SOME PLATINUM COMPLEXES CONTAINING PHOSPHORUS-FLUORINE LIGANDS

by

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To my parents

ACKNOWLEDGEMENTS

Firstly I would like to thank my supervisors, Professor E.A.V. Ebsworth and Dr D.W.H. Rankin for all the help and advice they have continually given me. I am also grateful to all the members of the inorganic research group for passing on their experimental skills to me, for discussing my work and lending me many useful suggestions, especially to Dr F.J.S. Reed for his encouragement in the early stages of my work, and to Mr S.G.D. Henderson for his help with experimental details and glass blowing. Thanks are also due to Miss Clare Shannon and Miss Jean Clarke for typing this thesis.

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SUMMARY

The work involved in this thesis was the study of the reactions of simple fluorophosphines with some platinum II complexes using n.m.r. spectroscopy and to attempt to isolate any stable complexes observed.

The first part was the study of the reactions of PF_2X with t-Pt $HX(PEt_3)_2$ (X = Cl, Br, I). The products isolated here were $X(PEt_3)_2Pt\ \mu PF_2Pt(X)_2(PEt_3)$. Attempts were made to solve the mechanism of this reaction and although a lot of information was obtained about the intermediates involved a complete mechanism could not be determined.

The second area studied was the reactions of HPF_2Y (Y = S or Se) with various Pt^{II} substrates. For these systems the products were $PtX(PF_2Y)(PEt_3)_2$ (X = H, Cl, Br, I). A lot of information was discovered about the mechanisms involved in these reactions from low temperature n.m.r. studies. Also, the X-ray crystal structure was obtained for $PtCl(PF_2S)(PEt_3)_2$.

Finally some work has been carried out to discover the type of reactions possible with these Pt-PF_2Y complexes.

CONTENTS

CHAPTER 1

Introduction

INTRODUCTION

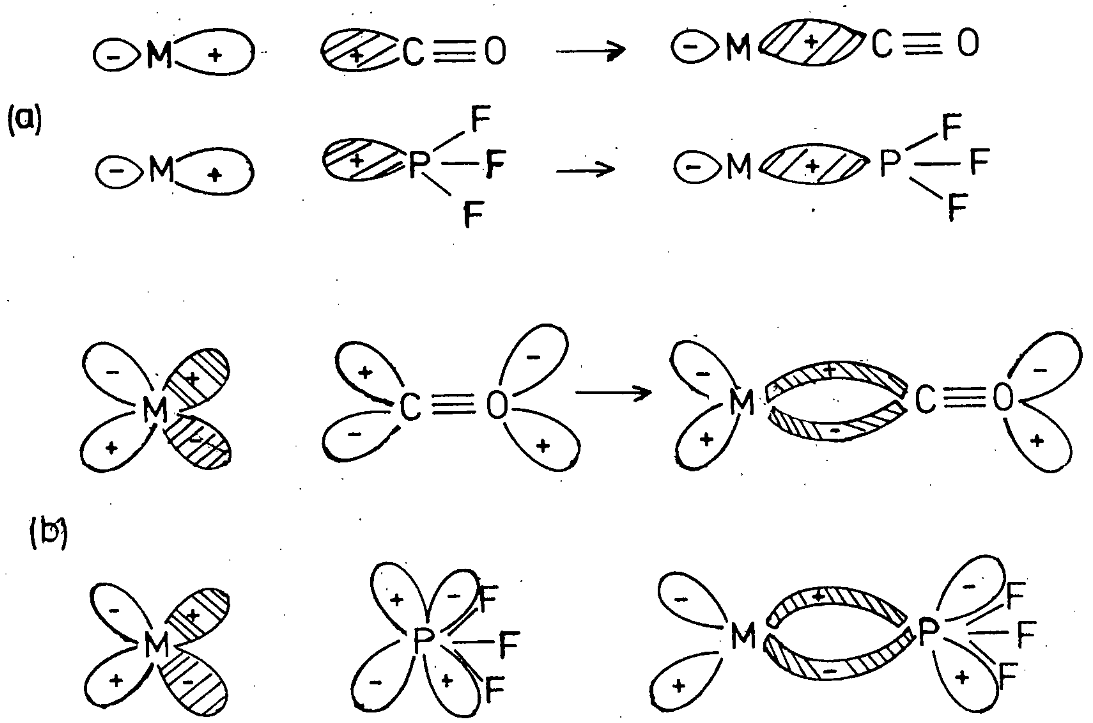
(i) Transition Metal Fluorophosphine Chemistry

This area of chemistry has been dominated by the interaction of PF_3 with transition metals. Some work has also been done with compounds of the form RPF_2 (where R can be C Cl_3 CF_3 R_2N)$^{1)}$. In most cases the metal is in the M^O oxidation state and the complexes formed are volatile liquids.

In this project we set out to investigate the interaction of simple fluorophosphines with some Pt^{II} substrates. The fluorides of phosphorus studied were PF_2X(X = Cl Br I) and HPF_2Y (Y = SorSe). Several interesting results were obtained. However, before discussing these results I shall give a review of some of the related Chemistry reported in the literature.

The first studies were made on the interaction of PF_3 with transition metals. The idea behind much of this work was a comparison of PF_3 and CO as ligands[1]. In general it seems that if a carbonyl complex can be formed then a similar PF_3 complex is possible. In fact one method of forming PF_3 complexes is via displacement of CO groups [1].

It is thought that both these ligands bond to transition metals in a similar way, in that both have available vacant orbitals of π symmetry relative to the M - L bond which can accept electrons. They also have available a lone pair which can be donated to the metal (Fig. 1)[2].



(a) Shows the formation of the M - L bond which involves donation of the lone pair from the ligand.

(b) Shows the formation of the M - L π bond which involves donation of electrons by the metal.

For phosphine ligands the extent of back donation from the metal depends on the electronegativity of the groups attached to the phosphorous. The more electronegative the groups are, the greater the π acceptor properties and hence the shorter the M - P bond is likely to be. In fact some i.r. spectral evidence and some photoelectron spectra shows that PF_3 is as good as CO as a π acceptor if not better.

Evidence to support this view of the bond between the metal and PF_3 came from electron diffraction studies on $Ni(PF_3)_4$[1]. The Ni - P distance was found to be 209.9(3) pm. The covalent radius of P is 110 pm and of atomic Ni 120 - 130 pm, so it seems reasonable to assume that the short bond length was due to π interactions between the metal and the ligand. This also compares with a bond length of around 230 pm for a $M - PR_3$ group (where R is alkyl) and 220 pm for a $M - P(OR)_3$ complex.

However, for platinum very few CO complexes exist; those that have been obtained have low thermal stability; for example $Pt(CO)_4$ can be detected via matrix isolation but it decomposes on warming. The PF_3 derivatives are thermally more stable as shown by one method of formation.

$$M + PF_3 \xrightarrow[\text{high P}]{\Delta} M(PF_3)_4 \qquad M = Ni, Pd, Pt.$$

Where well defined carbonyls are known, PF_3 complexes can be made via displacement of the CO groups[1] from the metal and here the process is usually thermally or photochemically induced, which again demonstrates the greater thermal stability of the PF_3 compounds.

Because of this greater stability the fluorophosphine chemistry of platinum is more extensive than the carbonyl chemistry. As well as $Pt^{o}(PF_3)_4$ a whole series of complexes of the form $Pt^{II}(RPF_2)_2Cl_2$ is known. On heating cis $Pt(PF_3)_2Cl_2$ we obtain $Pt_2(PF_3)_2Cl_4$ a chloro bridged dimer. All the monomeric complexes retain the cis configuration.

As in simple fluorophosphine chemistry the stability of the PF_2

group is again demonstrated in that the PF_2 group remains intact while various R groups may be exchanged. However, with one major exception, the PF_3 complexes of Pt^{II}, most fluorophosphine transition metal complexes are air stable, which is in contrast with the behaviour of free fluorophosphines. Most of the M^{o} complexes are thermally stable but at the same time are very volatile giving off strong-smelling vapours. In fact many fluorophosphine complexes can be distilled without significant decomposition.

The M^{II} complexes on the other hand, tend to have higher melting points and many are crystalline solids. Most of the known Pt^{II} fluorophosphine complexes have been reported since 1968.

In 1968 Nixon and Sexton[3] reported the formation of a series of complexes of the form cis $Pt\,X_2(RPF_2)_2$ or cis $Pt\,X_2\,(R_2PF)_2$ (X = Cl or Br, R = NEt_2, NMe_2, $N(C_5H_{10})_2$) and this was the first major study of Pt^{II} fluorophosphine complexes. Previous to this the only known examples were cis $PtCl_2(PF_3)_2$ and $(PtCl_2PF_3)_2$[4].

Since 1969 only a few papers have been published in this area, one of the major ones being by Grosse and Schmutzler[5] in 1976 who reported the following reactions:-

$$Pt\,Cl_2\,L_2 + PF_2OR \longrightarrow Pt\,Cl\,L_2\left(PF_2O\right) \quad (R = \text{alkyl},\ Pr^{\underline{n}},\ Bu^{\underline{n}})$$

These complexes are all air stable crystalline solids and were characterised using ^{31}P and ^{19}F n.m.r. spectroscopy. This was the first substantial n.m.r. investigation in this field and it is with the advances made in recording Fourier transform n.m.r. spectra that more information on these complexes can be obtained.

Also in 1976 Goggin and Goodfellow[6] reported the following reaction:-

$$2\ NBu_4^+ + Pt_2X_6^{2-} + PY_3 \longrightarrow 2[Pt\ X_3\ PY_3]^-\ NBu_4^+ \quad (X = Cl\ Br\ I;\ Y = Cl,\ F)$$

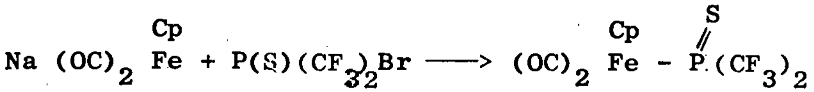
and in 1977 $Pt(PEt_3)\ Cl_2PF_3$[7] was reported as the product when PF_3 was bubbled through a solution of $Pt_2\ Cl_4\ (PEt_3)_2$ in $CH_2\ Cl_2$ which contained a little PCl_3. These complexes were also air stable crystalline solids and in fact the X - ray structure was obtained for $Pt(PEt_3)Cl_2PF_3$.

It is fairly obvious that the most useful technique available to study these systems is n.m.r. spectroscopy; with both ^{31}P and ^{19}F 100% spin ½ and ^{195}Pt 33.5% spin ½ the spectra obtained are very distinctive. Several features stand out in the ^{31}P spectra of a Pt - PF_2 complex. The PF_2 chemical shift tends to be to high frequency of the PEt_3 resonance and $^1J(PtPF_2)$is large, usually between 5000 and 7000 Hz. This has been attributed to π bonding in that the stronger a π acceptor the RPF_2 group is then the larger is the coupling constant[6]. Another consistent factor has been that $^1J(PF)$is generally lower for the bound PF_2 group than it is in the free fluorophosphine.

As mentioned before the work in this project involves the reactions of PF_2X (X = Cl Br I) and HPF_2Y (Y = SorSe) with some platinum substrates. Very little work has been carried out using these ligands and indeed the only example known is:-[8]

$$Ir(CO)Cl\,L_2 + PEF_2X \longrightarrow Ir(CO)Cl\,L_2\,PF_2E \quad (E = O\,or\,S;\ L = PPh_3, PPh_2Me)$$

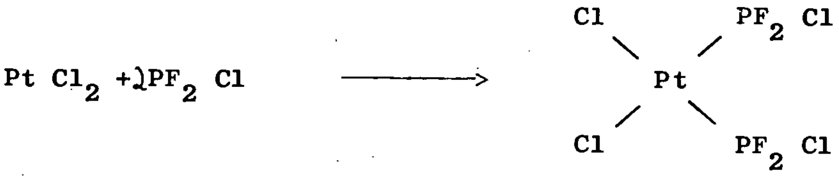
These complexes were characterised using i.r. spectroscopy. The compounds were too insoluble to allow an n.m.r. study to be carried out. However similar reactions on $NaCpFe(CO)_2$ gave more conclusive results. In this system $SP(CF_3)_2FeCp(CO)_2$ was isolated in 15% from the reaction[28].



$$\mathrm{Na\,(OC)_2\overset{Cp}{Fe} + P(S)(CF_3)_2Br \longrightarrow (OC)_2\overset{Cp}{Fe} - \overset{S}{\overset{/\!/}{P}}(CF_3)_2}$$

The n.m.r. data favoured the P^V form as representing the structure of the product.

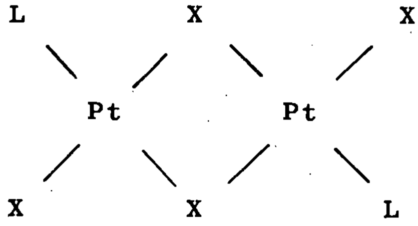
The only example of a Pt complex with a PF_2X ligand came from a reaction recently carried out in this department[9]:-



This complex was characterised using ^{31}P, ^{19}F n.m.r. spectroscopy.

(ii) Some recent progress in the formation of bridged binuclear Platinum complexes.

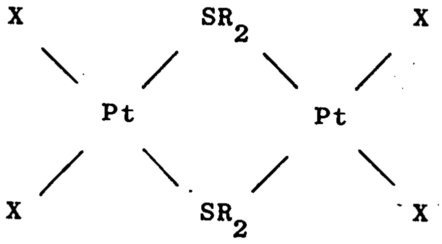
Until recently the only type of bridged platinum complex known was[2]

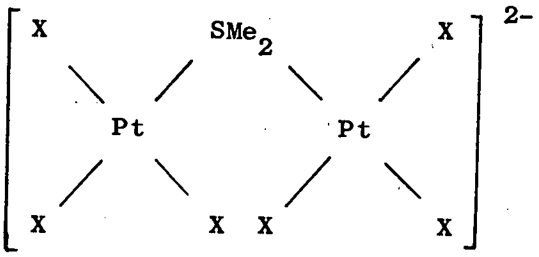


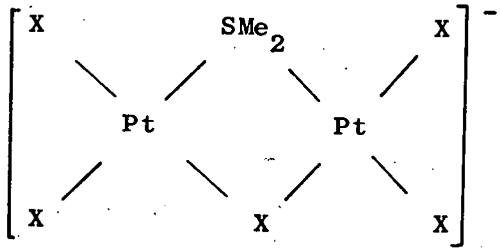
where X was an anionic ligand. Many examples of these compounds have been reported.

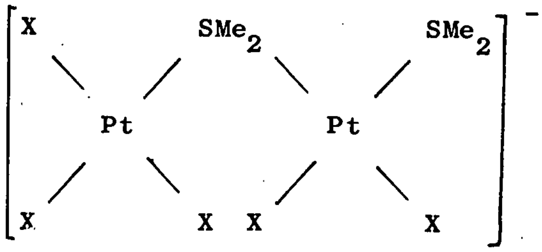
In this section I shall discuss and draw together several reports which have recently appeared where bridged complexes have been formed, the bridging ligand being a neutral species or a novel ligand acting as the bridge between two platinum atoms. This is relevant in that in the course of this project we have studied the formation of some novel bridged binuclear platinum complexes.

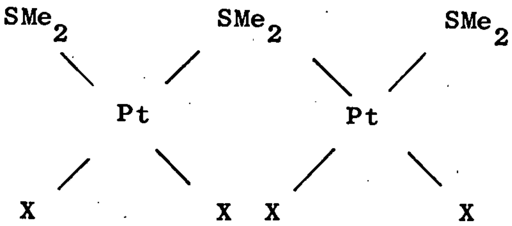
In 1974[10] the first examples of a neutral species acting as a bridge between two platinum atoms was reported. The bridging groups were SR_2 (R = Et or Me) and several novel types of complexes were formed.





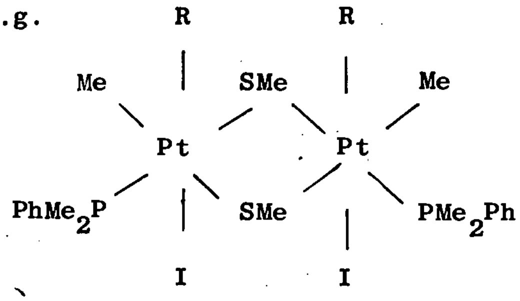




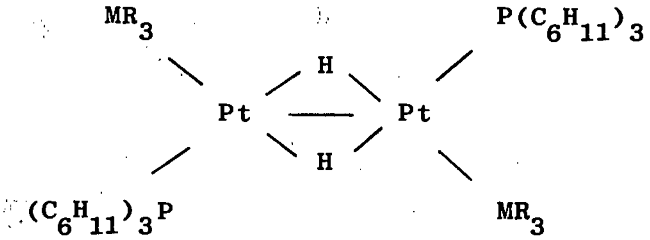


The structures were all assigned using ^{1}H n.m.r. and vibrational studies.

The next report was in 1976 when Brown and Puddephatt[11] carried out an extensive n.m.r. study on the oxidative addition reactions of some SR bridged complexes. They reported the formation of several Pt^{IV} bridged complexes as intermediates e.g.



