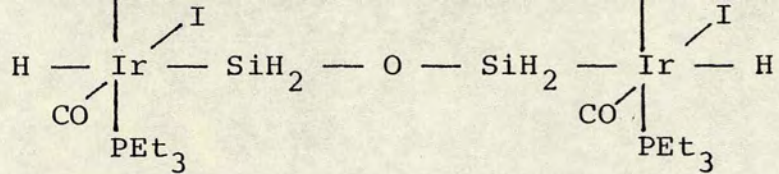
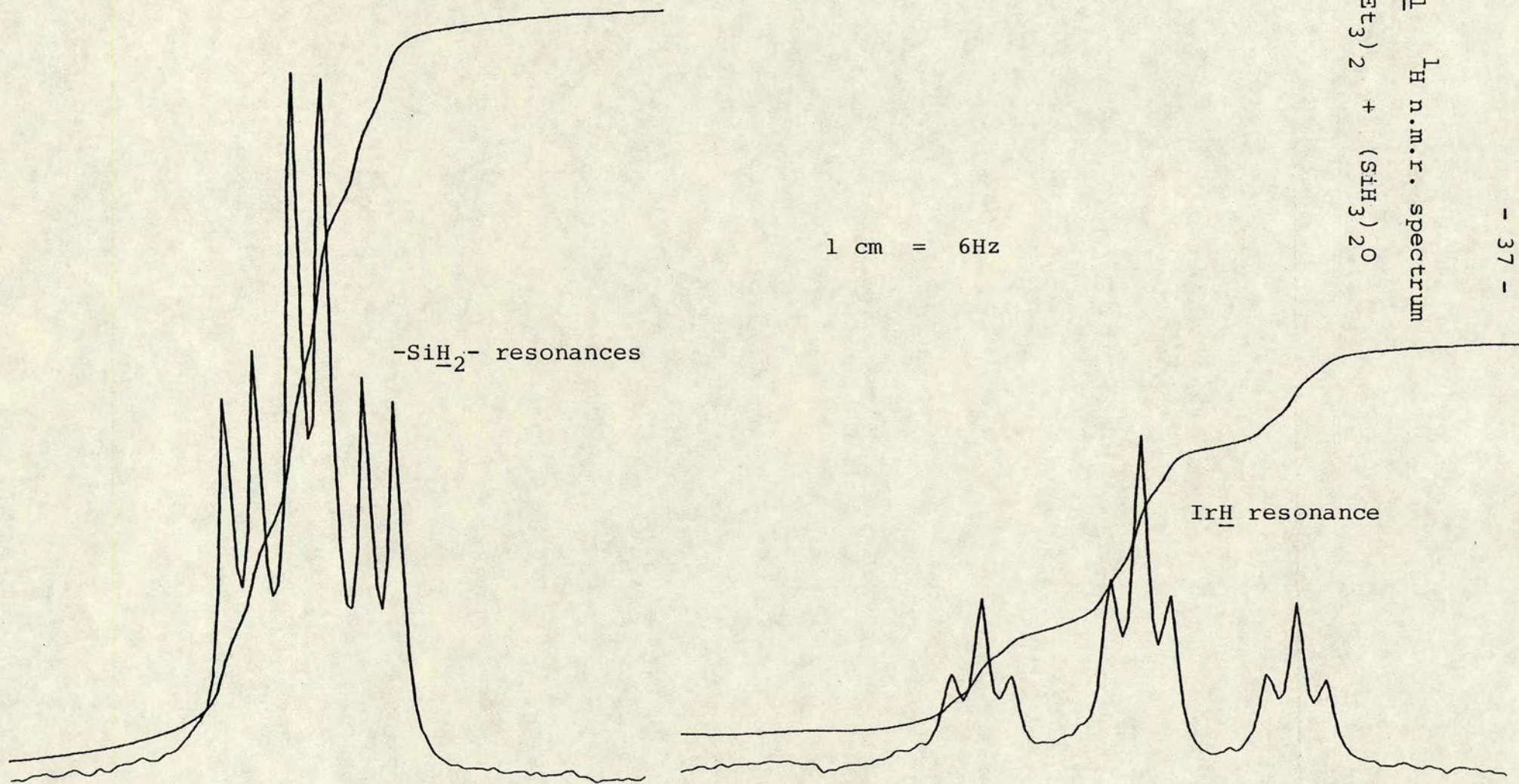
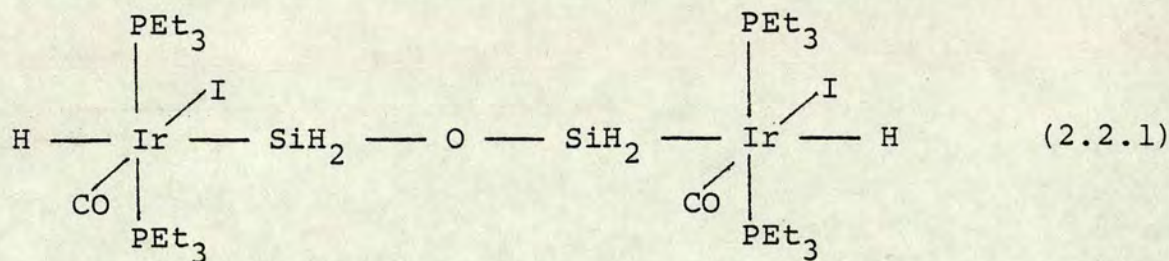


Figure 2.1  $^1\text{H}$  n.m.r. spectrum  
 $\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2 + (\text{SiH}_3)_2\text{O}$





All this information indicates the following structure:



Parameters are detailed in Table (2.2)

The compound was isolated as an air stable white solid which decomposed slowly in solution. Further agreement with the above structure was obtained from measurement of the compound's molecular weight in benzene and from carbon and hydrogen analysis.

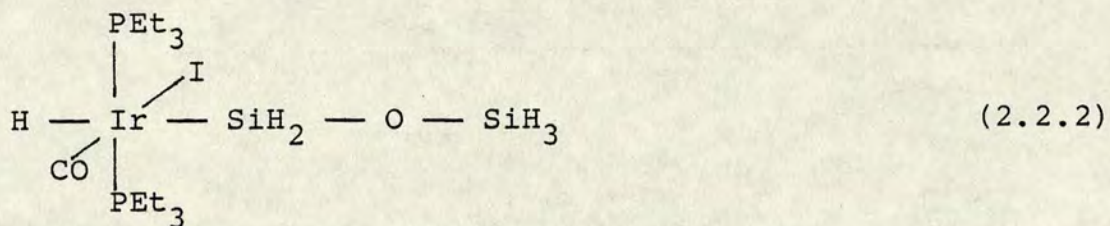
The infra-red spectrum was recorded showing characteristic absorptions for  $\nu_{\text{SiH}}$ ,  $\nu_{\text{CO}}$  and  $\nu_{\text{IrH}}$ .

On carrying out the reaction in light petroleum a gum dropped out of solution. When this was dissolved in benzene the  $^1\text{H}$  n.m.r. spectra showed resonances for complex (2.2.1) and resonances for a further compound. These appeared as a triplet of doublets very similar to those for complex (2.2.1) in the silyl region. There was also a singlet. This singlet was not due to unreacted disiloxane as the volatile materials had been removed from the system. The hydride resonance appeared as a triplet of triplets.

The chemical shifts and coupling constants were very similar to but different from those of complex (2.2.1).



These further resonances were assigned to:



Parameters are tabulated in Table (2.2)

When  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  was allowed to react with a very large excess of  $(\text{SiH}_3)_2\text{O}$  in benzene this species was again observed, as well as the bis-product.

### 2.2.2 Reaction of $(\text{SiH}_3)_2\text{O}$ with $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$

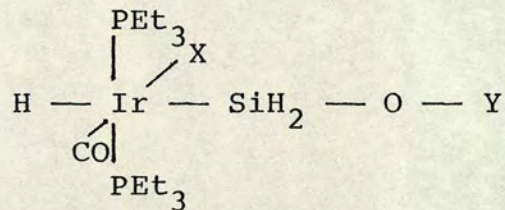
Reaction of  $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$  with  $(\text{SiH}_3)_2\text{O}$  followed a similar pattern to that with the iodide. No evidence was found for a mono added product though no real attempt was made to force one. A bis-added product was observed showing similar n.m.r. spectra to complex (2.2.1). This was further characterized by molecular weight, carbon and hydrogen analysis, and infra-red spectroscopy. Parameters are detailed in Table (2.2).

### 2.2.3 Discussion of reactions with $(\text{SiH}_3)_2\text{O}$

The observation that complex (2.2.1) was formed as the sole species when  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  reacted with an excess of disiloxane except when a very large excess of disiloxane was used indicates that the free  $\text{SiH}_3$  group of complex (2.2.2)



Table (2.2)  $\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2 + (\text{SiH}_3)_2\text{O} \longrightarrow$



	$\delta\text{P}$	$\delta\text{SiH}_2$	$\delta\text{SiH}_3$	$\delta\text{IrH}$	$^2\text{J}_{\text{HP}}$	$^3\text{J}_{\text{HP}}$	$^3\text{J}_{\text{HH}}$	$\delta^{29}\text{Si}$	$^2\text{J}_{\text{SiP}}$	$^1\text{J}_{\text{SiH}}$	$^2\text{J}_{\text{SiH}}$
A	-13.8	5.71	4.89	-9.83	15.9	6.7	3.1				
B	-13.8	5.78	-	-9.80	15.9	7.1	3.0	-30.1	10.7	196.0	10.4
C	-3.8	5.56	-	-7.92	15.9	6.2	2.5				

N.m.r. parameters obtained at room temperature using  $\text{C}_6\text{D}_6$  as solvent.

A X = I Y =  $\text{SiH}_3$   
 B X = I Y =  $\text{SiH}_2\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2\text{H}$   
 C X = Cl Y =  $\text{SiH}_2\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2\text{H}$



reacts faster with  $\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2$  than does disiloxane. When complex (2.2.1) is allowed to stand with a large excess of disiloxane there is no formation of complex (2.2.2), showing that if there is an equilibrium between disiloxane, mono-complex and bis-complex, it very much favours the bis-complex and free disiloxane. All that was observed was degradation of the peak due to  $(\text{SiH}_3)_2\text{O}$  and appearance of other peaks in this region as well as one due to  $\text{SiH}_4$ . Curtis et al<sup>3,4,5</sup> have observed the catalytic effect of iridium complexes on the disproportionation of  $(\text{SiMe}_2\text{H})_2\text{O}$  to give polymers and dimethylsilane.

### 2.3 Reaction of $\text{Si}_2\text{H}_6$ with $\text{Ir}(\text{CO})\text{I}(\text{PET}_3)_2$

T.E. Fraser investigated the reaction of disilane with  $\text{Ir}(\text{CO})\text{Cl}(\text{PET}_3)_2$  and observed formation of a mono product. J.E. Bentham<sup>6</sup> studied the reactions of  $\text{PtH}(\text{PET}_3)_2\text{X}$  with disilanyl and digermanyl compounds. He observed only mono added products except in the reaction of  $\text{ClH}_2\text{SiSiH}_2\text{Cl}$  with a two fold excess of trans  $\text{PtHI}(\text{PET}_3)_2$  which gave a symmetrical and complex  $^1\text{H}$ Si n.m.r. spectrum possibly consistent with the formation of  $\text{Cl}(\text{PET}_3)_2\text{PtSiHClSiHClPt}(\text{PET}_3)_2\text{Cl}$ .

#### 2.3.1 Using excess of $\text{Si}_2\text{H}_6$

The reaction was carried out in benzene and was complete as soon as the benzene had thawed out, the orange yellow of the starting material changing to colourless. The  $^1\text{H}$  n.m.r. spectra showed peaks for more than one species at first but after one hour at room temperature one species was observed.



The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectra showed a single line in the region associated with triethylphosphine bound to six-coordinated iridium(III). On selectively decoupling the ethyl and silyl frequencies a doublet was obtained indicating that there was one hydride bound to iridium.

The  $^1\text{H}$  n.m.r. spectra showed resonances in the silyl region, the triethylphosphine region, and the iridium hydride region.

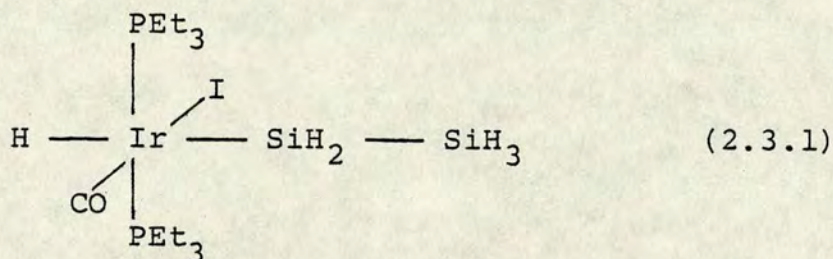
In the silyl region there were two resonances. The signal at higher frequency appeared as a triplet which could be collapsed by irradiation of the other silyl frequency. The other resonance in the silyl region was made up of seven lines. When the higher frequency silyl resonance was irradiated this collapsed to a triplet of doublets. The triplet was collapsed by irradiating the  $^{31}\text{P}$  frequency and the doublet was assigned to coupling with the hydride. Irradiating only the phosphorus frequency gave five lines caused by a doublet of overlapping quartets.

The signal at higher frequency was assigned to the free  $\text{SiH}_3$  group and that at lower frequency to the  $\text{SiH}_2$  bound to iridium. This is in contrast to the other systems examined where the  $\text{SiH}$  bound to the metal comes at higher frequency than the free  $\text{SiH}_3$  group.

The  $\text{IrH}$  was in the region associated with hydride trans to either carbonyl or silicon. It appeared as a triplet of triplets. The large triplet splitting was decoupled by irradiating the  $^{31}\text{P}$  frequency and the smaller



triplet by irradiating the SiH<sub>2</sub> frequency. Because of the size of <sup>3</sup>J<sub>H<sub>1</sub>IrSiH</sub> the hydride was assigned as trans to the SiH<sub>2</sub> group. From this information the structure was concluded to be:



Parameters are listed in Table (2.3)

### 2.3.2 Using excess of Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub>

This reaction was carried out in two stages, the mono-product first being generated in situ and isolated followed by addition of further Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub>.

The <sup>31</sup>P n.m.r. spectrum was similar to that of the mono species.

The <sup>1</sup>H n.m.r. spectrum showed resonances in the silyl region, the triethyl phosphine region, and the iridium hydride region.

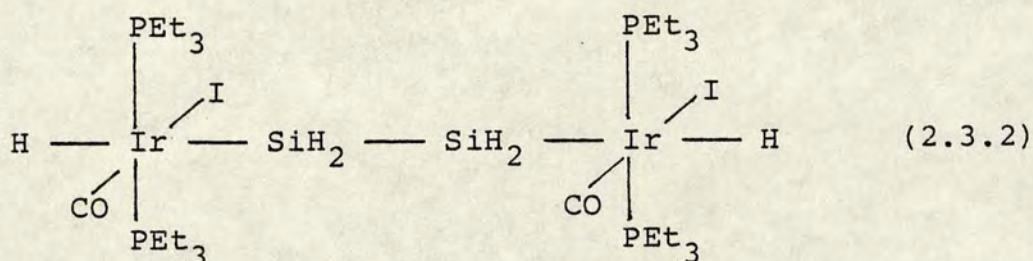
The SiH signal was symmetric, broad and structureless but sharpened to a singlet on decoupling at the phosphorus and IrH frequencies.

The IrH signal appeared as a broad triplet; on closer examination each line was found to have shoulders as if made up of broadened triplets. <sup>1</sup>H decoupling at the silyl



frequency removed these shoulders to give sharper lines. Irradiating the  $^{31}\text{P}$  frequency gave a broad singlet which sharpened on simultaneous irradiation of the silyl frequency. The hydride resonance appeared in the region associated with H trans to carbonyl or silicon and as most reactions with silyls appear to produce a trans added product is assigned as being trans to Si.

The information suggests the following structure:



Parameters are detailed in Table (2.3)

The breadth of the resonance and lack of structure is due to the  $\text{SiH}_2$  protons showing second order effects.

The compound was isolated as a white solid whose carbon and hydrogen analysis agreed with the above structure.

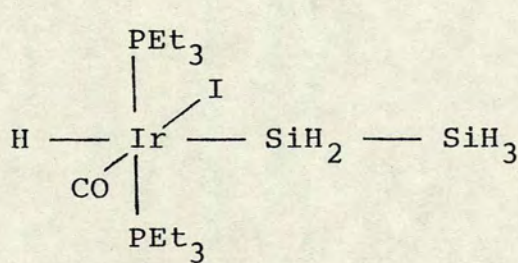
The infra-red spectrum was recorded showing characteristic absorptions for  $\nu_{\text{SiH}}$ ,  $\nu_{\text{CO}}$  and  $\nu_{\text{IrH}}$ .

#### 2.4 Reaction of $\text{SiH}_n\text{F}_{4-n}$ with $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$

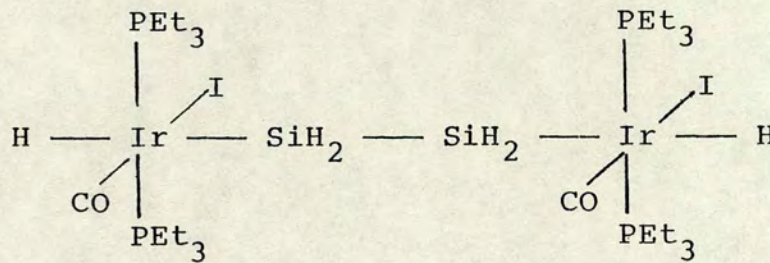
These reactions were carried out in order to characterize some of the novel species found in the reactions with  $\text{BF}_3$  discussed in the next section.



Table 2.3  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2 + \text{Si}_2\text{H}_6 \longrightarrow$



A



B

	$\delta_P$	$\delta_{\text{SiH}_2}$	$\delta_{\text{SiH}_3}$	$\delta_{\text{IrH}}$	$^3J_{\text{HSiSiH}}$	$^3J_{\text{HIrSiH}}$	$^2J_{\text{HIrP}}$	$^3J_{\text{HSiIrP}}$
A	-16.8	3.16	3.88	-9.74	3.2	3.5	15.7	8.1
B	-16.1	3.39	-	-9.46	-	nr	16.5	nr

N.m.r. parameters obtained at room temperature using  $\text{C}_6\text{D}_6$  as solvent.



#### 2.4.1 Reaction with SiH<sub>3</sub>F

Equimolar amounts of Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub> and SiH<sub>3</sub>F were allowed to react in toluene. Reaction started as soon as the toluene began to thaw, the solution going from orange yellow to almost colourless.

The <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectra (see Figure 2.2) showed a doublet assigned as <sup>3</sup>J<sub>PIrSiF</sub> in the region associated with triethylphosphine bound to six-coordinate iridium(III). On selectively decoupling the ethyl and silyl frequencies a triplet was obtained. The extra doublet causing this was due to one hydride bound to iridium.

The <sup>1</sup>H n.m.r. spectra showed resonances in the silyl region, the triethylphosphine region and the iridium hydride region.

The signal in the silyl region (see Figure 2.3) appeared as a wide doublet of triplets of doublets. The wide doublet was collapsed by irradiation of the frequency of the <sup>19</sup>F resonance and was assigned as <sup>2</sup>J<sub>HSiF</sub>. The triplet was collapsed by irradiating at the frequency of the <sup>31</sup>P resonance and was assigned as <sup>3</sup>J<sub>HSiIrP</sub>. The narrow doublet was assigned as <sup>3</sup>J<sub>HSiIrH</sub>.

The hydride was taken to be trans to the SiH<sub>2</sub>F group because of its chemical shift, and the sizes of <sup>3</sup>J<sub>HSiIrH</sub> and <sup>3</sup>J<sub>FSiIrH</sub>. The signal appeared as sixteen lines (see Figure 2.4) and could be interpreted as a triplet of doublets of triplets. The wide triplet was collapsed by irradiation



Figure 2.2

$^{31}\text{P}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2 + \text{SiH}_3\text{F}$

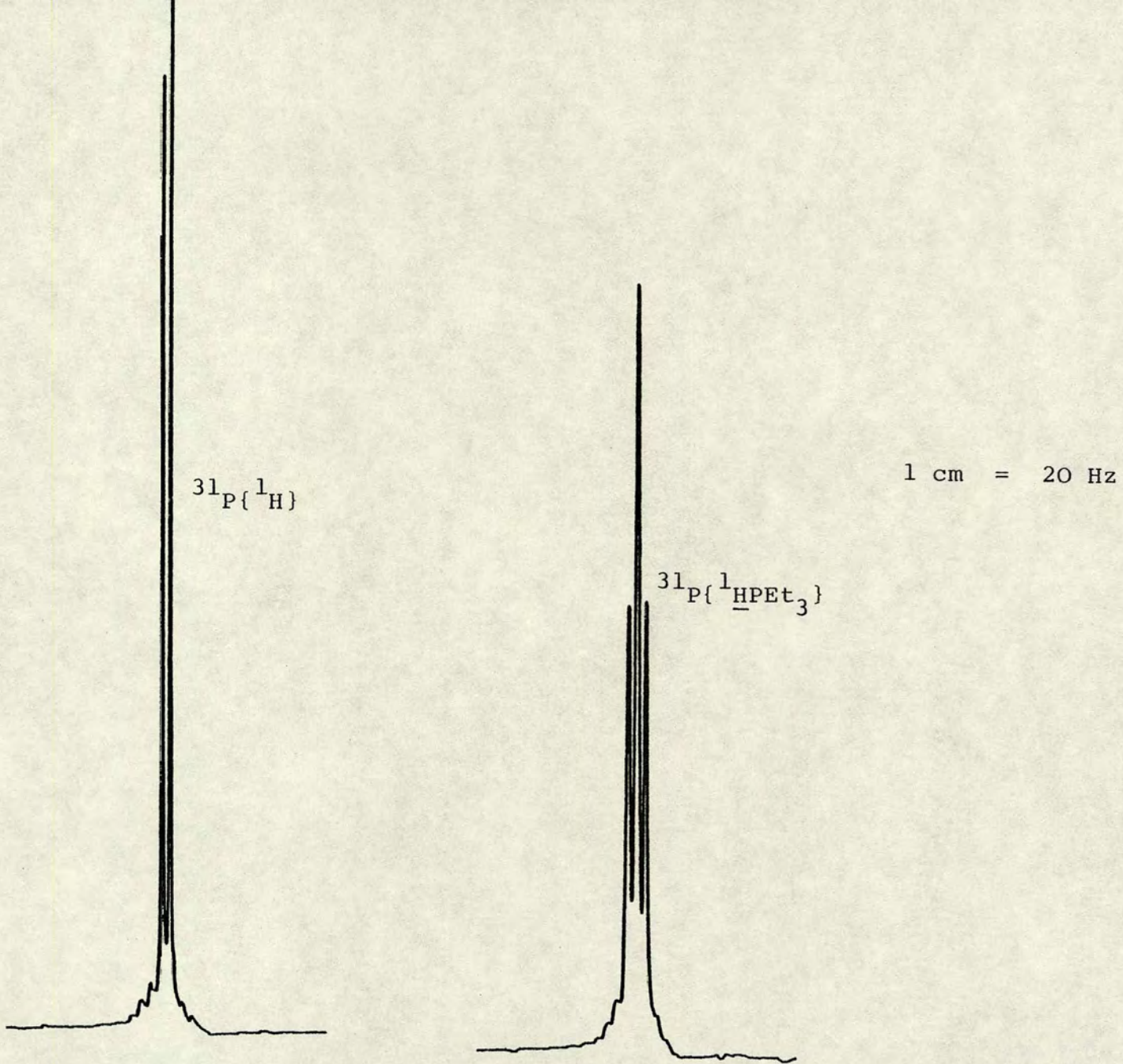
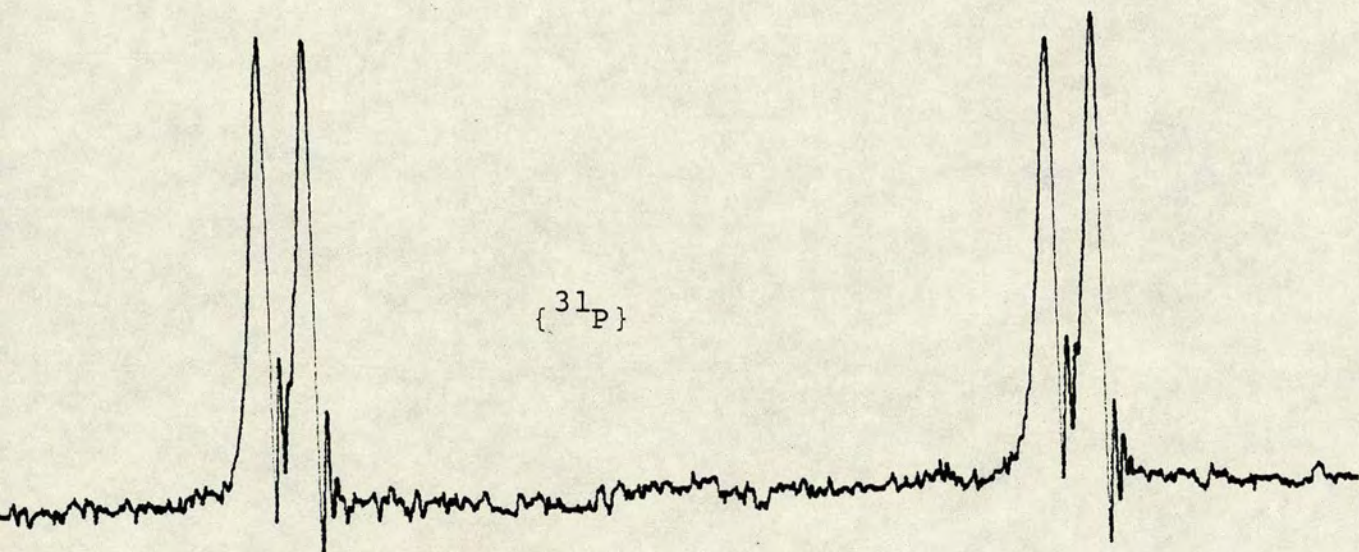
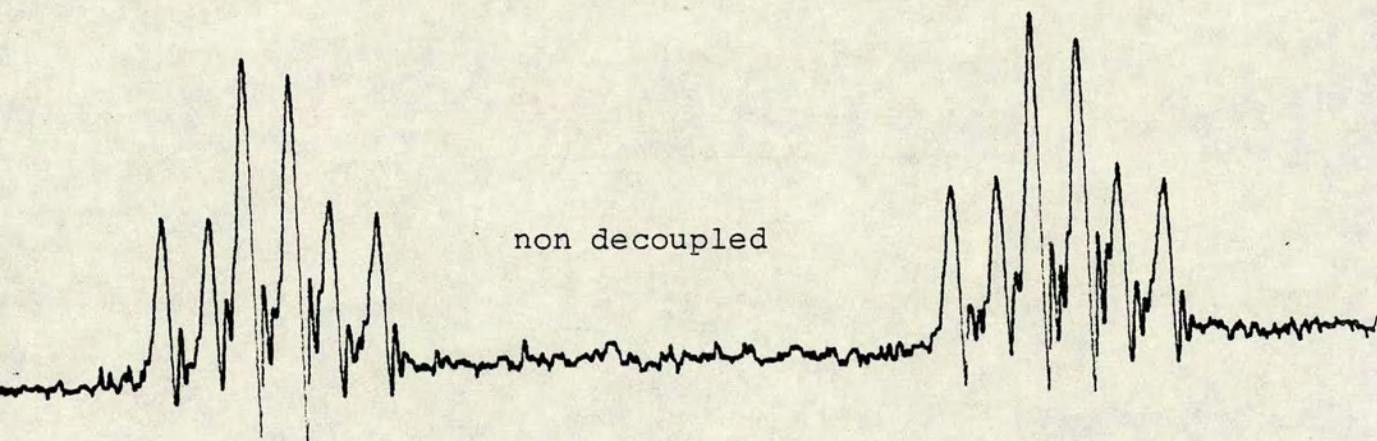


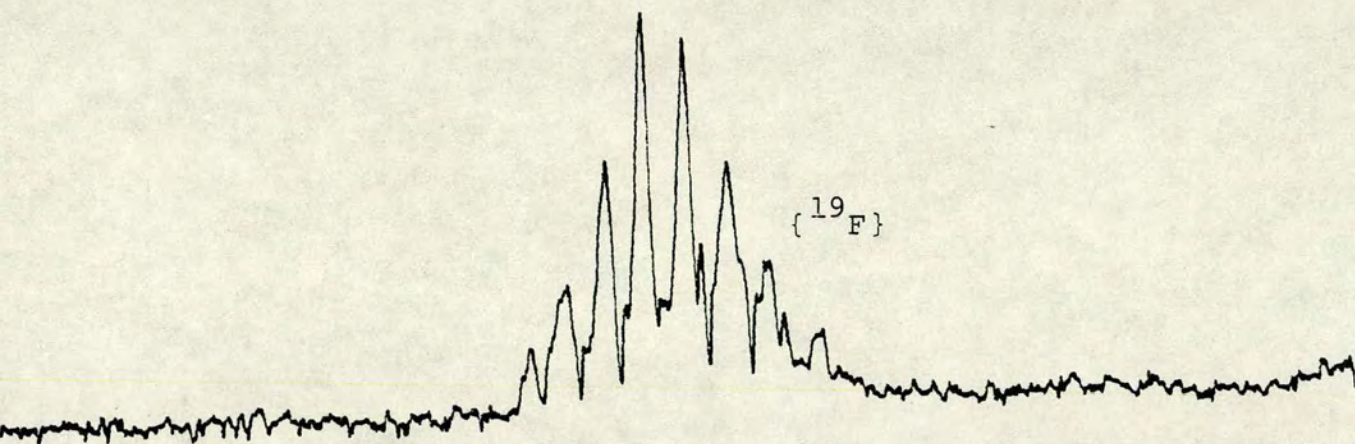


Figure 2.3

$^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2 + \text{SiH}_3\text{F}$



1 cm = 5 Hz

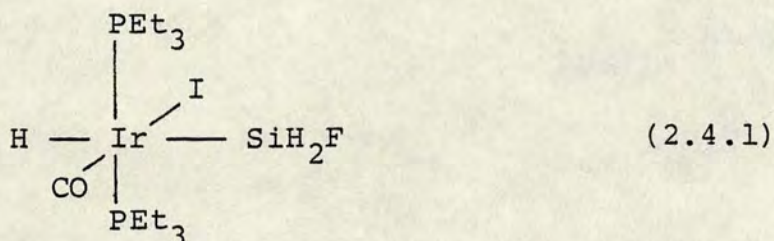




of the  $^{31}\text{P}$  frequency and the doublet by irradiation of the  $^{19}\text{F}$  frequency; the triplet had the same coupling constant as that already assigned as  $^3J_{\text{HIrSiH}}$ .

The  $^{19}\text{F}$  n.m.r. spectra (see Figure 2.5) appeared as a wide triplet of doublets of triplets. Each coupling had been previously assigned from the  $^1\text{H}$  or  $^{31}\text{P}$  n.m.r. spectra. The wide triplet was due to  $^2J_{\text{FSiH}}$ , the doublet to  $^3J_{\text{HIrSiF}}$ , and the triplet to  $^3J_{\text{FSiIrP}}$ .

This information suggests the following structure:



Parameters are detailed in Table (2.4)

The compound was isolated as a white solid whose carbon and hydrogen analysis fitted the above structure.

#### 2.4.2 Reaction with $\text{SiHF}_3$

The reaction was carried out in toluene using equimolar amounts of reactants. Reaction was slow compared to other oxidative additions with  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2$  and the solution took five minutes to lose its orange colour at room temperature.

The  $^{31}\text{P}$   $^1\text{H}$  n.m.r. spectra showed a narrow quartet assigned as  $^3J_{\text{PIrSiF}}$  in the region associated with



Figure 2.4  $^1\text{H}$  n.m.r. spectrum

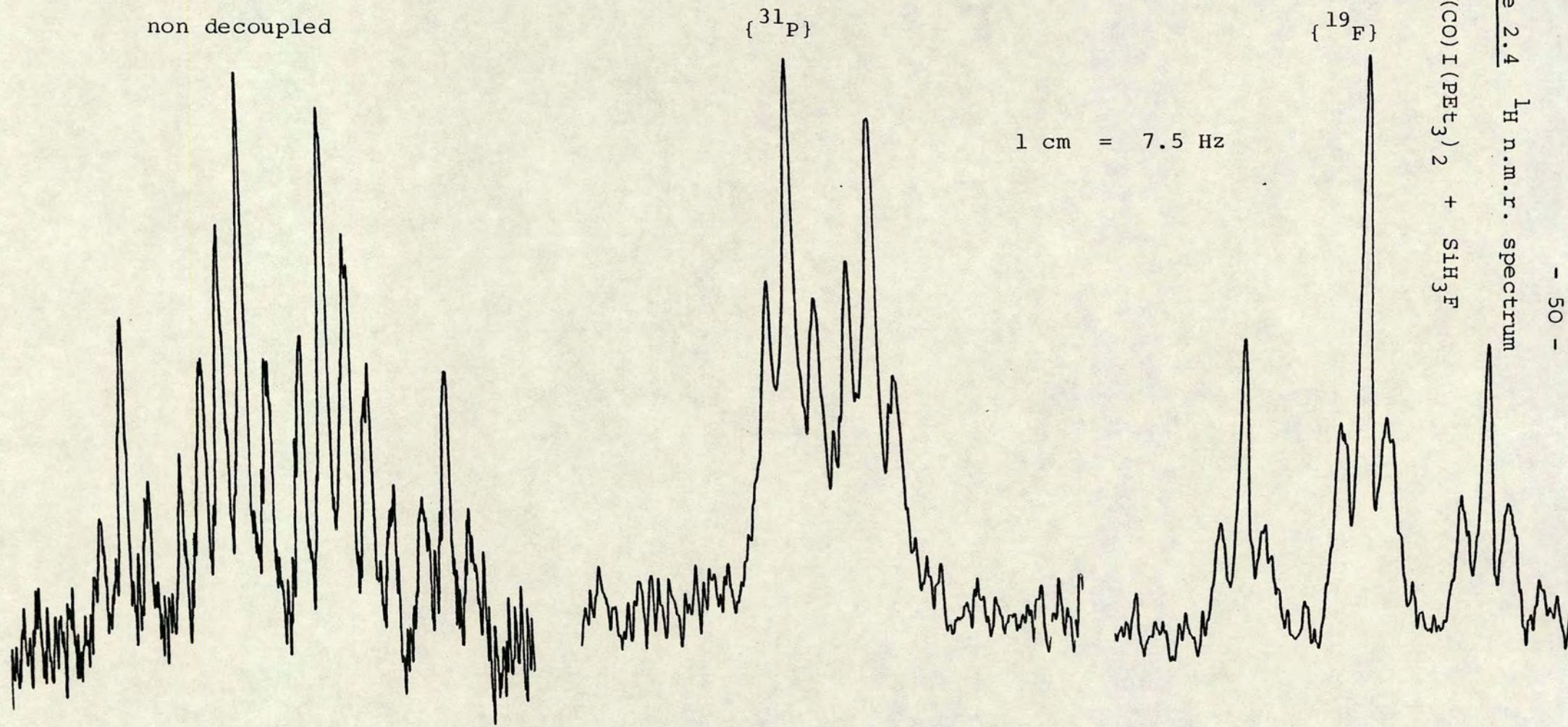
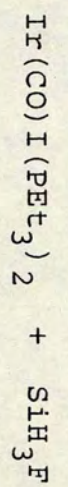
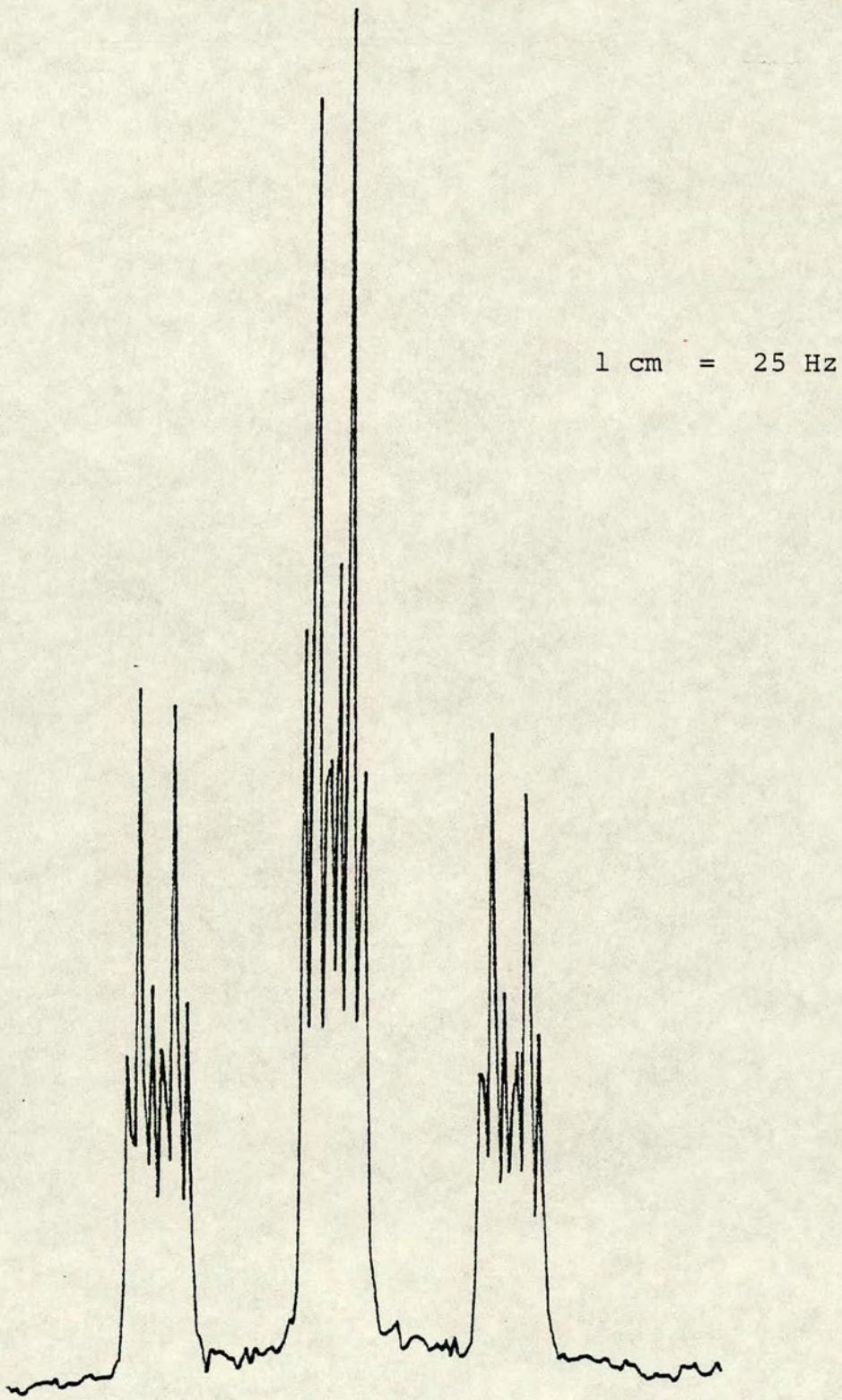




Figure 2.5  $^{19}\text{F}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2 + \text{SiH}_3\text{F}$





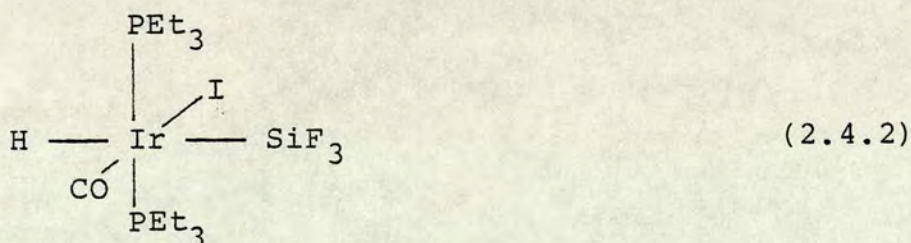
triethylphosphine bound to six-coordinated iridium(III). On selectively decoupling the ethyl and silyl frequencies this became six lines, the intensities indicating an overlapping doublet of quartets caused by coupling to one iridium hydride.

The  $^1\text{H}$  n.m.r. spectra showed resonances in the triethyl phosphine region and the iridium hydride region.

The hydride resonance was in the region associated with H trans to carbonyl or silicon and due to the wide coupling constant to the fluorine, H was assigned as trans to the  $\text{SiF}_3$  group. The signal appeared as a triplet of quartets. The quartet was collapsed by irradiation at the  $^{19}\text{F}$  frequency, and the triplet by irradiation at the  $^{31}\text{P}$  frequency.

The  $^{19}\text{F}$  n.m.r. spectrum showed a narrow doublet of triplets. Both couplings had been previously assigned from the  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectra, the doublet being due to  $^3J_{\text{FSiIrH}}$  and the triplet to  $^3J_{\text{FSiIrP}}$ .

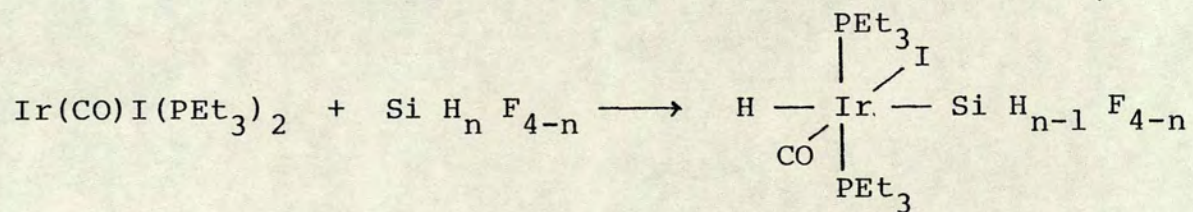
This information suggests the following structure:



Parameters are detailed in Table (2.4).



Table 2.4



	$\delta_{\text{P}}$	$\delta_{\text{P}}$	$\delta_{\text{H}}$	$\delta_{\text{H}}$	$^3\text{J}_{\text{PIrSiF}}$	$^2\text{J}_{\text{HSiF}}$	$^3\text{J}_{\text{HSiIrP}}$	$^2\text{J}_{\text{HIrP}}$	$^3\text{J}_{\text{HIrSiF}}$	$^3\text{J}_{\text{HIrSiH}}$
A	-13.71	-169.36	5.74	-9.99	3.4	50.5	5.6	15.4	10.1	2.9
B	-13.21	-91.07	-	-10.43	2.2	-	-	14.6	9.7	-

N.m.r. parameters recorded at room temperature using  $\text{C}_6\text{D}_5\text{CD}_3$  as solvent.

A  $\text{SiH}_3\text{F}$

B  $\text{SiHF}_3$



The compound was isolated as a white solid whose carbon and hydrogen analysis fitted the above structure.

## 2.5 Reactions of complexes formed in this Chapter

### 2.5.1 $[\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2\text{SiH}_2]_2\text{NSiH}_3 + \text{HCl}$

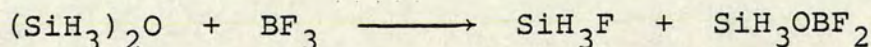
The reaction between  $\text{N}(\text{SiH}_3)_3$  and  $\text{HCl}$  to give  $\text{SiH}_3\text{Cl}$  is well documented<sup>7</sup>. Accordingly complex (2.1.2) was reacted with  $\text{HCl}$  to establish whether the coordinated silyl amine is susceptible to attack by  $\text{HCl}$ .  $^1\text{H}$  n.m.r. spectra confirmed that a reaction had occurred and by comparison with the parameters for  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2\text{SiH}_2\text{Cl}$  this was established to be the product of the reaction.

### 2.5.2 $[\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_2)]_2\text{O} + \text{base}$

At the present time there are no documented examples of four coordinate iridium(I) complexes containing an  $\text{SiH}_2\text{X}$  ligand. In an attempt to produce such a species compound (2.2.1) was reacted with a variety of bases ( $\text{Me}_3\text{N}$ , pyridene,  $\text{Bu}^t\text{Li}$ ) intended to abstract  $\text{HI}$ . No reaction was observed in any of the systems confirming the stability of iridium(III) relative to iridium(I).

### 2.5.3 $[\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_2)]_2\text{O} + \text{BF}_3$

The reaction between the Lewis acid  $\text{BF}_3$  and  $(\text{SiH}_3)_2\text{O}$  has been studied<sup>8</sup> and the following reaction observed:





Reaction of complex (2.2.1) did not show  $\text{BF}_3$  reacting as a Lewis acid but as a fluorinating agent to the silyl group.

Six iridium(III) species (see Figure 2.6 for idea of amounts) with silicon ligands were observed. The presence of  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_2\text{I})$  and of  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_3)$  was confirmed by comparison of their  $^{31}\text{P}$  and  $^1\text{H}$  n.m.r. spectra. Complex (2.4.1) was detected by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. and has been discussed in section 4. A species assigned as  $\text{Ir}(\text{CO})\text{H}_2(\text{PEt}_3)_2(\text{SiF}_3)$  from n.m.r. evidence will be discussed in the next section.

$^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  n.m.r. showed resonances for two other fluorinated silyl species.

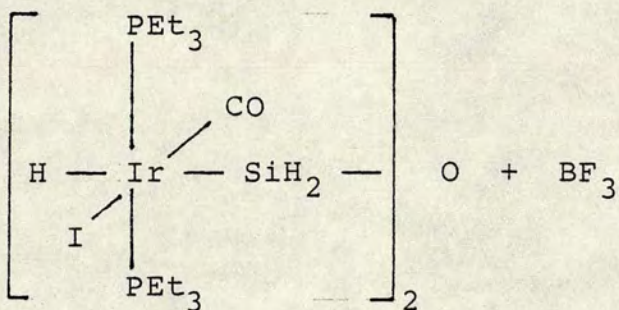
The more dominant of these will be discussed first.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum appeared as a triplet in the region associated with triethyl phosphine bound to six-coordinated iridium(III). On selectively decoupling the triethyl phosphine and silyl proton frequencies this resonance appeared as a quartet due to the additional coupling to one hydride bound to iridium.

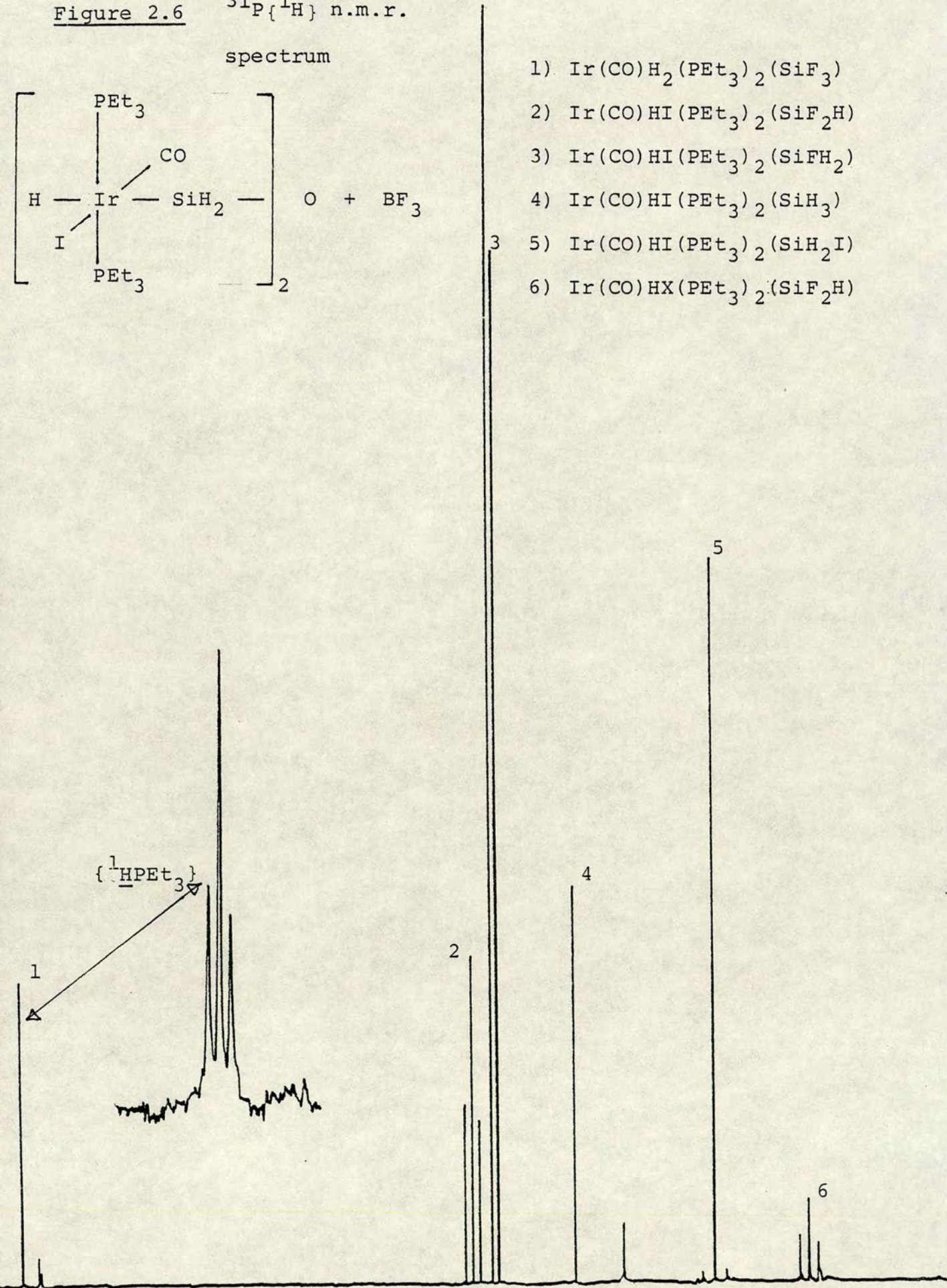
The  $^{19}\text{F}$  spectrum showed as a wide doublet of triplets of doublets. The wide doublet coupling was assigned as  $^2\text{J}_{\text{FSiH}}$ . The triplet coupling had the same coupling constant as the triplet observed in the  $^{31}\text{P}$  n.m.r. spectrum and was assigned as  $^3\text{J}_{\text{FSiIrP}}$ . The narrow doublet coupling was due to coupling to the trans hydride ( $^3\text{J}_{\text{FSiIrH}}$ ).



Figure 2.6  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum



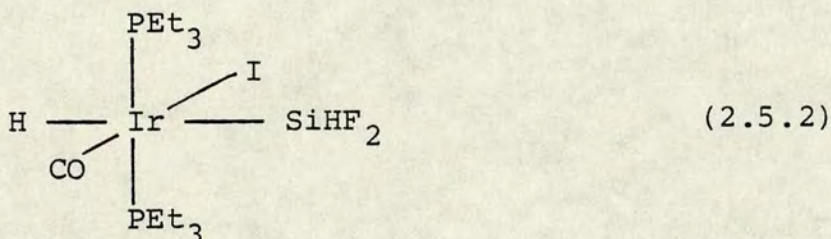
- 1)  $\text{Ir}(\text{CO})\text{H}_2(\text{PEt}_3)_2(\text{SiF}_3)$
- 2)  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiF}_2\text{H})$
- 3)  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiFH}_2)$
- 4)  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_3)$
- 5)  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_2\text{I})$
- 6)  $\text{Ir}(\text{CO})\text{HX}(\text{PEt}_3)_2(\text{SiF}_2\text{H})$





The  $^1\text{H}$  n.m.r. spectrum showed only a resonance in the hydride region attributed to this species. The resonance arising from the silyl proton would have been weak and may have been masked by the many other silyl resonances present. The resonance in the hydride region appeared as sixteen lines and could be interpreted as a triplet of triplets of doublets. The wider triplet coupling was assigned as  $^2\text{J}_{\text{HIrP}}$ . The narrower triplet coupling had been observed previously in the  $^{19}\text{F}$  n.m.r. spectrum and assigned as  $^3\text{J}_{\text{HIrSiF}}$ . The narrow doublet coupling was assigned as  $^3\text{J}_{\text{HIrSiH}}$ .

This information suggests the following structure:



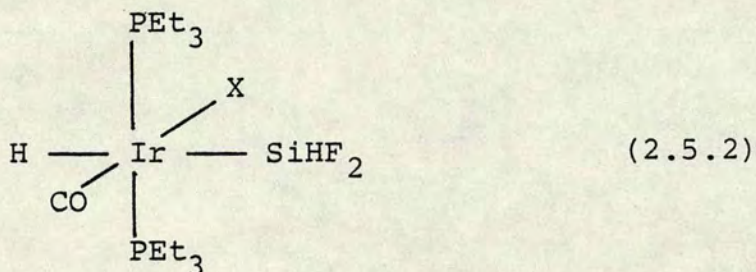
Parameters are detailed in Table (2.5(a)).

$^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. studies also showed the presence of an additional species giving spectra similar to those due to compound (2.5.1).



No  $^1\text{H}$  n.m.r. resonance due to the species was observed as it was a minor species and the areas in which its resonances occur would be masked by more dominant species.

The structure attributed to this was of the type:



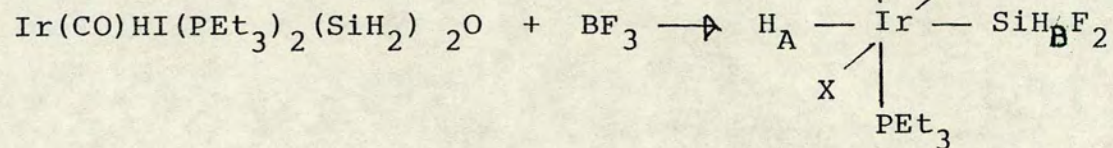
N.m.r. parameters are listed in Table (2.5(a)).

It is not certain what X is, the species where X = I already having been observed. A possible "pseudo halide" that could be in the reaction mixture is  $-\text{OSiH}_3$  but this is conjecture. The species was not observed in the reaction of compound (2.1.1) with  $\text{BF}_3$ .

Another worker<sup>9</sup> in this group has observed the following reaction.



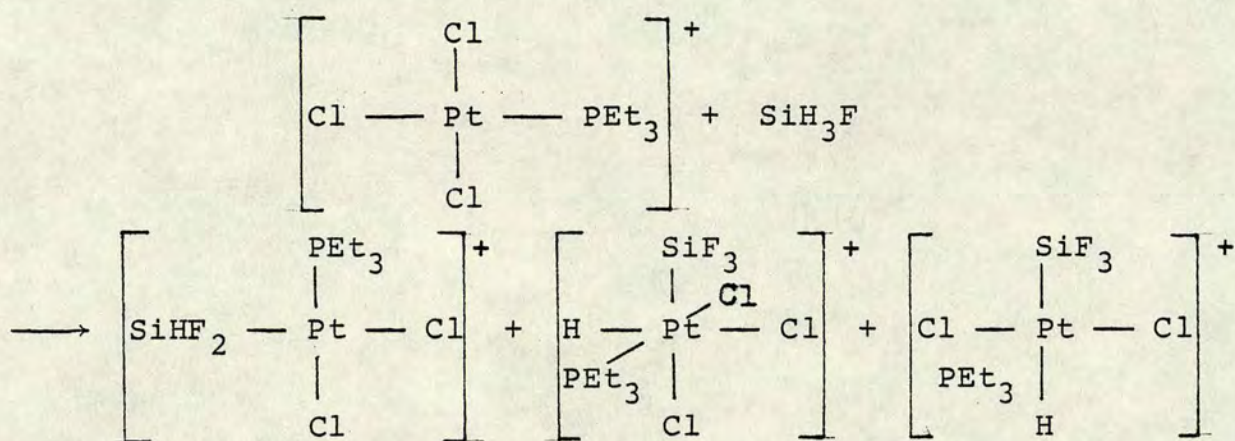
Table 2.5(a)



	$\delta_P$	$\delta_F$	$\delta_{H_A}$	$\delta_{H_B}$	$^3J_{\text{PIrSiF}}$	$^2J_{\text{FSiH}_B}$	$^3J_{\text{FSiIrH}_A}$	$^3J_{\text{H}_B\text{SiIrH}_A}$	$^2J_{\text{H}_A\text{IrP}}$
X = I	-12.97	-105.24	-9.79	n.o.	3.9	67.8	8.0	5.1	14.9
X = ?	-20.14	-111.79	n.o.	n.o.	4.8	61.9	8.5	n.o.	n.o.

N.m.r. parameters recorded at room temperature using  $\text{C}_6\text{D}_6$  as solvent.





No mono-fluoride species were observed and in the case of reaction with  $\text{GeH}_3\text{F}$  only trifluoro species were observed.

2.5.4  $\text{Ir}(\text{CO})\text{HI}(\text{PEt}_3)_2(\text{SiH}_2)\text{N}(\text{SiH}_3)_2 + \text{BF}_3$

Reaction of compound (2.1.1) with  $\text{BF}_3$  was confusing at first. The initial reaction with  $\text{BF}_3$  was fast but long term products were formed after several hours. These long term products were the same species as those formed when compound (2.2.1) was reacted with  $\text{BF}_3$ , except for compound (2.5.2).

The species assigned as  $\text{Ir}(\text{CO})\text{H}_2(\text{PEt}_3)_2(\text{SiF}_3)$  was characterized by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. studies.

The  $^{31}\text{P}$  resonance appeared as a singlet in the region associated with triethyl phosphine bound to six-coordinated iridium(III). Under conditions of the highest resolution a perturbed quartet was observed.  $^3\text{J}_{\text{FSiIrP}}$  is extremely small; this is unusual. However, three bond couplings vary in magnitude around zero and we must suppose that configurational changes are responsible for the small value



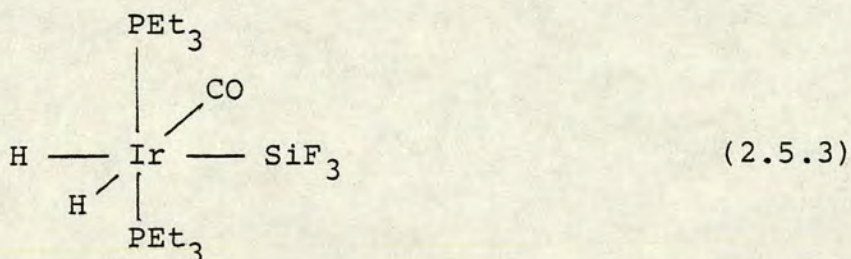
here. On selectively decoupling the ethyl proton frequencies a triplet was observed indicating two hydrides bound to iridium.

The  $^1\text{H}$  n.m.r. spectra (see Figure 2.7) showed two types of resonance in the region associated with a hydride trans to carbonyl or silicon. The signal at higher frequency appeared as a wide quartet of triplets of narrow doublets. The wide quartet coupling comes from the hydride being trans to an  $\text{SiF}_3$  group, two equivalent phosphorus nuclei give rise to the triplet pattern, and the narrow doublet coupling was assigned as  $^2J_{\text{HIrH}}$ .

The resonance at lower frequency showed as a triplet of pseudo quintets. The triplet coupling was due to  $^2J_{\text{HIrP}}$ . An overlapping doublet of quartets gave rise to the pseudo quintet where the doublet coupling was of similar magnitude to that already assigned as  $^2J_{\text{HIrH}}$ . The quartet coupling was due to coupling to the  $\text{SiF}_3$  group.

The  $^{19}\text{F}$  n.m.r. spectrum appeared as a wide doublet of doublets. The coupling constant for the wide doublet was due to coupling to a trans hydride and the smaller doublet from coupling to a cis hydride.

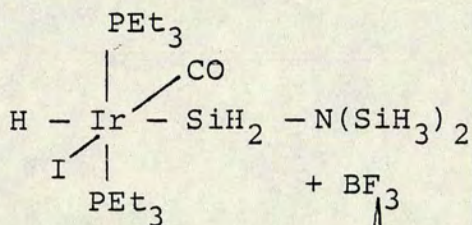
This information indicates the following structure:



Parameters are detailed in Table (2.5(b)).

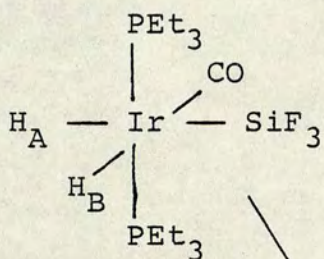
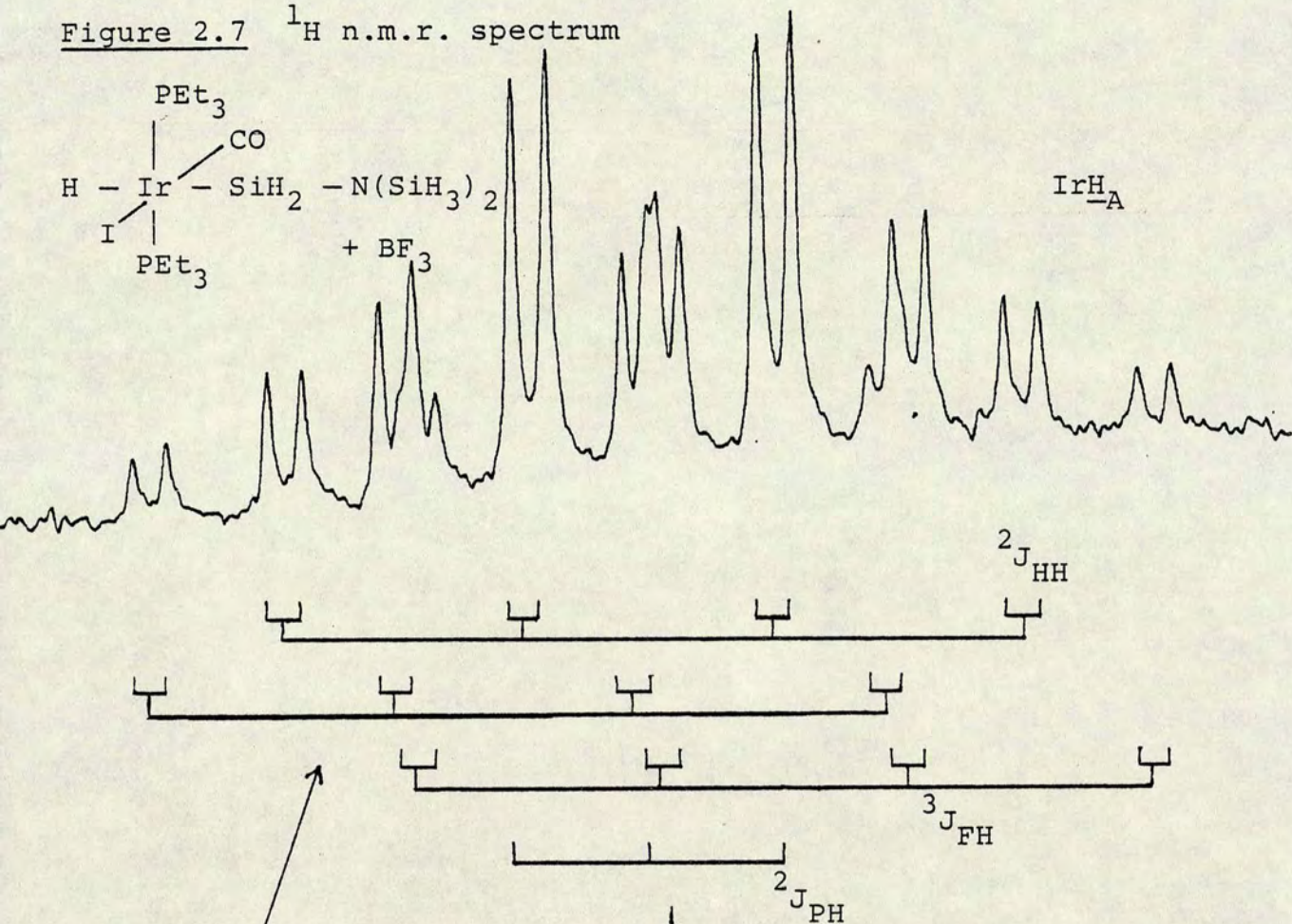


Figure 2.7  $^1\text{H}$  n.m.r. spectrum



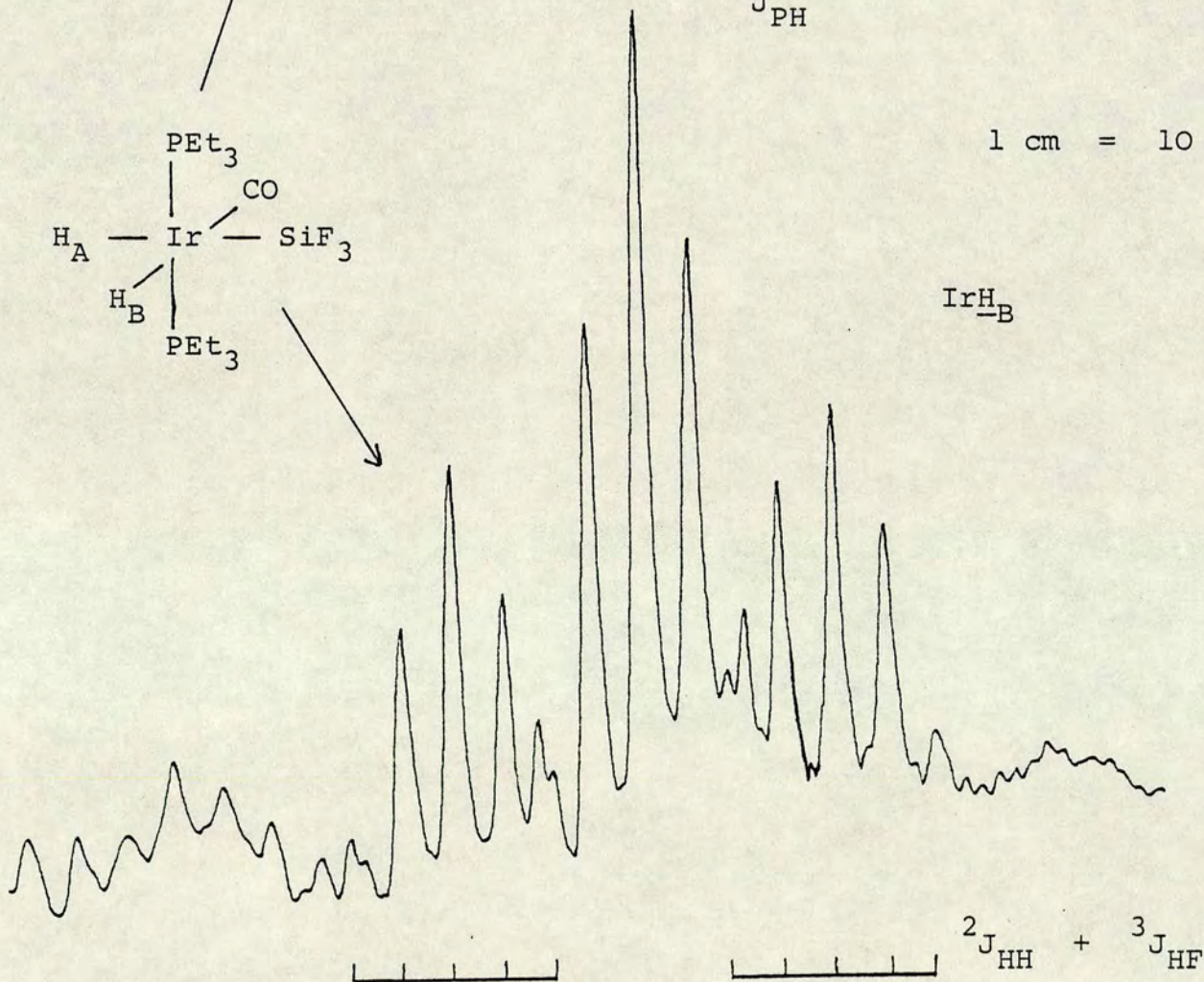
+  $\text{BF}_3$

$\text{IrH}_A$

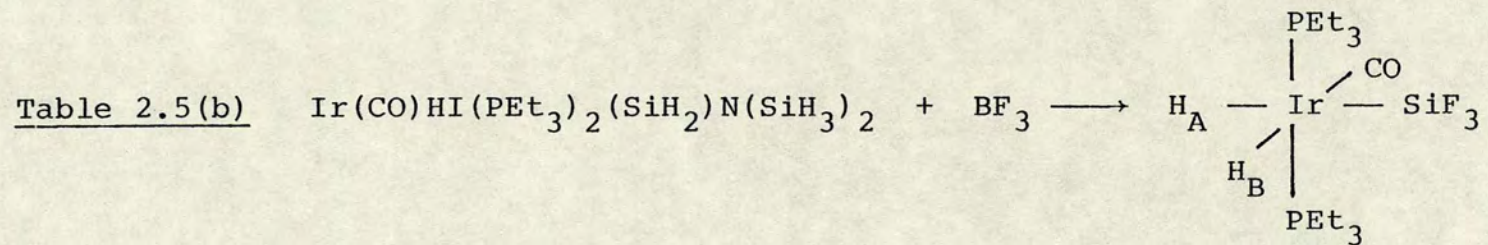


1 cm = 10 Hz

$\text{IrH}_B$







$\delta_{\text{P}}$	$\delta_{\text{F}}$	$\delta_{\text{H}_A}$	$\delta_{\text{H}_B}$	$^3J_{\text{PIrSiF}}$	$^3J_{\text{FSiIrH}_A}$	$^3J_{\text{FSiIrH}_B}$	$^2J_{\text{PIrH}_A}$	$^2J_{\text{PIrH}_B}$	$^2J_{\text{H}_A\text{IrH}_B}$
-3.22	-84.26	-10.96	-12.04	0.2	32.7	4.8	17.8	17.5	4.6

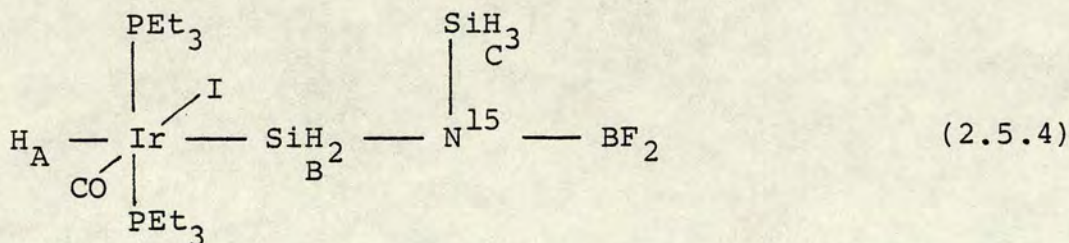
N.m.r. parameters recorded at room temperature using  $\text{C}_6\text{D}_6$  as solvent.



Complex (2.1.1) labelled with  $^{15}\text{N}$  was reacted with  $\text{BF}_3$  and the products immediately examined by n.m.r. spectroscopy. At  $-80^\circ\text{C}$  no reaction had occurred and only the  $^1\text{H}$  n.m.r. spectrum of the starting material observed.

On warming to  $-50^\circ\text{C}$  reaction took place. Observed were the species already discussed in this section, complex (2.1.1) and close to it a new species with similar but broadened resonances. These new resonances were presumed to be due to a similar complex with boron attached, the broadening being caused by  $^{11}\text{B}$  quadrupole relaxation. Its  $\text{SiH}_2$  resonance appeared as a broadened lump which was perturbed on irradiation of its hydride. The hydride signal appeared as a broadened triplet which sharpened on irradiation of the  $\text{SiH}_2$  frequency. A free  $\text{SiH}_3$  peak was observed split into a doublet by coupling to  $^{15}\text{N}$  and broadened by coupling to boron. The ratio of the  $\text{SiH}_3$  peak to the  $\text{SiH}_2$  peak was 3:2.