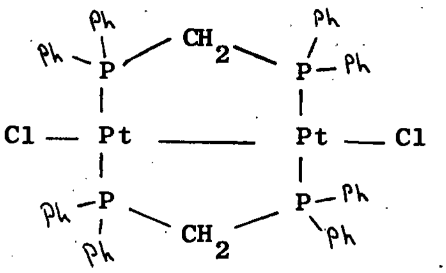
As well as these sulphur bridged complexes several compounds have been reported which contain hydride bridges. Most of the work in this area has been done by Spencer and Stone[12,13] who, since 1976 have published several papers on the synthesis and reactions of the following series of compounds:-



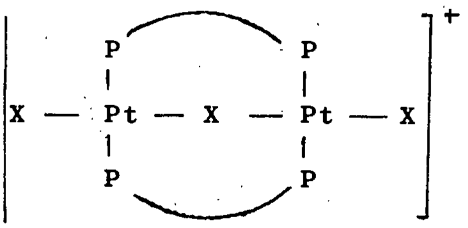
formed from the reaction of $Pt(C_2H_4)_2(P(C_6H_{11})_3)_2$ with MR_3H (M = Si or Ge; R = Cl, Me, Ph, CH_2Ph, Et or OEt).

The structure was established from X - ray studies and some vibrational work and although the bridging hydrides were not observed in the crystal structure, the fact that they are present is confirmed from the bridge cleavage reactions which these complexes undergo. Perhaps the most useful have been the reactions with olefins which show that the complexes catalyse the hydrosilylation[14] of both alkenes and alkynes.

Another major piece of work in this area stemmed from the reaction of $PtCl_2$ (dppm)[15)] [dppm = bis(diphenylphosphino)methane] with Na BPh_4 followed by HCl in boiling benzene which gave:-

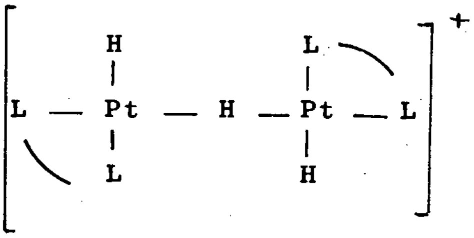


It was then observed that an intermediate in this reaction contained a hydrido bridging ligand and from this a series of complexes was prepared[16].



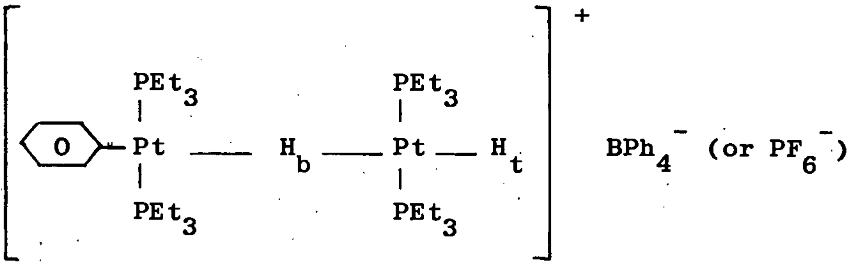
(X = H or Cl)

It was suggested that formation of this monohydride bridge could be associated with the presence of the bidentate donor ligands. There is some evidence that this may be the case from another example where a single hydride bridge is postulated[17]



Again a bidentate donor ligand is present. In this example fast exchange occurs between the bridging and terminal hydrides. Even when the n.m.r. spectrum is studied at temperatures below -100°C only one signal is observed. However terminal Pt - H stretching vibrations are observed in the i.r. spectrum. All the evidence supports the suggestion that a fast exchange is taking place.

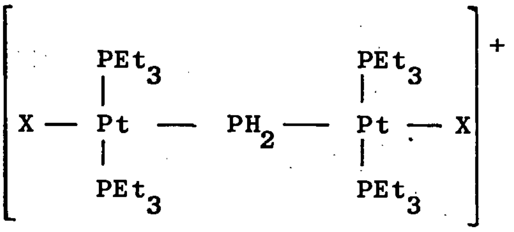
One example has been reported where bidentate donor ligands are absent and in this case we have a stable mono hydride bridged species[18].



Here there is no evidence for a fast exchange on the n.m.r. time scale and the structure was assigned on the basis of n.m.r. evidence and the X - ray crystal structure.

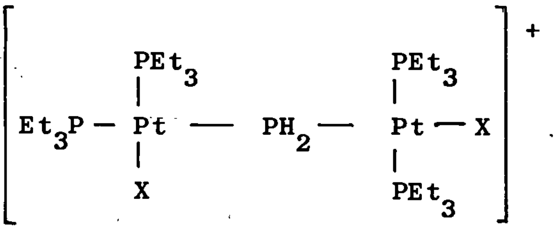
Apart from one report of a hydroxo bridged complex[19] $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ the other major advances in synthesising novel binuclear platinum complexes have come from work carried out in this department.

Most of the work has been done with bridging PH_2 groups[20] and several complexes have been characterised:-



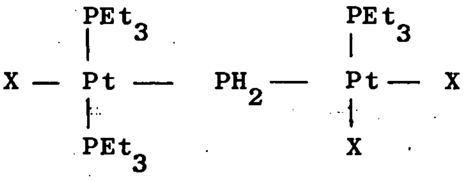
$[X-Pt(PEt_3)_2-PH_2-Pt(PEt_3)_2-X]^+$

trans - trans
cation
X = Cl Br I H



$[Et_3P-Pt(PEt_3)(X)-PH_2-Pt(PEt_3)_2-X]^+$

cis - trans
cation

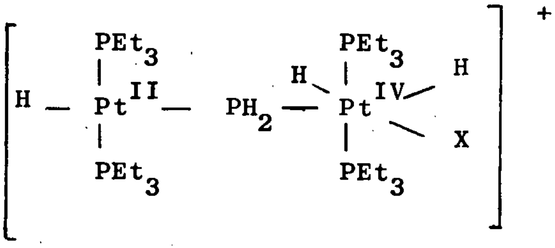


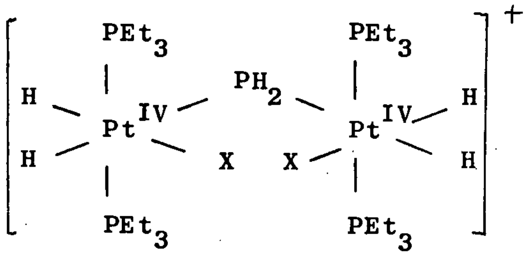
$X-Pt(PEt_3)_2-PH_2-Pt(PEt_3)(X)-X$

neutral complex

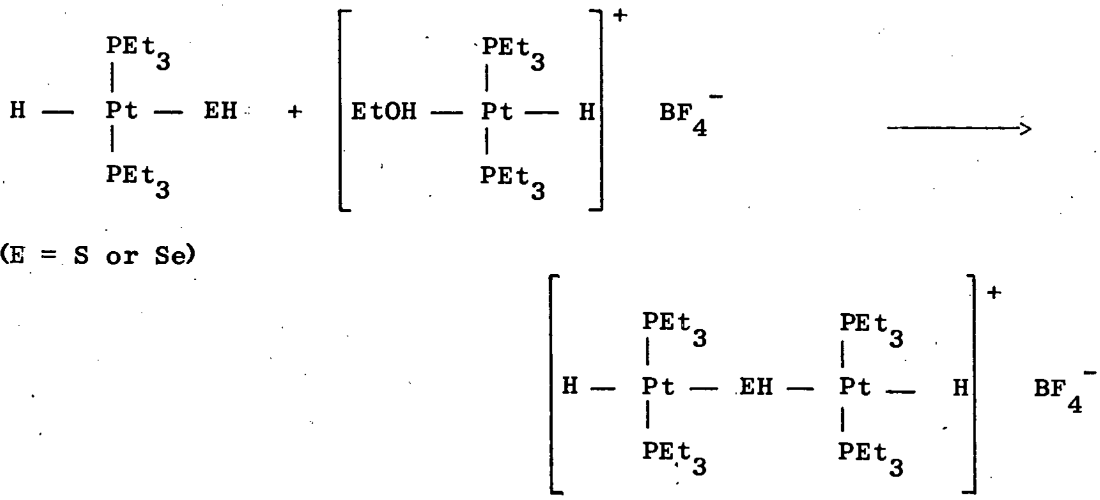
No evidence has been obtained for the cis - cis structure, and the heavier the halogen then the greater the tendency there is for the neutral complex to form. These complexes were formed by reacting either $PtHX(PEt_3)_2$ or $PtX_2(PEt_3)_2$ with Me_3SiPH_2.

Oxidative addition reactions with HX[21] have been carried out on these hydride complexes and evidence has been obtained to show that stepwise addition takes place with both of the following complexes being observed in the ^{31}P n.m.r. spectra.





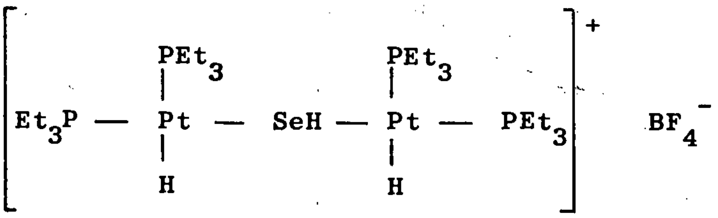
As well as the PH_2 systems a lot of work has been done on complexes containing an SH or SeH bridging group[22]. Here the compounds are formed from direct reaction of two platinum substrates:



$$H-\underset{PEt_3}{\overset{PEt_3}{Pt}}-EH + \left[EtOH-\underset{PEt_3}{\overset{PEt_3}{Pt}}-H\right]^+ BF_4^- \longrightarrow \left[H-\underset{PEt_3}{\overset{PEt_3}{Pt}}-EH-\underset{PEt_3}{\overset{PEt_3}{Pt}}-H\right]^+ BF_4^-$$

(E = S or Se)

For the Se system it was found that in solution isomerisation took place and the ^{31}P spectrum showed an $AA^1\ XX^1$ pattern which has been interpreted as arising from the cis - cis structure[2].



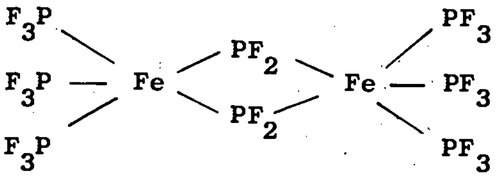
$$\left[\begin{array}{ccccccccc} & & PEt_3 & & & & PEt_3 & & \\ & & | & & & & | & & \\ Et_3P & — & Pt & — & SeH & — & Pt & — & PEt_3 \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}\right]^+ \quad BF_4^-$$

This is in direct contrast to the PH_2 system where isomerisation was from the trans - trans to the cis - trans structure. This could be due to the fact that we go from 4 coordinate phosphorous to 3 coordinate Se so the steric problems are different and the PH_2 system prefers the cis - trans structure while the SeH prefers the cis - cis configuration. For Se the cis - trans structure is not seen.

Attempts were made to carry out oxidative addition reactions, but in all cases the result was breaking of the bridge: for example, with H Cl cis, cis, trans $Pt(H)_2(Cl)_2(PEt_3)_2$ was the major product. Attempts have also been made to deprotonate the bridge but again these have proved unsuccessful.

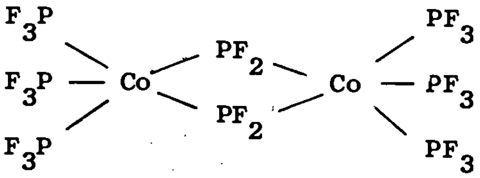
In this thesis we shall report the formation of similar complexes containing a PF_2 bridge. Very few examples of PF_2 acting as a bridging ligand are known and in fact only in one case is a singly bridged complex formed[24]. Two examples reported of doubly bridged PF_2 complexes are:

25)

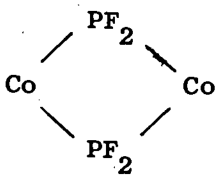


and

26)



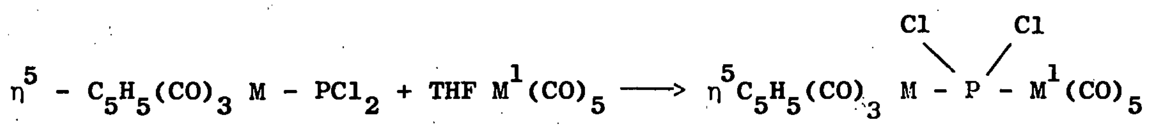
The iron complex was formed when Fe vapour was condensed with PF_3 at liquid nitrogen temperatures. The cobalt complex was the product when anhydrous <u>CoI_2</u> was reacted with Ca powder (Molar ratio 1:10) with PF_3 at 400 atm. and at temperatures above 170°C for 15 hours.

The iron complex was a red crystalline but volatile compound while the cobalt one was thermally stable up to and above 200°C. It was also stable in air for several days and from mass spectroscopy evidence it would appear that the  unit was the most stable part of the molecule, with an intense peak appearing at $^m/_e = 256$.

Similar complexes have also been prepared with CO bridges and in 1973 Kruck[27] et al reported the formation of complexes containing H and PF_2 bridges in the one molecule.

However, the first example of a singly bridged complex where the bridging ligand was PF_2 was reported in 1977 by Malisch and Panster[24].

The first stage in the preparation was formation of the PCl_2 complex:

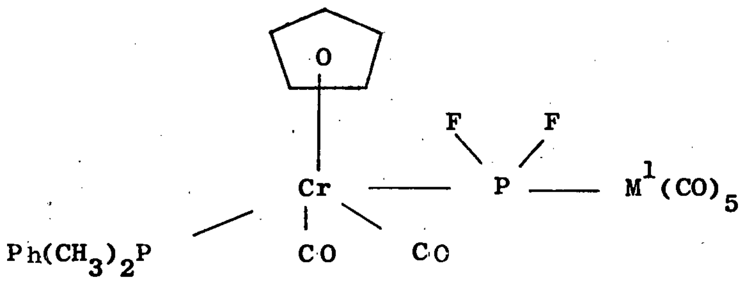


$$\eta^5 - C_5H_5(CO)_3\ M - PCl_2 + THF\ M^1(CO)_5 \longrightarrow \eta^5C_5H_5(CO)_3\ M - \overset{Cl\quad Cl}{P} - M^1(CO)_5$$

(M = Cr or W, M^1 = Cr or W)

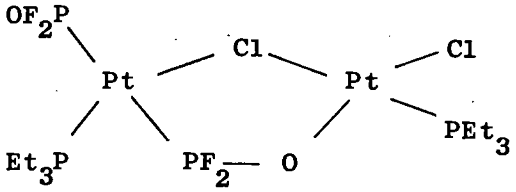
The Cl was then replaced by F, by reaction with BF_4^-.

The complexes were characterised using ^{31}P and ^{19}F n.m.r. spectroscopy and vibrational studies. They were all stable, crystalline yellow or green solids, the PF_2 complexes being less soluble and slightly more stable than the PCl_2 compounds. The PCl_2 series decomposed on melting to give $M(CO)_6$ while at no stage was the fragment $\eta^5C_5H_5(CO)_3M - PF_2$ observed, not even in the mass spectrum. Even the action of a strong base failed to decompose the PF_2 derivatives; in fact reaction with $P(CH_3)_2$ Ph led to displacement of a CO trans to the PF_2 to give the binuclear complex.



All the n.m.r. data was noted and for all complexes there was a downfield shift of δP for the bound PX_2 group compared to the free one.

Some recent work by Schmutzler[44] has resulted in the formation of a complex containing a $Pt-PF_2-O-Pt$ group. This complex had already been reported[5] and it was suggested that the complex had a monomer structure with two terminal PF_2O groups. However the X-ray crystal structure has now shown the structure to be



This complex is unusual in that it contains two distinct PF_2O groups. The 5 membered ring structure which contains the two Pt atoms means that the bond angles around Cl are much larger than they are in a normal Pt-Cl-Pt bridging group.

This complex was formed by the reaction of $PtCl(PF_2O)(PEt_3)_2$ with $PF_2(OC_3H_5)$ at 80°C.

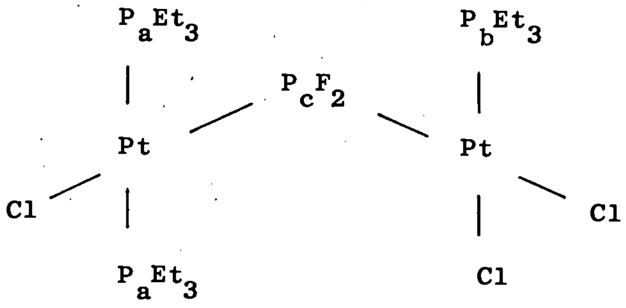
CHAPTER 2

The reaction of t-Pt $HX(PEt_3)_2$ with PF_2X

(X = Cl Br I)

2.1. Introduction

As part of my chemistry IV project a preliminary study of the reaction of t - Pt H Cl(PEt_3)$_2$ with PF_2Cl was carried out. The results obtained showed that complex I was being produced as one of the major products[29].



I

Other work carried out in this department had shown that it was possible to form binuclear platinum complexes containing a PH_2 bridging group[20]. We were therefore interested in synthesising these PF_2 bridged complexes and studying their reactions.

2.2 The reaction of t-Pt H Cl(PEt_3)$_2$ with PF_2Cl

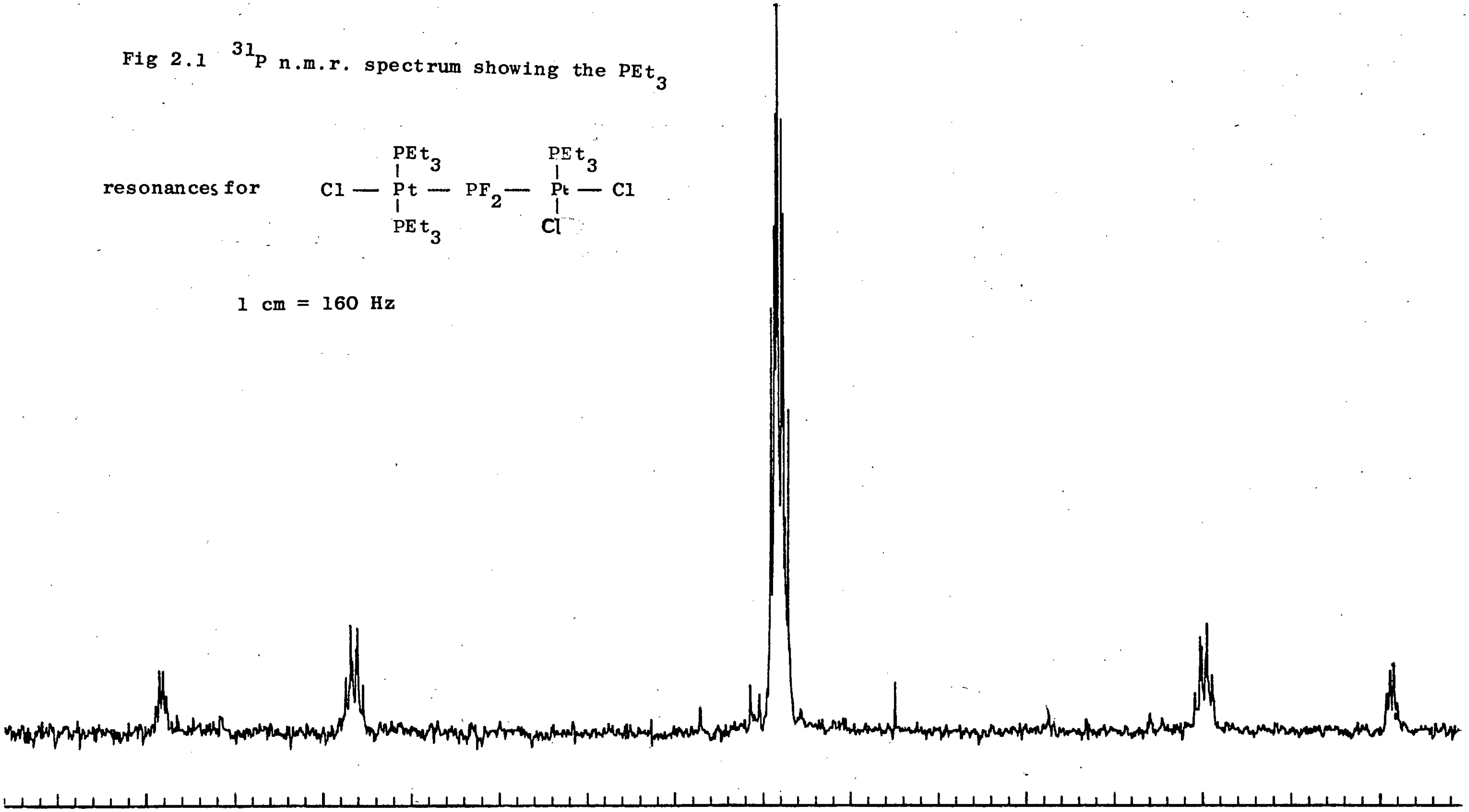
This reaction was carried out in CH_2Cl_2 and at room temperature complex A was obtained in approximately 60% yield. By removing the solvent once the reaction mixture had reached room temperature a white gum was obtained. By washing with ether and recrystallisation from methanol the product was obtained as clear, needle-like crystals.

Fig 2.1 ^{31}P n.m.r. spectrum showing the PEt$_3$

resonances for

$$\mathrm{Cl - \underset{PEt_3}{\overset{PEt_3}{Pt}} - PF_2 - \underset{Cl}{\overset{PEt_3}{Pt}} - Cl}$$

1 cm = 160 Hz

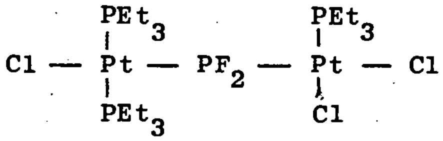


The reaction was studied and the final product identified using ^{31}P and ^{19}F n.m.r. spectroscopy. This proved particularly useful in this system as the presence of ^{195}Pt in 33% abundance, spin ½, meant that a lot of extra information could be obtained by studying the Pt satellites.

The ^{31}P spectra obtained for complex A were all first order and showed two distinct sets of resonances. At low frequency a complex multiplet was observed at ∿17 ppm and it was only by studying the Pt satellite patterns that this could be explained. Two sets of Pt satellites were observed, one showing a coupling of 2406Hz and the other of 3479Hz (Fig. 2.1). Both sets of satellites showed a doublet of triplets pattern although the size of the coupling constants were different. By taking the satellite patterns and fitting them over the central resonance it was possible to distinguish between two resonances which were both centered ∿17 ppm.

At high frequency a large triplet (Fig. 2.2) was observed with a splitting of 1058Hz. This corresponds to a PF_2 triplet pattern and confirms the presence of a PF_2 group in the complex. The satellites were also observed, but the pattern was complicated. This was due to the fact that two different Pt couplings were being observed. These couplings were very similar in size so the two sets of satellites overlapped. Each line in the central triplet was further split into a doublet of triplets and the couplings corresponded to the doublet couplings observed at low frequency.

Fig 2.2 ^{31}P n.m.r. spectrum showing the $\underline{P}F_2$ resonance for



$$\mathrm{Cl-\overset{PEt_3}{\underset{PEt_3}{Pt}}-PF_2-\overset{PEt_3}{\underset{Cl}{Pt}}-Cl}$$

1 cm = 400 Hz

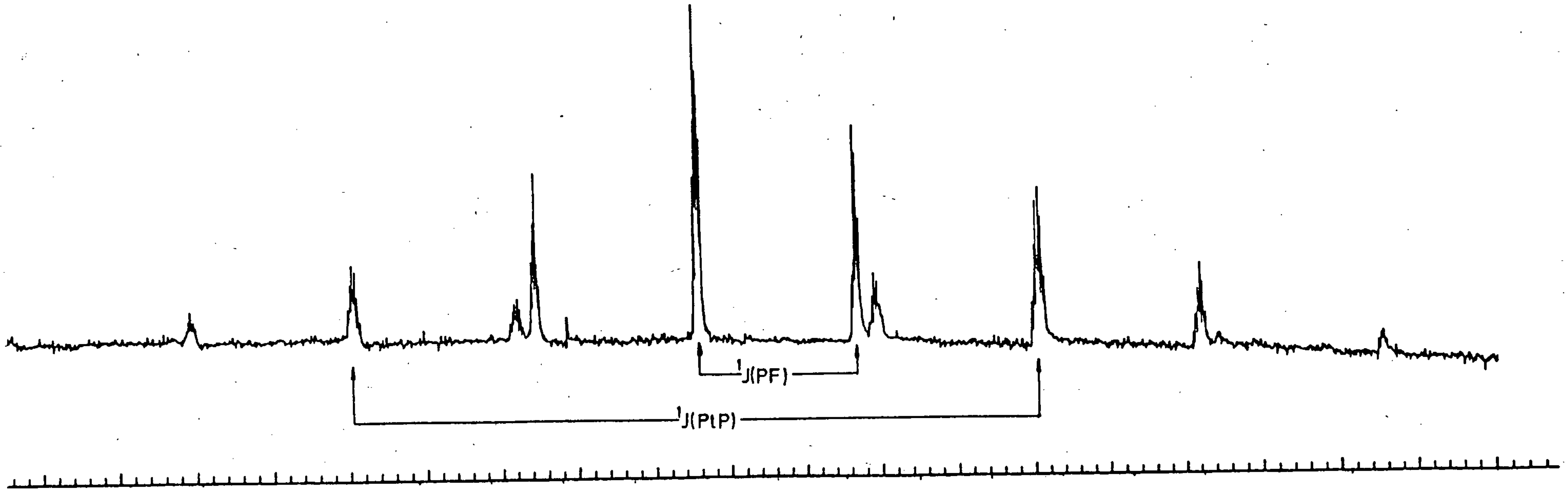
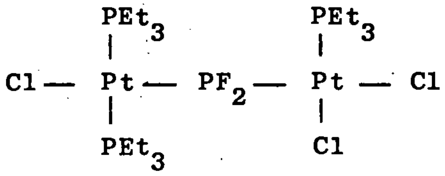
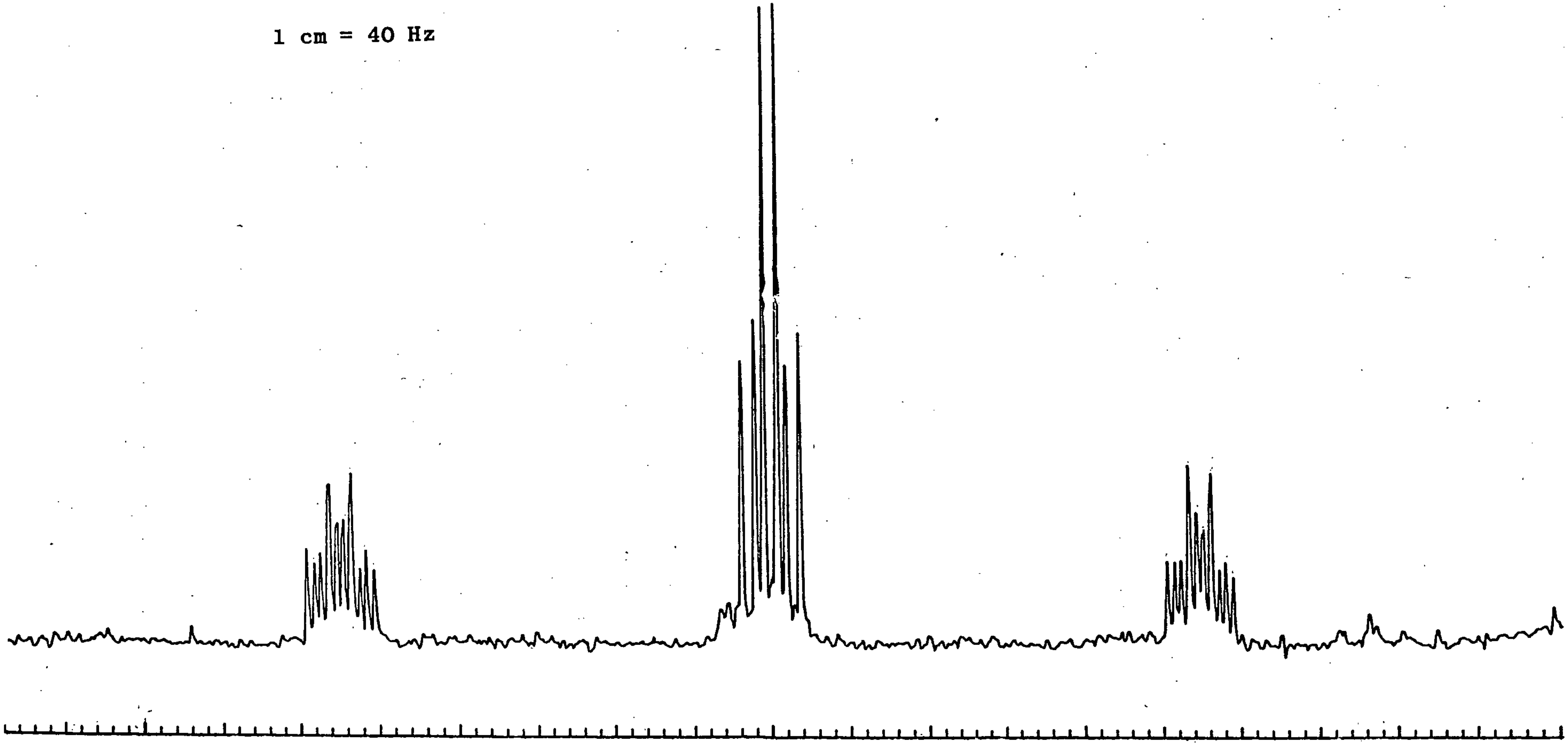


Fig 2.3 ^{19}F n.m.r. spectrum showing one part of the spectrum for



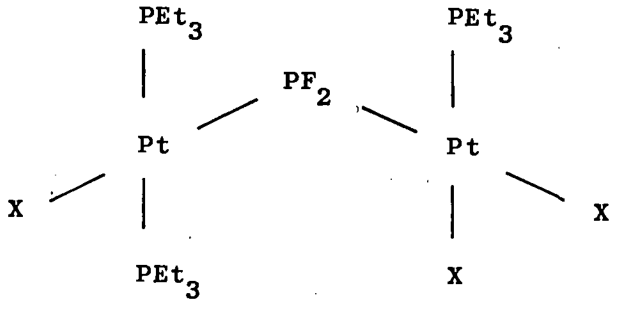
$$\mathrm{Cl-\overset{PEt_3}{\underset{PEt_3}{Pt}}-PF_2-\overset{PEt_3}{\underset{Cl}{Pt}}-Cl}$$



1 cm = 40 Hz

The ^{19}F spectra (Fig. 2.3) showed a large doublet splitting of 1058Hz and each line appeared as a doublet of triplets. Here the two coupling constants corresponded to the values for the small triplet couplings observed at the low frequency part of the ^{31}P spectra.

The evidence listed here suggests that complex A is of the form:



where X could be H or Cl. All the splittings observed in the ^{31}P and ^{19}F spectra can be accounted for on the basis of the structure shown and it is proposed the complex A is in fact complex I where all three X's are chlorides. This assignment was based on analysis and on i.r.spectra which showed no evidence for a Pt - H stretch.

2.3 Formation of similar Br and I complexes

The bromide and iodide analogues of I could be made by the same method as the chloride. However it was found that they were better prepared from the chloride by halogen exchange using Li Br or NaI. The products were again obtained as air stable crystalline solids and were identified using ^{31}P and ^{19}F n.m.r. spectroscopy.

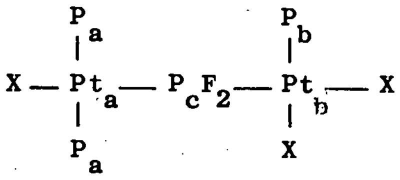
The results are summarised in Tables (i) and (ii). Some interesting trends in parameters are noted in the series Cl ——> I; some of these helped to make the spectra easier to interpret.

First, in the ^{31}P spectra δP_a shifts to low frequency on going from Cl ——> I while δP_b does not change much. On a simple basis one might expect δP_b to be more affected by changing the halogen since P_b is bound to a platinum which is attached to two halogen atoms, whereas P_a is bound to a platinum which is attached to only one halogen. However, by comparing the data with those for the PH_2 bridged complexes and with cis and trans $Pt\ X_2\ (PEt_3)_2$ it appears that the changes observed here are consistent with those observed in other series of complexes. The result of the increase in $\delta(P_b - P_a)$ is that we now obtain two distinct resonances in the PEt_3 region which simplifies the interpretation of the spectra.

Another factor which simplifies the spectra is the decrease in the size of one of the two values of $^1J(PtP_c)$. This means that two distinct pairs of satellites are observed instead of the overlapping patterns found with the Cl system. The same effect is noted in the ^{19}F spectra where one of the values of $^2J(PtF)$ decreases by more than the other.

Also for the iodide complex $^2J(P_aP_c)$ is small and unresolved so the ^{31}P spectra shows a triplet pattern as opposed to the expected doublet of triplets. There are several other slight differences in the chemical shifts and coupling constants, but these are to be expected as the halogen is changed.