This is consistent with the following structure:



The  $^1\text{H}$  n.m.r. parameters of the species are as follows:

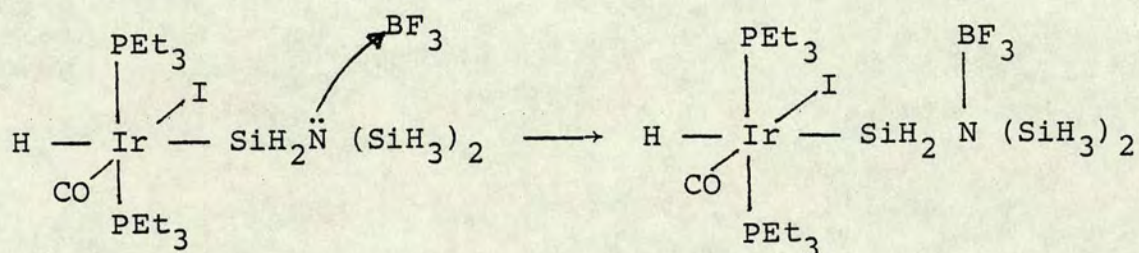
$\delta_{\text{H}_A}$	$\delta_{\text{H}_B}$	$\delta_{\text{H}_C}$	$^2J_{\text{H}_C\text{IrP}}$
-10.23	5.07	4.58	15.5



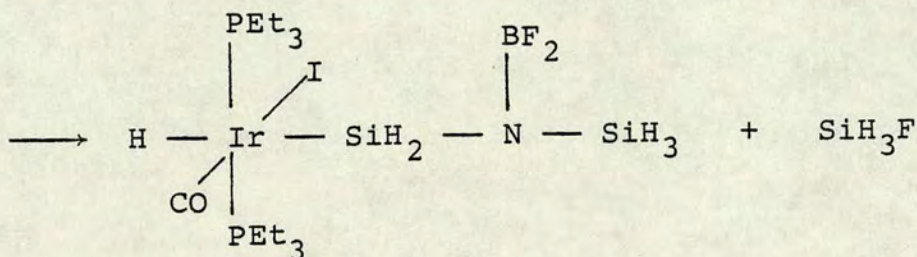
This would account for the ratio of the silyl peaks which are bound to  $^{15}\text{N}$ .

The other product would be  $\text{SiH}_3\text{F}$  and the first part of a mechanism can be postulated.

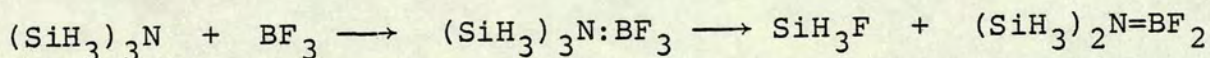
The first step although not observed is probably the Lewis acid  $\text{BF}_3$  accepting the lone pair of electron on nitrogen.



This is immediately followed by rearrangement and loss of  $\text{SiH}_3\text{F}$ .



Sujishi and Witz<sup>10</sup> have studied the reaction of  $\text{N}(\text{SiH}_3)_3$  with  $\text{BF}_3$  and report the following:

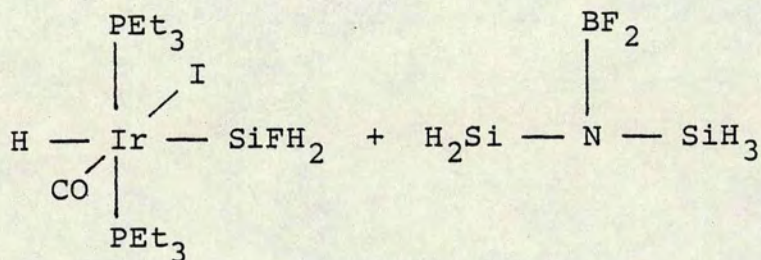
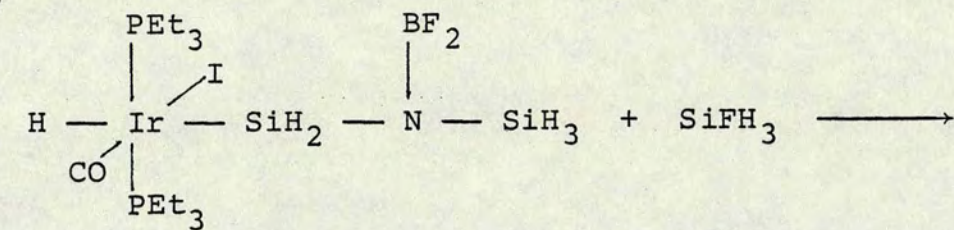


It has been shown in Section 2.1 that the bis species complex (2.1.2) can in the presence of excess  $\text{N}(\text{SiH}_3)_3$  rearrange to the mono species complex (2.1.1).



The next step could be rearrangement of the above with excess silyls present.

e.g.



After some time one of the products observed is  $\text{N}(\text{SiH}_3)_3$  but no starting material complex (2.1.1).

$\text{BF}_3$  or a boron species formed could act as a catalyst promoting the exchanges observed.



REFERENCES - CHAPTER 2

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CHAPTER 3

Reactions of Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>

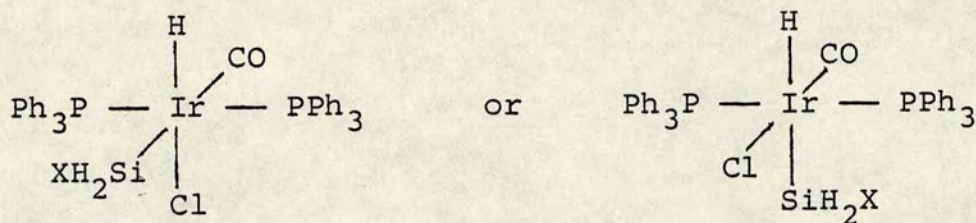
with O(SiH<sub>3</sub>)<sub>2</sub> and N(SiH<sub>3</sub>)<sub>3</sub>



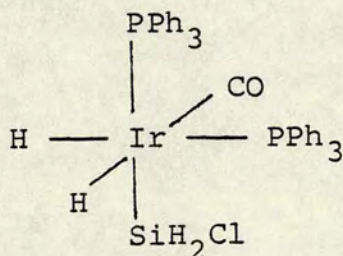
3. Reactions of Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>

Reactions of N(SiH<sub>3</sub>)<sub>3</sub> and O(SiH<sub>3</sub>)<sub>2</sub> with Vaska's compound<sup>1</sup> were carried out for comparison with their reactions with Ir(CO)X(PEt<sub>3</sub>)<sub>2</sub>.

Bridges<sup>2</sup> has previously studied reactions of Vaska's compound with SiH<sub>3</sub>X (X = H, Cl, Br, I), which gave two types of isomer:



Reaction with SiH<sub>3</sub>Cl was different: rearrangement to the dihydride species was observed.



No reactions of molecules containing more than one silyl (-SiH<sub>3</sub>) group with Vaska's compound had previously been studied.



### 3.1 Reaction of $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ with $\text{O}(\text{SiH}_3)_2$

This reaction took place in two stages. Equimolar amounts of Vaska's compound and disiloxane were allowed to react at room temperature in benzene. The yellow colour of Vaska's compound gave way to a colourless solution which was stable for half an hour.

After half an hour a white solid dropped out of solution: then after a period of two days this went back into solution.

The solution which was stable for half an hour was studied by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum appeared as a singlet having a chemical shift in the region associated with P bonded to six-coordinate iridium III. On selectively decoupling the phenyl and silyl proton frequencies a narrow doublet was obtained indicating P cis to one hydride.

The  $^1\text{H}$  n.m.r. spectrum showed resonances in three regions:- The phenyl region, the silyl region, and the iridium hydride region.

The resonance in the phenyl region gave no useful information.

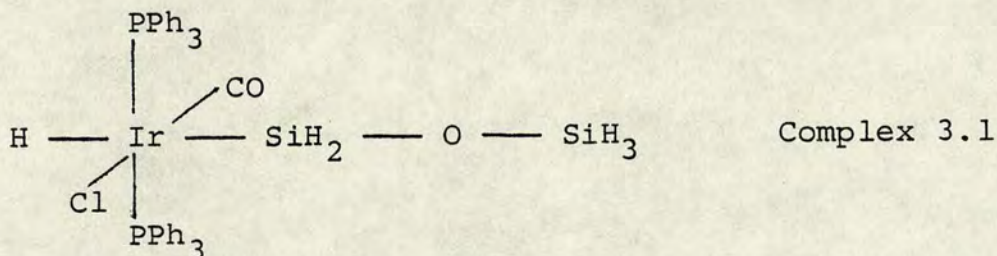
Two resonances were observed in the silyl region - a singlet and a multiplet. The integral of the area under the peaks gave a ratio of three to two.



The multiplet, at slightly higher frequency to the singlet, appeared as a triplet of doublets. The triplet coupling was assigned as  ${}^3J_{\text{HSiIrP}}$  and the doublet coupling as  ${}^3J_{\text{HSiIrH}}$ .

The resonance in the iridium hydride region appeared as a triplet of triplets. The wider triplet coupling was assigned as  ${}^2J_{\text{HIrP}}$ . The narrower triplet coupling was of the same magnitude as the doublet coupling in the silyl region assigned as  ${}^3J_{\text{HSiIrH}}$ .

This information is in agreement with the following structure:



N.m.r. parameters are listed in Table 3.1

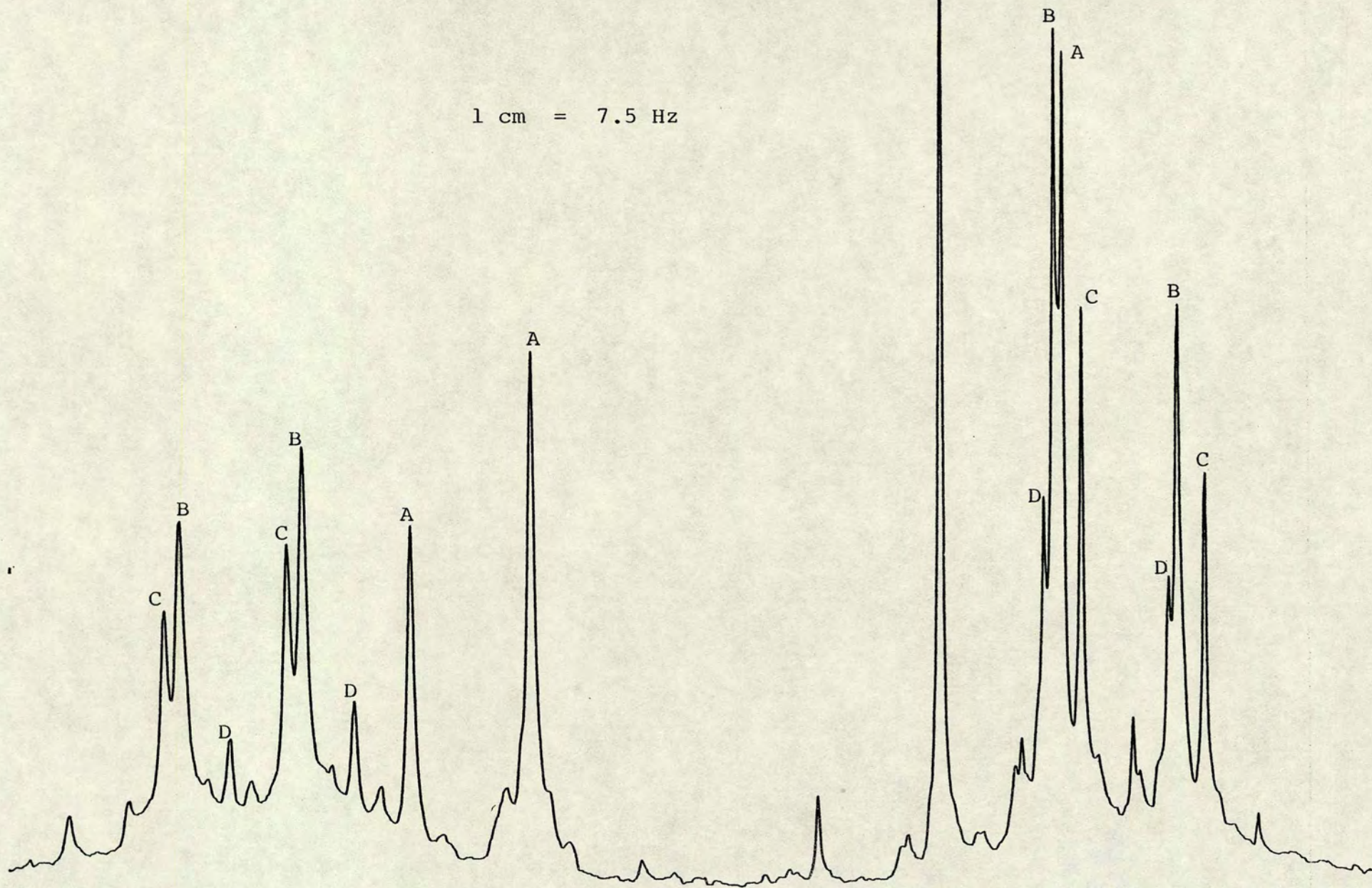
The solution obtained after standing for two days gave much more complicated spectra.

The  ${}^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum (see Figure 3.1) appeared as four AB quartets which shall be labelled as arising from species A, B, C and D. The dominant species was A, with only slightly less of B, and a bit less of C. Species D was a very minor species.

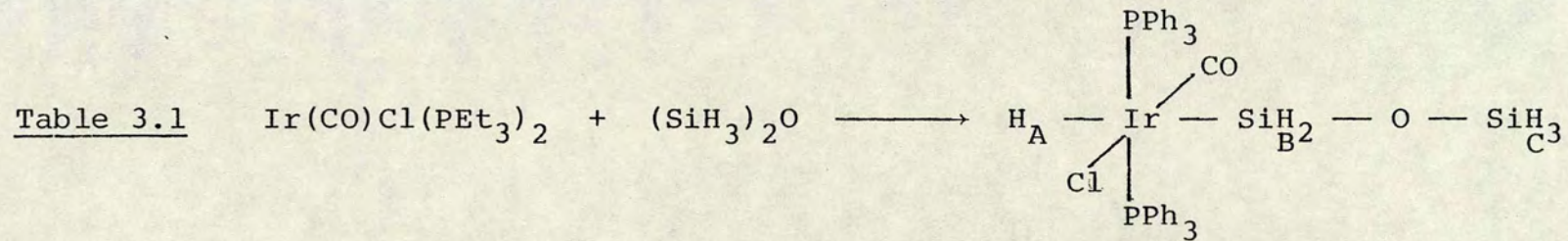
The chemical shifts and coupling constant ( ${}^2J_{\text{PIrP}}$ ) for species A were the same as the published parameters<sup>3</sup> for



Figure 3.1  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 + (\text{SiH}_3)_2\text{O}$



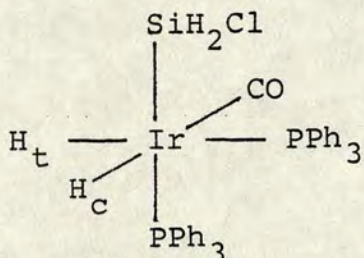




$\delta_P$	$\delta_{H_A}$	$\delta_{H_B}$	$\delta_{H_C}$	$^3J_{H_A \text{IrSiH}_B}$	$^2J_{H_A \text{IrP}}$	$^3J_{H_B \text{SiIrP}}$
8.05	6.37	4.89	4.42	3.0	14.5	6.8

N.m.r. parameters were recorded at 298 K using  $\text{C}_6\text{D}_6$  as solvent





On investigation by  $^1\text{H}$  n.m.r. the spectra showed further evidence for this species. There were two resonances due to it in the iridium hydride region (see Figure 3.2)  $\text{H}_t$  gave rise to a wide doublet of doublets of overlapping doublets of doublets.  $\text{H}_c$ , resonating at slightly higher frequency, gave rise to a doublet, of doublets, of doublets of doublets.

The two protons bonded to the silicon give rise to separate signals as they are magnetically inequivalent (an explanation can be found in the next chapter). Only one of these could be observed (see Figure 3.3) as the other was masked by peaks arising from other species resonating in the same region.  $\text{H}_q$ , the resonance (see figure 3.3) at lower frequency, appeared as an overlapping doublet, of doublets, of doublets of doublets.

All these resonances could be proved as belonging to the same species by decoupling experiments and the chemical shifts and coupling constants were in agreement for the structure above when compared with the published parameters.

Also observed in the low frequency  $^1\text{H}$  n.m.r. spectrum were resonances due to two other species, one being almost as strong as the resonances for species A but the other a more minor species. Both these resonances were very similar in appearance and were very close to each other.



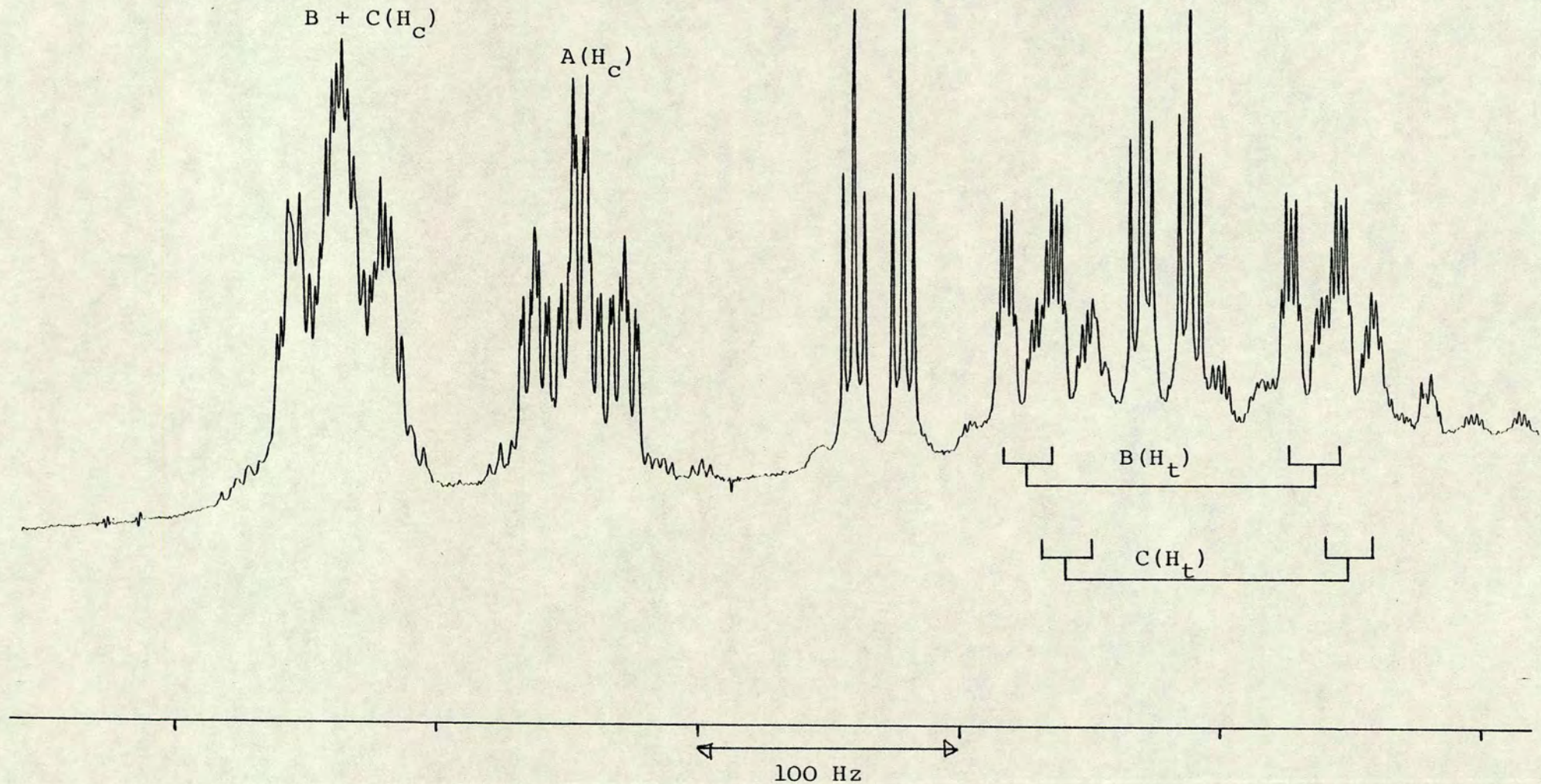
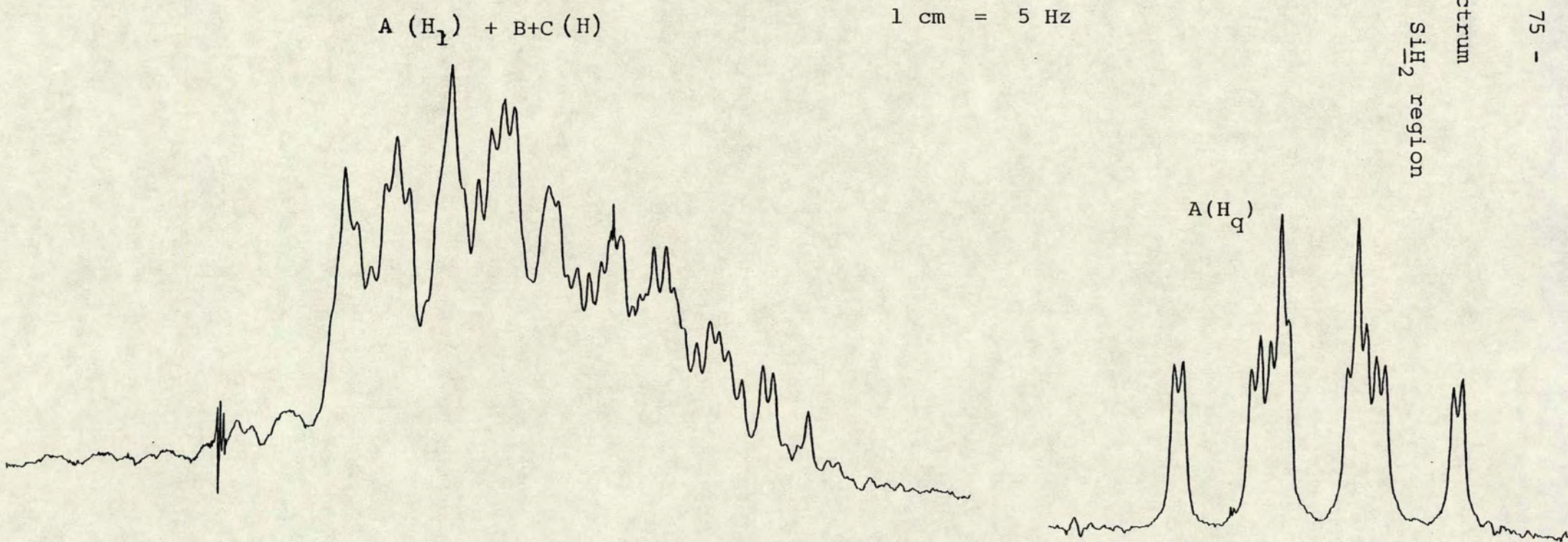


Figure 3.2  $^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 + \text{O}(\text{SiH}_3)_2$  IrH region



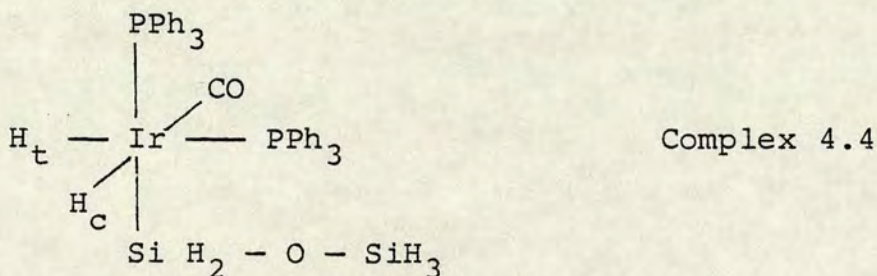
Figure 3.3  $^1\text{H}$  n.m.r. spectrum  
 $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 + \text{O}(\text{SiH}_3)_2$   $\text{SiH}_2$  region





In fact a lot of peaks were so close they overlapped and could not be distinguished.

The dominant of these and the peaks assigned as species B from the  $^{31}\text{P}$  n.m.r. spectrum could be attributed to:



This is discussed and the parameters are listed in the next chapter.

$\text{H}_t$  gave rise to a wide doublet of doublets of overlapping doublets of triplets and could be clearly characterized from the spectrum obtained. The resonance due to  $\text{H}_c$  at slightly higher frequency was masked by the similar  $\text{H}_c$  for the minor species.

The complex resonance for the  $-\text{SiH}_2-$  could not be resolved as it was also masked by other peaks. Decoupling using frequencies in the  $-\text{SiH}_2$  region, collapsed the  $\text{IrH}$  resonances to low frequency and thus established that the  $-\text{SiH}_2$  resonance, whilst obscured by other signals, was actually present and derived from the same molecule.

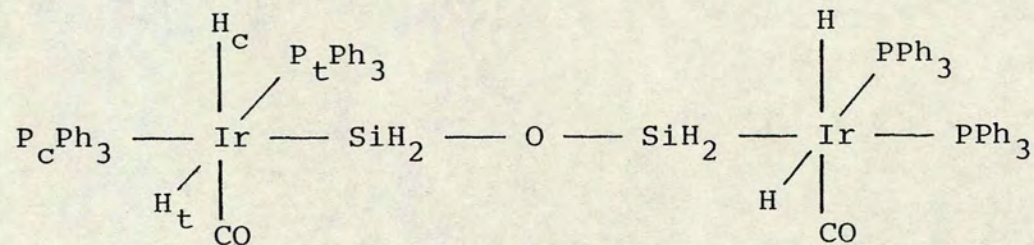
The remaining peaks in the  $^1\text{H}$  n.m.r. spectrum due to a minor species and the peaks due to species C in the  $^{31}\text{P}$  n.m.r. spectrum were taken to originate from the same molecule. Resonances observed were very similar to those for







Table 3.2  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 + (\text{SiH}_3)_2\text{O}$

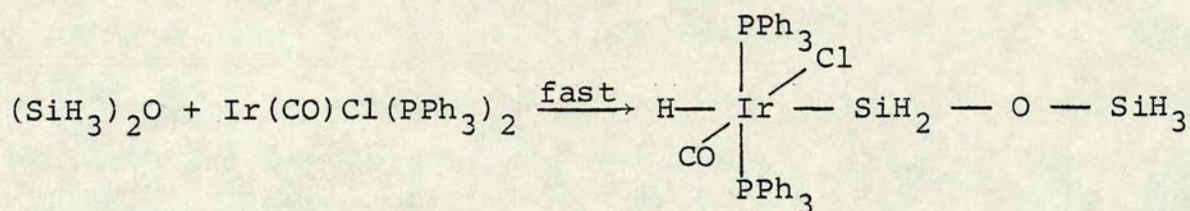


$\delta P_c$	$\delta P_t$	$\delta H_t$	${}^2J_{P_c\text{Ir}P_t}$	${}^2J_{H_t\text{Ir}P_t}$	${}^2J_{H_t\text{Ir}P_c}$	${}^2J_{H_t\text{Ir}H_c}$	${}^3J_{H_t\text{IrSiH}}$
0.9	3.9	-10.22	17.3	110.8	19.3	4.0	2.0

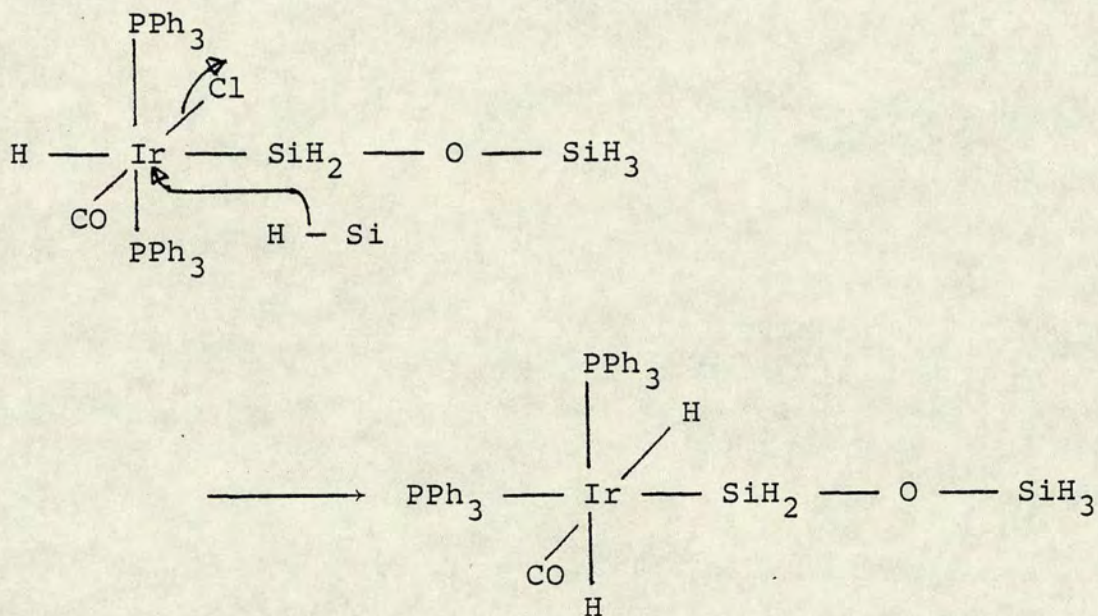
N.m.r. parameters were recorded at 298 K using  $\text{C}_6\text{D}_6$  as solvent.



The reaction can be summarized as :



In the next step a halogen is lost from the iridium centre and replaced by a hydride. The hydrogen comes from silyl that is present. It does not come from the solvent as the solvent was deuteriated.



What happens next is speculation. From the  $\text{BF}_3$  reactions in Chapter 2 it is known that these systems can exchange under certain conditions.

The silyl chloride adduct could be formed by exchange of  $-\text{Cl}$  for  $-\text{O-SiH}_3$  or by exchange of complete silyl groups. There is chlorine in the system that was lost from the iridium centre.



Also present in the reaction mixture was a lot of  $-O-SiH_3$  species shown by  $^1H$  n.m.r. This is another example of an iridium compound promoting exchange of siloxanes<sup>4,5,6</sup>.

### 3.2 Reaction of $Ir(CO)Cl(PPh_3)_2$ with $N(SiH_3)_3$

An excess of  $N(SiH_3)_3$  was allowed to react with  $Ir(CO)Cl(PPh_3)_2$  in benzene at room temperature. A white solid was immediately formed which further reacted over a period of two days to produce a clear solution. Only one product was observed. Comparison of its n.m.r. parameters with compound 4.1 discussed in the next chapter showed it to be  $[Ir(CO)H_2(PPh_3)_2(SiH_2^-)]_2NSiH_3$ .

There was no observation of a trans oxidatively-added intermediate. Presumably it is much less stable than that observed for the disiloxane reaction.

It was also interesting to notice there was no rearrangement to a  $-SiH_2Cl$  dihydride adduct.



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- (2) D.M. Bridges, Ph.D. Thesis, Edinburgh, (1976).
- (3) E.A.V. Ebsworth, T.E. Fraser, S.G. Henderson, D.M. Leitch, D.W.H. Rankin, J.Chem.Soc.(Dalton), p.1010, (1981).
- (4) M.D. Curtis, J. Greene, J.Amer.Chem.Soc., 99, p.5176, (1977).
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- (6) M.D. Curtis, J. Greene, W.M. Butler, J.Organometal.Chem., 164, p.371, (1979).



CHAPTER 4

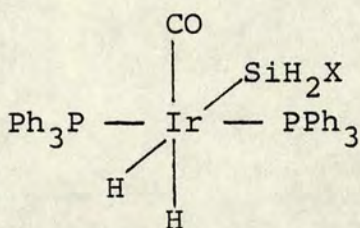
Reactions of  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$   
with some silyl compounds



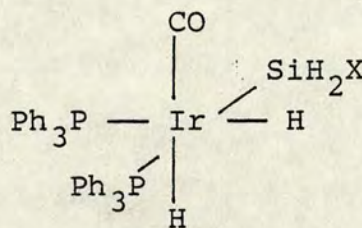
4. Reactions of  $\text{HIr}(\text{CO})(\text{PPh}_3)_3$  with some silyl compounds

Reactions of  $\text{HIr}(\text{CO})(\text{PPh}_3)_3$  with silyl compounds have been studied by D.M. Bridges<sup>1</sup> and T.E. Fraser<sup>2</sup>, but these studies were not conclusive. These reactions have been reexamined with the aid of a recently acquired 360 MHz FT n.m.r. spectrometer to establish fully the structures of the species formed<sup>3</sup>.

The products have been found to be of two types:-



(trans isomer)



(cis isomer)

The cis isomer appears to be the dominant isomer and in some reactions the only isomer formed.

The cis isomer has a chiral centre which leads to the SiH's being non-equivalent and giving rise to two signals in its <sup>1</sup>H n.m.r. Two resonances were observed for the hydrides. The splitting patterns, the sizes of the assigned coupling constants and the positions of the resonances were used to assign the stereochemistry.

The <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectra show as AB quartets due to the inequivalent, but similar, triphenyl phosphine groups.



#### 4.1 Reaction of $N(SiH_3)_3$ with $HIr(CO)(PPh_3)_3$

This reaction was studied in order to clarify the species observed in the reaction of  $N(SiH_3)_3$  with Vaska's compound.

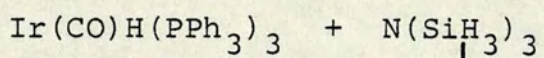
Trisilylamine was allowed to react with  $HIr(CO)(PPh_3)_3$  in toluene at  $-40^\circ C$  and reaction was complete in twelve hours. This was carried out using equimolar amounts.

The  $^{31}P\{^1H\}$  n.m.r. spectrum appeared as an AB quartet indicative of two mutually cis phosphines, but trans to different groups. When the silyl and phenyl frequencies were selectively decoupled, the low frequency half of the AB pattern appeared as five lines. This was due to coupling to two hydrides of the same type, and they must therefore be both cis to that phosphine. The higher frequency signals appeared as what, in first order terms, could be described as a wide doublet of doublets of doublets. One of the doublet couplings was due to the coupling to the other phosphorus,  $^2J_{PIrP}$ . The wide doublet was due to coupling to a trans hydride and the smallest coupling derived from a cis hydride. The spectrum is rather more complicated than this, perhaps because of second order effects (see Figure 4.1).

The  $^1H$  n.m.r. spectrum contained peaks in three regions:- in the phenyl region, the silyl region and in the iridium hydride region.

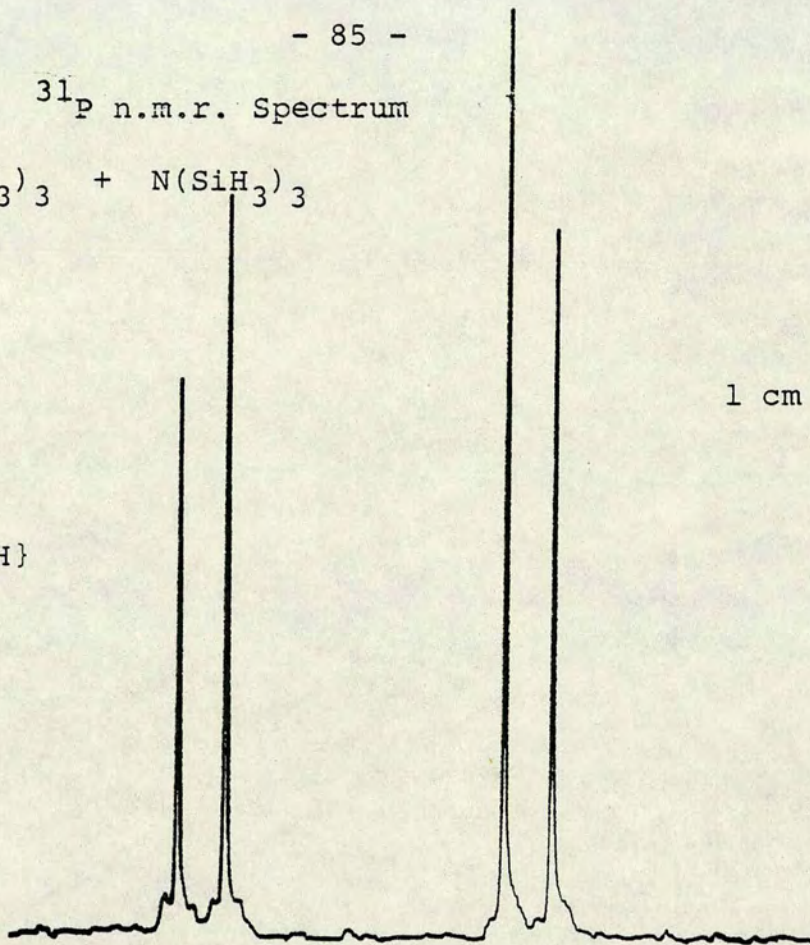


Figure 4.1  $^{31}\text{P}$  n.m.r. Spectrum

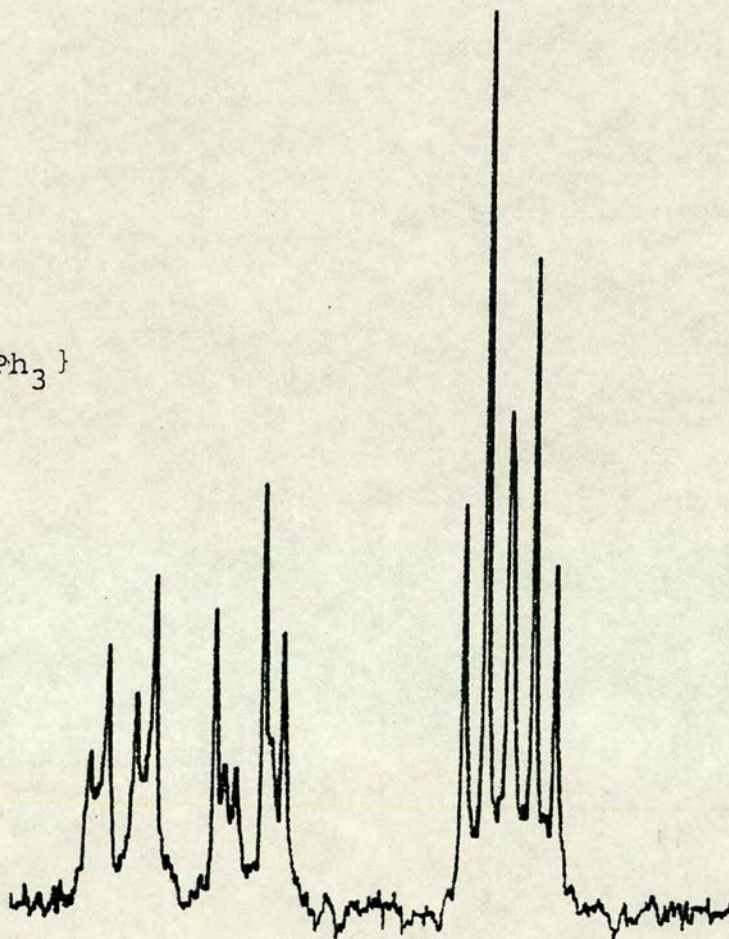


1 cm = 25 Hz

$^{31}\text{P}\{^1\text{H}\}$



$^{31}\text{P}\{^1\text{HPPH}_3\}$





The hydride region showed two resonances which will be discussed later.

There were three silyl resonances. Two of these were multiplets which, by integration, were shown to be of the same intensity and were assigned as arising from the two protons bound to Si in the grouping  $\text{H}_2\text{SiIr}(\text{CO})\text{H}_2(\text{PPh}_3)_2$ . Because of the chirality of the iridium centre, the two  $\text{SiH}$  protons would be inequivalent. The other resonance in the silyl region was a sharp singlet which was shown by integration to be of three quarters of the intensity of the combined signals for the protons on the silicon bonded to the metal. The signal was assigned to a free  $-\text{SiH}_3$  group. Because of the integral ratio of the free  $\text{SiH}_3$  resonance to the bonded  $\text{SiH}_2$  resonance, the complex was assigned as being the bis iridium species  $[\text{Ir}(\text{CO})\text{H}_2(\text{PPh}_3)_2\text{SiH}_2]\text{NSiH}_3$ .

The higher frequency multiplet ( $\text{H}_1$ ) appeared broadened and could not be analysed until a line narrowing programme was used to transform the F.I.D. when this was used, the multiplet could be interpreted as a doublet of doublets of doublets of doublets (see Figure 4.2).

The widest doublet coupling was assigned as arising from  ${}^3\text{J}_{\text{HSiIrP}(c)}$  by comparison with the  ${}^1\text{H}$  n.m.r. spectra for the silyl halide reactions. The next widest doublet was assigned as arising from  ${}^2\text{J}_{\text{HSiH}}$ . The second narrowest doublet coupling was assigned as arising from  ${}^3\text{J}_{\text{HSiIrP}(t)}$  and the narrowest doublet as arising from  ${}^3\text{J}_{\text{HSiIrH}}$ .



Only coupling to one hydride was observed and this was shown, by double irradiation, to be due to the hydride resonating at lower frequency.

The other  $\text{SiH}$  multiplet ( $\text{H}_q$ ) also interpreted as a doublet of doublets of doublets of doublets (see Figure 4.3).

The two largest couplings were assigned as arising from  ${}^3\text{J}_{\text{HSiIrP}(c)}$  and  ${}^3\text{J}_{\text{HSiIrP}(t)}$ . The next widest doublet coupling had the same coupling constant as that observed for the other  $\text{SiH}$  resonance and was assigned as arising from  ${}^2\text{J}_{\text{HIrSiH}}$ . Irradiation of the higher frequency hydride removed this doublet coupling; this was the only hydride to which coupling was observed. Low power irradiation at the frequency of each silyl multiplet affected the other multiplet, showing that they both arose from the same complex. Only low power irradiation could be used as their frequencies were so close.

Low power irradiation of the low frequency hydride signal and observation of the high frequency silyl resonance gave some information about the relative signs of their coupling constants.

${}^3\text{J}_{\text{H}_1\text{SiIrP}_t}$	${}^2\text{J}_{\text{H}_t\text{IrP}_t}$	Same
${}^3\text{J}_{\text{H}_1\text{SiIrP}_c}$	${}^2\text{J}_{\text{H}_t\text{IrP}_c}$	Opposite
${}^3\text{J}_{\text{H}_1\text{SiIrH}_c}$	${}^2\text{J}_{\text{H}_t\text{IrH}_c}$	Same

(as defined in Table 4.1)



Figure 4.2  $^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + \text{N}(\text{SiH}_3)_3$ .  
 $\text{SiH}_2$  region.

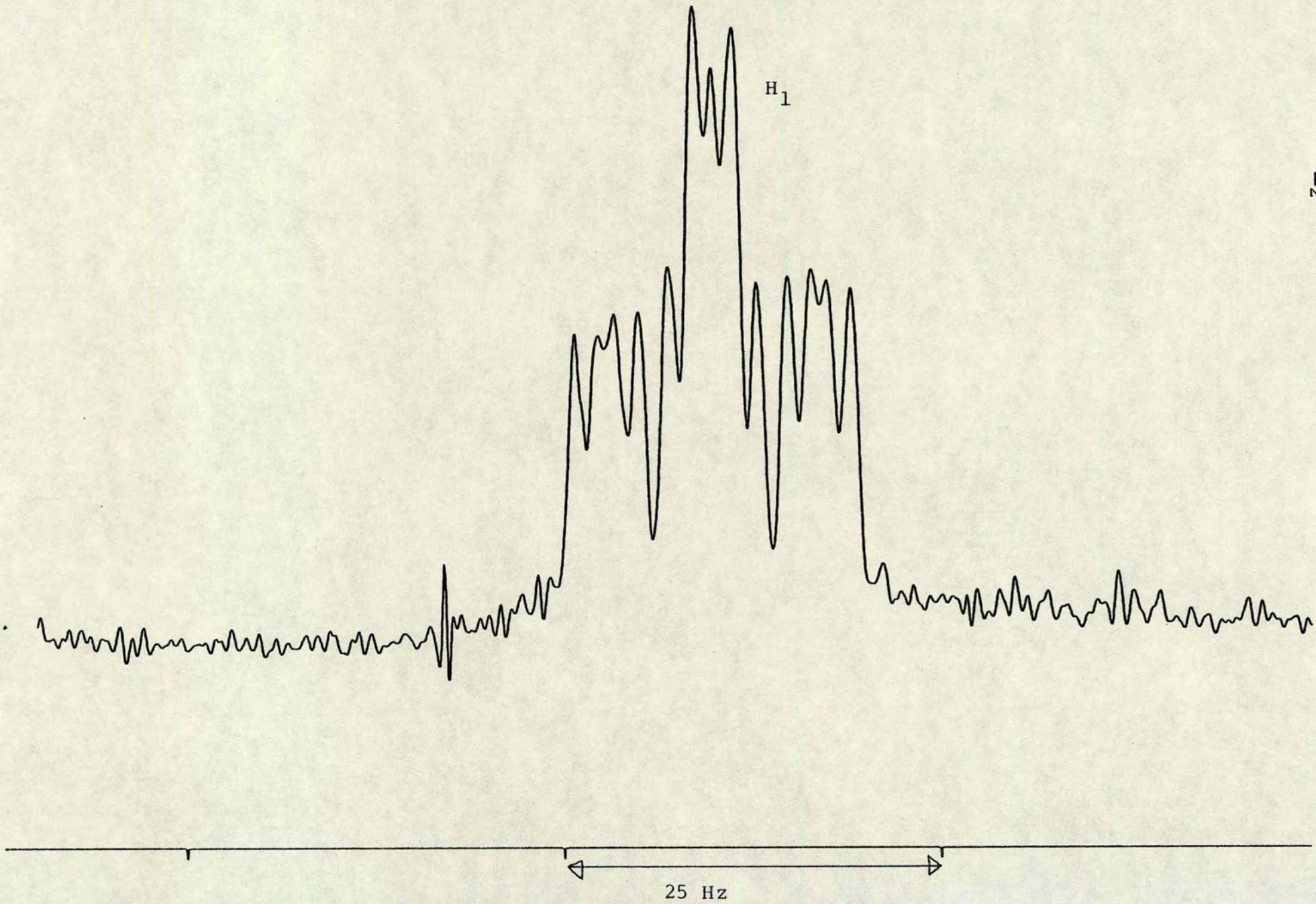
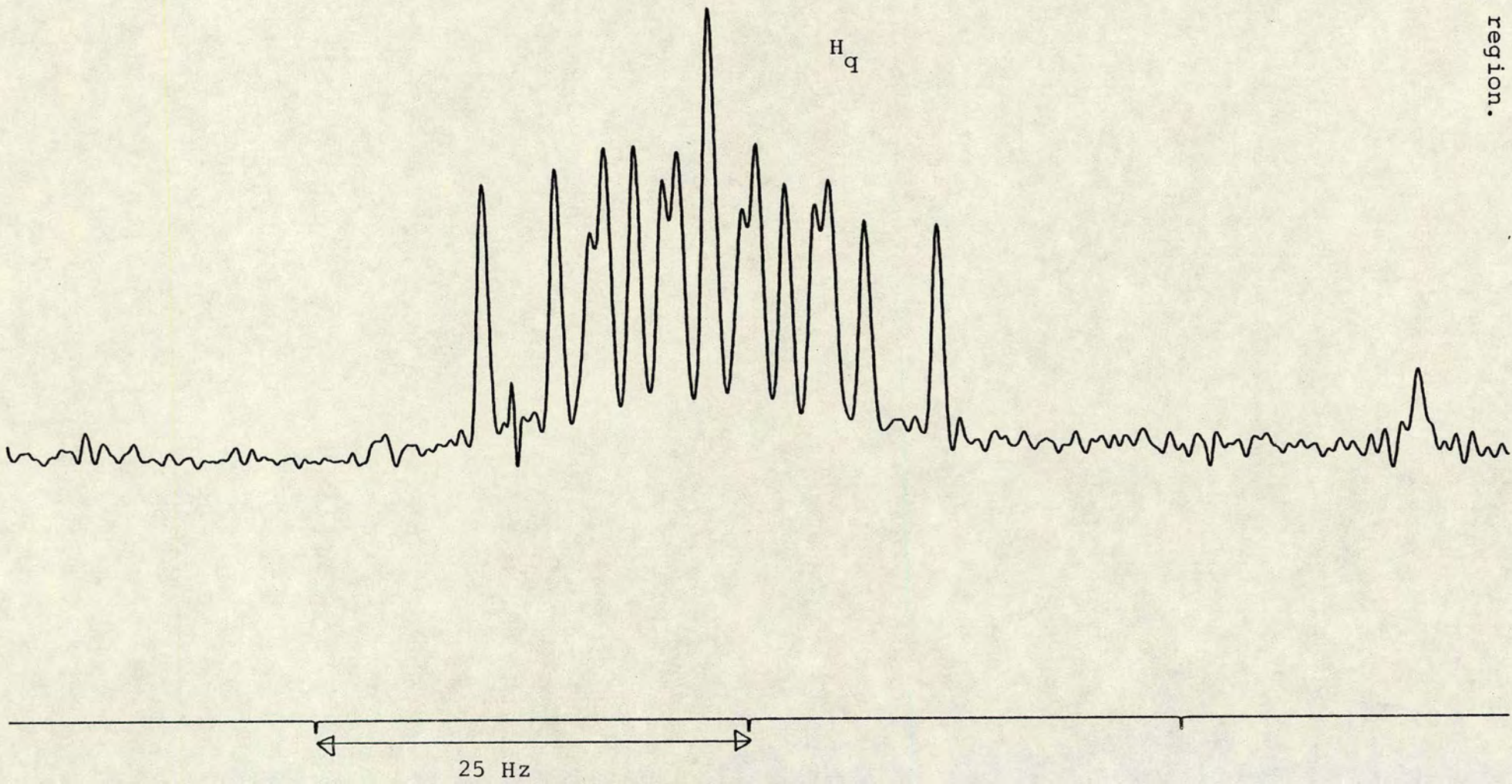




Figure 4.3

$^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + \text{N}(\text{SiH}_3)_3$   
 $\text{SiH}_2$  region.





The hydride region showed two types of resonance. The lower frequency signal ( $H_t$ ) (see Figure 4.4) appeared as a wide doublet of doublets of doublets of doublets. The widest of these doublet couplings was assigned as arising from  ${}^2J_{\text{HIrP}(t)}$  because of its large size, and the next widest coupling as arising from  ${}^2J_{\text{HIrP}(c)}$ . The second narrowest doublet was assigned as arising from  ${}^2J_{\text{HIrH}}$  and irradiation at the frequency of the other hydride affected it. The narrowest doublet had the same coupling constant as  ${}^3J_{\text{HIrSiH}}$  previously observed on the higher frequency silyl multiplet, and by its irradiation could be collapsed.

The higher frequency hydride signal ( $H_c$ ) also appeared as a doublet of doublets of doublets of doublets resonating in the region associated with H trans to a carbonyl (see Figure 4.5). The two wider doublet couplings were assigned as arising from  ${}^2J_{\text{HIrP}}$ . Both the other doublets had couplings previously observed, the smallest being  ${}^2J_{\text{HIrH}}$  and the second smallest,  ${}^3J_{\text{HIrSiH}}$ . Low power irradiation of the lower frequency hydride affected the former, and the latter could be collapsed by irradiation of the lower frequency silyl multiplet.

The experiments carried out using low power irradiation gave information on the relative signs of the coupling constants.

${}^2J_{\text{H}_t\text{IrP}_c}$	${}^2J_{\text{H}_c\text{IrP}_c}$	opposite
${}^2J_{\text{H}_t\text{IrP}_t}$	${}^2J_{\text{H}_c\text{IrP}_t}$	same

(as defined in Table 4.1)



Figure 4.4  $^1\text{H}$  n.m.r. spectrum  
 $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + \text{N}(\text{SiH}_3)_3$   
 $\text{IrH}$  region

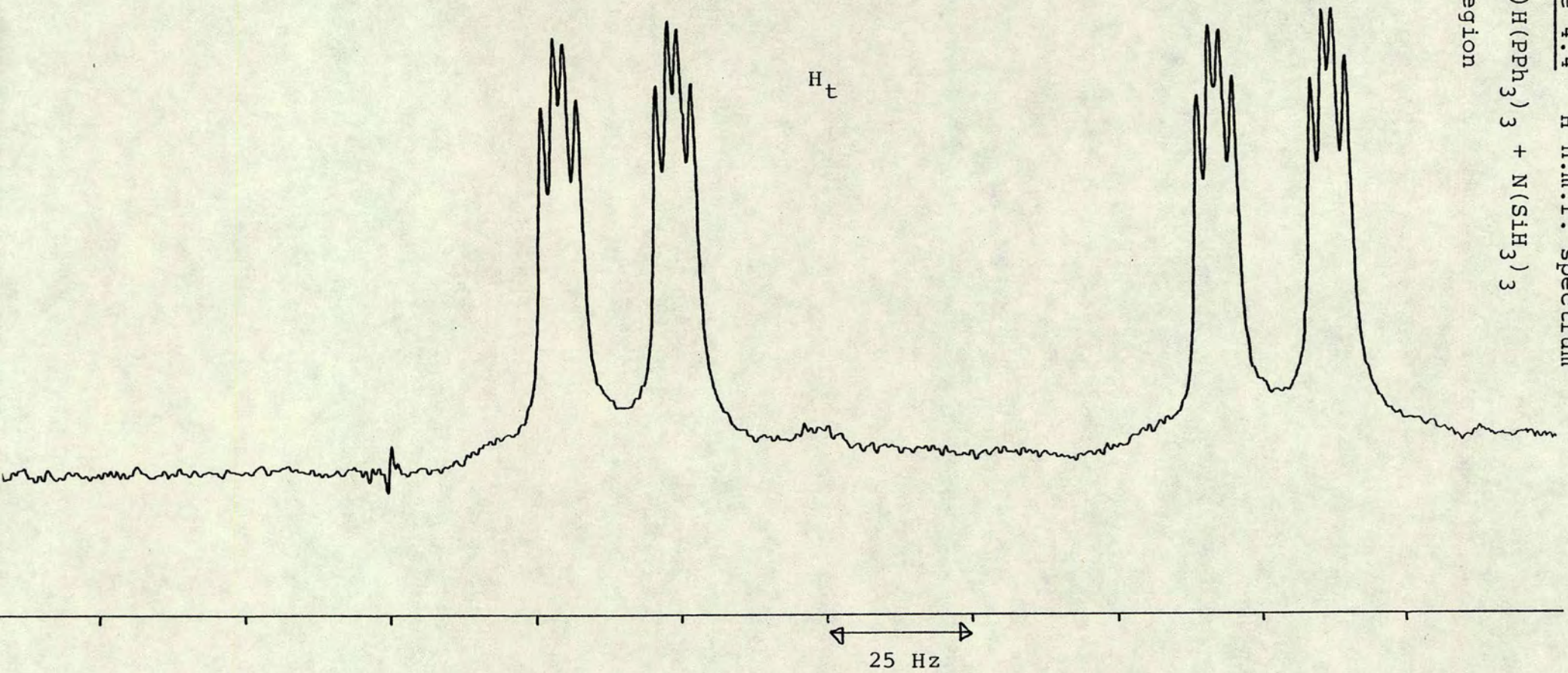
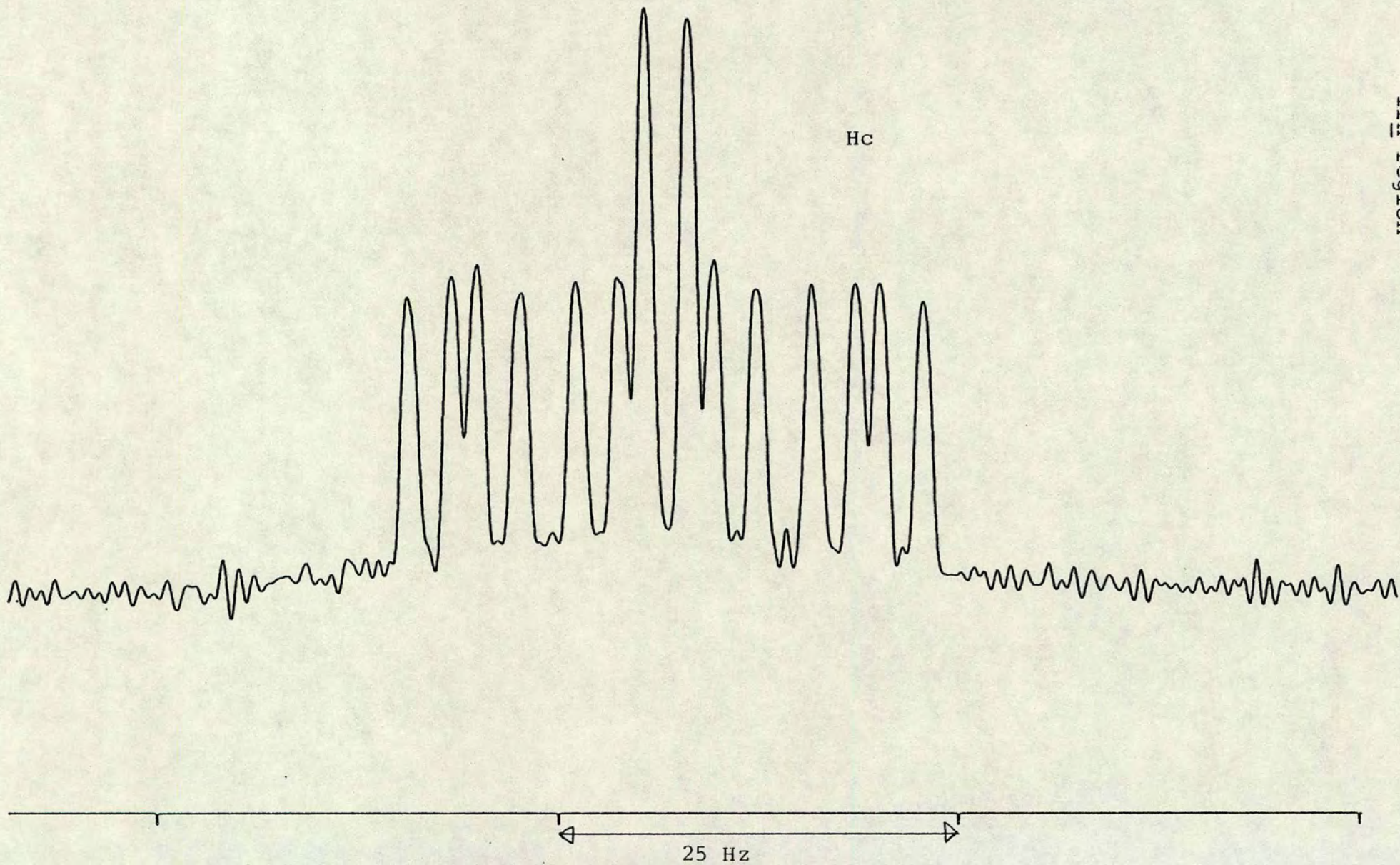


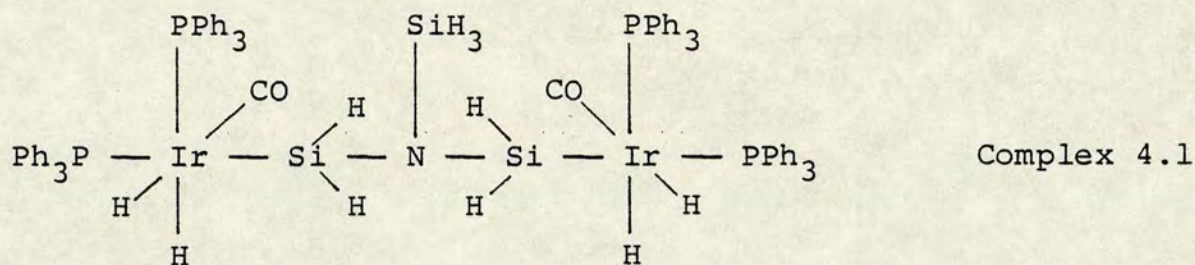


Figure 4.5  $^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + \text{N}(\text{SiH}_3)_3$   
 $\text{IrH}$  region



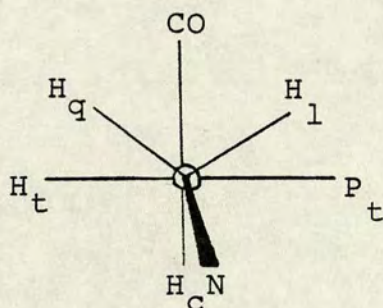


Collectively, this information suggests the following structure:-



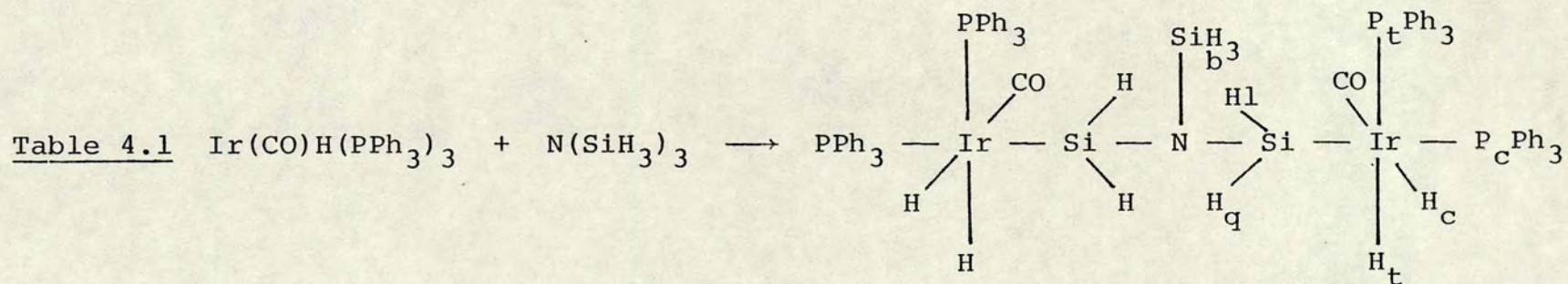
Parameters are detailed in Table 4.1

When the structure is drawn as a Fisher projection it is possible to see why the two protons on the silicon bonded to iridium are non equivalent. The view is along the projection of the silicon-iridium bond.



Irrespective of molecular rotation about this axis,  $H_q$  and  $H_l$  remain magnetically non equivalent. The projection also elucidates why  $SiH$  shows one large, and one small coupling to the cis phosphorus atoms, whereas for  $SiH$  they couple approximately equally. It is well documented that three bond coupling constants are very sensitive to angle change c.p.  ${}^3J_{HCCH}$  in ethane<sup>4,5</sup>.





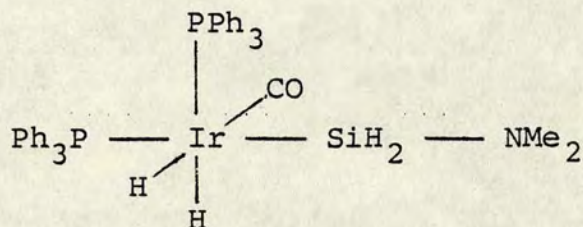
$\delta_{\text{H}_t}$	$\delta_{\text{H}_c}$	$\delta_{\text{H}_l}$	$\delta_{\text{H}_q}$	$\delta_{\text{H}_b}$	$\delta_{\text{P}_c}$	$\delta_{\text{P}_t}$	$^2J_{\text{P}_c\text{IrP}_t}$	$^2J_{\text{H}_c\text{IrP}_t}$	$^2J_{\text{H}_t\text{IrP}_c}$	$^2J_{\text{H}_t\text{IrH}_c}$
-10.31	-9.33	5.56	5.31	4.67	2.23	6.89	16.4	110.8	19.4	3.9

$^3J_{\text{H}_t\text{IrSiH}_l}$	$^3J_{\text{H}_c\text{IrSiH}_q}$	$^2J_{\text{H}_c\text{IrP}_t}$	$^2J_{\text{H}_c\text{IrP}_c}$	$^2J_{\text{H}_q\text{SiH}_l}$	$^3J_{\text{H}_q\text{SiIrP}_c}$	$^3J_{\text{H}_q\text{SiIrP}_t}$	$^3J_{\text{H}_l\text{SiIrP}_c}$	$^3J_{\text{H}_l\text{SiIrP}_t}$
2.2	6.2	15.2	21.1	9.0	10.1	12.7	3.8	11.2

N.m.r. parameters were recorded at 298 K using  $\text{C}_6\text{D}_5\text{CD}_3$  as solvent.



Robb<sup>6</sup> has recently carried out the reaction of  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  with  $\text{Me}_2\text{NSiH}_3$  and found formation of the mono-iridium species



Its n.m.r. parameters are very similar to those of complex 4.1.

#### 4.2 Reaction of $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$ with $\text{SiF}_3\text{H}$

The reaction of compounds 2.1.1 and 2.2.1 with  $\text{BF}_3$  yielded, as one of the products, complex 2.5.3.  $\text{SiF}_3\text{H}$  was allowed to react with  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  to see if a similar species could be produced. Reaction took place at  $-40^\circ\text{C}$  over 12 hours, the insoluble starting material disappearing to give a colourless solution.

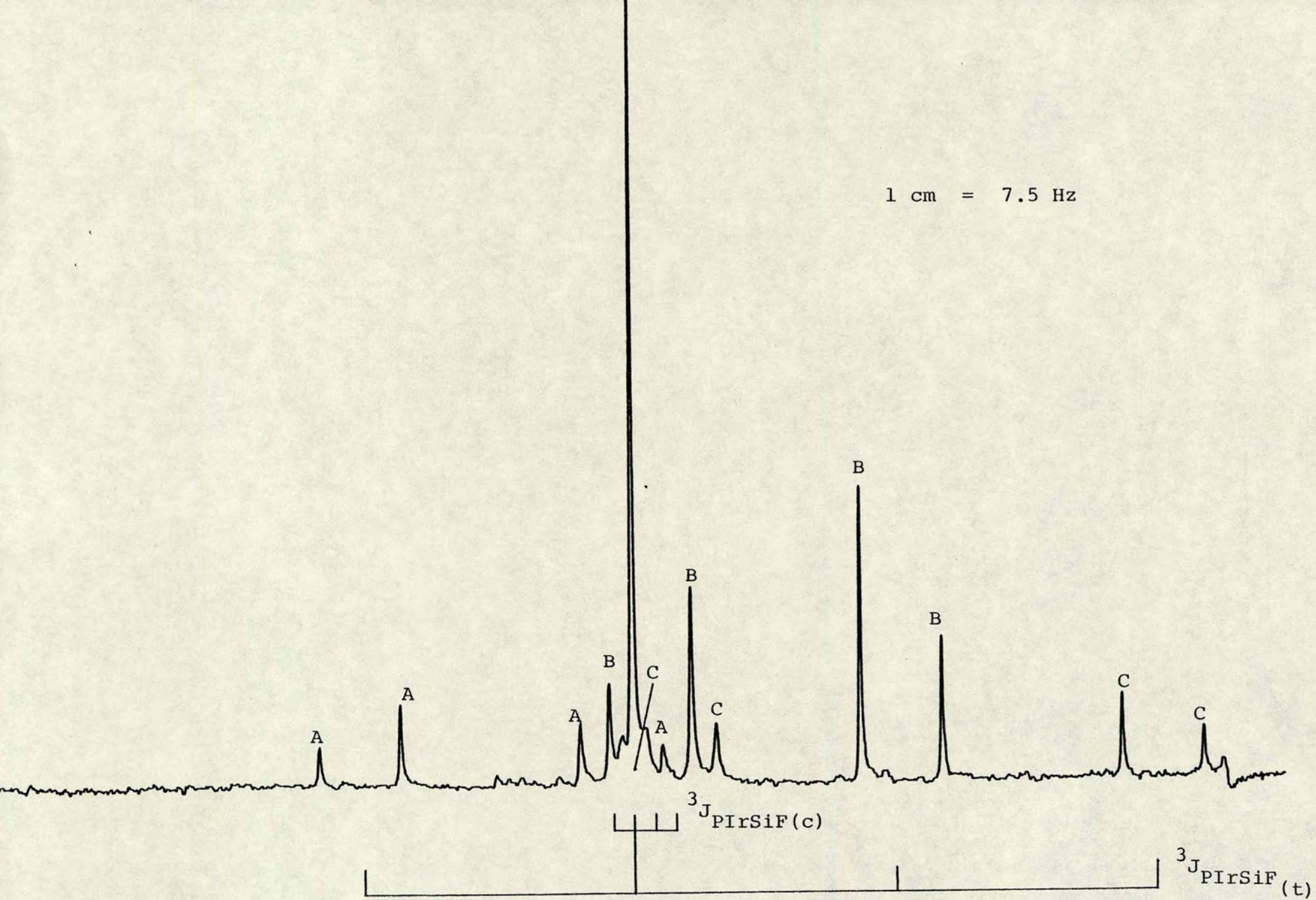
N.m.r. studies showed one major iridium species to be present.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum appeared as twelve lines which could be analysed as due to an  $\text{ABX}_3$  spin system. These twelve lines appeared as three AB quartets and a large singlet (see Figure 4.6). The singlet was due to an AB quartet where the internal chemical shift was roughly zero. It is not exactly zero though because, when solved numerically, the value of D has to be shifted from the indicated



Figure 4.6

$^3\text{P}\{\text{H}\}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + \text{SiF}_3\text{H}$





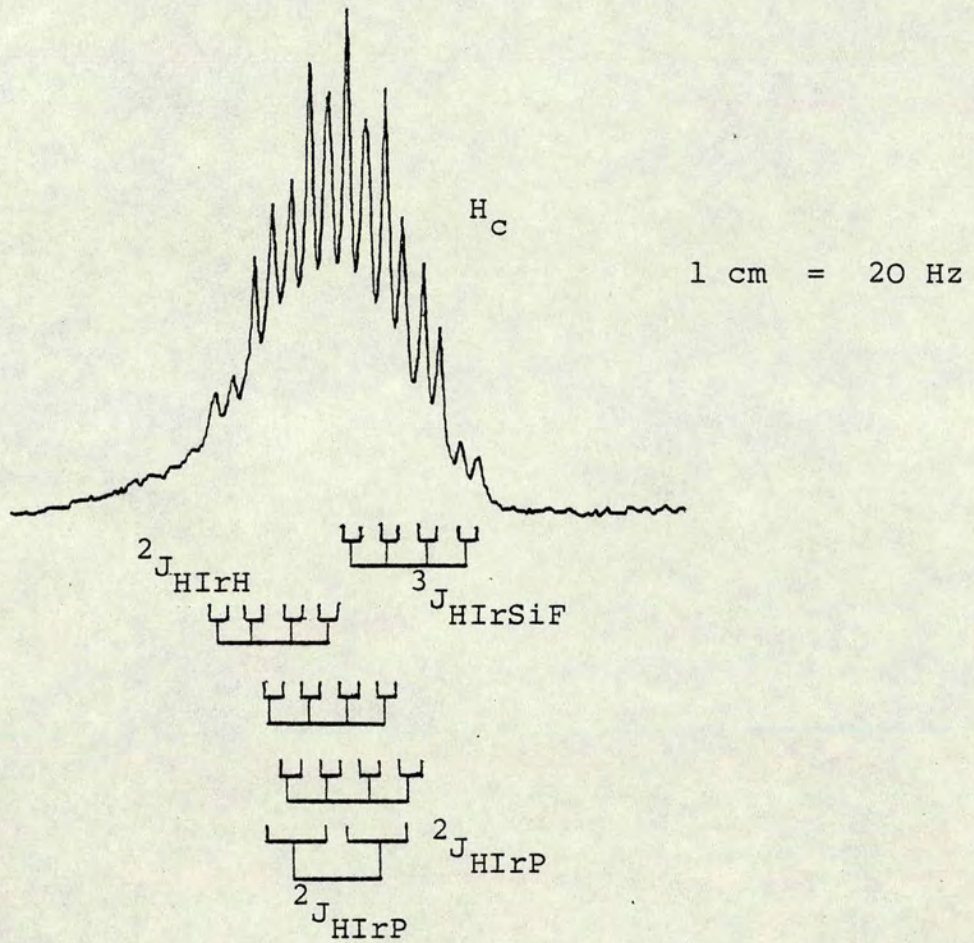
frequency by 0.7 and 0.8 Hz to each side, i.e. there was an internal chemical shift of 1.5 Hz. When this had been analysed the internal chemical shifts were calculated in Hz. These have been drawn in Figure 4.6, and it can be clearly seen that there are two quartets; the large quartet was assigned as arising from  ${}^3J_{\text{PIrSiF}(t)}$  and the small quartet as arising from  ${}^3J_{\text{PIrSiF}(c)}$ . The chemical shifts of the cis and trans phosphines were taken as the centres of both quartets.