Table 2.1 ^{31}P and ^{19}F n.m.r. data for



$X-\overset{\displaystyle P_a}{\underset{\displaystyle P_a}{Pt_a}}-P_cF_2-\overset{\displaystyle P_b}{\underset{\displaystyle X}{Pt_b}}-X$

X	Cl	Br	I
δP_a	17.3	12.7	4.70
δP_b	17.3	17.7	15.5
δP_c	211.02	208.8	204.6
$^1J(Pt\ P_a)$	2406	2430	2386
$^1J(Pt\ P_b)$	3479	3470	3330
$^1J(Pt\ P_c)$	4519 4452	4578 4280	4501 3869
$^2J(P_a\ P_c)$	19.3	15.5	14.4
$^2J(P_b\ P_c)$	10.1	7.6	N.R.
$^1J(P_c\ F)$	1059	1079	1112
$^3J(P_a\ F)$	14.1	15.5	14.0
$^3J(P_b\ F)$	10.0	17.2	12.0
δF	-30.9	-27.6	-27.5
$^2J(Pt\ F)$	541 551	512 566	453 570

Chemical shifts are in ppm, coupling constants in Hz

2.4 Possible Mechanisms of Formation

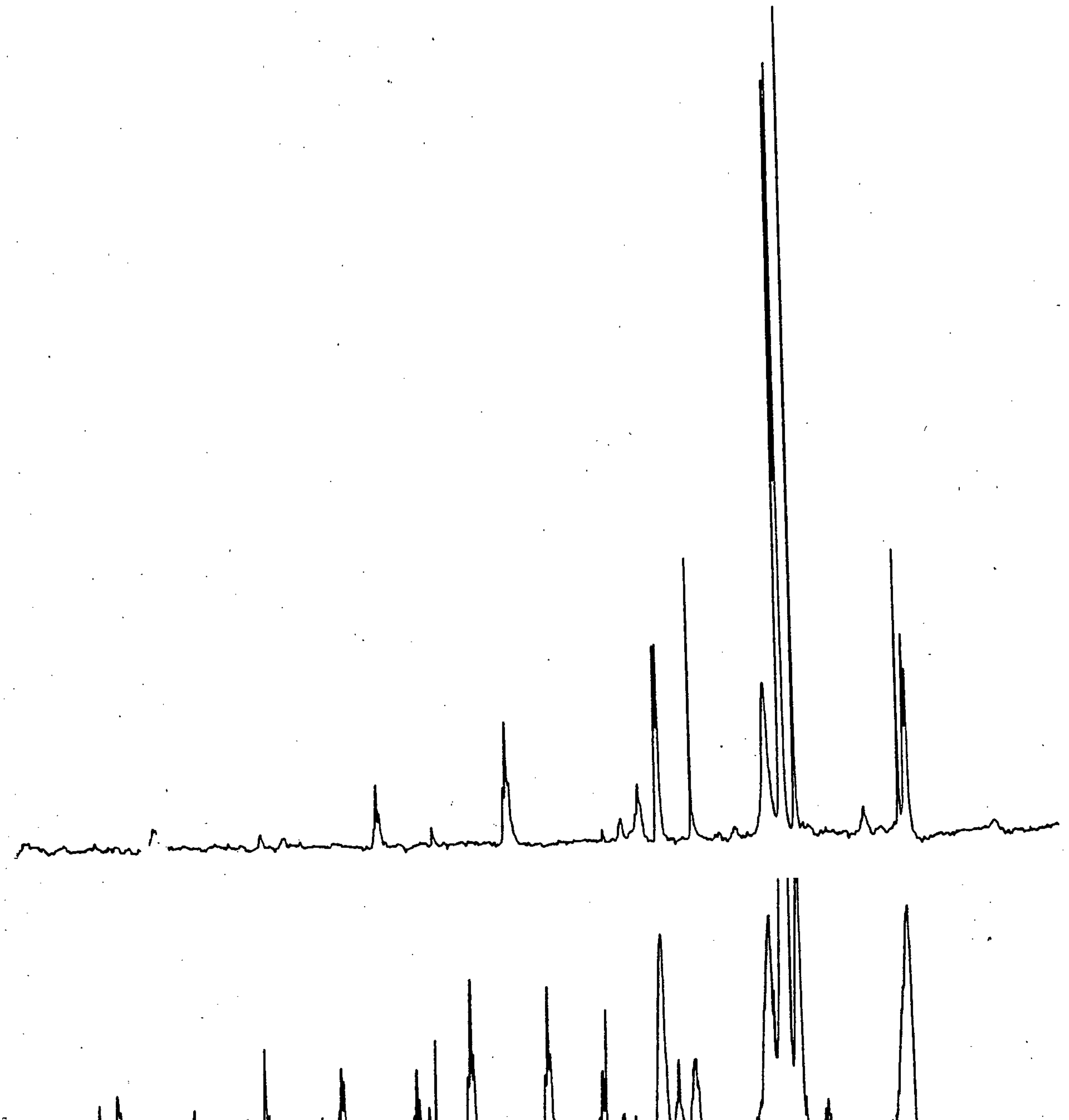
The reactions were all studied at low temperatures using ^{31}P and ^{19}F n.m.r. spectroscopy in an attempt to find out something about the mechanism which leads to formation of these bridged complexes. If we compare the PF_2 and the PH_2 systems we see that for the PH_2 reaction the neutral complex is only formed on decomposition of the ionic species whereas the only observed product for the PF_2 system is the neutral complex. It was hoped that the low temperature studies would explain the difference.

The ^{31}P spectrum of the reaction of t-$PtHCl(PEt_3)_2$ with PF_2Cl was recorded at -90°C in CD_2Cl_2. The spectrum showed one strong resonance, a singlet with Pt satellites, which could be assigned as being due to cis, cis, trans $PtH_2Cl_2(PEt_3)_2$. There was also a broad peak at +20 ppm but this could not be assigned to any known species.

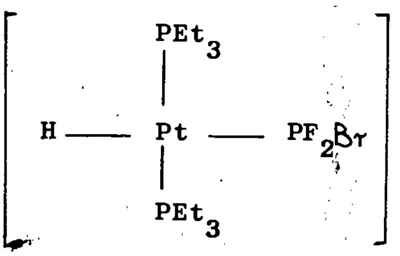
When the reaction of t $PtHBr(PEt_3)_2$ with PF_2Br was in turn studied, the results were far more useful. In this system two strong resonances were observed in the PEt_3 region, one of which corresponded to cis, cis, trans $PtH_2Br_2(PEt_3)_2$. The other resonance showed a doublet splitting and also had Pt satellites. In the PF_2 region there was a triplet of triplets with Pt satellites. The large triplet coupling confirmed the presence of a PF_2 group while the smaller coupling is equal to the doublet coupling observed in the PEt_3 region. This would correspond to a Pt complex containing one PF_2 group and two PEt_3 groups. When the proton coupling was retained, the PF_2 resonance showed an additional doublet coupling of

Fig 2.4 ^{31}P n.m.r. spectrum at -90°C showing a Pt-PF_2X intermediate. Above ^1H decoupled below ^1H non-decoupled. $PtH_2Br_2(PEt_3)_2$ is also observed.

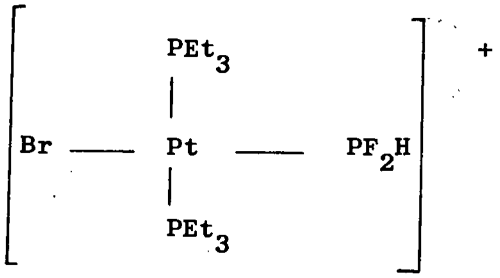
1 cm = 600 Hz



600 Hz (Fig. 2.4). This coupling is due to a hydrogen, which suggests that the complex observed could have one of the two possible structures A and B:



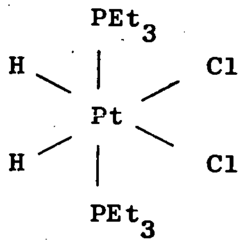
A

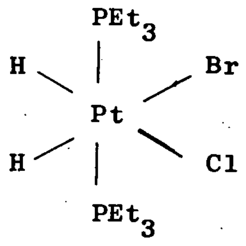


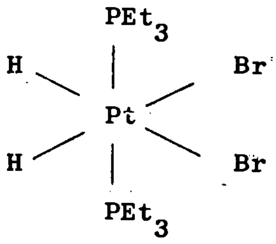
B

The evidence given so far does not show that there is a Br group in the complex let alone show where it is bound. To shed further light on this question the following mixed halogen reactions were carried out: PF_2Br was allowed to react with t-Pt-HCl$(PEt_3)_2$, and PF_2Cl to react with t-Pt HBr$(PEt_3)_2$.

The ^{31}P spectrum of the first of these showed three complexes to be present at -90°C. They were all derivatives of Pt^{IV} and were identified as







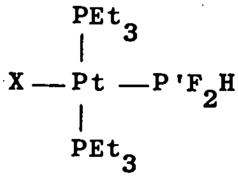
from their chemical shifts and $^1J(PtP)$ coupling constants. The reaction of t-PtHBr$(PEt_3)_2$ with PF_2Cl on the other hand gave a $PtPF_2$ complex very similar to that observed from the reaction with PF_2Br. However several differences were noted; for example δP = 12.57 ppm for PF_2Br system and 14.35 ppm for the PF_2Cl

derivative with δP^1 = 106.53 ppm and 101.80 ppm. The values for the coupling constants differed slightly as well: $^1J(PtP)$ = 5817 Hz and 5927 Hz for the PF_2Br and PF_2Cl systems respectively. These differences are small and significant and help to confirm that two different complexes have been observed and that a change in halogen must be associated with these differences. Hence the complexes must contain halogen; however there is still no evidence to say whether the halogen is bound to the Pt or the PF_2 group.

The most obvious explanation would be to propose that the PF_2X group is replacing Br bound to the Pt, giving the complexes $PtH(PF_2X)(PEt_3)_2$ (X = Cl,Br). However, the value of 600 Hz for $^2J(PH)$ is very large and does not fit in with other observed values for $^2J(PH)$; for example $^2J(PH)$ for the complex $PtH(PF_2S)(PEt_3)_2$ was observed as 273 Hz which is less than half the value obtained here. This fact tends to support the idea that some sort of exchange has occurred and that PF_2H is bound to the Pt.

Several other observations also suggest that it is PF_2H which is bound to the Pt. Firstly, an experiment performed earlier has shown that PF_2H reacted with $PtHCl(PEt_3)_2$ to produce a Pt-PF_2 complex which could contain a PF_2H group. The chemical shift for P^1 was 184 ppm and $^1J(PtP)$= 3000 Hz. This would at first appear to be completely different from the complexes observed here but again comparison with the PF_2Y (Y = S or Se) work is necessary. In the PF_2S and PF_2Se studies the complexes $PtX(PF_2Y(PEt_3)_2$ (X = Cl,Br) have been isolated and the complexes $PtH(PF_2Y)(PEt_3)_2$ observed as intermediates. When the H replaced a halogen there was a large shift of δP^1 to high frequency (Cl-δP^1 = 132 ppm. H δP^1 = 230 ppm),

Table 2.2 ^{31}P and ^{19}F n.m.r. data for



$$\begin{array}{c} PEt_3 \\ | \\ X-Pt-P'F_2H \\ | \\ PEt_3 \end{array}$$

(X = H,Cl or Br)

X	Cl	Br	H
δP	14.4	12.6	19.5
δP'	101.8	106.5	184
^{1}J(Pt P)	2119	2076	2329
^{1}J(Pt P')	5927	5817	3000
^{2}J(PP')	24.4	24.4	24.4
^{3}J(PF)	NR	NR	NR
^{1}J(PF)	1068	1080	1050
δF	-71.7	-72.6	NO
^{2}J(Pt F)	515	510	NO
^{1}J(PH)	647	635	NO
^{2}J(FH)	60.7	59.5	NO

Chemical shifts are in ppm, coupling constants in Hz

NR - not resolved

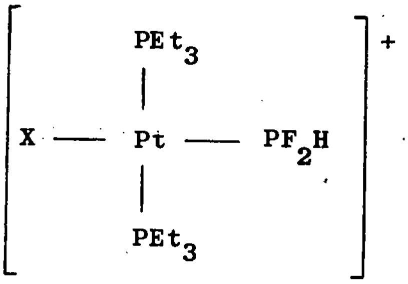
NO - not obtained

also $^1J(PtP)$ goes down from ~5000 to 3000, as is to be expected on replacing a trans-halogen with a trans-hydride.

This could also be what happens with the PF_2H complexes. The observed chemical shifts were δP^1 = 101 for the PF_2Cl system, 106 for the PF_2Br and 184 for the PF_2H reaction. If it was the PF_2H which was bound to the Pt then the trans-ligand would have changed from Cl to Br → H and this would fit with the large shift to high frequency. Also the $^1J(PtP)$ values observed were PF_2Cl - 5900 Hz PF_2Br 5800 Hz and PF_2H - 3000 Hz which would again fit for changing the ligand trans to a PF_2H group from Cl → Br → H.

Another piece of evidence comes from the observed n.m.r. parameters for the complex cis $PtCl_2(PF_2Cl)_2$. Here there are PF_2Cl groups trans to Cl and δP = 110 ppm, $^1J(PtP)$ = 5996 Hz. If the complex we were observing in the reactions here had the PF_2Cl group bound to the Pt then the trans ligand would be a hydride and a shift to high frequency would be expected for δP, also the $^1J(PtP)$ coupling constant would be lowered to ~3000 Hz. Therefore it would seem that the complexes observed have had the PF_2 group trans to a halogen and the PH-coupling observed was due to H directly bound to PF_2.

The best way to prove that this was indeed what was happening was to obtain ^1H n.m.r. spectra. If the H was bound to the Pt then δH would be ~-10 ppm. If on the other hand it was bound to the PF_2 then δH would be ~+10 ppm. The spectra were obtained and the pattern observed was the expected doublet (~600 Hz) of triplets (~60 Hz) with Pt satellites. δH was found to be +9 ppm which is conclusive evidence that the H is bound to the PF_2 group and that the complexes observed were:



$$\left[\begin{array}{ccccc} & & PEt_3 & & \\ & & | & & \\ X & — & Pt & — & PF_2H \\ & & | & & \\ & & PEt_3 & & \end{array}\right]^+$$

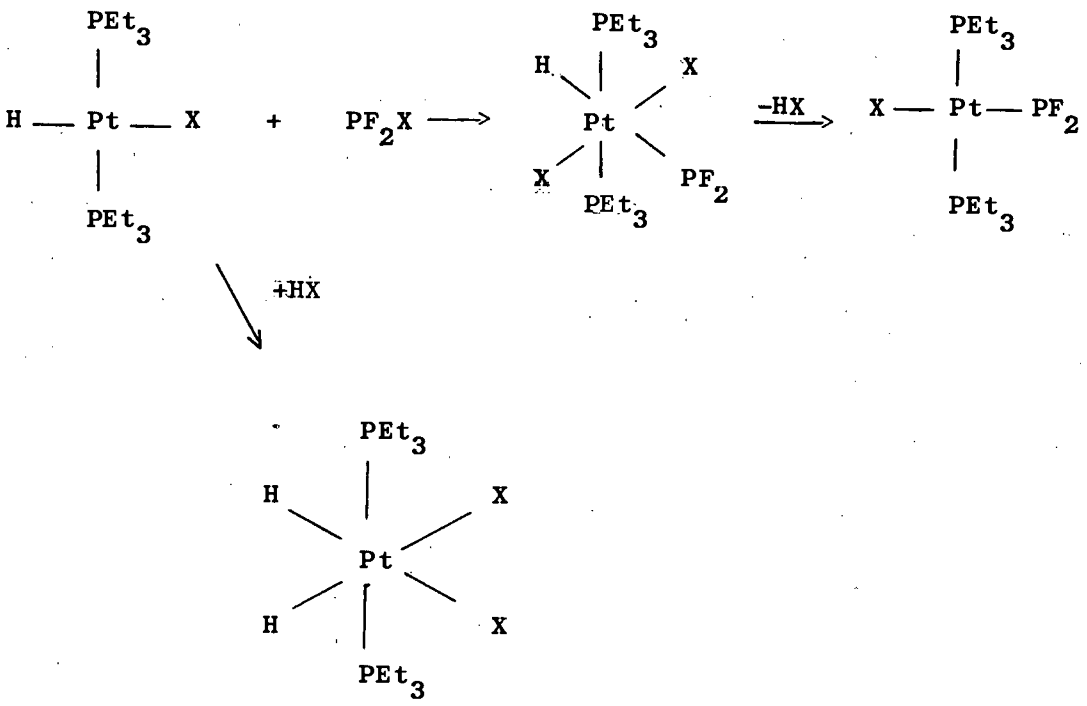
(X = Cl or Br)

As the reaction mixtures were allowed to warm up it was found that the amount of $Pt(H)_2(X)_2(PEt_3)_2$ present decreased and that a singlet appeared at +20 ppm, corresponding to the cation $HPEt_3^+$. Then as the temperature reached $+10^{o}C$ the bridged complexes began to appear.

All the bits of information gathered from these low temperature studies have now to be put together into formulating possible mechanisms for this reaction. The first thing to say is that no satisfactory mechanism can be proposed with any certainty. Indeed small pieces of information have been found which can give ideas as to what could be happening in this system.

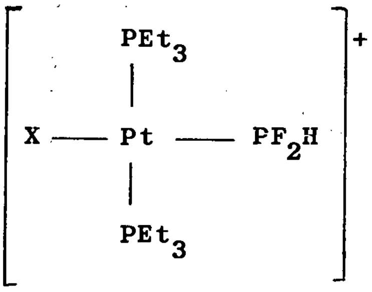
The only species which appeared in all the reactions was cis, cis trans $Pt(H)_2(X)_2(PEt_3)_2$. This could have been formed by addition of HX to the starting material. So a source of HX has to be found.

From the reaction of t-$PtHCl(PEt_3)_2$ with PF_2Br where three complexes of the form cis, cis, trans $PtH_2X_2(PEt_3)_2$ were observed it can be seen that the X from the PF_2X starting material is now bound to the metal. This would suggest an initial oxidative addition of PF_2X followed by loss of HX which can in turn add to the starting material, i.e.



However, neither of the two PF_2-Pt intermediates postulated here were observed in the n.m.r. spectra. Formation of a terminal Pt-PF_2 group would give a possible route to bridge formation in that this group would be reactive and could then attack another platinum molecule.

When evidence was obtained for a Pt-PF_2 intermediate from the reactions of t-$PtHBr(PEt_3)_2$ with PF_2Br and PF_2Cl it had a hydrogen bound to the PF_2 group. We have proposed that these intermediates were of the form:



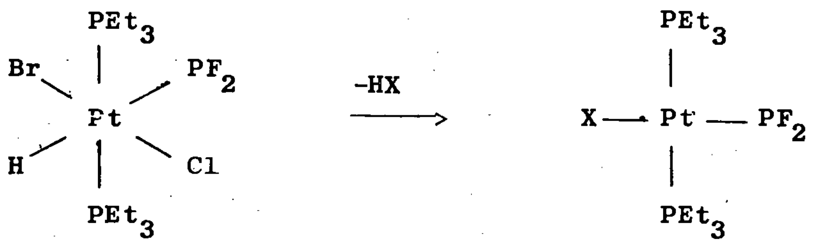
$$\left[X-Pt(PEt_3)_2-PF_2H \right]^+$$

(X = Cl or Br)

One would have expected that the intermediates would be of the form $PtH(PF_2X)(PEt_3)_2$ but the halogen bound to the PF_2 has been exchanged for an H. This exchange of an H for X bound to a phosphorus is very unusual. However it could be formed by attack of HX on a terminal PF_2 group.

From the observations made so far two complexes have been seen at -90°C in the ^{31}P spectrum, $[PtX(PF_2H)(PEt_3)_2]^+$ and $PtH_2X_2(PEt_3)_2$. However only one H was present per platinum in the starting materials and three are required for every two Pt atoms in these intermediates. This lends to the suggestion that the solvent CD_2Cl_2 could be involved. For the complex $PtX(PF_2H)(PEt_3)_2$ a ^1H spectrum has been obtained so the proton now bound to the PF_2 must be the one which was originally on the Pt so any terminal PF_2 group formed did not abstract a proton from the solvent. Also, all the couplings expected, $^1J(PH)$ and $^2J(FH)$, were observed with no sign of deuterium coupling.

If the first stage of the reaction is oxidative addition of PF_2X then the complex formed from the reaction of $PtHBr(PEt_3)_2$ with PF_2Cl would be:

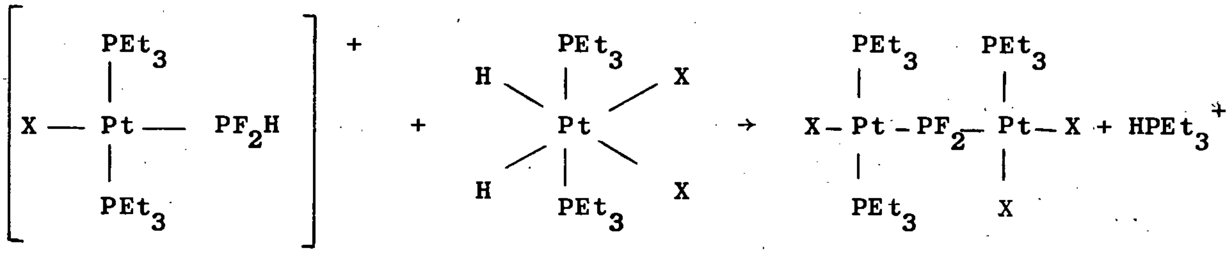


(X = Cl or Br)

which could lose HX to give two possible four coordinated complexes. However only one PF_2H intermediate was observed. This could be due to the fact that the Cl complex is the thermodynamically preferred product. If this is the case then $PtCl(PF_2H)(PEt_3)_2$ would be the expected intermediate for the reaction of t-$PtHCl(PEt_3)_2$ with PF_2Br

However for this system no PF_2 intermediate was observed. This could be explained if the rate of addition of HX to t-$PtHX(PEt_3)_2$ differed for X = Cl and Br so that in the Br case HX addition onto the PF_2 is allowed to occur. For the $PtHCl(PEt_3)_2$ reactions the Pt complex mops up all the HX before reaction to the PF_2 species occurs. This may seem unlikely although we cannot be sure and because of this we cannot say that the trans-halogen in the PF_2H complexes was the one which was originally bound to the PF_2 group. Formation of the PF_2H intermediate may involve a four-coordinated phosphorus as an intermediate but we have no evidence to support this.

As yet we still do not know where the extra H atom comes from and because of this any proposal as to the origin of the intermediates observed here will be somewhat uncertain. However, now that we have identified the two intermediates we now have to allow them to react to give the observed products.



If H_2 gas was evolved then this would be a balanced equation, however at no stage was there any sign of a gas being given off and no non-condensable components were found in the reaction vessel. Yet again the proposed mechanism does not fit with the experimental observations.

In summing up this work it can be noted that several interesting results have been found by studying these reactions at low temperature but so far no satisfactory mechanism can be postulated. Because of this, the formation of other PF_2 bridged complexes, other than the three which have been characterised, has not been possible. Until a better route to formation of these binuclear complexes can be found it does not seem as if this will be possible. A method has to be found whereby the step which forms the bridge can be controlled by selection of different starting materials. We therefore set out to make Pt-PF_2S complexes in the hope that removing the S would lead to a Pt-PF_2 group which could then form a bridged complex. The work on these PF_2S complexes is described in the next chapter.

2.5. Difficulties found in the reaction.

Several attempts were made before the PF_2 bridged complex was obtained in a reasonable yield. One of the main difficulties was that the major by-product found was Pt Cl $PF_2O(PEt_3)_2$ which suggested that water was being allowed into the system.

This source of error was removed by drying all the reagents thoroughly. The solvent was dried over CaH_2 and freshly distilled before use. The Pt H Cl $(PEt_3)_2$ was finely powdered and dried on a vaccuum line before use. The vaccuum line itself was completely dried using SiH_3Br before use. Another source of PF_2O could have come from some being present in the PF_2 Cl so freshly prepared PF_2 Cl was used to obtain the best results.

The first experiments carried out had shown a yellow colour and it was thought that the desired product might be yellow. It was only when extreme care was taken that the solution stayed clear and white crystals were obtained. Some of these crystals were suitable for X - ray data to be collected but the disorder in the crystal meant that the structure could not be solved. All that was confirmed was that two Pt atoms were in close association possibly forming a bridged complex.

The samples obtained tended to smell strongly of PEt_3 and it was thought that perhaps the first product obtained was the symmetrical cationic complex and that the neutral complex was in fact a decomposition product. However, no evidence whatsoever has been found in the n.m.r. spectra for the cationic bridged complex. Also the final crystalline product gave very good C and H analysis which ruled out any significant amount of the cationic species being present. Certainly the most stable complex in solution is the unsymmetrical neutral complex.

However, even the neutral complexes are slightly unstable in solution, the iodide being the least stable followed by the bromide then the chloride. Decomposition occurs yielding t-Pt X_2 $(PEt_3)_2$ as the only known Pt complex. This means that the n.m.r. data is more difficult to obtain especially for the iodide complex. Problems arise due to the fact that the PF_2 resonance seems to be less sensitive than the PEt_3 part. Although they should be in the ratio PF_2 : PEt_3, 1:3 it doesn't appear this way in the spectra. The PEt_3 region can be collected in ∿1000 pulses whilst it can require up to 100,000 pulses to collect reasonable data for the PF_2 part. This could be due to the PF_2 resonance having a different relaxation time. Meanwhile, the bridged complex is slowly decomposing.

This slow decomposition in solution also explains the low yield from the final recrystallisation where crystals of t-Pt X_2 $(PEt_3)_2$ were also obtained. The only answer to this problem was to have the complexes in solution as little as possible. This meant that in the initial preparation a higher yield was obtained if the solvent was removed immediately the reaction was warmed to room temperature.

Another problem arises from the structure determination. From the n.m.r. data collected we can say that there are two inequivalent Pt atoms linked by a PF_2 group and that one Pt atom contains two PEt_3 groups cis to the bridge and that the other Pt contains one cis PEt_3 group. From the i.r. spectra and the analysis results it is proposed that the other sites on the Pt atoms are filled by halogen atoms. The possibility must now be considered that an H atom may also be involved in linking the two Pt atoms or that another group may also be bound to the PF_2.

It seems unlikely that another group is bound to the PF_2 since the band should be visible in the i.r. if a P - H bond existed. Also were there a halogen still bound then a P - X stretch would have been observed.

The possibility that there may be a Pt - H - Pt linkage is more difficult to discount. Examples are known where mixed PF_2 and H bridging complexes have been formed. However by comparison with the PH_2 system where ^1H studies were carried out it seems unlikely that a hydride is present. Also there was no evidence of coupling to a hydride in the PF_2 region, and no evidence was found for a Pt - H - Pt stretch in the i.r. but this may be hidden by the other bands.

CHAPTER 3

The reaction of t-Pt $HX(PEt_3)_2$ with HPF_2Y
(X = Cl Br I, Y = S or Se)

3.1 Introduction

The complexes Pt Cl (PF_2O) $(PR_3)_2$ have been fully characterised[5]. Our interest in these complexes derived from the possibility that by removing the oxygen a terminal Pt - PF_2 group might be formed and this could then form a bridged complex. This would enable a wider range of bridged complexes to be formed.

However an attempt to remove the O using Si_2 Cl_6 was unsuccessful. In analogous compounds of simple phosphoranes, it is easier to remove S from the phosphorus than to remove O. It was hoped that a method of forming Pt - PF_2S complexes could be found and if this was successful then attempts could be made to remove the S.

A Pt - PF_2S complex was in fact observed as one of the products from the reaction of $(PF_2)_2$ S with Pt Cl H $(PEt_3)_2$ but other products were also observed. Since this did not appear to be a good synthetic route to the Pt - PF_2S complexes, another method was attempted. In this chapter we report the results of studying the reactions of HPF_2Y (Y = S or Se) with Pt HX $(PEt_3)_2$ (X = Cl Br or I).

3.2 Isolation of Products

The reactions were carried out in CH_2 Cl_2 and by allowing the system to warm to room temperature and then removing the solvent the products were isolated as air stable white crystalline solids. These products were identified by ^{31}P and ^{19}F n.m.r. spectroscopy and the crystal structure was obtained for Pt Cl (PF_2S) $(PEt_3)_2$.

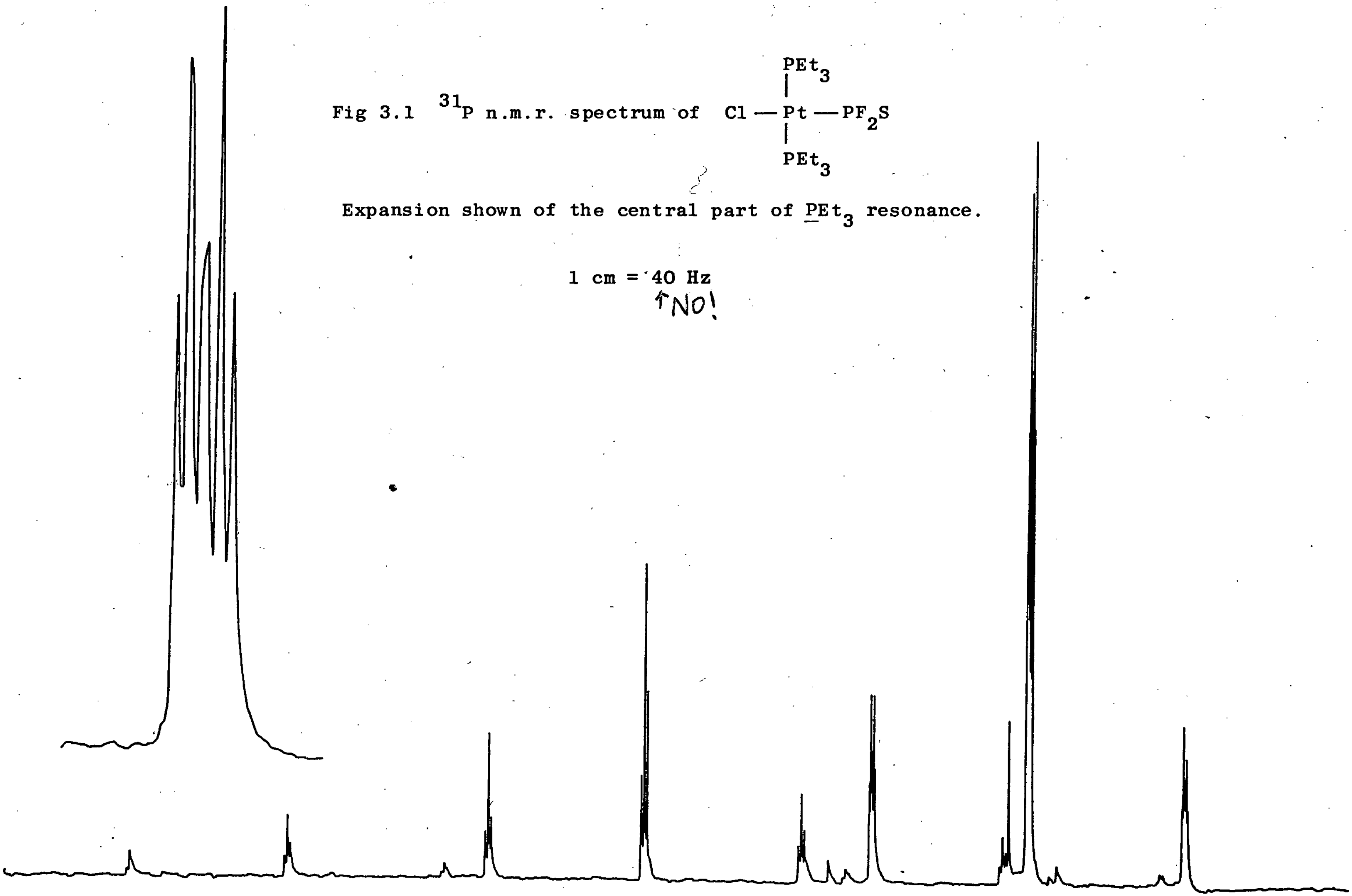


Fig 3.1 ^{31}P n.m.r. spectrum of $\mathrm{Cl}-\underset{\underset{\displaystyle\mathrm{PEt_3}}{|}}{\overset{\overset{\displaystyle\mathrm{PEt_3}}{|}}{\mathrm{Pt}}}-\mathrm{PF_2S}$

?

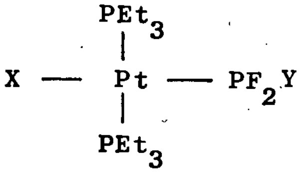
Expansion shown of the central part of $\underline{\mathrm{P}}\mathrm{Et_3}$ resonance.

1 cm = 40 Hz

↑NO!

The spectra obtained were all first order and showed similar patterns for all the products isolated. The ^{31}P spectrum (Fig. 3.1.) showed two distinct resonances. To low frequency, which is the PEt_3 region, a doublet of triplets was observed while at high frequency, the PF_2 region, a triplet of triplets was observed. In the high frequency pattern the first triplet coupling is ∿1100 Hz and is due to ^1J (PF), confirming the presence of a PF_2 group. The other triplet coupling is the same as the doublet coupling in the PEt_3 resonance. With Pt satellites being observed for both resonances, the evidence confirms that we have a Pt complex containing a PF_2Y and two PEt_3 groups. The fact that the S and Se are still bound to the PF_2 is suggested from CH analysis; moreover in the ^{19}F spectra there was a suggestion that ^2J(F Se) was being resolved, giving selenium satellites very close to the main resonance.