The  ${}^1\text{H}$  n.m.r. spectra showed resonances in the triphenyl-phosphine region, and in the iridium hydride region.

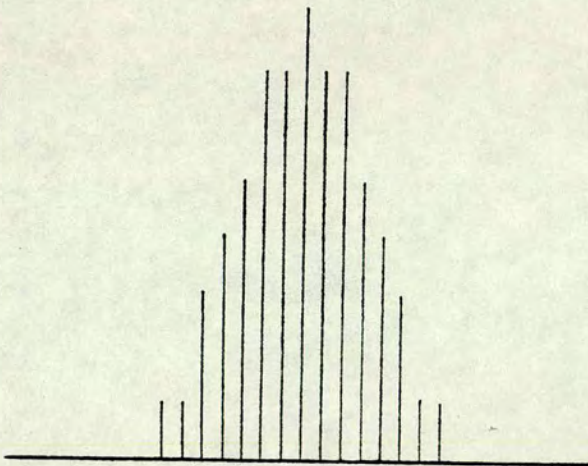
The iridium hydride region showed two resonances. The resonance at higher frequency ( $\text{H}_c$ ) could be interpreted as a doublet of doublets of quartets of doublets (see Figure 4.7), and appeared in the region associated with H trans to carbonyl or silicon. It was taken as being trans to carbonyl, because from the  ${}^{31}\text{P}$  n.m.r. spectrum silicon is almost certainly trans to phosphorus. The actual interpretation had to be carried out by line intensity analysis knowing that the outer lines appeared as parts of quartets of doublets. Two possible arrangements with couplings to two non-equivalent phosphorus nuclei and giving a fifteen line pattern could be arrived at. Only one was similar to the pattern observed. The larger two doublets were assigned as arising from  ${}^2J_{\text{HIrP}}$ , the quartet as arising from  ${}^3J_{\text{HIrSiF}}$  and the narrow doublet as arising from  ${}^2J_{\text{HIrH}}$ .



Figure 4.7  $H^1$  n.m.r. spectrum  $Ir(CO)H(PPh_3)_3 + SiF_3H$   
 $IrH$  region.



Line intensity analysis using above couplings





The lower frequency hydride ( $H_t$ ) appeared as a wide doublet of overlapping doublets of quartets of doublets (see Figure 4.8). The very wide doublet was assigned as arising from  ${}^2J_{HIrP(t)}$  and the next widest doublet as arising from  ${}^2J_{HIrP(c)}$ . The quartet was assigned as arising from  ${}^3J_{HIrSiF}$ . The narrow doublet coupling was previously observed in the resonance of the other hydride and was assigned as arising from  ${}^2J_{HIrH}$ . There is a problem with this, in that the outer two lines at the high frequency end of the high frequency half of the signal appear to be missing. There is a broad lump which could be due to them, but if so, they are perturbed for some reason.

Low power irradiation of each hydride resonance affected the other hydride resonance. An experiment was carried out to determine the relative signs of the coupling constants, using low power tickling of the outermost lines.

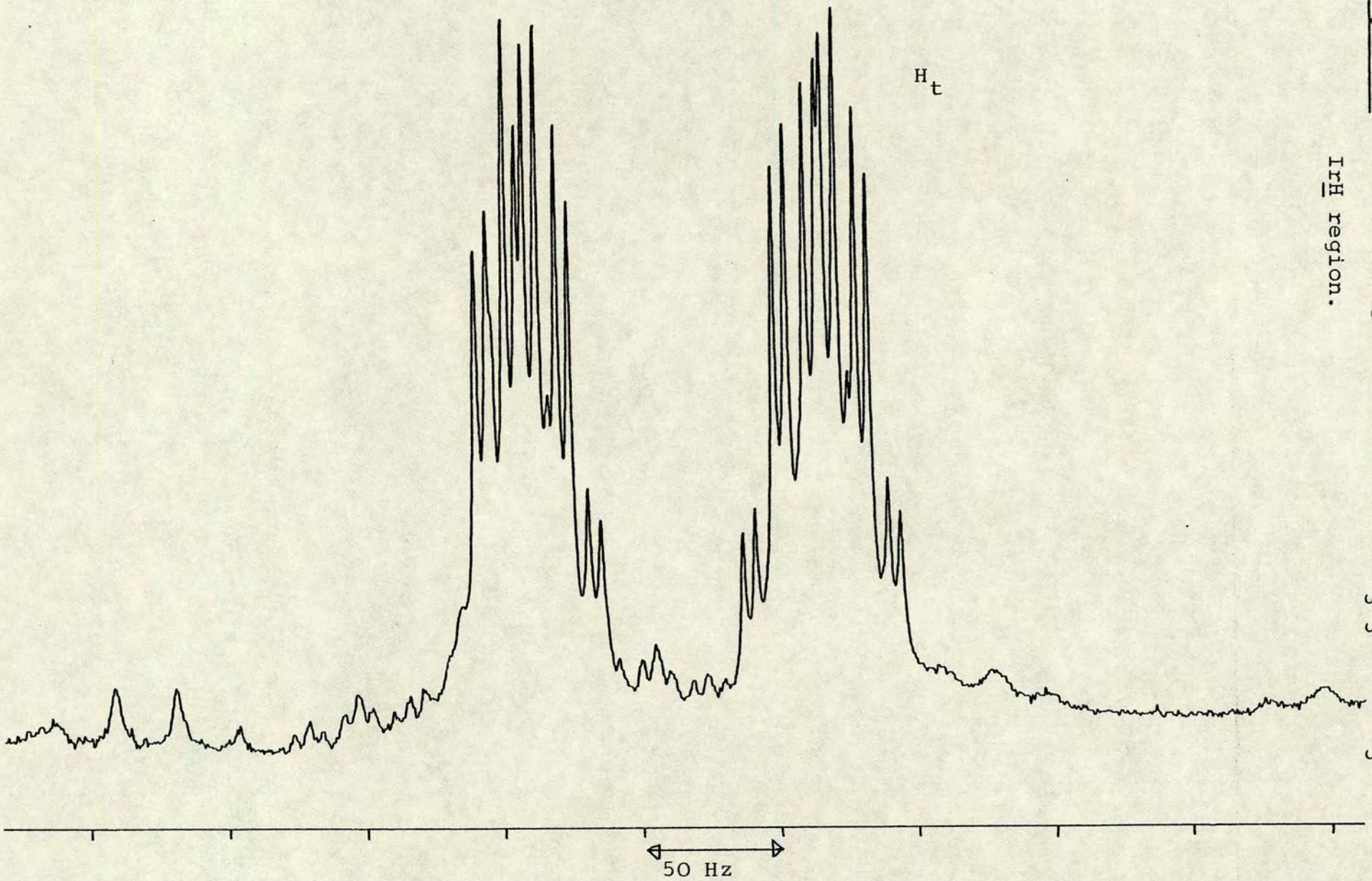
${}^2J_{H_t IrP_t}$	${}^2J_{H_c IrP_t}$	opposite
${}^2J_{H_t IrP_c}$	${}^2J_{H_c IrP_c}$	same
${}^3J_{H_t IrSiF}$	${}^3J_{H_c IrSiF}$	same

(as defined in Table 4.2)

The  ${}^{19}F$  n.m.r. spectrum was more complicated, and the resonance pattern was not symmetric. When  ${}^{31}P$  was decoupled it simplified to a triplet due to coupling to two similar hydrides.



Figure 4.8  $^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + \text{SiF}_3\text{H}$   
 $\text{IrH}$  region.

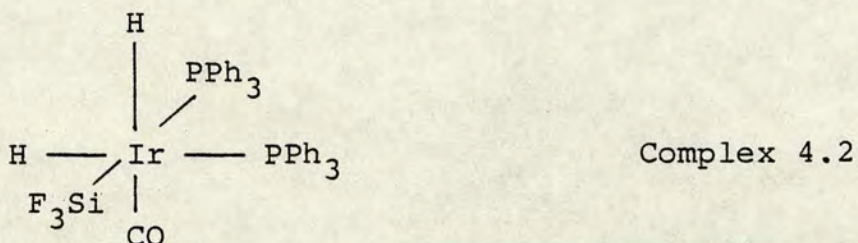




The non-decoupled spectrum showed a definite wide doublet, due to coupling to a trans phosphorus.

The spectrum was complicated for two reasons - the spectrum was being run under conditions of the highest resolution, and the couplings observed were to two phosphorus nuclei which themselves gave rise to a second order spectrum.

This information is in harmony with the following structure.



The n.m.r. parameters are documented in Table 4.2.

There is evidence from the  $^{19}\text{F}$  and  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectra that there was a very small amount of trans isomer present (i.e. the isomer with mutually trans phosphines). The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum showed a resonance with a narrow quartet coupling assumed to be due to  $^3J_{\text{PIrSiF}}$ . The  $^{19}\text{F}$  n.m.r. spectra showed a doublet of triplets; when irradiated at its  $^{31}\text{P}$  frequency the triplet splitting collapsed. The  $^1\text{H}$  n.m.r. spectra of this species was not observed, presumably because it was masked by that of the dominant cis isomer.

The structure assigned to the trans isomer was-



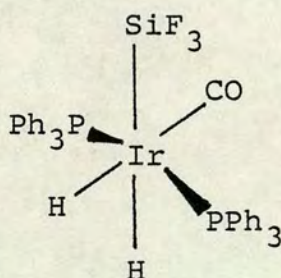


Its parameters are:-

$\delta_F$	$^3J_{FP}$	$^3J_{FH(t)}$	$^3J_{FH(c)}$
-90.01	2.5	9.8	no

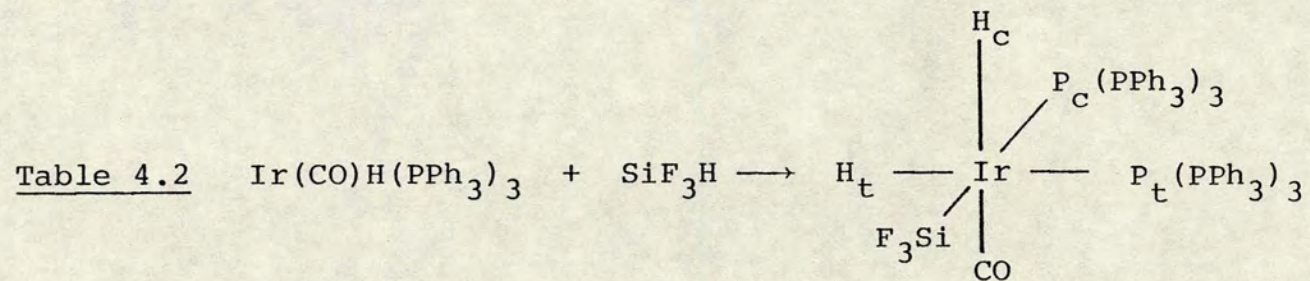
### Discussion

With this trans species we clearly observe the three-bond phosphorus-fluorine coupling, but do not observe the three-bond fluorine coupling to the cis hydride. This is opposite to the case with the analogous complex containing triethyl phosphine formed in the  $BF_3$  reactions in Chapter 2. Coupling of the fluorine to the trans hydride is also very much smaller than in the triethyl phosphine complex. Triphenyl phosphine is a bulkier ligand than triethyl phosphine and might tend to distort the molecule by forcing away from the  $SiF_3$  and CO groups down to the less crowded area where there are just hydrides.



Two and three bond couplings in molecules like these are often very sensitive to changes in molecular arrangements.





$\delta_{\text{H}_t}$	$\delta_{\text{H}_c}$	$\delta_{\text{P}_t}$	$\delta_{\text{P}_c}$	$\delta_{\text{F}}$	${}^2J_{\text{H}_t\text{IrH}_c}$	${}^2J_{\text{H}_t\text{IrP}_t}$	${}^2J_{\text{H}_t\text{IrP}_c}$
-10.86	-9.86	1.60	1.50	-84.51	4.5	106.3	17.7

${}^3J_{\text{H}_t\text{IrSiF}}$	${}^2J_{\text{H}_c\text{IrP}}$	${}^2J_{\text{H}_c\text{IrP}}$	${}^3J_{\text{H}_c\text{IrSiF}}$	${}^2J_{\text{P}_t\text{IrP}_c}$	${}^3J_{\text{P}_c\text{IrSiF}}$	${}^3J_{\text{P}_t\text{IrSiF}}$
11.2	14.3	19.5	9.7	18.9	61.5	4.8

N.m.r. parameters were recorded at 298 K using  $\text{C}_6\text{D}_5\text{CD}_3$  as solvent.



#### 4.3 Reaction of $\text{HIr}(\text{CO})(\text{PPh}_3)_3$ with $(\text{SiH}_3)_2\text{O}$

When disiloxane was reacted with  $\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2$  it was found that a bis iridium species was formed readily, but a mono iridium species only with great difficulty. This was attributed to the  $-\text{OSiH}_3$  group of the metal complex being more reactive than that of disiloxane. Disiloxane was reacted with Vaska's compound and a mono iridium species was observed as the initial product which then disproportionated to several species. The reaction of disiloxane with  $\text{HIr}(\text{CO})(\text{PPh}_3)_3$  was carried out in order to clarify the disproportionation and also to see how easily a mono iridium species could be formed.

$\text{HIr}(\text{CO})(\text{PPh}_3)_3$  and  $(\text{SiH}_3)_2\text{O}$  were reacted in a 1:2 molar ratio at  $-40^\circ\text{C}$  over a period of twelve hours until all the solid  $\text{HIr}(\text{CO})(\text{PPh}_3)_3$  was used up and the solution went colourless.

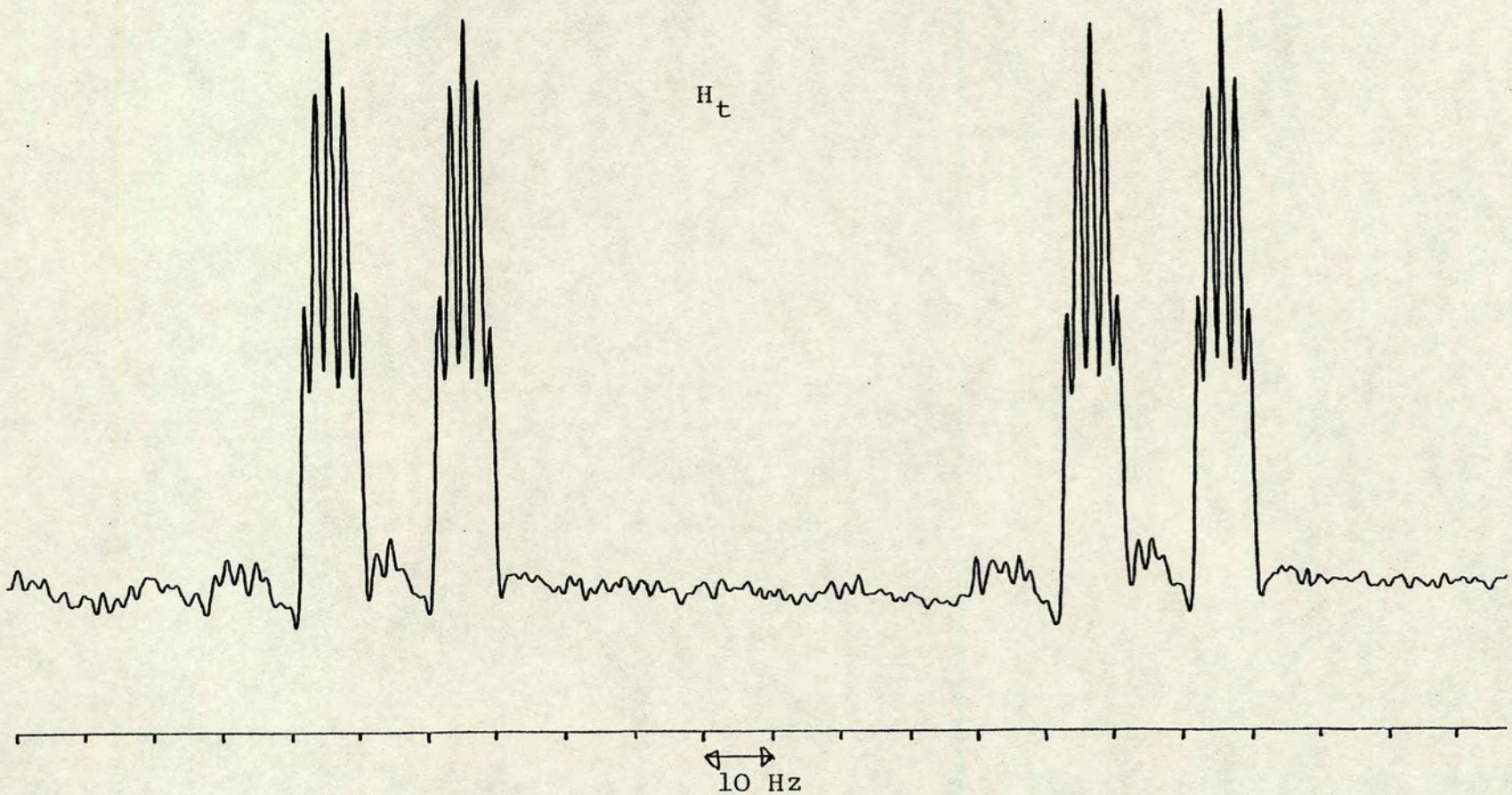
The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum appeared as an AB quartet and a singlet, the singlet arising from free triphenyl phosphine. The AB quartet arose from two mutually cis phosphines trans to different groups.

The  $^1\text{H}$  n.m.r. spectrum showed three groups of resonances - in the phenyl region, the silyl region and in the iridium hydride region.

There were two resonances in the hydride region, both of which were multiplets. The resonance at lower frequency ( $\text{H}_t$ ) (see Figure 4.9) could be interpreted as a wide



Figure 4.9  $^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + (\text{SiH}_3)_2\text{O}$   
 $\text{IrH}$  region





doublet of doublets of doublets of triplets; the triplet coupling was half the smallest doublet coupling, so that the peaks had the appearance of quintets.

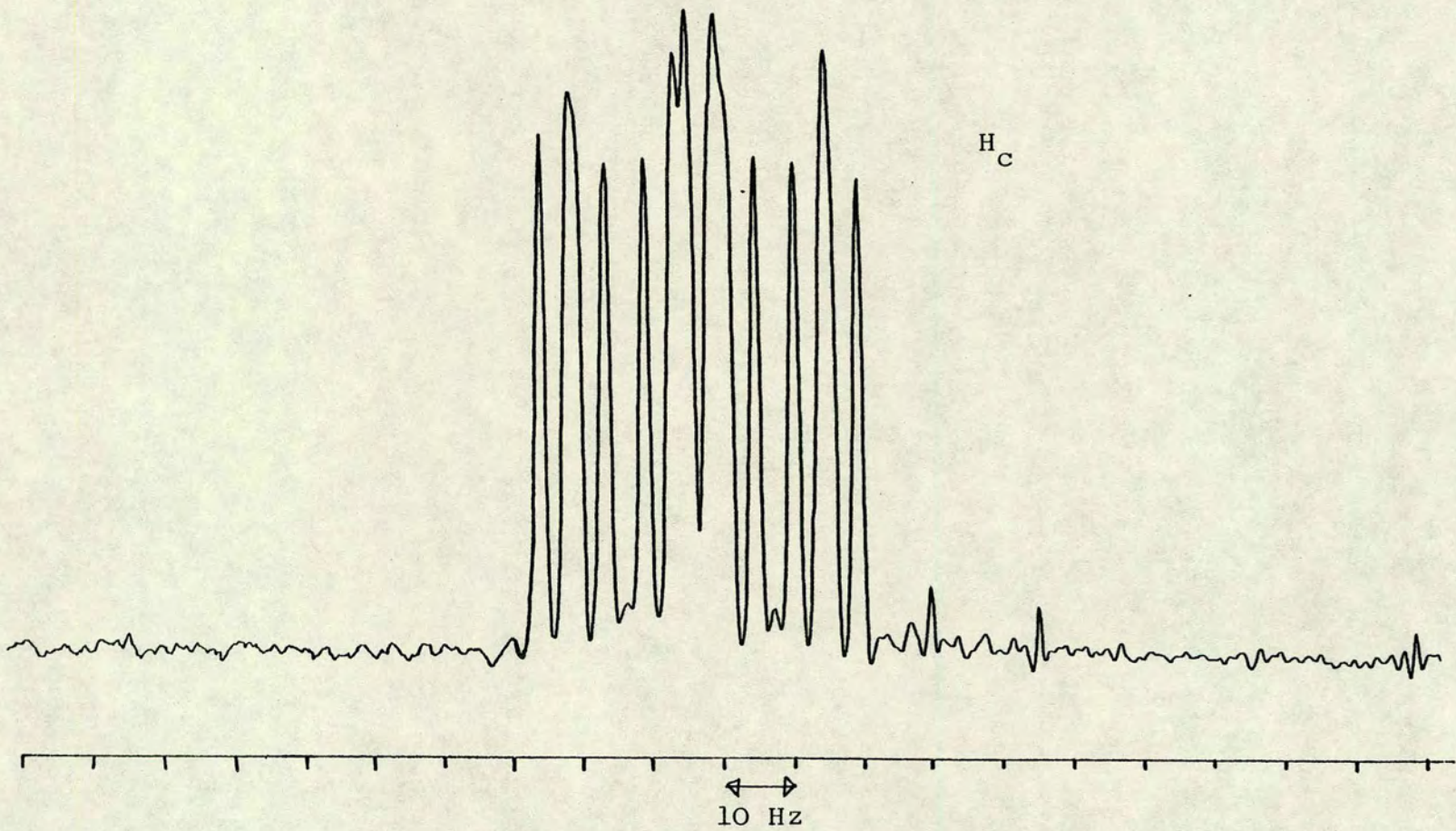
The wide doublet was assigned as arising from  ${}^2J_{\text{HIrP}(t)}$  and the next widest doublet as arising from  ${}^2J_{\text{HIrP}(c)}$ . The triplet coupling was assigned as arising from  ${}^3J_{\text{HIrSiH}}$ . However, the two protons that it couples to are not magnetically equivalent. The small doublet was assigned as arising from  ${}^2J_{\text{HIrH}}$ .

The higher frequency hydride ( $H_c$ ) multiplet could be interpreted as a doublet of doublets of doublets of doublets (see Figure 4.10). The wider two couplings were assigned as arising from  ${}^2J_{\text{HIrP}(c)}$ , and the narrowest doublet as  ${}^2J_{\text{HIrH}}$ , which has been observed in the other hydride resonance. The remaining doublet coupling was assigned as due to one of the protons on the  $-\text{SiH}_2-$  group.

There were many resonances observed in the silyl region which could be divided into two types - those from H bound to Si which was also bound to iridium and those from H bound to Si which was not bound to iridium. Of those not directly bonded to iridium, there were two large singlets, one being due to unreacted  $(\text{SiH}_3)_2\text{O}$  and the other due to a free  $-\text{SiH}_3$  of the iridium complex. It was difficult to assign them by integration, but the resonance at higher frequency was assumed to be the  $-\text{SiH}_3$  group of the metal complex. This was also assigned from a reaction where no excess of disiloxane had been used. There were also many



Figure 4.10  $^1\text{H}$  n.m.r. spectrum  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3 + (\text{SiH}_3)_2\text{O}$   
 $\text{IrH}$  region

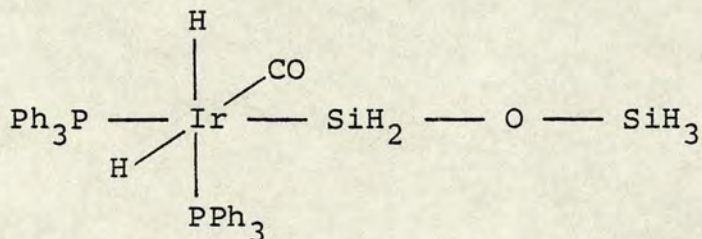




small peaks due to rearrangement of Si-O and Si-H bonds caused by the metal complex. This has already been observed for similar types of species<sup>7,8,9</sup>.

The other silyl resonance was a complex multiplet (see Figure 4.11). In these systems the SiH<sub>2</sub> protons are magnetically non-equivalent and give rise to two signals in the <sup>1</sup>H n.m.r. spectrum labelled H<sub>1</sub> and H<sub>q</sub>. With this system these two protons are almost equivalent and give rise to a complex second order pattern. A computer simulation was carried out to determine the six <sup>1</sup>H n.m.r. parameters which could not be measured directly. The results of this simulation are compared with the experimentally observed spectrum (Figure 4.11) and provide a near perfect fit.

This information is consistent with the following structure:



Complex 4.4

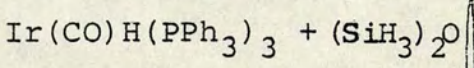
N.m.r. parameters are detailed in Table 4.3.

Here again is another example of disiloxane oxidatively adding to an iridium I complex and forming a mono-iridium species. This can be contrasted with the reaction of Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub> with disiloxane where a bis-iridium species was readily formed but a mono-iridium species could only be obtained with great difficulty.

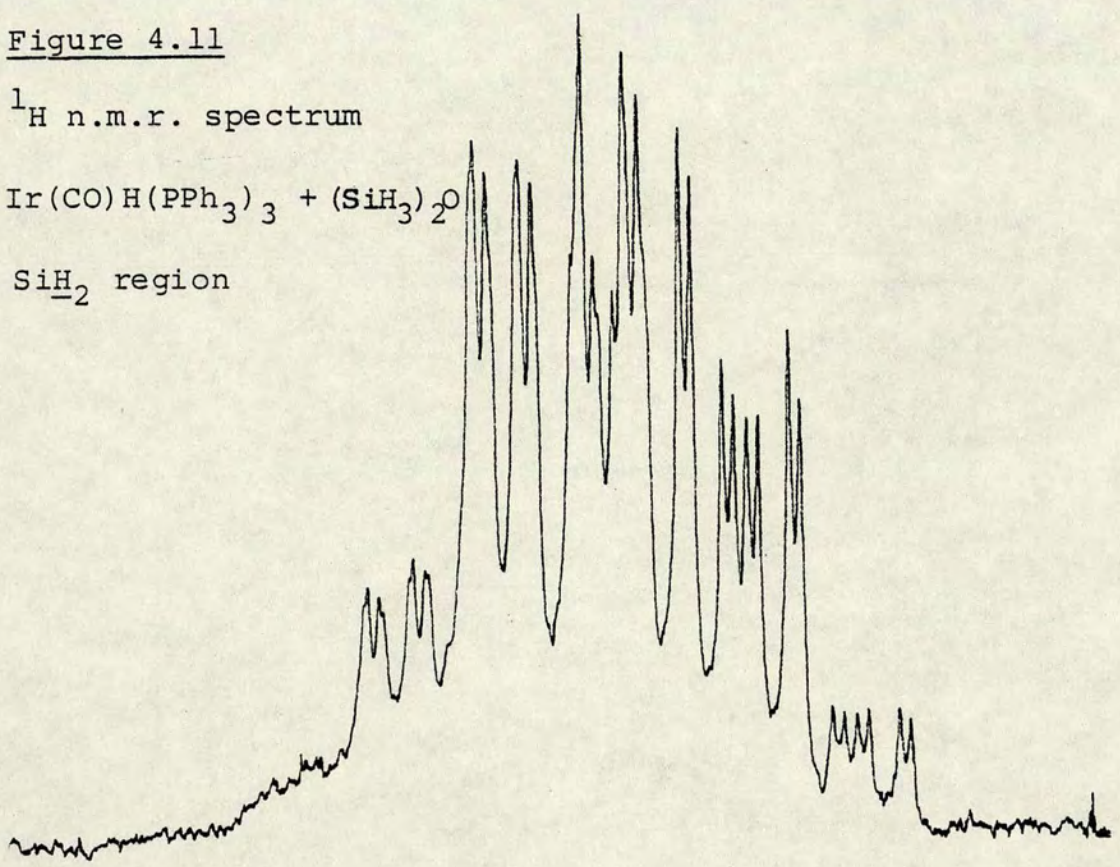


Figure 4.11

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



$\text{SiH}_2$  region



25 Hz

Computer Simulation

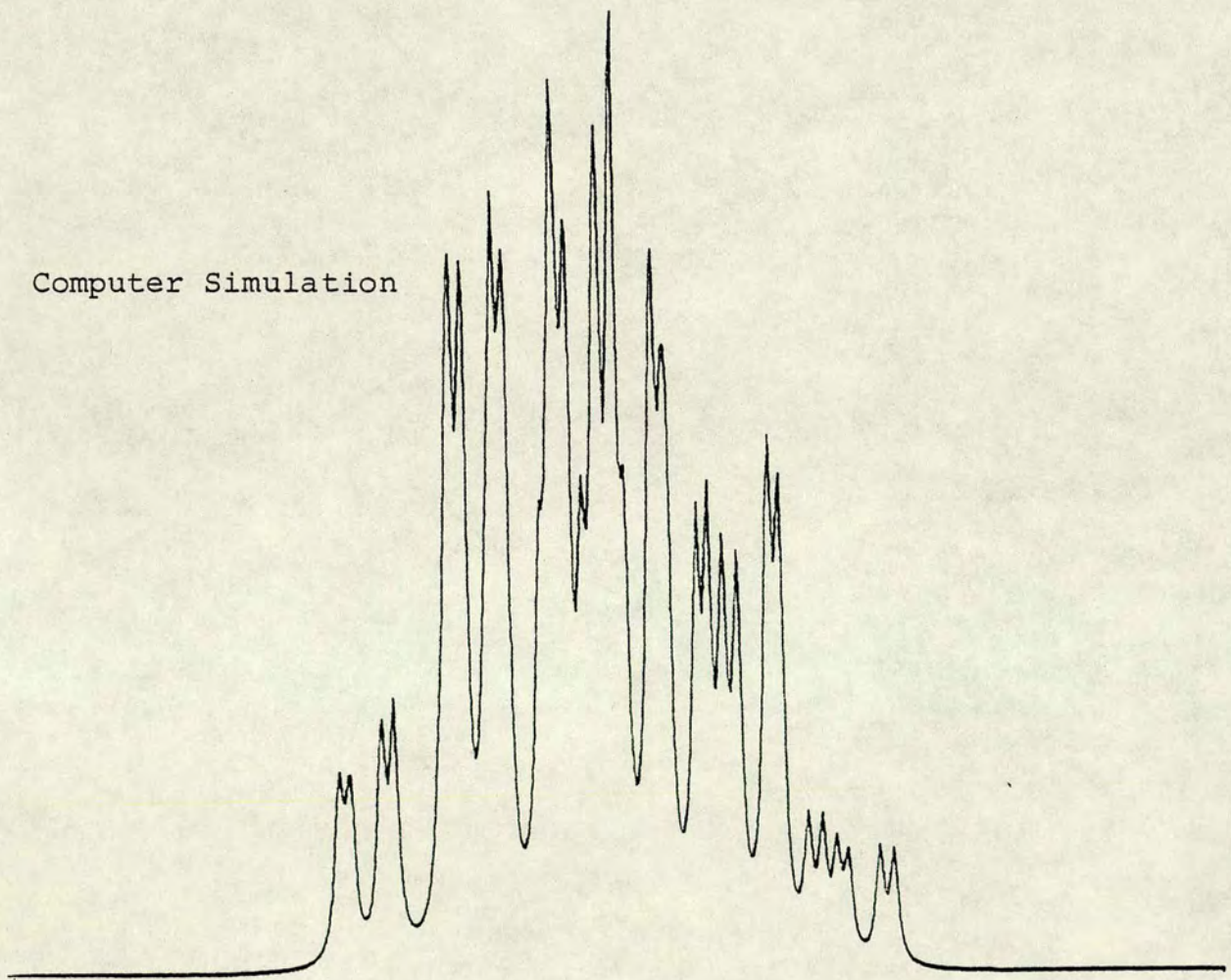
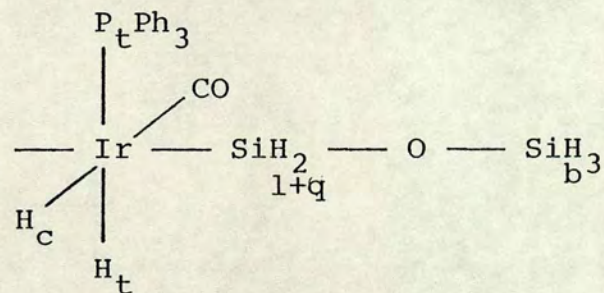
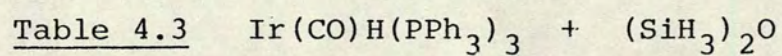




Table 4.3



$\delta_{P_t}$	$\delta_{P_c}$	$\delta_{H_c}$	$\delta_{H_D}$	$\delta_{H_L}$	$\delta_{H_q}$	$\delta_{H_b}$	$^2J_{P_t IrP_c}$	$^2J_{H_t IrP_t}$	$^2J_{H_t IrP_c}$	$^3J_{H_t IrSiH}$
7.29	1.93	-9.32	-10.25	9.15	5.95	4.85	17.3	110.9	19.4	1.7

$^2J_{H_c IrH_t}$	$^2J_{H_c IrP}$	$^2J_{H_c IrP}$	$^3J_{H_c IrSiH}$	$^2J_{H_1 H_q}$	$^3J_{H_q SiIrP_t}$	$^3J_{H_1 SiIrP_t}$	$^3J_{H_q SiIrP_c}$	$^3J_{H_1 SiIrP_c}$
3.9	21.4	14.7	6.0	13.7	15.0	5.0	9.0	14.0

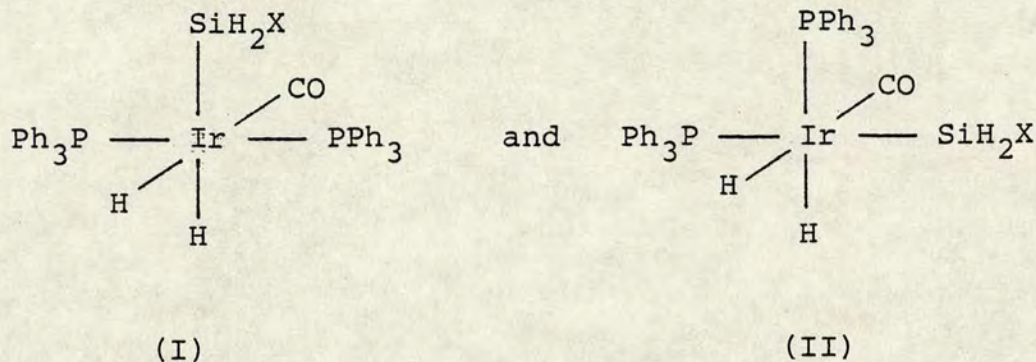
N.m.r. parameters recorded at 298 K using  $\text{C}_6\text{D}_5\text{CD}_3$  as solvent.