The substituent trans to PF_2Y in the Pt complex is not identified by any of the evidence so far presented. Several pieces of evidence show that this substituent is halogen. Firstly, different chemical shifts and coupling constants are observed depending on which halogen is present in the Pt starting material. Also when the spectra were recorded with the proton coupling retained the pattern of the PF_2 region was unchanged. This shows that the trans ligand is definitely not a hydride. Finally the analysis figures are consistent with a halogen being trans to the PF_2Y group. With this evidence plus that obtained from the ^{31}P spectra it is proposed that the following complexes have been isolated:



$$X - \underset{PEt_3}{\overset{PEt_3}{Pt}} - PF_2Y$$

(i) X = Cl Y = S

(ii) X = Br Y = S

(iii) X = I Y = S

(iv) X = Cl Y = Se

(v) X = Br Y = Se

(vi) X = I Y = Se

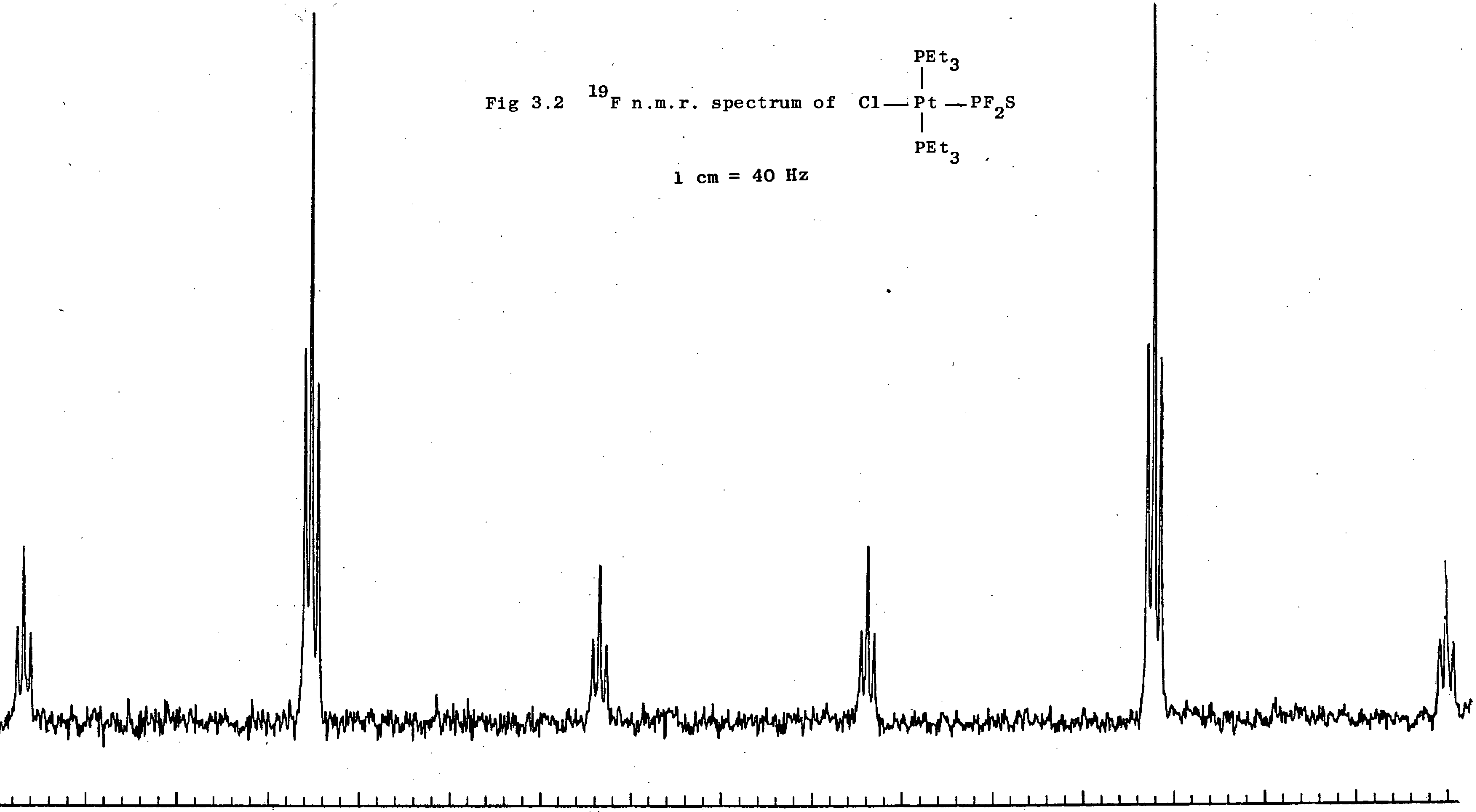


Fig 3.2 ^{19}F n.m.r. spectrum of $\mathrm{Cl{-}\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}{-}PF_2S}$

1 cm = 40 Hz

The ^{19}F spectra all confirm the suggested structures, showing a doublet $^{1}J(PF)$ of triplets $^{3}J(PF)$ all with Pt satellites.

The n.m.r. parameters are consistent with values for known transition metal fluorophosphine complexes in that δP for the PF_2 part is to high frequency when bound to the Pt. Also the slight differences in the chemical shifts and coupling constants seen in Table (i) are consistent with the halogen varying with the halogen in the starting material and with replacement of PF_2S by a PF_2 Se group.

3.3. Reaction Mechanism

The synthetic reactions were all studied at low temperatures using ^{31}P and ^{19}F n.m.r. spectroscopy. Several interesting complexes were observed and a reasonable mechanism can be postulated from the observations noted. The intermediates observed depended on the amount of HPF_2Y added. Two ratios of Pt to PF_2 were studied, 1:1 and 1:4. Each of these will be considered in turn.

(i) Pt H X $(PEt_3)_2$ + HPF_2Y 1:1.

For this system the S and Se reactions behaved similarly with, if anything, the S reactions being cleaner. In all cases no reaction took place until -50°C and at this temperature 3 complexes were observed in the ^{31}P spectra. The first showed a singlet with Pt satellites which could be assigned as cis, cis, trans Pt H_2 X_2 $(PEt_3)_2$. The other two complexes each showed a doublet pattern in the PEt_3 region both with Pt satellites. The species responsible for one of these doublets was present in only a trace amount. In the PF_2 region only one resonance was observed, as a triplet of

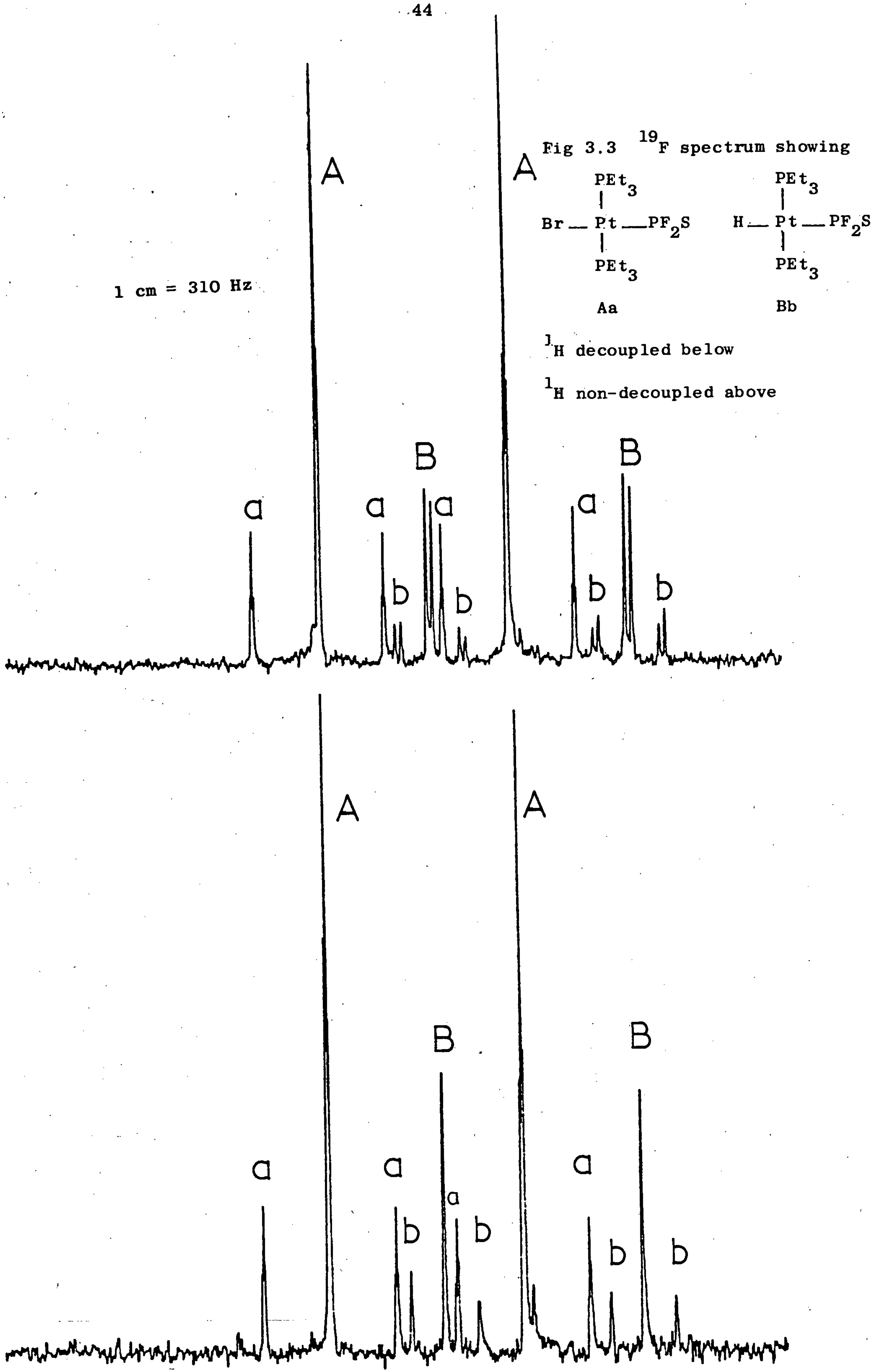


Fig 3.3 ^{19}F spectrum showing

$$\begin{array}{c} PEt_3 \\ | \\ Br - Pt - PF_2S \\ | \\ PEt_3 \end{array} \qquad \begin{array}{c} PEt_3 \\ | \\ H - Pt - PF_2S \\ | \\ PEt_3 \end{array}$$

Aa Bb

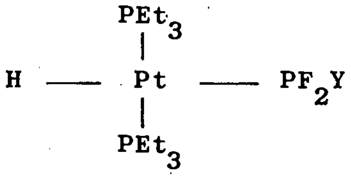
^1H decoupled below

^1H non-decoupled above

triplets with Pt satellites. The smaller triplet splitting here corresponded with one of the doublet couplings observed at low frequency.

The spectra were then observed with the proton coupling retained The PF_2 resonance showed a large additional doublet splitting which suggests a trans hydride. The protons on the ethyl groups are too far away to couple to the P nucleus of the PF_2 group. The ^{19}F spectra showed a doublet of triplets with Pt satellites, each line of which was further split into a doublet (Fig. 3.3) when the proton coupling was retained. The same parameters were obtained no matter which Pt starting material was used, the only difference being observed when Se replaced the S in the PF_2 group.

From this evidence it is proposed that we are observing here two Pt^{II} complexes.



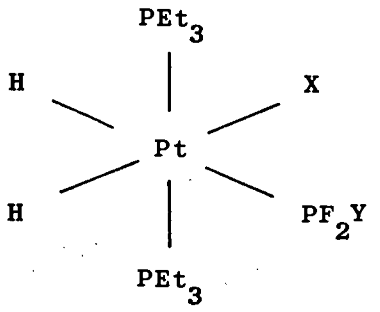
$$H-\overset{\overset{PEt_3}{|}}{\underset{\underset{PEt_3}{|}}{Pt}}-PF_2Y$$

(vii) Y = S

(viii) Y = Se

The $^3J(PF)$ coupling might well be small which would explain why only a doublet is seen at low frequency in the ^{31}P spectra instead of the expected doublet of triplets.

The other doublet observed at low frequency would be due to the PEt_3 groups of the Pt^{IV} six coordinate complex formed by oxidative addition of HPF_2Y to the Pt starting material.



(ix) X = Cl Y = S (xii) X = Cl Y = Se
(x) X = Br Y = S (xiii) X = Br Y = Se
(xi) X = I Y = S (xiv) X = I Y = Se

The high frequency part of the spectra of these complexes was not observed here, but it would seem likely that they are formed. Loss of H X from complexes (ix) - (xiv) would give the four coordinate Pt^{II} complexes (vii) and (viii) which are observed as the major intermediates. This H X could then add to unreacted starting material to give the other observed intermediates cis, cis, trans Pt H_2 X_2 $(PEt_3)_2$. Ultimately, loss of H_2 gas from the complexes (ix) - (xiv) would give the final products, complexes (i) - (vi). Further evidence will be mentioned later which will confirm the existence of complexes (ix) - (xiv).

The reaction does in fact produce 1 mole of H_2 gas which again supports the formation of the six coordinate intermediates (ix) - (xiv). As the system is warmed from -50°C the amount of Pt H (PF_2Y) $(PEt_3)_2$ present goes down and the final product appears.

To sum up the observations made here, the following reaction mechanism is proposed (Fig.3.4.). The first step involves oxidative addition of HPF_2Y to Pt H X $(PEt_3)_2$ to give the Pt^{IV} complexes (ix) - (xiv). These complexes can then undergo reductive elimination in two ways: they can lose H X (step A) which is a fast at low temperatures and reversible; or they can lose H_2 (step B) which is slower and irreversible and gives the final product. Fig 3.5 shows one case where all three Pt-PF_2 complexes involved were observed.

Fig 3.5 ^{31}P n.m.r. spectrum recorded at -30°C of the reaction $PtHCl(PEt_3)_2 + HPF_2S$, showing the 3 different $Pt-PF_2Y$ complexes

1 cm = 250 Hz

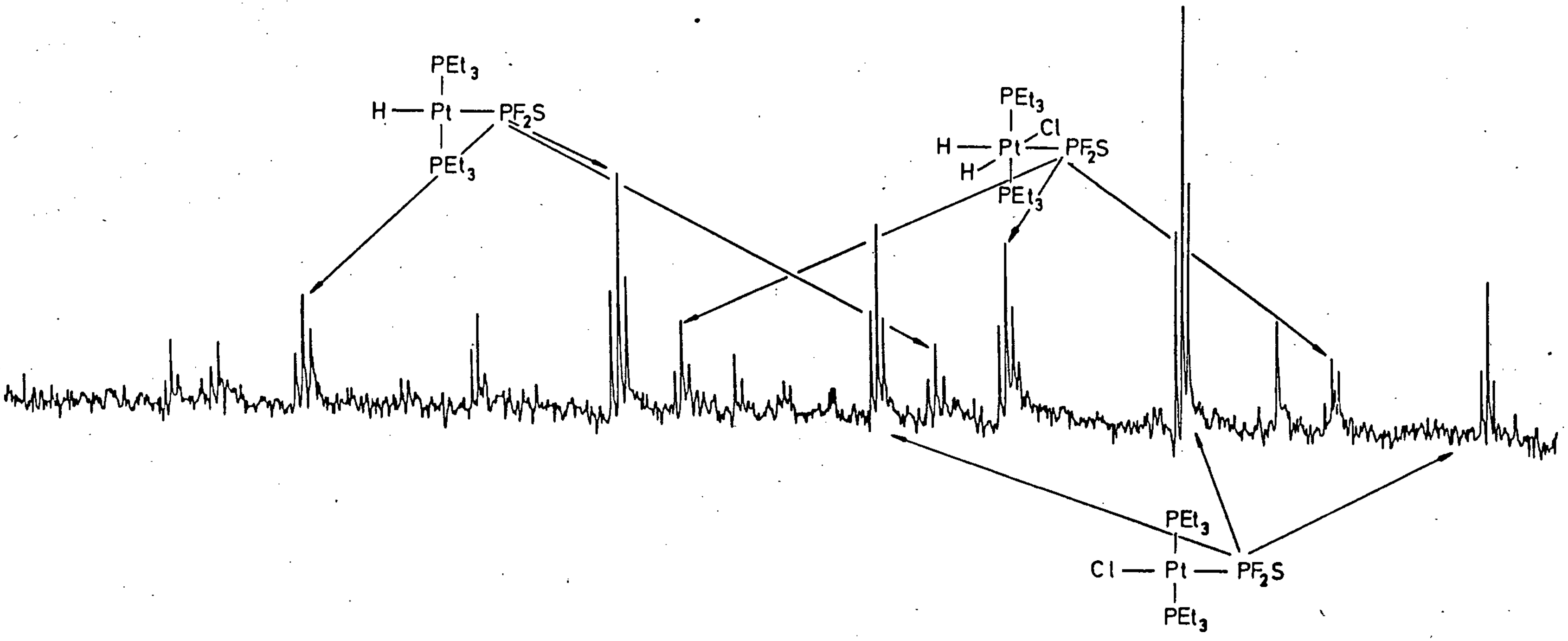
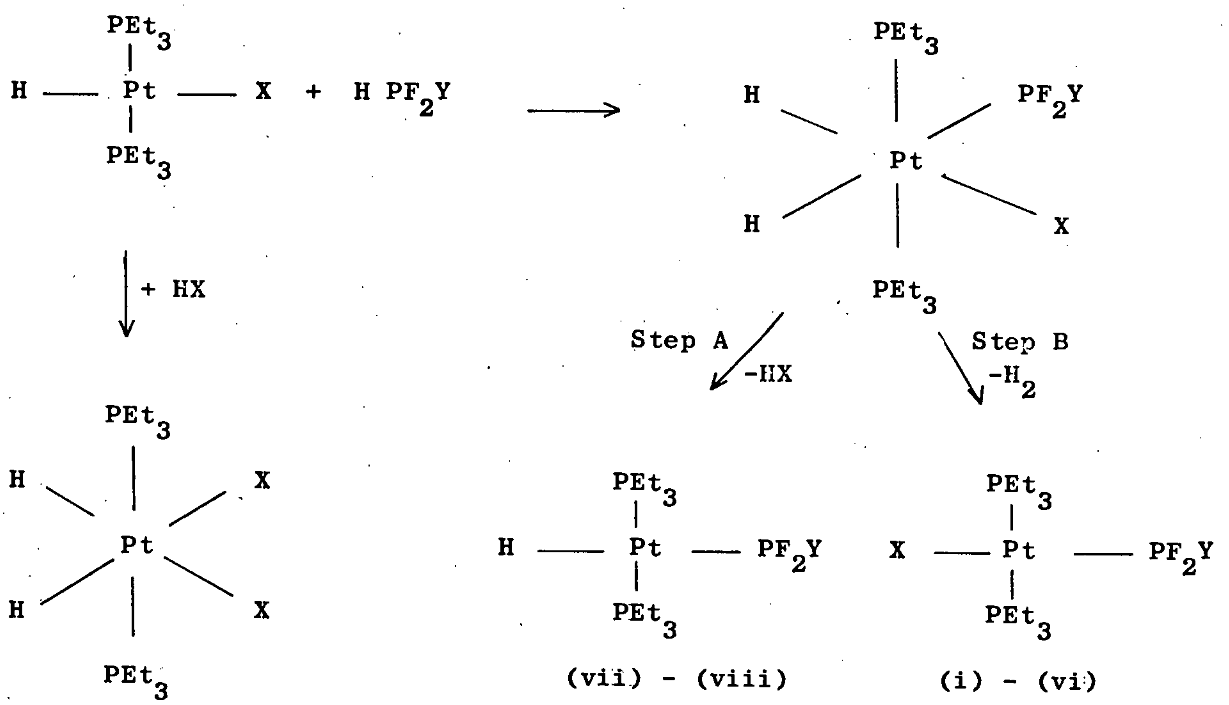


Fig 3.4



3(ii) Pt H X $(PEt_3)_2$ + H P F_2Y 1:4

The results obtained from these reactions helped to confirm the observations made in the previous section. However there were also some interesting developments in that the sulphur and selenium systems behaved in different ways. I shall deal with the sulphur system first.

When a large excess of HPF_2S was added a different intermediate was observed at low temperature. Again no reaction took place until -50°C but at this temperature the main complex observed was the complex which was present in only trace amounts in the 1:1 reaction. The ^{31}P spectra each showed a doublet with Pt satellites at low frequency and at high frequency a triplet of triplets was observed with Pt satellites. The size of the Pt couplings suggested that these products are Pt$^{(IV)}$ six coordinate complexes. If the proton coupling is retained then the high frequency

Table 3.1 ^{31}P and ^{19}F n.m.r. data for complexes (i) - (viii)

Complex	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)*
δP	18.9	15.7	10.7	17.8	14.6	9.5	19.0	18.5
δP'	132.7	133.7	135.7	137.7	138.4	141.0	222	2346
^1J(Pt P)	2346	2326	2305	2354	2339	2302	2500	2502
^1J(Pt P')	5322	5337	5217	5054	5039	5002	3032	2827
^2J(PP')	24	22	22	22	22	19.5	29.3	29.3
^3J(PF)	9.8	9.8	9.8	9.8	9.8	9.8	4.3	4.9
^1J(PF)	1162	1169	1184	1181	1191	1201	1199	1210
^2J(PH)	-	-	-	-	-	-	273	273
δF	-5.7	-5.2	-5.1	-7.0	-6.9	-6.1	-13.9	-16.0
^2J(Pt F)	792	796	772	720	725	699	400	358
^3J(FH)	-	-	-	-	-	-	37.6	34.4

Chemical shifts are in ppm, coupling constants in Hz.

*in CD Cl_3

resonance shows an additional doublet coupling which is due to the presence of a trans hydride. Also if the n.m.r. parameters (Table 3.2) are considered it can be seen that slight variations in the chemical shifts and coupling constants with changing halogen are noted. This would be consistent with the presence of a halogen on the Pt.

From this evidence it is suggested that when a large excess of HPF_2S is added then the equilibria react in such a way that the product of oxidative addition of HPF_2S to Pt H X $(PEt_3)_2$ is the stable product at -50°C, so that complexes (ix) - (xi) are observed.

When these systems are allowed to warm up, loss of hydrogen gas occurs and the products Pt X (PF_2S) $(PEt_3)_2$ are formed. These exist in solution with the excess HPF_2S. No evidence was seen of further addition of HPF_2S. It might have been expected that further addition of HPF_2S might occur to either Pt H (PF_2S) $(PEt_3)_2$ or to Pt X (PF_2S) $(PEt_3)_2$ but this does not seem to happen.

From this evidence it can be seen that as excess of HPF_2S is added then the first effect is to shift step one to the right and more of complexes (ix) - (xi) is observed. These complexes can react in two ways, losing H X or H_2, but in the case where excess of HPF_2S is present no evidence was found for Pt H PF_2S $(PEt_3)_2$, ie loss of H X is inhibited. This could be due to the absence of Pt starting material to react with to give cis, cis, trans Pt H_2 X_2 $(PEt_3)_2$ so the driving force for loss of H X has been removed from the system. The result of this is that complexes (ix) - (xi) are observed in greater concentration and as the system warms up H_2 is lost and the final products, complexes (i) - (iii) are formed.

One other fact which emerged was that the iodide system reacts faster than the chloride so that by -50°C the iodide six-coordinate complex has lost H_2 to give the final product. This again shows that a halogen is involved in the intermediate since the same rate of reaction would be expected if the halogen was not present in the intermediate.

For the reactions with HPF_2Se a much more complicated set of results was obtained. From the 1:1 reactions it was noted that the intermediate $PtH(PF_2Se)(PEt_3)_2$ was never present in as high a concentration as with the sulphur analogue. However, at that stage no explanation was available. It was also found that the final products were more difficult to obtain as pure compound for the selenium systems.

When the reactions were studied with a large excess of HPF_2Se the ^{31}P spectra at -90°C showed two PF_2Se intermediates. These were identified from their chemical shifts and coupling constants to be $PtH(PF_2Se)(PEt_3)_2$ and $Pt(H)_2X(PF_2Se)(PEt_3)_2$. $PtH_2X_2(PEt_3)_2$ was also present.

When the system was allowed to warm to -70°C a change took place and at low frequency in the ^{31}P spectrum a triplet with Pt satellites was observed. At high frequency the PF_2 peaks were broad showing no distinct coupling to the PEt_3 part. When the H coupling was retained the PF_2 part showed the additional doublet splitting expected for a trans hydride.

The fluorine spectra showed the pattern expected for a Pt-PF_2 complex (Fig 3.6). The couplings indicated that this was a Pt^{IV}

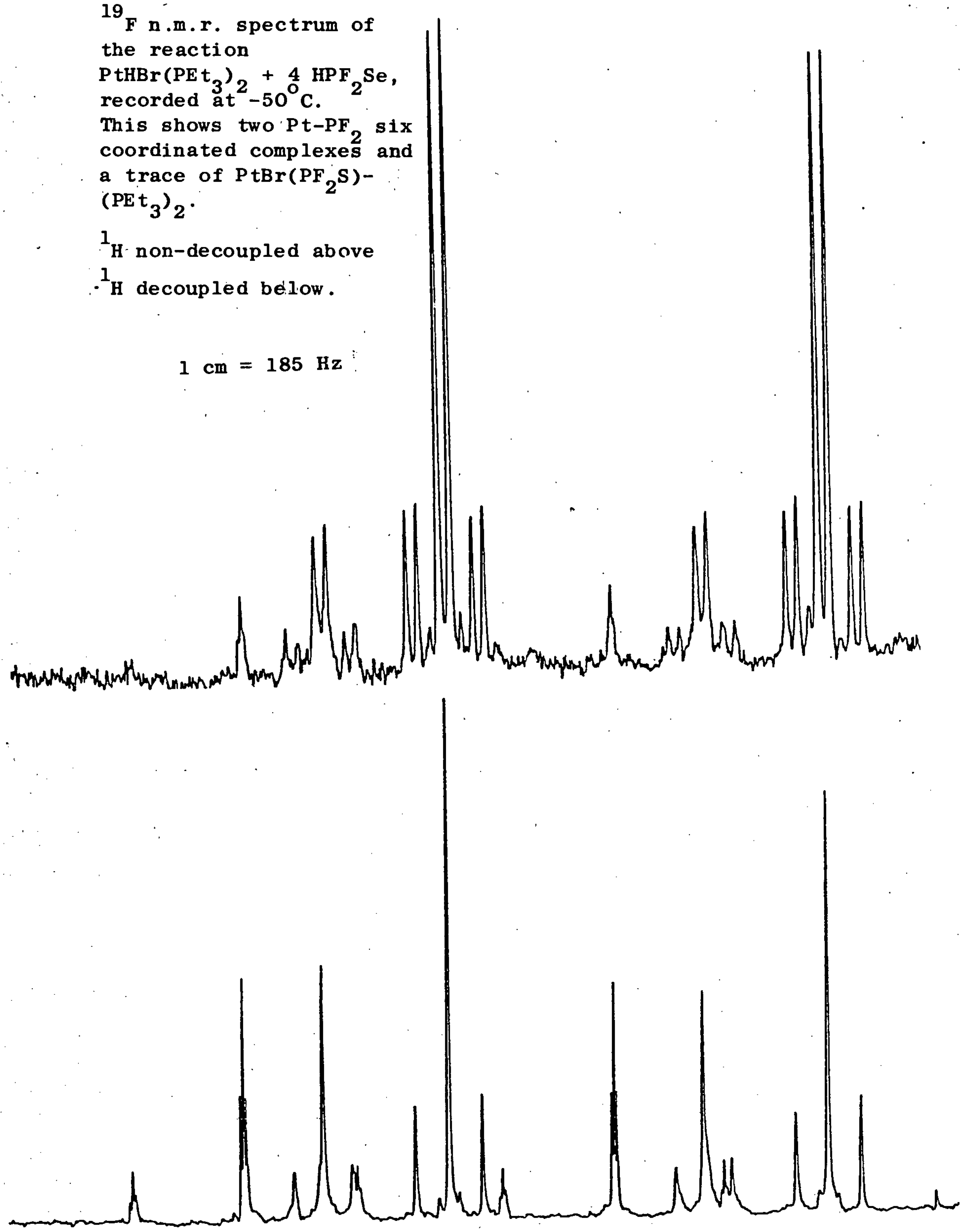
Fig. 3.6

^{19}F n.m.r. spectrum of the reaction $PtHBr(PEt_3)_2$ + 4 HPF_2Se, recorded at $-50^{\circ}C$. This shows two Pt-PF_2 six coordinated complexes and a trace of $PtBr(PF_2S)(PEt_3)_2$.

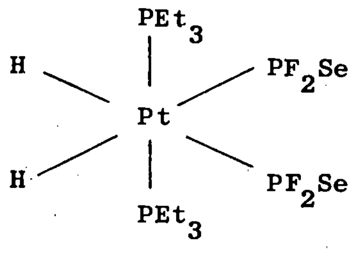
^{1}H non-decoupled above

^{1}H decoupled below.

1 cm = 185 Hz



complex. The same parameters were noted for the Br reaction. This suggested that no halogen was involved in the intermediate. From this evidence it would appear that the complex observed is



(XV)

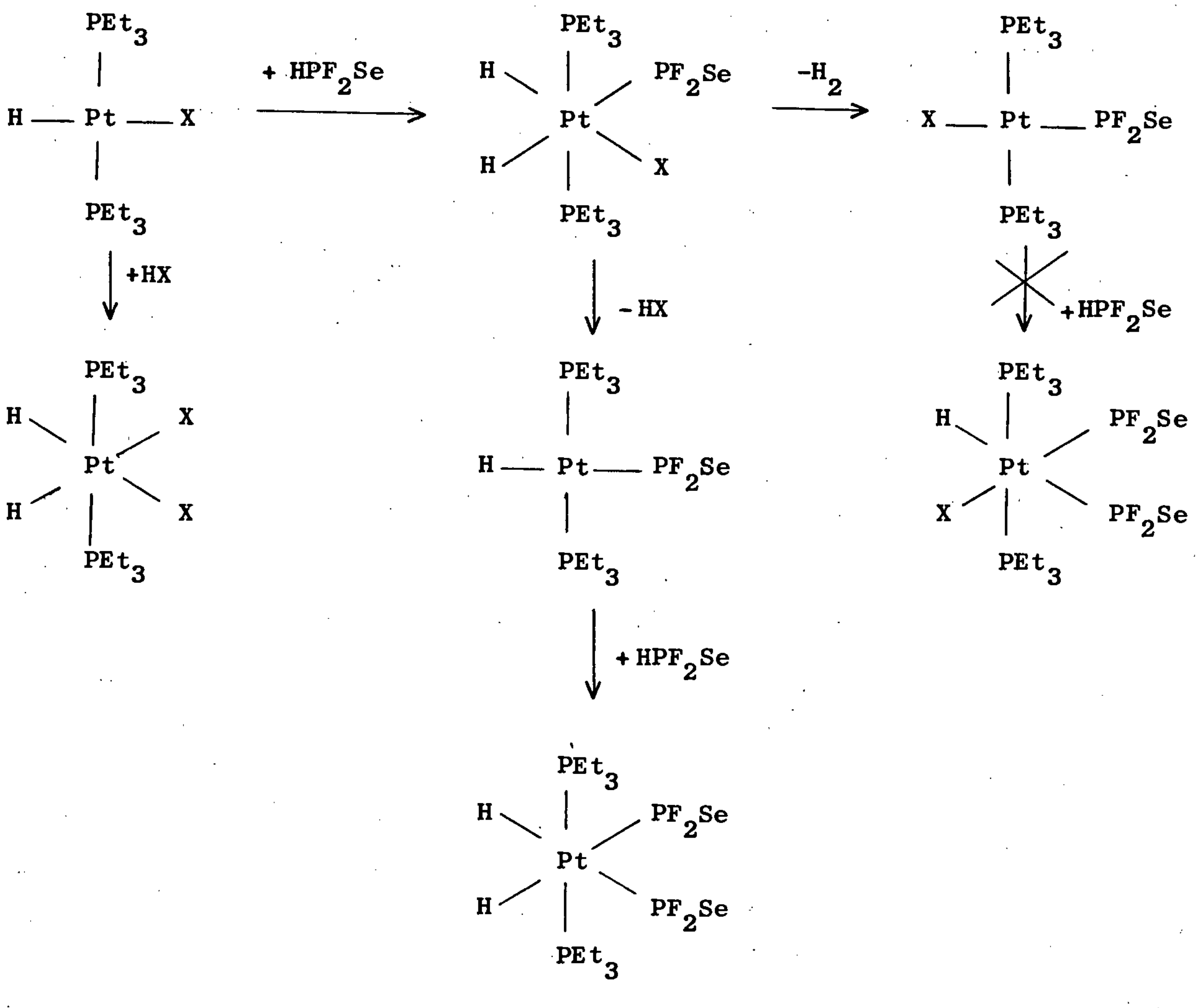
This would seem to be the only complex which would fit with the observed spectra, i.e. a triplet coupling with PEt_3 region and the same complex appearing in both the Br and Cl reactions.

This means that addition of a second HPF_2Se molecule is occurring. However, this addition only takes place to the complex $PtH(PF_2Se)(PEt_3)_2$. As the system was warmed the intermediate disappears and the product obtained was $PtX(PF_2Se)(PEt_3)_2$, and this exists in solution with the excess HPF_2Se. No evidence was obtained for the complex $PtHX(PF_2Se)_2(PEt_3)_2$ (Fig. 3.7).

It would therefore appear that all these complexes exist in equilibrium, and at room temperature the thermodynamically favoured product is $PtX(PF_2Se)(PEt_3)_2$.

Loss of the H_2 from complex (XV) would give $Pt(PF_2Se)_2(PEt_3)_2$. However, no evidence was obtained for this species. One would expect a complex second order spectrum if two PF_2Se groups were bound trans to each other across a Pt but in the 6-coordinated complex where they are cis to each other a simple first order spectrum was observed.

Fig 3.7 Proposed mechanism for the HPF_2Se reactions



Complex (XV)

There seems to be no obvious reason why HPF_2S and HPF_2Se should react differently. For the S reaction when an excess of HPF_2S is added formation of $PtH(PF_2S)(PEt_3)_2$ is inhibited yet for the selenium system it appears to be enhanced in that further addition to $PtH(PF_2Se)(PEt_3)_2$ takes place. Perhaps the fact that this further addition occurs promotes the loss of HX from complexes (xii) - (xiv) in the selenium reaction.

The reason why addition of the second HPF_2Se molecule occurs is uncertain. It could be that the PH bond is slightly weaker for the Se molecule compared with HPF_2S: however there is no direct evidence to

Table 3.2

^{21}p and ^{19}F n.m.r. data for complexes (IX) - (XV)

Complex	(IX)	(X)	(XII)	(XIII)	(XIV)	(XV)
δP	9.1	6.4	9.25	6.5	2.3	6.8
δP'	162.6	156.2	NR	170	152	148.1
^{1}J(PtP)	1643	1636	1632	1607	1716	1533
^{1}J(PtP')	2066	2078	NR	NR	NR	1878
^{2}J(PP)	26.9	26.9	24.4	24.4	24.4	22
^{3}J(PF)	NR	NR	NR	NR	NR	NR
^{1}J(PF)	1234	1231	1234	1236	1228	1229
^{2}J(PH)	NR	NR	NR	NR	NR	NR
δF	-11.6	-10.6	-15.5	-14.1	-11.9	-10.4
^{2}J(PtF)	240	233	210	212	210	187
^{3}J(FH)	41	40	36	37	36	37

NR - not resolved

The data for complex (XI) $PtH_2I(PF_2S)(PEt_3)_2$ was not obtained

Chemical shifts are in ppm and coupling constants in Hz prove this. The vibrational stretching frequencies for P-H are 2444.5 cm^{-1} for HPF_2Se[30] and 2458 cm^{-1} for HPF_2S[31]. This could suggest that the P-H bond is shorter for the HPF_2S molecule and hence stronger but this is not really very convincing evidence. The vibrational frequency for P-H in HPF_2O is 2500 cm^{-1} so there is a greater chance that the P-H bond here is much stronger.