#### 4.4 Discussion

When  $\text{SiH}_3\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{H}, \text{Me}, \text{SiH}_3$ ) is reacted with  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$ , two types of product are formed.

These are:



The dominant of these, and sometimes the only isomer produced, is (II).  $\text{SiH}_3(\text{CH}_3)$  and  $\text{SiH}_3\text{F}$  form exclusively isomer (II).

The reaction of  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  with  $\text{O}(\text{SiH}_3)_2$  and  $\text{N}(\text{SiH}_3)_3$  yields exclusively isomer type (II). Another worker in this Department has found that reaction with  $\text{SiH}_3(\text{NMe}_2)$  gives exclusively isomer (II).

This is in keeping with the previous observation that all the reactions which produce 100% of isomer type (II) are with silyls bonded to a non-metal in row 1 of the periodic table, i.e. C, O, N and F.

Reaction of  $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3$  with  $\text{SiF}_3\text{H}$  forms mostly isomer (II) and a very small amount of isomer (I). This anomaly is probably due to the fact that there are three non-metals other than hydrogen bonded to the silicon instead of one.



In a recent paper<sup>3</sup> on this work it was pointed out that the most striking observation in relation to the chemical shifts was the internal shift between  $H_1$  and  $H_q$  in isomers of type (II). The magnitude of the shift depended dramatically on the nature of the substituent at Si: it was very small when the substituent was F,  $CH_3$  or  $SiH_3$  but large when the substituent was Cl, Br or I and increased in that order. It seemed likely that the shift was derived from conformational effects.

This can be observed even in the study with  $N(SiH_3)_3$  and  $O(SiH_3)_2$  where with disiloxane the internal chemical shift is so small that a second order pattern is observed, but with  $N(SiH_3)_3$  two separate easily interpreted signals are observed.



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CHAPTER 5

Reactions of  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$



5. Reactions of  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$

Reactions of  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  have previously been investigated by myself as part of a fourth year project<sup>1</sup>. Further reactions were carried out to add to the information already obtained. As part of the earlier study, low temperature oxidative addition by HCl was observed giving species where HCl oxidatively added to either one or both platinum depending on the concentration of HCl used.

5.1  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{HI}$

$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  was allowed to react with HI in a 1:4 molar ratio in methylene chloride. The reaction took place in two temperature dependent steps.

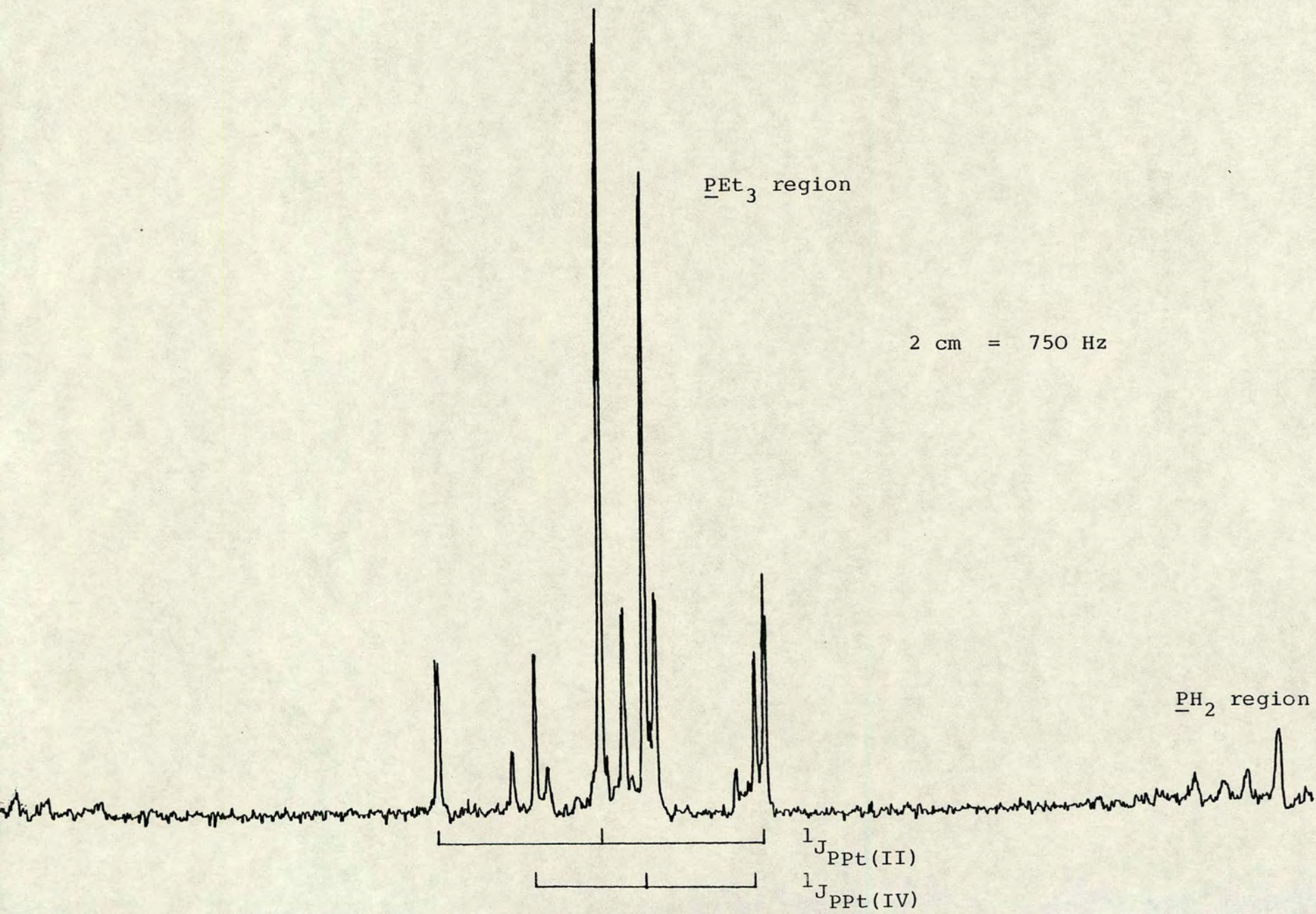
At  $-90^\circ\text{C}$  a species was formed where HI had oxidatively added to one of the platinum in the bridged complex.

The  $^3\text{1P}\{^1\text{H}\}$  n.m.r. spectra showed three resonances associated with the product. Two of these appeared in the  $\text{PEt}_3$  region and were each of twice the intensity of the other resonance which appeared in the  $\text{PH}_2$  region.

The two  $\text{PEt}_3$  resonances (see Figure 5.1) appeared as narrow doublets with  $^{195}\text{Pt}$  satellites. The narrow doublet splittings were assigned as arising from  $^2\text{J}_{\text{PptP(c)}}$ . The value of  $^1\text{J}_{\text{PtP}}$  associated with the higher frequency resonance was indicative of a four-coordinate Pt(II) species, and the coupling associated with the lower frequency resonance



Figure 5.1  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum  $[\text{HPt}(\text{PEt}_3)_2]_2 \text{PH}_2^+ \text{Cl}^- + \text{HI}$



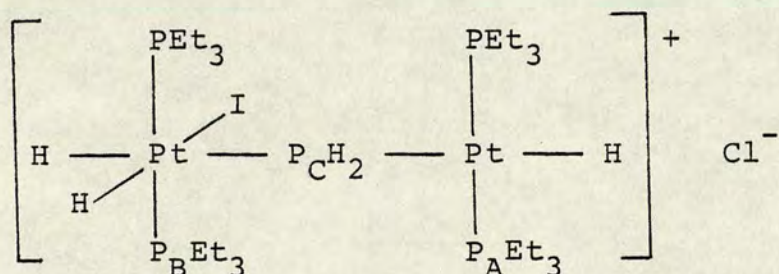


was indicative of a six-coordinate Pt(IV) complex.

Both these signals were of the same intensity.

The resonance in the  $\underline{\text{P}}\text{H}_2$  region (see Figure 5.2) appeared as a strong central resonance with two sets of  $^{195}\text{Pt}$  satellites. The lines showed signs of splitting but this could not be resolved. The wider of these sets of satellites was taken as  $^1\text{J}_{\text{Pt(A)P(C)}}$  where the coupling was to a four coordinate Pt(II) nucleus. The narrower of these was taken as  $^1\text{J}_{\text{Pt(B)P(C)}}$  where the coupling was to a six coordinate Pt(IV) nucleus.

This information suggests that the following species was present:



N.m.r. parameters are listed in Table 5.1

On warming to  $-70^\circ\text{C}$  the resonances attributed to this species disappeared and another set of signals appeared in the  $^{31}\text{P}$  n.m.r. spectrum.

One of these resonances appeared in the  $\underline{\text{P}}\text{Et}_3$  region (see Figure 5.3) as a narrow doublet with  $^{195}\text{Pt}$  satellites. The narrow doublet was assigned as arising from  $^2\text{J}_{\text{PpTP}}$ . The size of the coupling to  $^{195}\text{Pt}$  was indicative of being a six-coordinate Pt(IV) species.



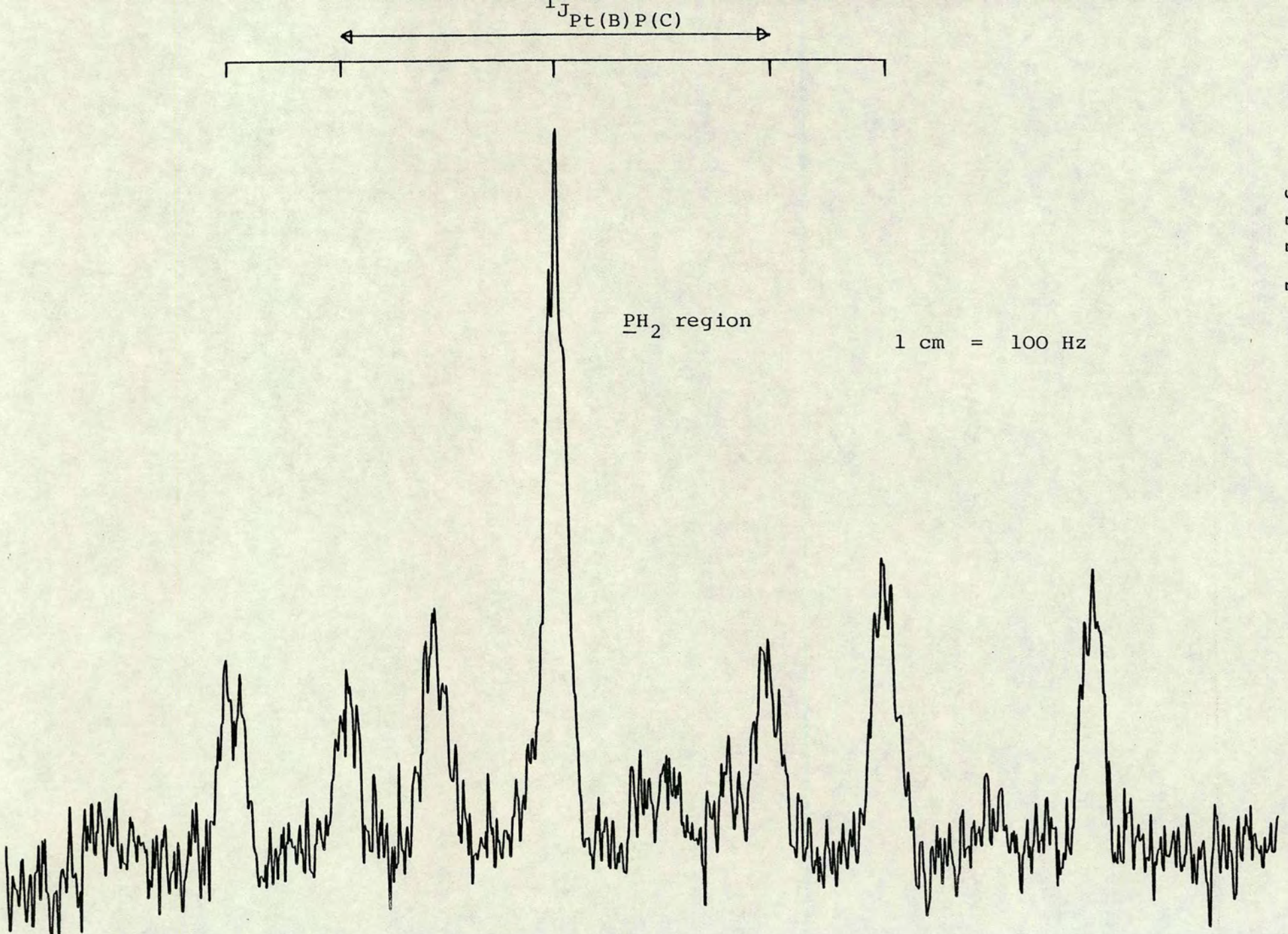
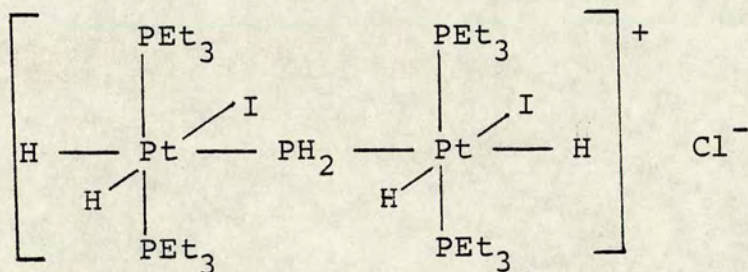


Figure 5.2  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum  
[HPt(PEt<sub>3</sub>)<sub>2</sub>]<sub>2</sub>PH<sub>2</sub><sup>+</sup>Cl<sup>-</sup> + HI



The other resonance was in the  $\underline{\text{P}}\text{H}_2$  region (see Figure 5.4) and appeared as a pseudo quintet of narrow quintets. The coupling constant of the narrow quintet coupling was of the same size as the doublet coupling observed in the  $\underline{\text{P}}\text{Et}_3$  region. The pseudo quintet showed intensities of 1 : 8 : 18 : 8 : 1 which arose from the probabilities of there being two, one or no  $^{195}\text{Pt}$  nuclei in the complex, which is indicative of a phosphorus bonded to two equivalent platinum nuclei.

This information suggests the following species was present:



The reaction was different to that of the reaction with HCl in that it took place at lower temperature and the step-wise addition of HI could be controlled by slightly increasing the temperature.

Decomposition products after warming were not studied.



Figure 5.3  $^3\text{P}\{^1\text{H}\}$  n.m.r. spectrum  $[\text{HPt}(\text{PEt}_3)_2]_2\text{P}^+\text{H}_2\text{Cl}^- + \text{HI}$

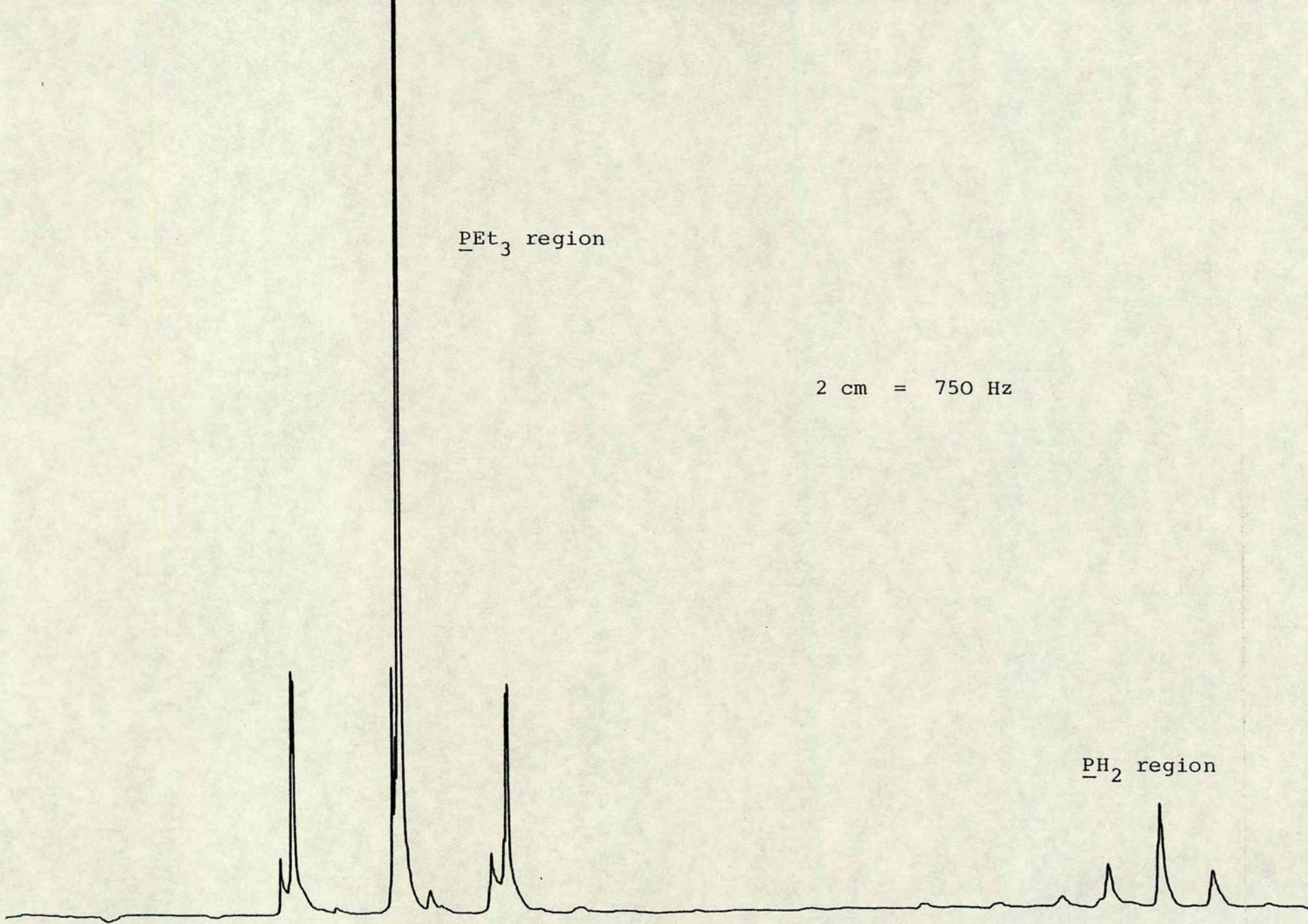




Figure 4.4  $^{31}\text{P}\{^1\text{H}\}_n$ .m.r. spectrum  $[\text{HPt}(\text{PEt}_3)_2]_2 \text{PH}_2^+ \text{Cl}^- + \text{HI}$

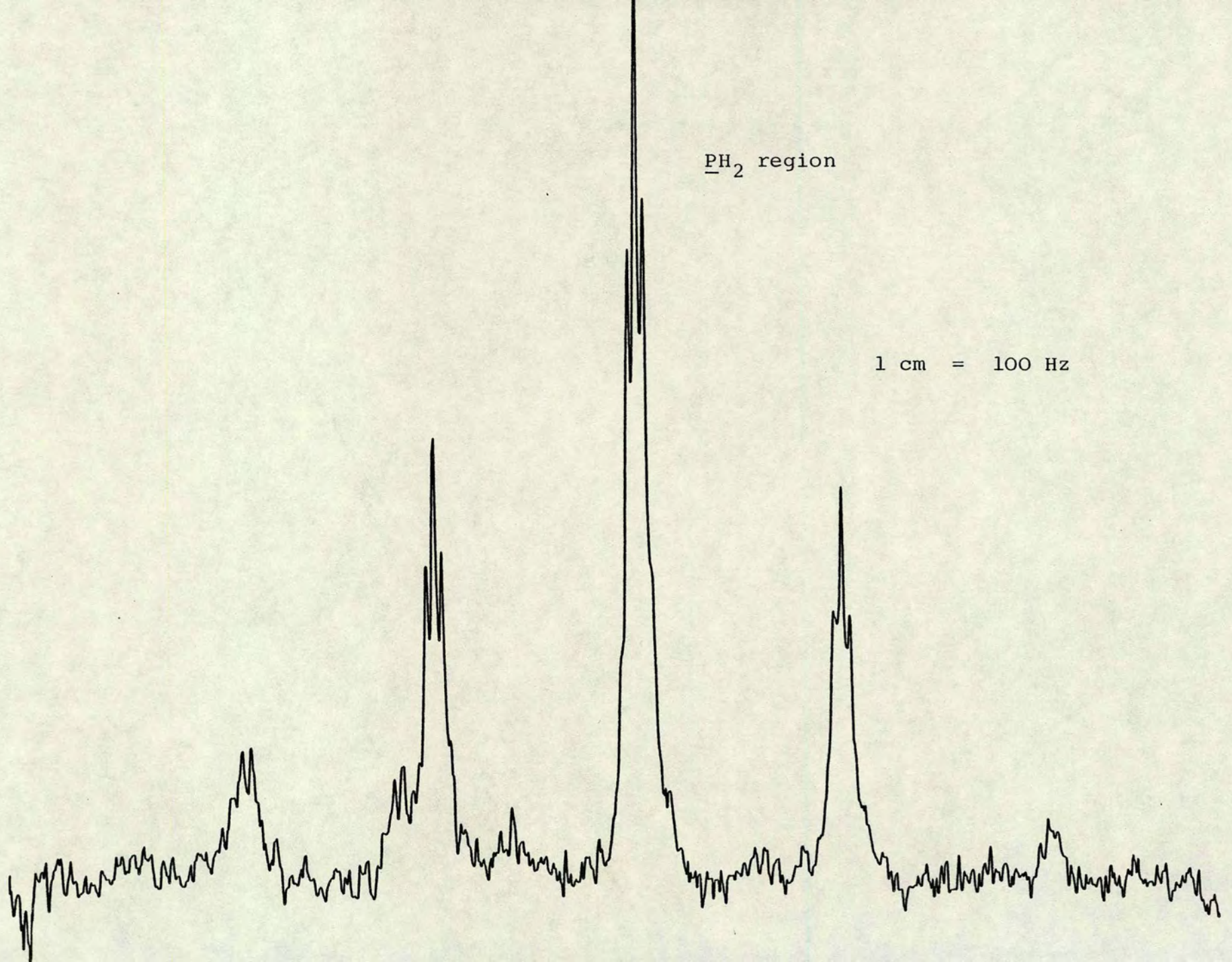




Table 5.1  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{HI}$

	$\delta_{\text{P}_A}$	$\delta_{\text{P}_B}$	$\delta_{\text{P}_C}$	$^1J_{\text{P}_A\text{Pt}}$	$^1J_{\text{P}_B\text{Pt}}$	$^1J_{\text{P}_C\text{Pt}(A)}$	$^1J_{\text{P}_C\text{Pt}(B)}$	$^2J_{\text{P}_A\text{P}_C}$	$^2J_{\text{P}_B\text{P}_C}$
	16.6	-	-169.7	2537	-	1202	-	18	-
	14.7	1.1	-197.8	2490	1671	1392	832	17	10
	-	-2.5	-242.7	-	1646	-	791	-	15

N.m.r. parameters obtained at 298 K, 13 K, and 13K respectively using  $\text{CD}_2\text{Cl}_2$  as solvent.



5.2  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{H}_2\text{Se}$

$[\text{H}_2\text{Pt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  was allowed to react with  $\text{H}_2\text{Se}$  in both 1:1 and 1:2 molar ratios. This was attempted to see if similar bridged species containing six-coordinated platinum could be formed as were observed in the reactions with hydrogen halides.

Reaction was investigated at temperatures down to as low as  $-120^\circ\text{C}$ .  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. studies showed no evidence for oxidative addition to the bridged species but immediate cleavage of the  $\text{PH}_2$  bridge.

Several SeH-platinum species were observed which had been synthesised before in this group<sup>2</sup> (see Table 5.2 for a summary of species formed and their  $^{31}\text{P}$  n.m.r. parameters). The complex assigned as  $[\text{H}_2\text{Pt}(\text{PEt}_3)_2(\text{SeH})\text{PH}_3]^+$  however was novel.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectra showed two resonances arising from it. The resonance in the  $\underline{\text{PEt}}_3$  region appeared as a narrow doublet assigned as arising from  $^2\text{J}_{\text{PPtP}}$ , with  $^{195}\text{Pt}$  satellites. The coupling to platinum  $^1\text{J}_{\text{PtP}}$  was characteristic of being a six-coordinate Pt(IV) complex. On selectively decoupling the ethyl  $^1\text{H}$  frequencies the signals broadened to have shoulders and were taken as being triplets, indicating that two hydrides were bonded to the platinum. The resonance in the  $\underline{\text{PH}}$  region appeared as a triplet with  $^{195}\text{Pt}$  satellites of intensity 1 : 4 : 1 indicating it was not from a bridged species. The triplet coupling was assigned as arising from  $^2\text{J}_{\text{PPtP}}$  and had been observed for the resonance in the  $\underline{\text{PEt}}_3$  region.

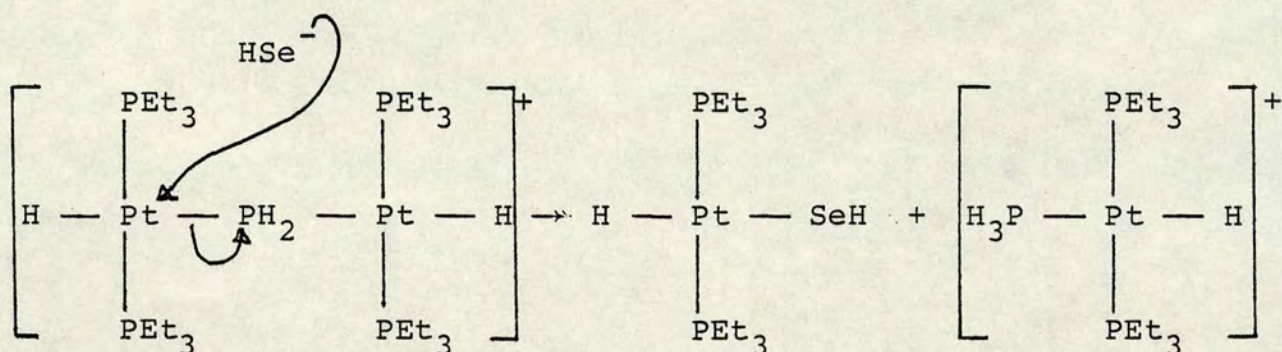


Table 5.2  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{H}_2\text{Se}$

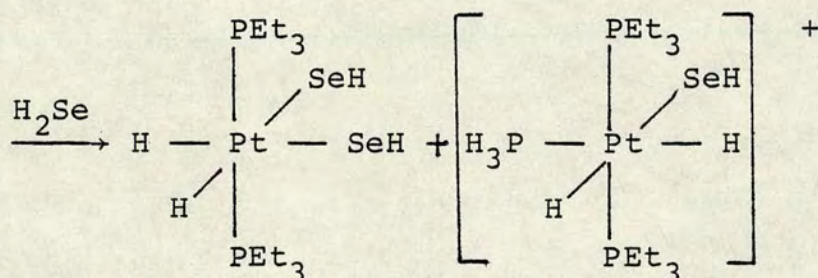
$\delta_p$	Types of Resonance	$^1J_{\text{PtP}}$	$^2J_{\text{PPtP}}$	Species	$\{^1\text{HPet}_3\}$
18.8	singlet + $^{195}\text{Pt}$ satellites	2600	-	$\text{HPt}(\text{PEt}_3)_2(\text{SeH})$	doublet
0.9	doublet + $^{195}\text{Pt}$ satellites	1586	22	$\text{H}_2\text{Pt}(\text{PEt}_3)_2(\text{SeH})_2\text{PH}_3^+$	broad triplet
-0.6	singlet + $^{195}\text{Pt}$ satellites	1762	-	$\text{H}_2\text{Pt}(\text{PEt}_3)_2(\text{SeH})_2$	triplet
6.7	singlet + $^{195}\text{Pt}$ satellites	1770	-	$\text{ClH}_2\text{Pt}(\text{PEt}_3)_2\text{SeH}$	triplet
-169.5	triplet + 1:4:1 satellites	1162	22	$\text{H}_2\text{Pt}(\text{PEt}_3)_2(\text{SeH})_2\text{PH}_3^+$	—



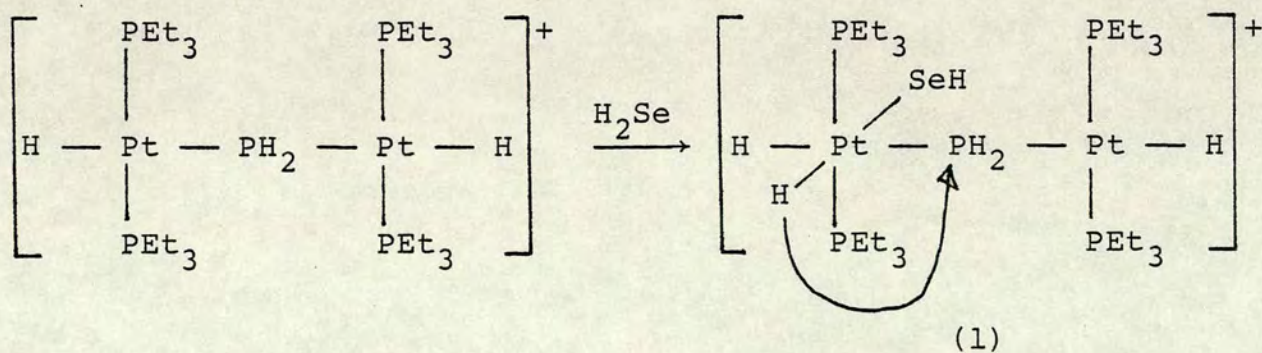
No evidence for an oxidative addition to the bridged complex was observed, but cleavage of the  $\text{PH}_2$  bridge seemed to be the initial reaction step. This probably took place by nucleophilic or ionic attack by  $\text{H}_2\text{Se}$ .



These species then undergo oxidative addition with  $\text{H}_2\text{Se}$ .



The alternative is that the initial step is an oxidative addition which immediately leads to cleavage of the  $\text{PH}_2$  bridge. This eventually happened with the  $\text{HCl}$  adduct.









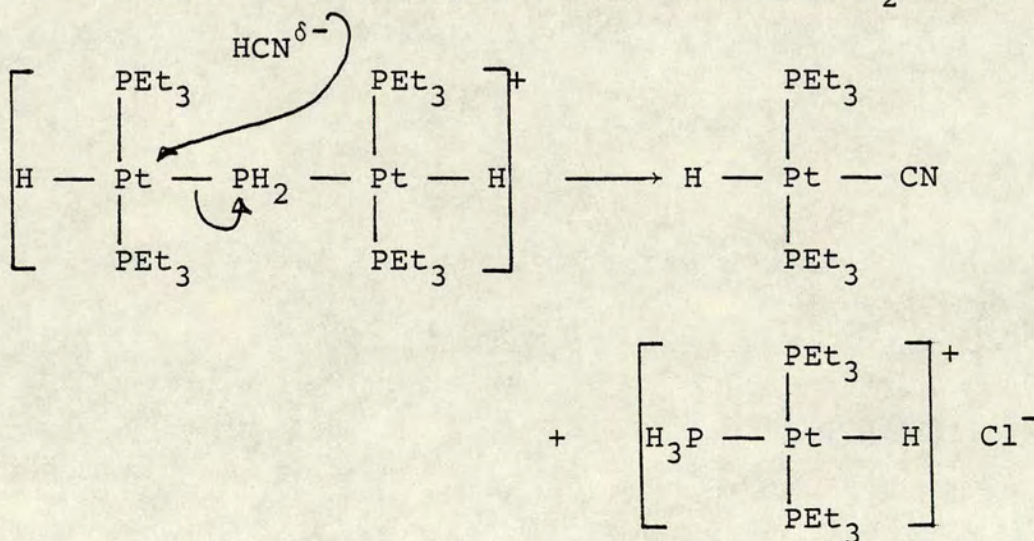
5.3  $[HPt(PEt_3)_2]_2PH_2^+Cl^- + HCN$

$[HPt(PEt_3)_2]_2PH_2^+Cl^-$  was allowed to react with HCN in a 1:2 molar ratio in dichloromethane. No reaction was observed until a temperature of  $20^\circ C$  was reached. Three species were observed and characterized by their published parameters<sup>3</sup>. These were:-

$\delta_P$	$^1J_{PtP}$	Species
19.8	2553.7	$HPt(PEt_3)_2CN$
15.3	2255.8	$ClPt(PEt_3)_2$
-240.5	-	$PH_3$

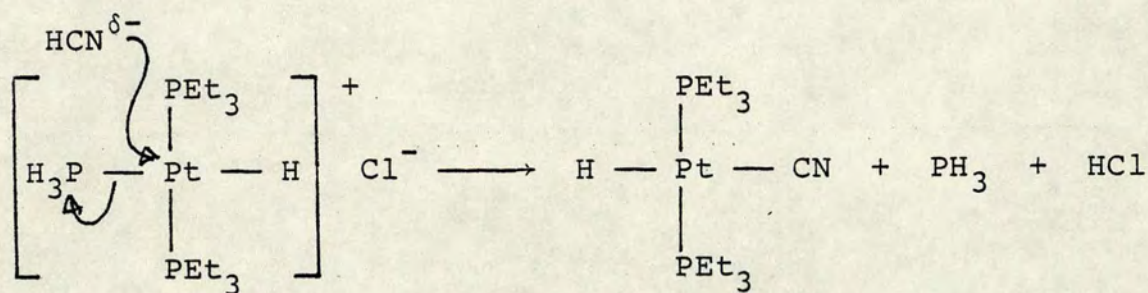
No six-coordinate complexes were observed.

A possible mechanism could involve an initial nucleophilic attack by HCN to cleave the  $PH_2$  bridged.

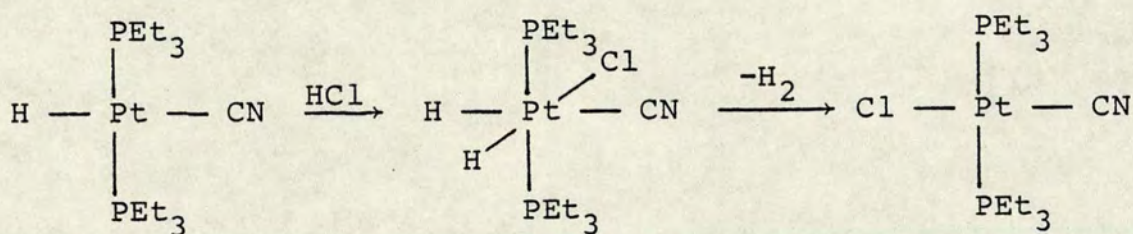


This is followed by nucleophilic attack on the cation formed, losing  $PH_3$  to become a neutral compound.



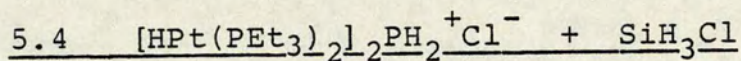


$\text{HPt}(\text{PEt}_3)_2\text{CN}$  then undergoes oxidative addition with the  $\text{HCl}$  formed followed by reductive elimination of  $\text{H}_2$ .



This reaction and that of  $\text{H}_2\text{Se}$  seem to indicate that if the attacking group is a strong nucleophile the first reaction step is nucleophilic attack cleaving the  $\text{PH}_2$  bridge.

If on the other hand, as in the hydrogen halide case, the attacking group is less nucleophilic the first reaction step is oxidative addition.



$[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  was allowed to react with a 1:2 molar excess of  $\text{SiH}_3\text{Cl}$  but no six-coordinate bridged species was observed.



The products were studied by  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. and many peaks were observed making interpretation difficult.

There were resonances in the  $\underline{\text{P}}\text{H}_2$  region indicating two types of bridged species (see Figure 5.5).

The resonance at lowest frequency appeared as a 1:8:18:8:1 pseudo-quintet of quintets. The outermost lines of the pseudo-quintet were not observed, but were assumed from the intensities of the observed lines. The quintet coupling was assigned as arising from  $^2\text{J}_{\text{PpPtP}}$ . This resonance appeared shifted to very low frequency compared to the starting material, which seemed to indicate that the ligand trans to the  $\underline{\text{P}}\text{H}_2$  had been changed. A ligand such as  $-\text{SiH}_2\text{Cl}$  might account for such a low frequency shift.

This was the first species formed. At the same time a resonance appeared in the  $\underline{\text{P}}\text{Et}_3$  region to slightly lower frequency of the starting materials resonance and similar in appearance (see Figure 5.6). It appeared as a doublet assigned as arising from  $^2\text{J}_{\text{PpPtP}}$  and had the same coupling constant as that previously assigned as  $^2\text{J}_{\text{PpPtP}}$  from the  $\underline{\text{P}}\text{H}_2$  region. This doublet had  $^{195}\text{Pt}$  satellites where the coupling constant  $^1\text{J}_{\text{PtP}}$  was indicative of a four-coordinate Pt(II) complex.

The structure attributed to these resonances was:

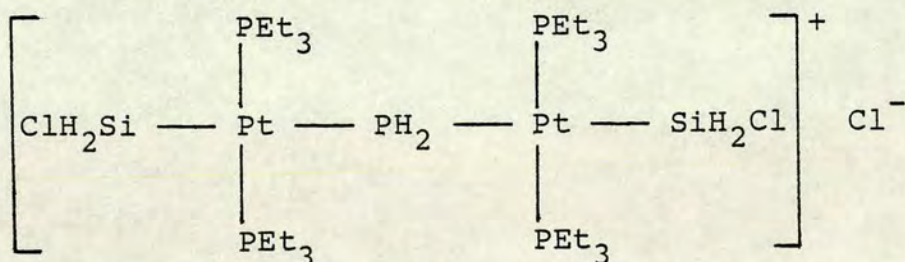




Figure 5.5  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum  
 $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{SiH}_3\text{Cl}$   $\text{PH}_2$  region

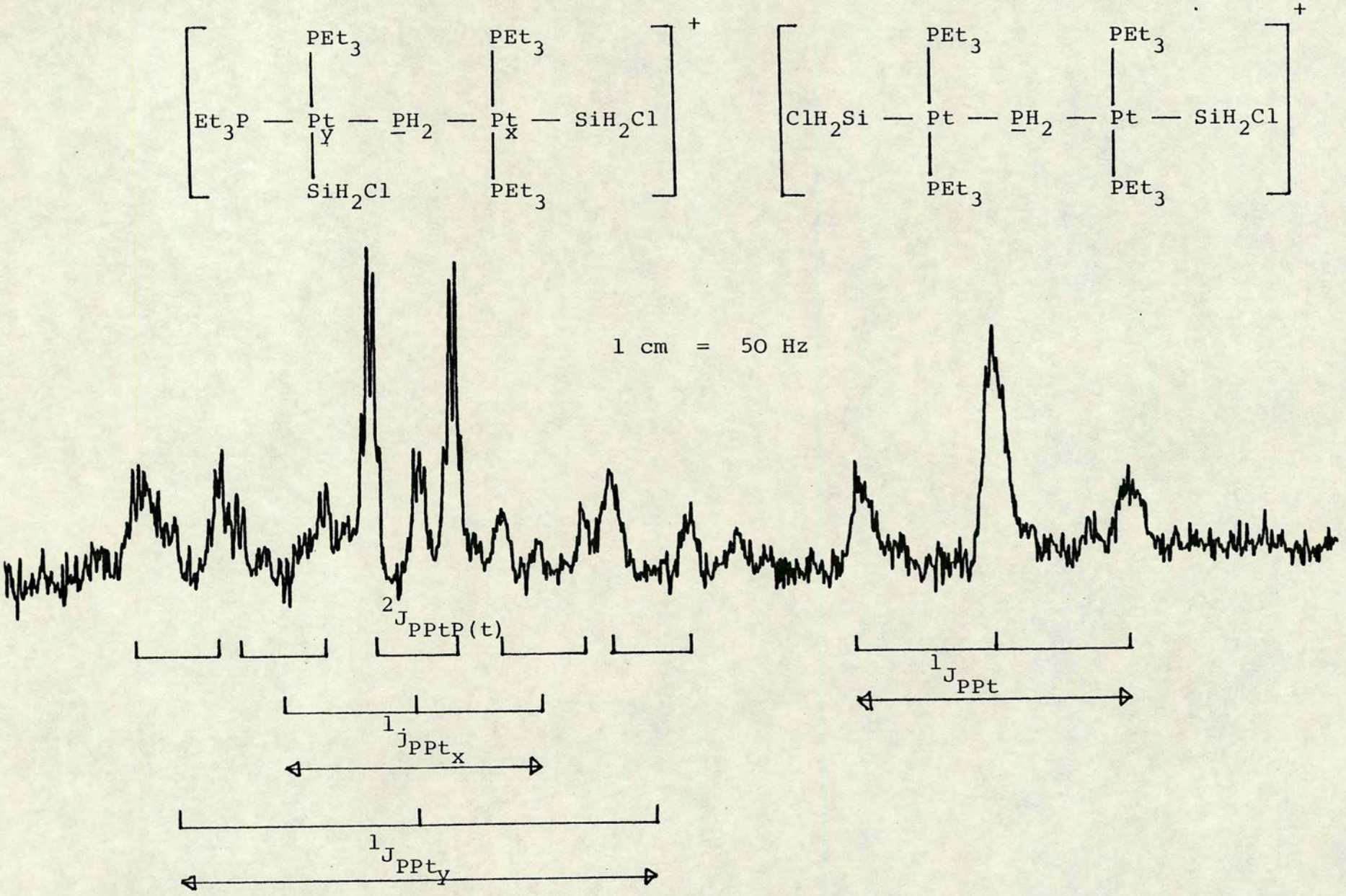
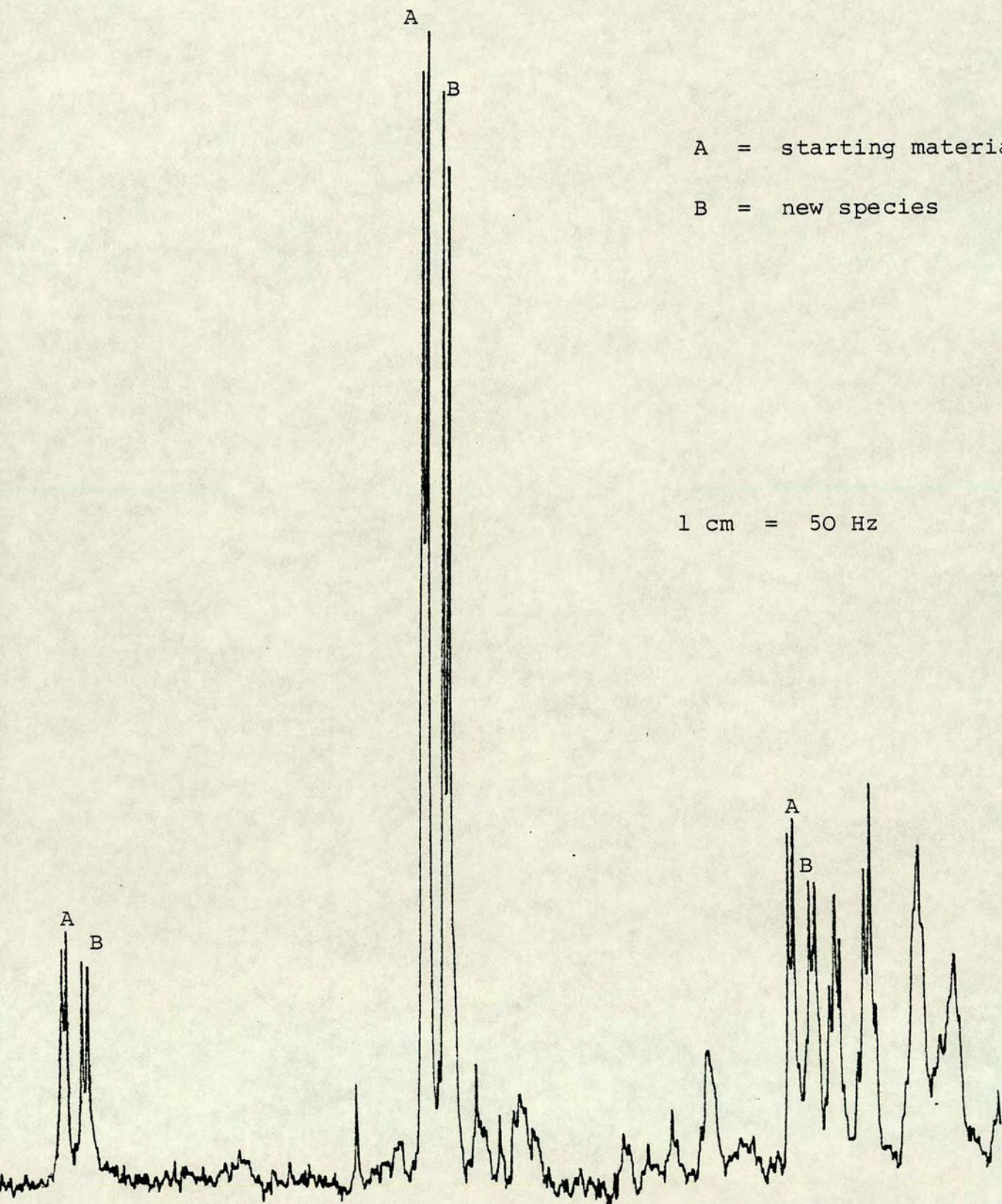
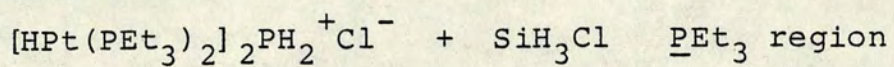




Figure 5.6  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum

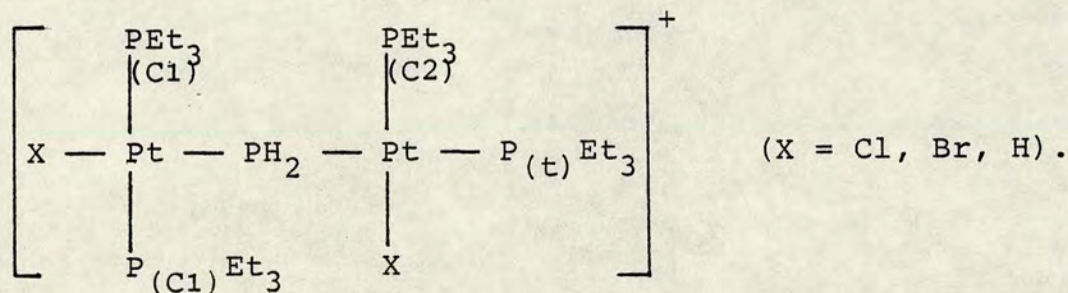




See Table 5.3 for n.m.r. parameters.

Very soon after this species was observed another species appeared.

This new species showed resonances in the  $\underline{\text{P}}\text{H}_2$  region (see Figure 5.5) at higher frequency than that of the first species which interpreted as a doublet of narrow quartets with two sets of  $^{195}\text{Pt}$  satellites. The satellites were of about one quarter of the intensity of the central resonances. This type of pattern had been observed before for the  $\underline{\text{P}}\text{H}_2$  region for the following type of complex<sup>4</sup>.



The wider doublet coupling arose from  $^2\text{J}_{\text{P}(\text{t})\text{PtP}(\text{C})}$  i.e. coupling to a trans phosphine. The quartet splitting arose from  $^2\text{J}_{\text{P}(\text{C})\text{PtP}(\text{t})}$ . These three triethylphosphines are all cis and couple roughly the same.

The two sets of satellites arose from the fact that the platinum on each side of the bridge were no longer magnetically equivalent and so gave rise to two different  $^1\text{J}_{\text{PtP}}$  values.

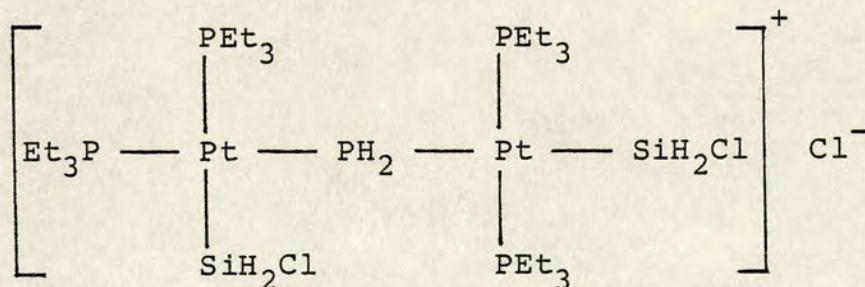
If  $\text{X} = \text{SiH}_2\text{Cl}$  it is in harmony with this structure that the chemical shift of the  $\underline{\text{P}}\text{H}_2$  group moves to higher frequency because it has become trans to only one  $\text{SiH}_2\text{Cl}$  ligand.



Similar species to this show three resonances in the  $\underline{PEt}_3$  region all with  $^{195}\text{Pt}$  satellites.  $P_{(Cl)}$  appeared as a narrow doublet having the same intensity as  $P_{(C2)} + P_{(t)}$ .  $P_{(C2)}$  appeared as a narrow triplet and  $P_{(t)}$  as a doublet of narrow doublets.

A doublet of doublets (see Figure 5.7) with  $^{195}\text{Pt}$  satellites was picked out easily,  $^1J_{PtP}$  being indicative of a four-coordinate Pt(II) complex. The wider doublet had the same coupling constant as  $^2J_{PPTP(t)}$  previously assigned from the  $\underline{PH}_2$  resonance. A triplet was observed with  $^{195}\text{Pt}$  satellites,  $^1J_{PtP}$  being indicative of a four coordinate Pt(II) complex. Its intensity was comparable with that of the previous resonance. A doublet was observed with  $^{195}\text{Pt}$  satellites,  $^1J_{PtP}$  being indicative of a four coordinate Pt(II) complex. This resonance was of twice the intensity of the doublet of doublets.

These observations would account for the following species:



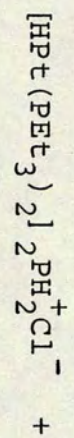
See Table 5.3 for n.m.r. parameters.

No  $^1\text{H}$  n.m.r. spectra were obtained.

Henner<sup>4</sup> has observed the following slow rearrangement:

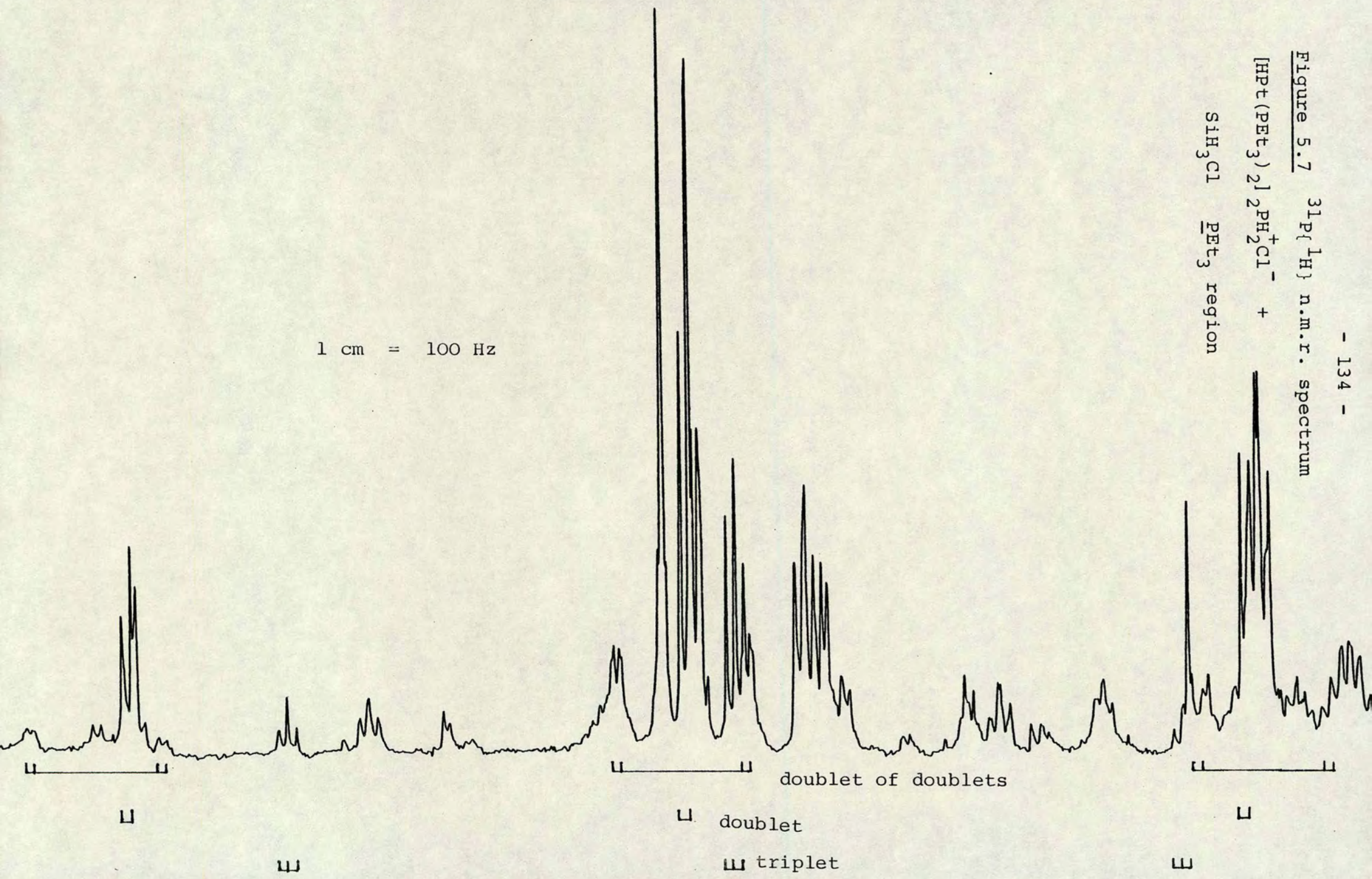


Figure 5.7  $^{31}\text{P}\{\text{H}\}$  n.m.r. spectrum

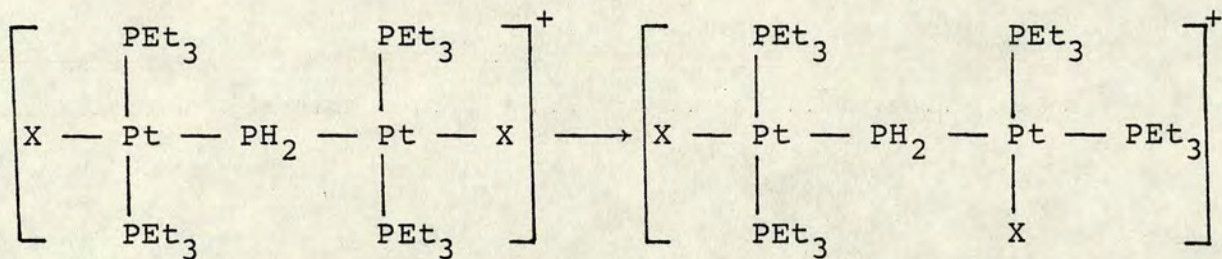


$\text{SiH}_3\text{Cl}$   $\text{PET}_3$  region

1 cm = 100 Hz







(X = Cl, Br)

This seems to be what is happening in this reaction where X = SiH<sub>2</sub>Cl.

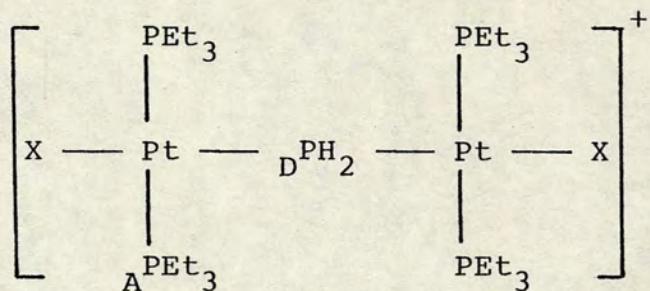
Formation of the first complex probably arises from oxidative addition by SiH<sub>3</sub>Cl followed by immediate reductive elimination of H<sub>2</sub>.

Another bridged species appeared in the reaction mixture which did not appear to be PH<sub>2</sub> bridged. No <sup>2</sup>J<sub>PtPt</sub> was observed. This showed as a singlet with two sets of <sup>195</sup>Pt satellites. One set of satellites, <sup>1</sup>J<sub>PtP</sub> was indicative of being a four-coordinate Pt(II) complex. The other set of satellites was from a long range coupling, <sup>3</sup>J<sub>PtP</sub>. What this species is is not known but it could be silicon or chlorine bridged.

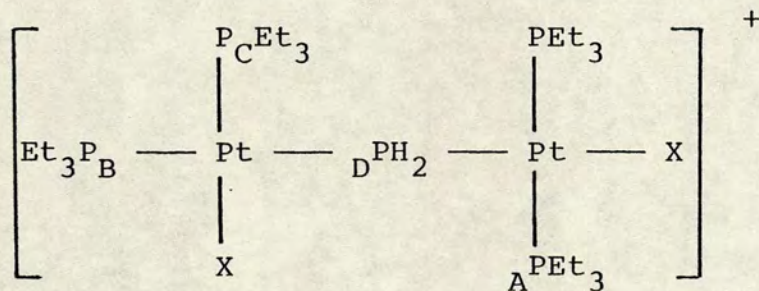
On allowing the reaction to warm to room temperature the spectrum simplified to show four species. Two contained no platinum and were PH<sub>3</sub> and (HPEt<sub>3</sub>)<sup>+</sup>X<sup>-</sup> whose resonance grew in intensity as the reaction got warmer. The two platinum species appear to be ClPt(PEt<sub>3</sub>)<sub>2</sub>SiH<sub>2</sub>Cl and Cl<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub> by comparison with published parameters<sup>5</sup>, though this does seem to involve a lot of halide.



Table 5.3  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{SiH}_3\text{Cl}$



trans-trans



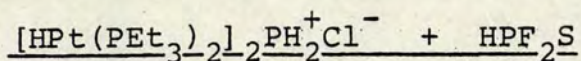
cis-trans

X = SiH<sub>2</sub>Cl

	$\delta_{\text{P}_A}$	$\delta_{\text{P}_B}$	$\delta_{\text{P}_C}$	$\delta_{\text{P}_D}$	$^1J_{\text{P}_A\text{Pt}}$	$^1J_{\text{P}_B\text{Pt}}$	$^1J_{\text{P}_C\text{Pt}}$	$^1J_{\text{P}_D\text{Pt}_A}$	$^1J_{\text{P}_D\text{Pt}_{BC}}$	$^2J_{\text{P}_D\text{PtP}_B}$	$^2J_{\text{P}_D\text{PtP}(\text{cis})}$
trans-trans	15.0	-	-	-262.8	2335	-	-	930	-	-	18
cis-trans	15.5	12.8	15.8	-211.4	2499	2008	~2400	928	1635	293	20

N.m.r. parameters recorded at 213 K using CD<sub>2</sub>Cl<sub>2</sub> as solvent.





Whitelock has studied reactions of  $\text{PF}_2$  species with Pt(II) compounds<sup>6,7</sup>. He observed that  $\text{HPF}_2\text{S}$  oxidatively adds to  $\text{HPt}(\text{PEt}_3)_2\text{X}$  and then undergoes reductive elimination of  $\text{H}_2$  or  $\text{HX}$  to form  $\text{XPt}(\text{PEt}_3)_2\text{PF}_2\text{S}$  or  $\text{HPt}(\text{PEt}_3)_2\text{PF}_2\text{S}$ .  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$  was allowed to react with  $\text{HPF}_2\text{S}$  in a 1:2 molar ratio at  $-60^\circ\text{C}$  in dichloromethane.

No bridged complex was detected; resonances due to two species were observed. One was identified as  $\text{HPt}(\text{PEt}_3)_2\text{PF}_2\text{S}$  by comparison with the published  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. parameters. Its  $^1\text{H}$  n.m.r. spectrum was also studied. The spectra for the familiar complex will be described first.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectra showed two resonances for this complex. The resonance in the  $\underline{\text{PEt}_3}$  region appeared as a doublet of triplets with  $^{195}\text{Pt}$  satellites. The doublet coupling was assigned as arising from  $^2\text{J}_{\text{PPtP}}$  and the triplet coupling as arising from  $^3\text{J}_{\text{PPtPF}}$ . The resonance in the  $\underline{\text{PF}_2}$  region appeared as a wide triplet of triplets with  $^{195}\text{Pt}$  satellites. The wide triplet coupling was assigned as arising from  $^1\text{J}_{\text{PF}}$  and the narrow triplet coupling as arising from  $^2\text{J}_{\text{PPtP}}$  already observed in the  $\underline{\text{PEt}_3}$  region.

The  $^{19}\text{F}$  n.m.r. spectrum appeared as a wide doublet of doublets with  $^{195}\text{Pt}$  satellites. The wide doublet coupling was assigned as arising from  $^1\text{J}_{\text{FP}}$  already observed in the  $^{31}\text{P}$  n.m.r. spectrum. The narrow doublet coupling was



assigned as arising from  ${}^3J_{\text{FPtH}}$ . The coupling  ${}^3J_{\text{FPtP}}$  was not resolved. Irradiation at the  $\text{PF}_2$  frequency collapsed the wide doublet.

The  ${}^1\text{H}$  n.m.r. spectrum was obtained which had not been observed before for this species. It appeared as a wide doublet of overlapping triplets of triplets with  ${}^{195}\text{Pt}$  satellites. The wide doublet splitting was assigned as arising from  ${}^2J_{\text{HPtP}(t)}$ . The wider triplet coupling was assigned as arising from  ${}^3J_{\text{HPtPF}}$  and had already been observed in the  ${}^{19}\text{F}$  n.m.r. spectrum. The narrow triplet coupling was assigned as arising from  ${}^2J_{\text{HPtP}(C)}$ .

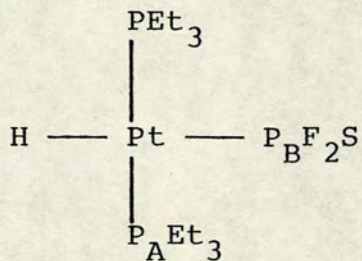
N.m.r. parameters are listed in Table 5.4.

Besides peaks due to this complex, another resonance in the  $\text{PEt}_3$  region of the  ${}^{31}\text{P}\{{}^1\text{H}\}$  n.m.r. was also observed. It appeared as a broadened singlet with  ${}^{195}\text{Pt}$  satellites.  ${}^1J_{\text{PtP}}$  was indicative of a four-coordinate Pt(II) compound. No other  $\text{PF}$  resonances were observed. This was strange because the  ${}^{19}\text{F}$  n.m.r. spectrum did show peaks due to another  $\text{PF}_2$  complex which appeared as a wide doublet of triplets with  ${}^{195}\text{Pt}$  satellites of second ordered appearance. The wide doublet was assigned as arising from  ${}^1J_{\text{PF}}$  and the narrow triplets as arising from  ${}^3J_{\text{FPtP}}$ . The wide doublet was collapsed by  ${}^{31}\text{P}$  irradiation.

The  ${}^1\text{H}$  n.m.r. spectrum also showed another resonance which appeared as a broadened triplet with  ${}^{195}\text{Pt}$  satellites. The triplets were assigned as arising from  ${}^2J_{\text{HPtP}}$ .



Table 5.4  $[\text{Hpt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^- + \text{HPF}_2\text{S}$



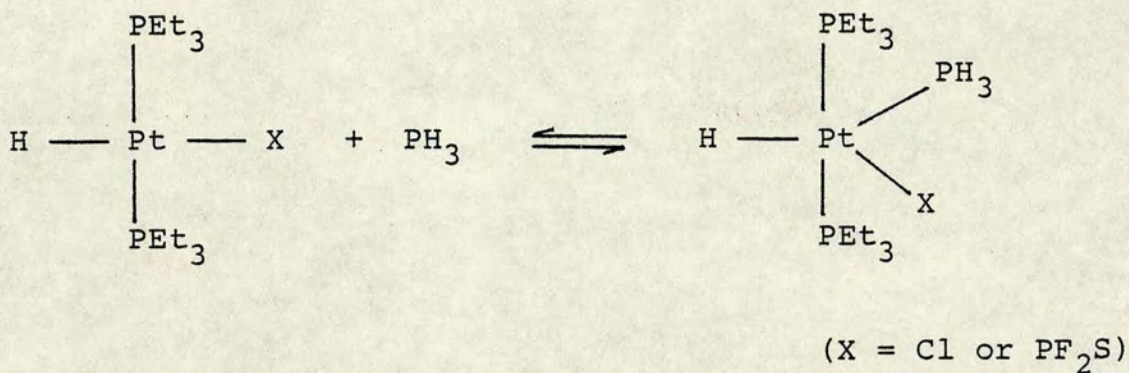
$\delta_{\text{P}_\text{A}}$	$\delta_{\text{P}_\text{B}}$	$\delta_{\text{H}}$	$\delta_{\text{F}}$	$^1\text{J}_{\text{P}_\text{A}\text{Pt}}$	$^1\text{J}_{\text{P}_\text{B}\text{Pt}}$	$^1\text{J}_{\text{HPt}}$
18.4	222	-7.83	-13.7	2475	2680	831.3

$^2\text{J}_{\text{P}_\text{A}\text{PtP}_\text{B}}$	$^2\text{J}_{\text{P}_\text{A}\text{PtH}}$	$^3\text{J}_{\text{P}_\text{A}\text{PtPF}}$	$^1\text{J}_{\text{P}_\text{B}\text{F}}$	$^3\text{J}_{\text{HPtPF}}$	$^2\text{J}_{\text{FPtP}}$
29	16.1	5	1199	37.6	393

N.m.r. parameters recorded at 213 K using  $\text{CD}_2\text{Cl}_2$  as solvent



The  $^{31}\text{P}$  n.m.r. spectrum also showed a broad resonance for free  $\text{PH}_3$ . The  $\text{PH}_3$  must be exchanging with something to cause the broadening. The extra resonances in the  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectra were broad so maybe the exchange was with the complex giving rise to them.



This type of exchange has been observed by a previous worker<sup>8</sup> but for  $\text{PH}_3$  the equilibrium lies well over to the left.



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CHAPTER 6

Experimental



## 6.1 General Experimental Methods

All volatile compounds were handled on a Pyrex vacuum system of conventional design<sup>1</sup>. The vacuum line was built up from detachable sections; Apiezon L and N greases were used on taps and ground glass joints respectively. Most of the detachable reaction ampoules were fitted with Rotaflo or Sovirel teflon greaseless taps. A high vacuum necessary for the exclusion of air and moisture from the materials being handled, was maintained by a mercury diffusion pump assisted by a rotary oil pump. The pressures of the materials inside the apparatus were measured using a spiral gauge with a mirror, employed as a null point instrument with a lamp and scale, and the pressure in the system was checked by a pirani gauge. Using a molecular weight bulb the line was calibrated for volume which, combined with pressure readings, allowed rapid calculation of the amount of volatile materials present.

Air-sensitive compounds were prepared on a Schlenk vacuum-and-nitrogen line. High purity nitrogen (B.O.C. white spot nitrogen specified less than 0.5% H<sub>2</sub>O and O<sub>2</sub>) was passed through columns of NaOH pellets and activated charcoal before being admitted to the line. Preparations were carried out in Pyrex reaction vessels and agitated with Pyrex or Teflon coated magnetic stirrer bars. Solutions and slurries were transferred between vessels using Pyrex syringes with stainless steel needles, or by Pyrex dropping-pipettes.



Air-sensitive solids or solutions of them were transferred between vessels in a V.A.C. Model HE-493 glove box equipped with a V.A.C. Model HE-493 Dri-Train. High purity nitrogen was fed directly from a cylinder into the body of the box and then continually circulated through the Dri-Train to remove contaminants. The pressure in the box was maintained marginally above atmospheric pressure by means of a Pedatrol attachment supplied by V.A.C. California, U.S.A.

## 6.2 Instruments

$^{31}\text{P}$  n.m.r. spectra were recorded using a Jeol FX60Q or a Varian Associates XL100 spectrometer, both of them operating in the Fourier transform mode and providing selective proton decoupling facilities. A deuterated solvent was employed as lock; variable temperature facilities were provided by both spectrometers.

Some  $^1\text{H}$  n.m.r. spectra were measured using a Bruker WH360 Fourier transform spectrometer; the  $^1\text{H}$  n.m.r. spectra of the remaining complexes were recorded on a Varian Associates HA100 spectrometer. All proton resonances were measured using a reference frequency which was locked to the resonating frequency of T.M.S. Both instruments provided facilities for recording the spectra at low temperatures.

$^{19}\text{F}$  n.m.r. spectra were recorded using the Varian Associates multinuclear XL100 spectrometer.  $^{29}\text{Si}$  spectra were obtained using the Bruker WH360 multinuclear spectrometer.



The heteronuclear double resonance or "spin tickling" technique provided a very convenient means of obtaining chemical shifts and coupling constants for nuclei other than hydrogen from the proton spectra. The HA100 instrument was used for this experiment; the technique involved connecting a second radio frequency, provided by a Schlumberger FS30 frequency synthesiser, to the double-tuned probe. Operating on frequency sweep, the spectrometer chart recorder pen was positioned over the peak to be decoupled, and the second radio frequency was then varied until the pen dropped toward the base line. More selective "tickling" was achieved by decreasing the power of the decoupling frequency.

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

Infra-red spectra were recorded using Perkin Elmer 457 or 577 double-beam spectrometers ( $250-4000\text{ cm}^{-1}$ ). Gas phase spectra were obtained using a gas cell fitted with KBr or CsI plates.

Analysis for carbon, hydrogen and nitrogen were carried out using a Perkin Elmer 240 elemental analyser.



### 6.3 Preparation of Starting Materials

#### 6.3.1 Metal-complex Starting Materials

##### Cis-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>

Cis- and trans-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> were made by reacting either PtCl<sub>2</sub> or K<sub>2</sub>PtCl<sub>4</sub> with PEt<sub>3</sub>. 2.0 g of K<sub>2</sub>PtCl<sub>4</sub> was dissolved in water and 1.4 ml of PEt<sub>3</sub> added. This mixture was left stirring for one hour, giving a pink-brown mixture of cis- and trans-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>. This mixture can be converted entirely to the cis-isomer by suspending it in hexane, adding one drop of PEt<sub>3</sub> and leaving the system stirring for several hours. The pure sample of cis-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> could then be collected. When PtCl<sub>2</sub> was used the first stage of the method was carried out in acetone, otherwise the procedure was the same.

##### Trans-PtHCl(PEt<sub>3</sub>)<sub>2</sub>

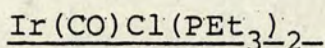
A suspension of 2.0 g of cis-dichloride in 20 ml of H<sub>2</sub>O and 1.0 ml of hydrazine hydrate was refluxed for one hour, during which time an oil formed. On cooling the oil solidified to give the impure product. This was purified using activated charcoal and a final recrystallization from methanol.

##### [HPt(PEt<sub>3</sub>)<sub>2</sub>]<sub>2</sub>PH<sub>2</sub><sup>+</sup>Cl<sup>-</sup>

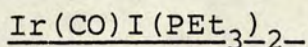
0.467 g of trans-hydride chloride was dissolved in 4 ml of dry degassed toluene in a Schlenk tube. 0.5 mM of H<sub>2</sub>PSiMe<sub>3</sub> was condensed in from the standard vacuum line and the solution shaken vigorously as it thawed. After ten minutes a pale yellow solid precipitated which was left for an hour. The solution was removed by syringe on the Schlenk



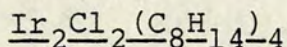
vacuum line under nitrogen and the yellow solid washed with 5 ml of ether. This solid was stored in the Dri-Train and even in this inert atmosphere decomposed over two weeks.



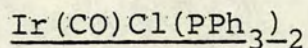
Under nitrogen, 0.45 g of  $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4$  was stirred in 5 ml of degassed acetone. At room temperature CO was bubbled at a slow rate through this orange slurry for four minutes during which time it turned deep blue. A solution of 0.3 ml of triethylphosphine in 5 ml of acetone was degassed and added slowly to this deep blue slurry with vigorous stirring to yield a yellow solution. The solvent was pumped off and the product maintained at  $80^\circ\text{C}$  while pumping for 90 minutes. The product was sublimed at  $120^\circ\text{C}$  in vacuum giving yellow crystals which could be handled for short periods in air<sup>2</sup>.



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

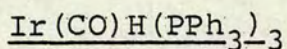


The dimer was prepared under nitrogen by refluxing  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  with cyclo-octene in isopropyl alcohol and  $\text{H}_2\text{O}$ <sup>3</sup>.



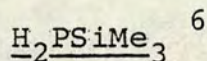
Vaska's compound was prepared by refluxing  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  and triphenylphosphine in dimethylformamide for twelve hours<sup>4</sup>.





Vaska's compound, triphenylphosphine and sodium tetrahydroborate were reacted in boiling ethanol under nitrogen for fifteen minutes<sup>5</sup>.

### 6.3.2 Non-metal Starting Materials



This was prepared from the reaction of  $\text{P}(\text{SiMe}_3)_3$  with water. A stock solution of 0.5 ml of water in 1.5 ml of diglyme was made up. In a greaseless tap ampoule 2.4 ml of  $(\text{SiMe}_3)_3\text{P}$  and 0.75 ml of this water/diglyme mixture was measured under nitrogen and when shaken vigorously left overnight. The products were separated by distillation to give a mixture of  $\text{H}_2\text{PSiMe}_3$  and  $(\text{Me}_3\text{Si})_2\text{O}$ . The ratio of these components was measured by  $^1\text{H}$  n.m.r. and this mixture was used in for preparation of  $[\text{HPt}(\text{PEt}_3)_2]_2\text{PH}_2^+\text{Cl}^-$ .

### 6.3.3 Volatile Reagents

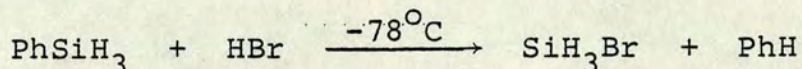
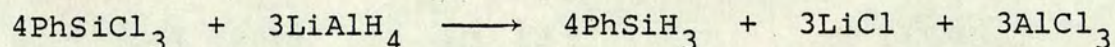
Procedures for the preparation and purification of the volatile compounds used during the course of this work are listed below. Appropriate references and any modifications to the standard technique are detailed. Purity checks were applied to commercial starting materials as appropriate.

Phenylsilane and silyl bromide were prepared by a variation on the method of Kummer and Fritz<sup>7</sup> on a 50 m mole scale. 50 m moles of phenylsilane and 100 m moles of HBr were condensed in a 250 ml ampule fitted with a Soveril tap.

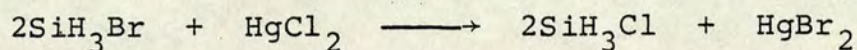


The ampule was immersed in a  $-78^{\circ}\text{C}$  bath overnight.

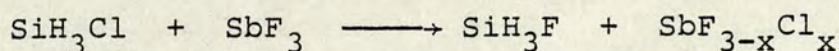
Fractionation was achieved as usual.



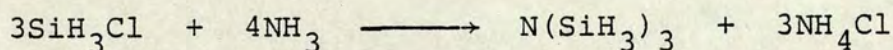
Silyl Chloride was prepared by streaming silyl bromide vapour through an excess of mercury(II)chloride<sup>8</sup>.



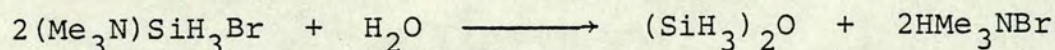
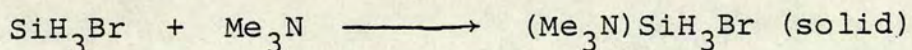
Silyl Fluoride was prepared by streaming silyl chloride vapour through an excess of antimony(III)fluoride<sup>9</sup> diluted with powdered glass.



Trisilylamine was prepared by the room temperature gas phase reaction of silyl chloride with ammonia.



Disiloxane was prepared by reacting small amounts of water with the 1:1 trimethylamine adduct of silyl bromide.



Hydrogen iodide was prepared by dehydrating aqueous hydriodic acid by phosphorous pentoxide<sup>10</sup>.



Hydrogen selenide was prepared by reacting aluminium selenide with 2M sulphuric acid<sup>11</sup>.

Hydrogen cyanide was prepared by reacting sodium cyanide with sulphuric acid, a variation on Brower<sup>11</sup>.

#### 6.3.4 Solvents

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

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

#### 6.4 Details of Experimental Technique

Two methods have been used to carry out experiments:-

##### Sealed n.m.r. tubes

0.1 m moles of metal substrate was weighed into an n.m.r. tube glass-blown onto a BlO cone and connected to the vacuum line. 3 cm depth of the relevant solvent or solvent mixture was then condensed in and the metal complex allowed to dissolve. Then the relevant reactant was condensed in its appropriate amount and the tube sealed and stored under liquid nitrogen until it was time to examine it.

##### Ampule with n.m.r. tube side-arm

This method was used when it was required to remove the volatiles from a reaction, or when a reaction of an excess of metal was required to promote formation of bis- and tris-species.



0.1 m moles of the metal complex was weighed into the ampule under nitrogen. The ampule was then attached to the vacuum line via a B10 cone where the relevant solvent and reactant was condensed in.

If the aim was to remove the volatiles then the solvent and excess reactant were pumped off. The residue was then dissolved in the relevant solvent which was condensed into the ampule and tipped down the side arm into the n.m.r. tube. The n.m.r. tube was then sealed and stored under liquid nitrogen.

If the aim was to study a reaction of the complex formed in the first stage with another involatile species, the solvent and excess reactant were also pumped off initially. The ampule was then detached from the vacuum line and the other involatile reagent weighed in under nitrogen. The ampule was then reconnected to the vacuum line and the appropriate solvent condensed in, dissolving the residue, and then tipped into the n.m.r. tube. The tube was sealed and stored under liquid nitrogen.

#### Isolation of products from n.m.r. tubes

After the n.m.r. investigation had shown the product formed to be clean an attempt was made to retrieve this from the tube. The sealed tube was opened under nitrogen (in the Dri-Train) and its contents tipped into a Schlenk tube with careful washing with the appropriate solvent. This was connected to the Schlenk line and the solvent



and any volatiles present pumped off. For all isolations in this thesis this yielded a gum which could be forced to a solid by triturating in light petroleum. The solid formed was stored under nitrogen.

Analysis figures for the solids obtained are give in Table 6.1.



Table 6.1 Analysis figure of iridium-silyl species in Chapter 2

Complexes	Found			Required		
	%C	%H	%N	%C	%H	%N
$[\text{HIr}(\text{CO})\text{Cl}(\text{PET}_3)_2\text{SiH}_2]_2\text{O}$	29.4	6.2	-	29.4	6.2	-
$[\text{HIr}(\text{CO})\text{I}(\text{PET}_3)_2\text{SiH}_2]_2\text{O}$	25.3	5.3	-	25.1	5.3	-
$\text{HIr}(\text{CO})\text{I}(\text{PET}_3)_2\text{SiH}_2\text{N}(\text{SiH}_3)_2$	22.7	5.4	2.3	22.6	5.6	2.0
$[\text{HIr}(\text{CO})\text{I}(\text{PET}_3)_2\text{SiH}_2]_2\text{NSiH}_3$	24.3	5.5	1.0	24.5	5.4	1.1
$[\text{HIr}(\text{CO})\text{I}(\text{PET}_3)_2\text{SiH}_2]_2$	25.2	5.3	-	25.4	5.4	-
$\text{HIr}(\text{CO})\text{I}(\text{PET}_3)_2\text{SiH}_2\text{F}$	24.4	5.0	-	24.6	5.2	-
$\text{HIr}(\text{CO})\text{I}(\text{PET}_3)_2\text{SiF}_3$	23.4	4.5	-	23.3	4.6	-



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List of Courses Attended

Fortran IV Programming - 10 lectures - C.N.M. Pounder

IMP Programming - 8 lectures

Multiple Resonance - 5 lectures - W. MacFarlane

Neutron Diffraction - 5 lectures - Various Lecturers

Mass Spectrometry - 5 lectures - H.L. Roberts

Aspects of Bio Inorganic Chemistry - 5 lectures - G.A. Heath

Evening Inorganic Seminars - 3 years



## Reactions of Silanes and Germanes with Iridium Complexes. Part 3.1 Reactions of some Silyl Derivatives of O, S, Se, N, and P with *trans*-Carbonylido-bis(triethylphosphine)iridium(I)

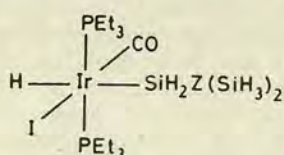
By E. A. V. Ebsworth,\* Hugh M. Ferrier, and Thomas E. Fraser, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The title complex, *trans*-[Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub>], (1), reacts with Y(SiH<sub>3</sub>)<sub>2</sub> (Y = O, S, or Se) in benzene to give [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>YSiH<sub>3</sub>)] or [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>)<sub>2</sub>Y], although when Y = O the formation of the former species is difficult to detect. Reaction between (1) and P(SiH<sub>3</sub>)<sub>3</sub> leads to the formation of [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>P(SiH<sub>3</sub>)<sub>2</sub>)] or [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>)<sub>2</sub>PSiH<sub>3</sub>], or [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>)<sub>3</sub>P], depending on the proportions of the reactants taken. Reaction between (1) and N(SiH<sub>3</sub>)<sub>3</sub> gives [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>N(SiH<sub>3</sub>)<sub>2</sub>)] and [Ir(CO)HI(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>)<sub>2</sub>NSiH<sub>3</sub>], but no tris(irdiosilylamine) was detected. The compounds have been characterised by <sup>1</sup>H and <sup>31</sup>P n.m.r. spectroscopy and in some cases by analysis.

OUR studies of the reactions between *trans*-[PtHX(PEt<sub>3</sub>)<sub>2</sub>] (X = Cl, Br, or I) and Y(SiH<sub>3</sub>)<sub>2</sub> (Y = O, S, or Se) or Z(SiH<sub>3</sub>)<sub>3</sub> (Z = N or P) have led<sup>2</sup> to the identification of derivatives such as [PtX(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>)<sub>2</sub>Y] or [PtX(PEt<sub>3</sub>)<sub>2</sub>(SiH<sub>2</sub>)<sub>2</sub>PSiH<sub>3</sub>] when X = I; when X = Cl, exchange processes complicate the reactions. We were not able to detect the formation of a tris(platinosilyl)phosphine, even when P(SiH<sub>3</sub>)<sub>3</sub> was allowed to react with a large excess of the platinum hydride starting material. As part of our study of the oxidative addition of silanes to *trans*-[Ir(CO)X(PEt<sub>3</sub>)<sub>2</sub>] and related compounds, we have investigated the reactions between *trans*-[Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub>], (1), and O(SiH<sub>3</sub>)<sub>2</sub>, S(SiH<sub>3</sub>)<sub>2</sub>, Se(SiH<sub>3</sub>)<sub>2</sub>, N(SiH<sub>3</sub>)<sub>3</sub>, and P(SiH<sub>3</sub>)<sub>3</sub>. The products of the reactions have initially been characterised by n.m.r. spectroscopy.

### RESULTS

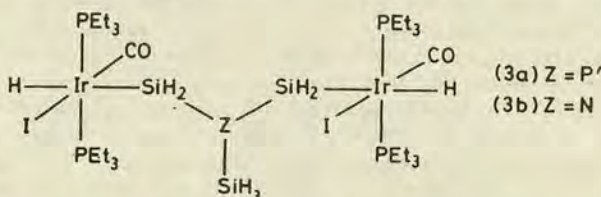
*Reactions of trans*-[Ir(CO)I(PEt<sub>3</sub>)<sub>2</sub>].—(a) With P(SiH<sub>3</sub>)<sub>3</sub>. Reaction of (1) with an excess of P(SiH<sub>3</sub>)<sub>3</sub> in benzene at room temperature was apparently complete within about one minute; we interpret the <sup>1</sup>H and <sup>31</sup>P n.m.r. spectra as showing that the main product formed under these conditions was complex (2a), below. Our reasons for this conclusion are as follows. The <sup>31</sup>P spectrum consists of two resonances, the stronger in the region associated with PEt<sub>3</sub> bound to six-co-ordinated Ir<sup>III</sup>, and the weaker a very long way to low frequency, in the region associated with P bound to three silicon atoms. With all proton



(2a) Z = P'

(2b) Z = N

bound. The <sup>1</sup>H n.m.r. spectrum confirms this analysis. The IrH region contains a single multiplet, a triplet of doublets of triplets. The larger triplet coupling is collapsed by irradiating in the <sup>31</sup>P region at the frequency of the PEt<sub>3</sub> resonance, while the doublet splitting is collapsed by irradiating at the P'Si<sub>3</sub> frequency. Thus the IrH proton is equally coupled to two PEt<sub>3</sub> nuclei (which must therefore both be *cis* to it) and shows resolved coupling both to the P'Si<sub>3</sub> phosphorus nucleus and to two other protons. In the SiH region there are two overlapping resonances. One is a simple doublet. The other, the weaker, appears as a doublet of triplets of doublets. The larger doublet splitting is collapsed by irradiating at the frequency of the P'Si<sub>3</sub> resonance, which also collapses the coupling in the simple doublet. Thus the two SiH resonances are associated with silicon atoms bound to the same P atom. The triplet splitting in the weaker multiplet is collapsed by irradiating at the PEt<sub>3</sub> frequency, while the splitting of the small



(3a) Z = P'

(3b) Z = N

doublet is of the same magnitude as that of the triplet in the IrH resonance. The chemical shift of the IrH resonance is consistent with H *trans* to Si or CO but not to I; the resolution of <sup>3</sup>J(HIrSiH) and <sup>3</sup>J(PSiH) is also in keeping with a structure in which H is *trans* to Si.

Reaction of (1) in 2 : 1 molar ratio with P(SiH<sub>3</sub>)<sub>3</sub> gave a different product. As before, the <sup>31</sup>P-{<sup>1</sup>H} spectrum consisted of two sets of resonances. The peak at the higher frequency, due to the PEt<sub>3</sub> nuclei, was a doublet; that at low frequency, which was much weaker, showed a quintet splitting of the same magnitude as the doublet coupling in the PEt<sub>3</sub> resonance. This implies that the P'Si<sub>3</sub> nucleus is equally coupled to four PEt<sub>3</sub> nuclei, and so that oxidative addition from two different SiH<sub>3</sub> groups of a molecule of P(SiH<sub>3</sub>)<sub>3</sub> has given the product (3a). The H resonances were qualitatively similar to those obtained from the reaction between (1) and an excess of P(SiH<sub>3</sub>)<sub>3</sub>, except that the chemical shifts and coupling constants were somewhat different and the simple doublet was relatively

coupling eliminated, the higher-frequency resonance appeared as a doublet and the lower as a triplet, the couplings in the two multiplets being equal: this is consistent with a product in which P'Si<sub>3</sub> is linked to an iridium atom to which two mutually *trans* PEt<sub>3</sub> groups are already



much less strong. All these observations are consistent with our formulation of the product as the bis(iridiosilyl)-phosphine.

Reaction of a four-fold molar excess of (1) with  $P(SiH_3)_3$  was also complete in a few minutes at room temperature. This time the  $^{31}P\{-^1H\}$  spectrum was less helpful in characterising the product. By working under conditions of the highest resolution, we were able to resolve the peak due to the  $PEt_3$  groups of the  $^{31}P\{-^1H\}$  spectrum as a doublet; the resonance due to the  $P'Si_3$  nucleus was clearly a multiplet and could have been a septet, but the envelope was not well enough defined for us to be sure. However, the  $PEt_3$  resonance was a clear doublet when only SiH and

and small amounts of both (2a) and (4) were obtained in the reaction between  $P(SiH_3)_3$  and (1) in two-fold molar excess; but (4) could be obtained in solution free of (2a) or (3a). We have succeeded in isolating (4) as a white solid, and confirming its constitution by analysis.

(b) *With*  $N(SiH_3)_3$ . Reaction of (1) with an equimolar quantity of  $N(SiH_3)_3$  in benzene at room temperature gave a single product whose  $^{31}P\{-^1H\}$  n.m.r. spectrum showed a single peak. In the  $^1H$  spectrum there were resonances in the regions associated with SiH, with the protons of co-ordinated  $PEt_3$  groups, and with IrH groups. The IrH resonance appeared as a triplet of triplets: the chemical shift was in the region associated with H *trans* to CO or to Si

TABLE I

N.m.r. parameters for complexes formed by reaction of (1) with  $N(SiH_3)_3$  and  $P(SiH_3)_3$ <sup>a</sup>

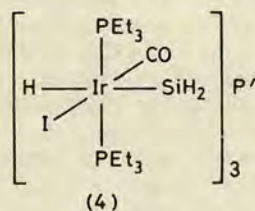
Complex	Chemical shifts/p.p.m.					
	$\delta(^{15}N/P')$	$\delta(P)$	$\delta(SiH_2)$	$\delta(SiH_3)$	$\delta(IrH)$	
(2b)	-6.5	-16.9	4.74	5.33	-9.82	
(3b)	-5.2	-16.7	4.85	5.47	-9.75	
(2a)	-343.7	-16.9	3.9	4.1	-10.0	
(3a)	-299.1	-17.6	4.1	4.2	-9.8	
(4) <sup>b</sup>	-259.0	-19.0	4.2		-9.7	

Complex	Coupling constant/Hz						
	$^2J(HP)$	$^2J(H_2Si^{15}N/P')$	$^2J(H_3Si^{15}N/P')$	$^2J(^{15}N/P'P)$	$^3J(HSiIrP)$	$^3J(HH)$	$^3J(HIrSi^{15}N/P')$
(2b)	15.2	4.9	4.3	0.2	6.9	2.3	1.9
(3b)	15.5	4.9	4.1		7.1	2.5	n.r.
(2a)	15.5	ca. 10	16.0	0.6	7.0	2.8	7.5
(3a)	15.6	10.4	15.7	1.2	6.3	1.8	7.9
(4) <sup>b</sup>	17.0	12.0		0.7	6.0	1.6	10.0

<sup>a</sup> Measurements in  $C_6H_6$  at room temperature, and considered accurate to  $\pm 2$  in last figure quoted. All shifts are measured as positive to high frequency of 85%  $H_3PO_4$  ( $^{31}P$ ),  $NMe_4^+$  ( $^{15}N$ ), or  $SiMe_4$  ( $^1H$ ); n.r. = not resolved. <sup>b</sup>  $^1J(^{29}SiP) = 62.8$  Hz. By homonuclear double resonance,  $^2J(HP)$  opposite in sign to  $^3J(HSiIrP)$ ,  $^3J(HP)$  opposite in sign to  $^2J(H_2SiP')$ .

CH protons were decoupled, showing that there was one IrH for each iridium centre, while under the same conditions the  $P'Si_3$  resonance was a well defined quartet, showing that there were three IrH groups around the central phosphorus. The IrH resonance appeared as a doublet of triplets, each line of which was broadened but could not be resolved further. The doublet splitting was collapsed by irradiating at the frequency of the  $P'Si_3$  resonance, and the triplet coupling by irradiating at the  $PEt_3$  frequency. The SiH resonance appeared as a roughly 1:2:2:2:1 quintet; this pattern was shown by heteronuclear double resonance to arise from coupling to the  $P'Si_3$  and the  $PEt_3$  phosphorus nuclei,  $^2J(HP)$  being roughly twice  $^3J(HP)$ . Under the highest resolution, a further small doublet splitting could be resolved on each line; we assign this to  $^3J(HH)$ . The



most important point, however, is that there was no doublet analogous to the resonances assigned to the  $SiH_3$  groups of (2a) and (3a). We conclude that the product we obtained from this system was the tris(iridiosilyl) complex, (4).

Small amounts of complex (3a) were formed in the reaction between equimolar proportions of (1) and  $P(SiH_3)_3$

but not to I; the larger of the triplet couplings could be collapsed by irradiating at the frequency of the  $PEt_3$  resonance. In the SiH region, there were two resonances: the stronger appeared as a singlet, and the weaker as a triplet of narrow doublets, in which the doublet splitting was the same as the smaller triplet splitting in the IrH resonance. The triplet coupling was collapsed by irradiating at the frequency of the P resonance, and the narrow doublet coupling by irradiating at the IrH frequency. We conclude that this product is a species analogous to (2a), with the  $SiH_2$  group *trans* to hydride; the strong singlet in the SiH region is assigned to the unco-ordinated  $SiH_3$  groups. When the experiment was repeated using  $^{15}N\text{-}(SiH_3)_3$ , each line in the SiH and the IrH regions showed an additional small doublet splitting, which was collapsed by irradiating at the same frequency in the  $^{15}N$  region. This shows that the three resonances come from the same molecule. The n.m.r. parameters are given in Table 1. The  $^{31}P\{-^1H\}$  resonance of the product obtained for  $^{15}N\text{-}(SiH_3)_3$  was a narrow doublet. When an excess of (1) was allowed to react with  $N(SiH_3)_3$ , a similar but different product was obtained. The  $^{31}P\{-^1H\}$  resonance was a singlet, as before. The IrH resonance showed a similar pattern, but at a slightly different chemical shift. The two SiH resonances were qualitatively similar, but the singlet due to the free  $SiH_3$  protons was relatively much weaker. The  $^{15}N$  chemical shift was also rather different, and we were unable to resolve  $^3J(H^{15}N)$ . We conclude that under these conditions the product is a bis(iridiosilyl)amine, (3b), analogous to (3a). Its n.m.r. parameters are set out

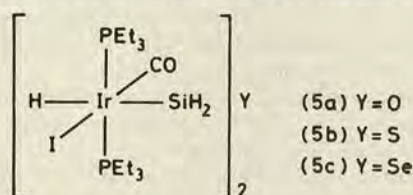


in Table 1. We were never able to detect the formation of a tris(iridosilyl)amine analogous to (4), despite using a variety of reaction conditions. Both of the products [(2b) and (3b)] were isolated as white solids and analysed.

It is worth noting that the bis(iridosilyl)amine is an initial product of the reaction between (1) and  $N(\text{SiH}_3)_3$ , even when an initial excess of the latter is taken; over a period of hours the bis product reverts to the mono-species.

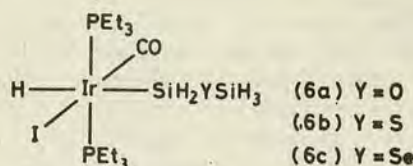
(c) *With*  $O(\text{SiH}_3)_2$ . Reaction between  $O(\text{SiH}_3)_2$  and (1) in 1:2 mol ratio gave a product whose  $^{31}\text{P}\{-^1\text{H}\}$  spectrum consisted of a single line. We believe this to have been the complex (5a).

The proton resonance spectrum contained peaks due to IrH, to  $\text{PEt}_3$ , and to SiH protons. The IrH resonance appeared as a triplet of triplets; the SiH resonance as a triplet of doublets. The larger triplet coupling in each case was shown by heteronuclear double resonance to derive



from coupling to phosphorus nuclei; the smaller triplet coupling in the IrH resonance was of the same magnitude as the doublet splitting in the SiH resonance. The absence of any resonance that could be assigned to protons of a free  $\text{SiH}_3$  group is significant. The complex was isolated as a white air-stable solid and characterised by analysis and by determining its molecular weight in solution. The n.m.r. parameters are given in Table 2. Reaction between (1) and an excess of  $O(\text{SiH}_3)_2$  in benzene gave a solution with the

Weak peaks corresponding to those of complex (6a) were observed in addition to those due to (5a) in a solution in benzene containing (1) and a large molar excess of  $O(\text{SiH}_3)_2$ . In this solution the resonance due to excess of  $O(\text{SiH}_3)_2$  degraded over a period of hours, and a peak due to  $\text{SiH}_4$



became progressively stronger, together with a number of weak peaks in the region normally associated with  $\text{SiHO}$  species.

(d) *With*  $S(\text{SiH}_3)_2$ . The reaction of (1) with  $S(\text{SiH}_3)_2$  followed a slightly different course. With the reactants in a 2:1 mol ratio, two singlets of roughly equal intensity were observed in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum. When only protons resonating at about  $\delta = 0-5$  p.p.m. were irradiated, each  $^{31}\text{P}$  line split into a doublet, showing that each species was a monohydride complex; when only  $\text{PEt}_3$  protons were decoupled, each  $^{31}\text{P}$  line appeared as a doublet of triplets, showing that in each complex there were two equivalent protons coupling to P and with chemical shifts around  $\delta = 4-6$  p.p.m. The  $^{31}\text{P}$  chemical shifts were in the region associated with  $\text{PEt}_3$  bound to  $\text{Ir}^{\text{III}}$ . All these observations are consistent with the formation of complexes (5b) and (6b), analogous to (5a) and (6a) above, and this interpretation is confirmed by the  $^1\text{H}$  spectrum. In this, two IrH resonances were observed, each appearing as a triplet of triplets, with the larger triplet coupling associated with coupling to P. In the SiH region we observed a sharp singlet and two triplets of doublets, with each of the triplet

TABLE 2

N.m.r. parameters for complexes formed by reaction of (1) with  $Y(\text{SiH}_3)_2$  ( $Y = \text{O}, \text{S}, \text{and Se}$ )<sup>a</sup>

Complex	Chemical shift/p.p.m.				Coupling constants/Hz		
	$\delta(\text{P})$	$\delta(\text{SiH}_2)$	$\delta(\text{SiH}_3)$	$\delta(\text{IrH})$	$^2J(\text{HP})$	$^3J(\text{HP})$	$^3J(\text{HH})$
(6a)	-13.8	5.71	4.89	-9.83	15.9	6.7	3.01
(6b)	-16.6	4.4	4.5	-10.2	16.7	8.0	3.2
(6c)	-17.1	4.3	4.6	-10.1	16.0	8.0	3.2
(5a) <sup>b</sup>	-13.8	5.78		-9.80	15.9	7.1	3.0
(5b)	-17.2	5.3		-9.95	15.5	8.0	2.3
(5c)	-17.3	5.2		-9.95	16.2	7.2	2.5

<sup>a</sup> Measurements in  $\text{C}_6\text{H}_6$  at room temperature; considered inaccurate to  $\pm 2$  in last figure quoted. All shifts taken as positive to high frequency of 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) or  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{29}\text{Si}$ ). <sup>b</sup>  $\delta(^{29}\text{Si}) = -30.1$  p.p.m.;  $^2J(\text{SiP}) = 10.7$ ;  $^3J(\text{SiH}) = 196.0$ ;  $^3J(\text{SiH}) = 10.4$  Hz. By homonuclear double resonance,  $^2J(\text{PH})$  opposite sign to  $^2J(\text{P}^1\text{rSiH})$ .

same  $^{31}\text{P}\{-^1\text{H}\}$  spectrum; the  $^1\text{H}$  spectrum was also the same except for a sharp singlet at a chemical shift corresponding to the resonance of free  $O(\text{SiH}_3)_2$ . This peak had  $^{29}\text{Si}$  satellites, and  $^1J(\text{SiH})$  was the same as in  $O(\text{SiH}_3)_2$ . On removing all volatile materials, a white solid residue remained which gave the same analytical results and the same molecular weight as did the product from the equimolar reaction described above. We conclude that under these conditions we have again obtained complex (5a), leaving an excess of  $O(\text{SiH}_3)_2$ . When the reaction was allowed to occur in light petroleum, an immediate precipitate was formed; this was soluble in benzene, and the proton resonance spectrum contained peaks due to (5a) and additional resonances that we assign to the complex (6a). The n.m.r. parameters are included in Table 2.

couplings associated with phosphorus. The triplet splittings in the higher frequency of the IrH and the higher frequency of the SiH multiplets were both collapsed by irradiating at the same frequency, which corresponded to the lower frequency of the two  $^{31}\text{P}$  resonances. These three resonances are therefore due to the same molecular species. Reaction with the reagents in 1:1 mol ratio gave spectra with the same resonances, but in which the singlet in the SiH region and the lower frequency SiH and IrH multiplets were relatively stronger. We conclude that these peaks and the higher frequency of the two  $^{31}\text{P}$  resonances are due to the complex of type (6b). We were unable to obtain samples of either species uncontaminated by the other. The n.m.r. parameters are given in Table 2.

(e) *With*  $\text{Se}(\text{SiH}_3)_2$ . The products of the reactions



between (1) and  $\text{Se}(\text{SiH}_3)_2$  in both 1 : 1 and 2 : 1 molar ratio gave  $^{31}\text{P}$  and  $^1\text{H}$  n.m.r. spectra that were qualitatively the same as those described above. We conclude that similar products of types (5c) and (6c) have been formed, and the n.m.r. parameters are included in Table 2.

#### DISCUSSION

The process of oxidative addition by which these species are formed is essentially the same as that invoked to explain the reactions between (1) and silyl halides;<sup>1</sup> the  $^1\text{H}$  n.m.r. parameters suggest that the stereochemical arrangement of ligands round iridium is the same. The relatively easy formation of the tris(irdiosilyl)phosphine is surprising, because the molecule must be stereochemically crowded; we hoped to determine the crystal structure,<sup>4</sup> but have been unable to grow crystals. It should be noted that reaction between  $[\text{PtHI}(\text{PEt}_3)_2]$  and  $\text{P}(\text{SiH}_3)_3$  gave  $[\{\text{PtI}(\text{PEt}_3)_2(\text{SiH}_3)_2\}_2\text{PSiH}_3]$  as the most substituted product formed, even though  $\text{Pt}^{\text{II}}$  is presumably less stereochemically demand-

TABLE 3

Analytical, molecular weight, and i.r. spectral data

Complex	Analysis (%) <sup>a</sup>			Infrared data <sup>b</sup>		<i>M</i> <sup>c</sup>
	C	H	N	$\bar{\nu}(\text{IrH})/\text{cm}^{-1}$ (w)	$\bar{\nu}(\text{CO})/\text{cm}^{-1}$ (s)	
(5a)	25.1 (25.3)	5.3 (5.3)		2 090	1 940	1 323 (1 242)
(2b)	22.7 (22.6)	5.4 (5.4)	2.3 (2.0)	2 090	1 980	
(3b)	24.3 (24.5)	5.6 (5.4)	0.9 (1.1)	2 090	1 960	
(4)	24.9 (24.9)	5.2 (5.3)		2 025	1 968	

<sup>a</sup> Found (calc.). <sup>b</sup> w = Weak, s = strong.

ing than is six-co-ordinated iridium(III). A similar change in degree of substitution is found with  $\text{N}(\text{SiH}_3)_3$ ; here we were able to identify mono- and bis-(irdiosilyl)-amines but no tris species, whereas with  $[\text{PtHI}(\text{PEt}_3)_2]$  we were only able to identify a mono-platiniosilyl species. Reaction between (1) and  $\text{S}(\text{SiH}_3)_2$  or  $\text{Se}(\text{SiH}_3)_2$  gave both mono- and bis-(irdiosilyl) complexes, but the reaction between (1) and  $\text{O}(\text{SiH}_3)_2$  was somewhat different. Even with an excess of  $\text{O}(\text{SiH}_3)_2$  the only product we could detect in benzene was the bis species (6a), save in the presence of a large excess of  $\text{O}(\text{SiH}_3)_2$ , and we were only able to determine the n.m.r. parameters of (6a) by allowing the reaction between (1) and  $\text{O}(\text{SiH}_3)_2$  to occur in a solution from which the products were precipitated as soon as they were formed. This implies that the free  $\text{SiH}_3$  group of (6a) reacts with (1) significantly faster than does  $\text{O}(\text{SiH}_3)_2$ . The alternative explanation that exchange of Si led to the formation of (5a) and  $\text{O}(\text{SiH}_3)_2$  is shown to be wrong by our observing peaks due to (5a) and (6a) together from the product of reaction in light petroleum after redissolving it in benzene. The

decomposition of excess of disiloxane in the presence of (5a) recalls the catalytic effect of  $[\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2\text{-(Si}_2\text{Me}_4\text{O)}]$  on the redistribution of Si-O and Si-H bonds in organosiloxanes.<sup>3</sup>

#### EXPERIMENTAL

Volatile materials were manipulated using a standard vacuum system fitted with greased or with Sovirel Teflon taps; involatile materials that were sensitive to air were handled in a V.A.C. model HE-493 glove-box fitted with a model HE-493 Dri-Train under dried nitrogen gas. Infrared spectra were obtained of gases or of solids dispersed in Nujol by means of Perkin-Elmer 457 (250–4 000  $\text{cm}^{-1}$ ) or 577 (200–4 000  $\text{cm}^{-1}$ ) instruments. N.m.r. spectra were recorded by means of the following spectrometers: FX90Q ( $^{31}\text{P}$ ), XL100 ( $^{31}\text{P}$ ), WH 360 ( $^1\text{H}$ ,  $^{29}\text{Si}$ ), and HA100 CW, whose probe had been double-tuned<sup>4</sup> to accept an additional radiofrequency for  $^1\text{H}\{-^{31}\text{P}\}$  or  $^1\text{H}\{-^{15}\text{N}\}$  experiments. Compounds were dissolved in  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{D}_6$ , and where necessary  $\text{SiMe}_4$  was added as a proton lock.

Silyl starting materials were prepared by established methods; *trans*- $[\text{Ir}(\text{CO})\text{I}(\text{PEt}_3)_2]$ , (1), was made from the corresponding chloride<sup>5</sup> and NaI.

Most of the reactions between (1) and silyl compounds were carried out in the following manner. Compound (1) (0.2 mmol) was weighed into an ampoule fitted with a Teflon tap and to whose side an n.m.r. tube was attached. Benzene was then distilled into the ampoule and (1) was allowed to dissolve; the appropriate silyl compound was then distilled into the solution and reaction allowed to occur for a few minutes. Volatile material was distilled away and fresh benzene distilled into the ampoule to dissolve the residual gum, and this process was repeated. Finally, the reaction products were washed into the n.m.r. tube using  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{D}_6$ , any locking material added, and the tube sealed. In some cases reactions were allowed to occur in n.m.r. tubes without removing any volatile material. The isolation of solid products was achieved using Schlenk equipment in conjunction with the glove-box. Products were analysed by microanalysis, and solution molecular weights determined osmometrically using Perkin-Elmer model 115 molecular weight apparatus. Analytical and i.r. data for the compounds that were isolated are summarised in Table 3.

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