3.4 The X-ray Crystal Structure

The single crystal X-ray structure was obtained for complex (i) $PtCl(PF_2S)(PEt_3)_2$ (Fig. 3.8). Several interesting features were noted about the structure. The main feature was the presence of a pseudo two-fold axis about the Pt-Cl bond which related adjacent molecules and showed the two possible orientations of the PF_2S group (Fig. 3.9).

From this crystal structure and by comparing it with other structures already published it was hoped that some information could be obtained as to the character of the PF_2S group.

Firstly the Pt-P distance can give an indication as to the π acceptor properties of the PF_2S group. The value obtained was 221.3(5) pm which is short compared with the value expected when alkyl groups are attached to the phosphorous, eg. 233.8(3) pm in complex (i). However it is not as short as the value 214.1 pm recorded for the Pt-PF_3 distance in cis $PtCl_2(PF_3)(PEt_3)$[7]. It is still apparent that the PF_2S group has strong π acceptor properties to give a Pt-P bond length of 221.3 pm. The π acceptor properties are usually dependent on the groups attached to the phosphorus and the enhancement here is due to the highly electronegative fluorine atoms bound to the phosphorus.

Fig 3.8 X-ray crystal structure of $PtCl(PF_2S)(PEt_3)_2$

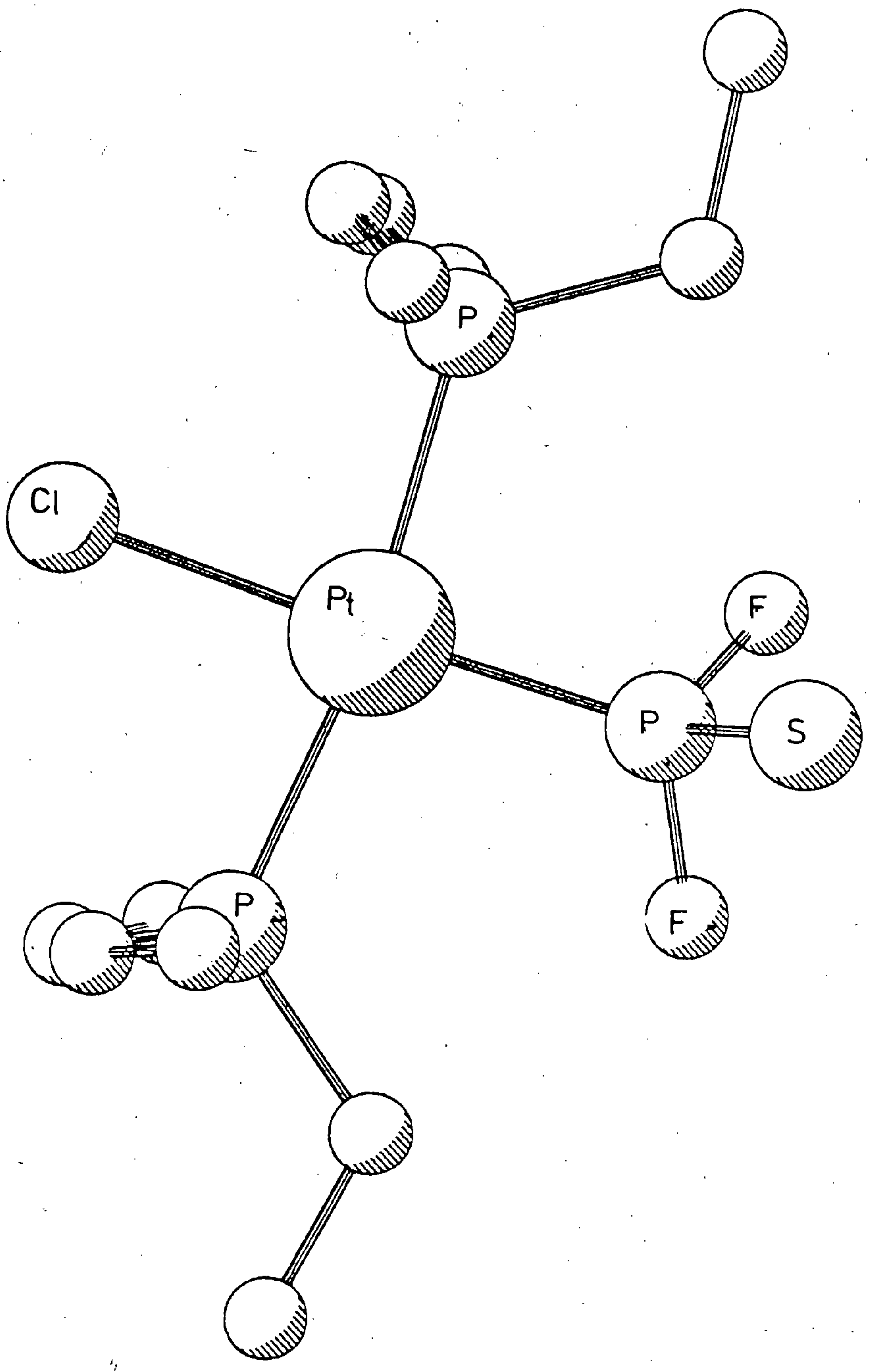
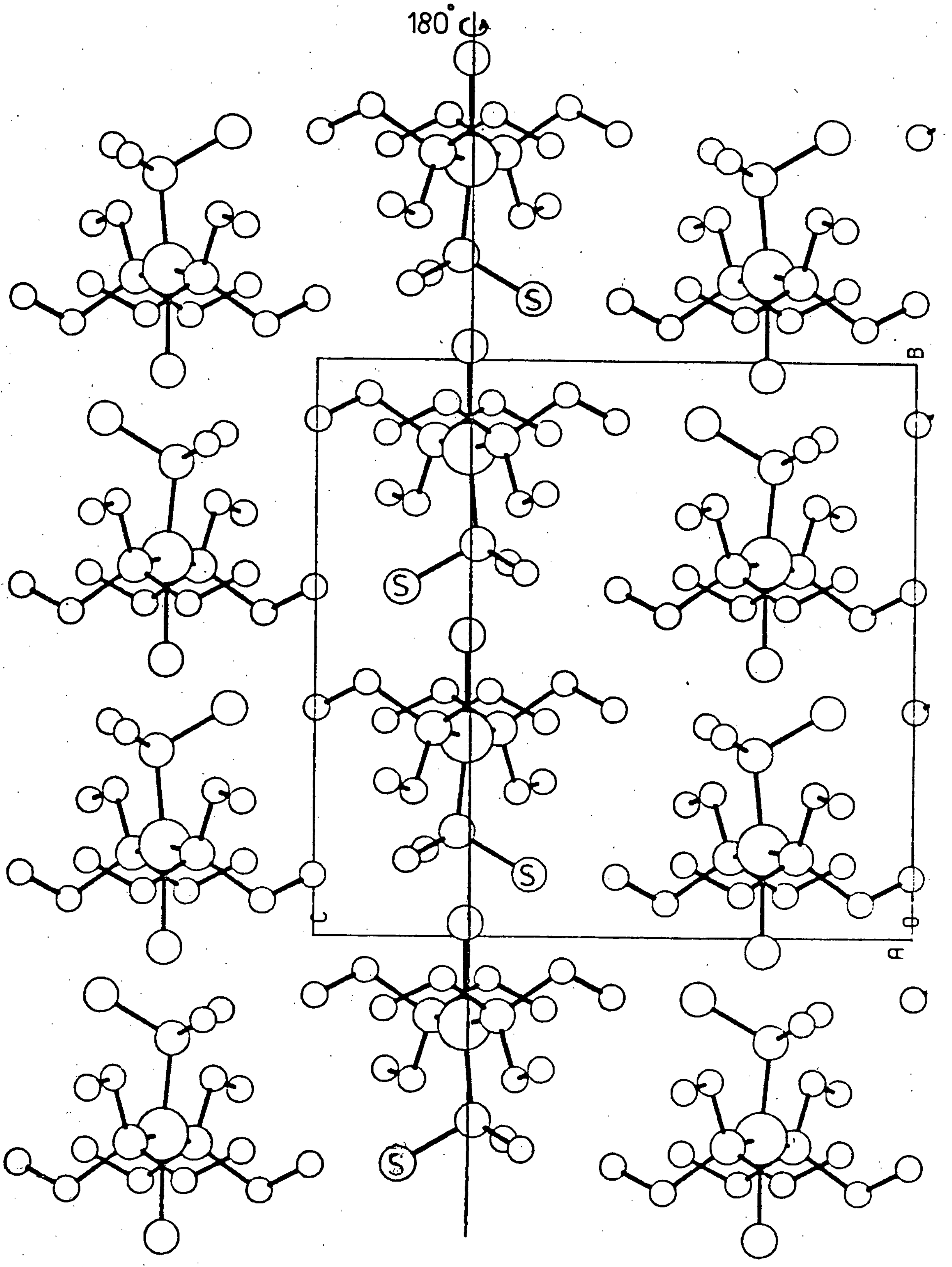
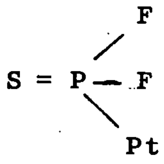


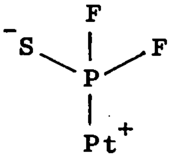
Fig 3.9 Crystal packing in $PtCl(PF_2S)(PEt_3)_2$, showing the presence of the two-fold rotation axis which relates adjacent molecules



The next question to be answered is whether the PF_2S group is bound to the platinum as PF_2S^- or $S = PF_2$, ie



or



Some idea about this can be found by considering the P-S bond length and the angles observed around the PF_2S group. Some comparisons can also be drawn with the structure of Pt Cl(PF_2O) (PEt_2Ph)$_2$ which was published in 1976[32]. The interpretation then was that the PF_2O was bound as PF_2O^-, ie isoelectronic with PF_3: however, if we consider the P-O bond length observed (147.1(17) pm) this is slightly longer than would be expected for a P=O (143.6 pm in $O=PF_3$)[33] but it is nowhere near as large as the value that might be expected for a P-O single bond (160 pm)[34]. Therefore there must be some doubt that the group is bound as PF_2O^-.

If we now consider the PF_2S system the P-S bond length observed was 195(1) pm. Typical values for P=S are 188.1(3) pm in SPF_2Br and 187.6(1) pm in HPF_2S[33] while the value obtained for P-S in PF_2S GeH_3 was 212 pm[35]. In the Pt complex the P-S bond length is in between the expected single and double bond distances. This could suggest that there is a slight negative charge on the sulphur.

The bond angles observed should also give some indication as to the character of the bond. For $S = PF_2Br$ the bond angles noted were: <SPF 118°, <SPBr 118° <BrPF 100° <FPF 98° which are typical values[33]

for a S = PX_3 group. If the P-S were a single bond then the values expected should be closer to those observed for a bound PF_3 group, for example, Pt $Cl_2(PF_3)(PEt_3)$ the angles observed were: <FPF 97.3°, 99.7° and 98.3°, <PtPF 117.3° 116.1° 123.7°[7]. If we now consider the angles observed in the PF_2S-Pt complex we find: <SP Pt 114.7° <$SPF_{(1)}$ 110.4°, <$SPF_{(2)}$ 108.0° <$F_{(1)}$ P Pt 112.3 <$F_{(2)}$ P Pt 115.8° <FPF 93.8°. Here, again, as with the bond length, the values obtained are not those for a P=S system and the suggestion again is that the bonding is intermediate between double and single bond character

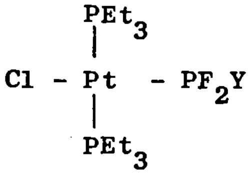
By comparing the P-O bond length obtained for the Pt-PF_2O complex and this P-S bond distance we might be able to draw some conclusions about the values expected for the PF_2Se system. On the basis of the observed bond lengths it would appear that the P-S is exhibiting more single bond character than the P-O system, ie the value of 195 pm is farther away from the 188 pm expected for P=S than the 147 pm observed for P-O is from the 143.6 expected for P=O.

This is a somewhat simple argument but if this is the case then when the selenium system is studied it might be expected that the PF_2Se group would show more PF_2Se^- character and hence the P-Se bond would be longer. This could also reduce the electron widthdrawing properties of the group which would make it a less effective π acceptor hence lengthening the Pt-P bond. Some evidence to support this idea comes from the Pt-P bond lengths observed, Pt-PF_2O 219.9(6) pm, Pt-PF_2S 221.3(5) pm. If the PF_2Se group does show more negative charge then this might explain the different mechanisms shown by the two systems.

To support this idea of there being a slight negative charge on the sulphur we can also draw on some n.m.r. evidence. Firstly the value for $^{1}J(PtP)$ was 4322 Hz in complex (i). This is a large value compared to those expected for trialkyl phosphines but it is not as large as the value obtained for bound PF_3 ~7000 Hz or bound PF_2Cl ~6000 Hz.

The theory put forward is that the size of the coupling constant depends on the trans ligand and on the electron withdrawing properties of the groups on the phosphorus. The more electron withdrawing there is then the larger is the coupling constant. The presence of a negative charge on the sulphur would lower the π acceptor properties of the PF_2S group and hence lower the size of the $^{1}J(PtP)$ coupling constant.

If we now consider the complexes:



$$\begin{array}{c} PEt_3 \\ | \\ Cl - Pt - PF_2Y \\ | \\ PEt_3 \end{array} \qquad (Y = O,\ S \text{ or } Se)$$

for Y = O $\delta P'$ = 34.0 ppm, Y = S $\delta P'$ = 132.7 ppm, Y = Se $\delta P'$ = 134.7 ppm and for all three complexes $^{1}J(PtP)$ ~5000 Hz when the Cl is replaced by H we find that for Y = S $\delta P'$ = 222 ppm, Y = Se $\delta P'$ - 237.2 ppm and $^{1}J(PtP)$ for both complexes ~3000 Hz.

In most cases when a halogen is replaced by a hydride then $^{1}J(PtP)$ is lower due to the smaller trans influence of the hydride ligand. This would lead to a longer Pt-P bond. If the Pt-P bond increases in length then this would be consistent with a reduction in the π acceptor properties of the PF_2S group and with a larger negative charge in the sulphur. The n.m.r. evidence suggests that this might be the case. A shift to high frequency was observed when the halogen was replaced by a hydride and if we consider that a value of 275 ppm has been recorded for δP of a free PF_2S^- ion then it would appear that this shift is consistent with a larger -ve charge on the sulphur. We can now predict that if the structure of Pt $H(PF_2S)(PEt_3)_2$ was solved then a long P-S bond would be found and in turn a long Pt-P bond.

Finally some information can be obtained as to the cis and trans influence of the PF_2S group by studying the bond lengths of the groups on the Pt. One theory says that the Pt-Cl bond depends only on the trans ligand and it increases in length as the trans influence increases. For PF_2S it would be expected that this has a large trans influence due to the π acceptor properties and that the Pt-Cl bond would be long. The value observed was 236.8(4) pm which is the normal value expected for a Cl trans to a PR_3 group as the PF_2S group appears to behave as a normal PR_3 group. This could be explained if it has to be a σ effect which determines the Pt-Cl bond length and the PF_2S ligands exert mainly a π effect. In the complex $cisPtCl_2(PF_3)(PEt_2)$ the trans influence of the PF_3 would be expected to lengthen the PtCl bond but the value obtained was 230.5 pm. This was explained as being due to the weak σ donor properties of the PF_3 which enhanced the ~σ properties of the Pt-Cl bond which increased the σ donation from Cl, which shortened the bond.

For the cis ligands the Pt P bond length depends on the relative π interactions and the greater the π acceptor properties of the cis ligands then the longer the Pt-P bond will be. For complex (i) Pt-P was 233.8(3) which is slightly longer than in complexes without PF ligands present so this could be due to an effect of the PF_2S ligand. However, it is apparent from studying the literature that several arguments have been put forward concerning cis and trans effects and that most structural parameters can be explained in more ways than one. It seems likely that the structure depends on σ and π effects and it is difficult to argue about the trans influence of various ligands on the basis of bond lengths only.

CHAPTER 4

The reaction of $[Pt X(PEt_3)_3]^+ BPh_4^-$ with HPF_2Y (X = H Cl or I, Y = Sor Se)

4.1 Introduction

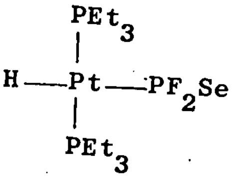
This work came as a natural follow up to the systems studied in Chapter 3. There were several possibilities as to what could happen in the reaction of the Pt cations with HPF_2Y. There was the possibility that oxidative addition could occur. Some other work in the research group had shown that HCl would oxidatively add to the cations so a similar reaction may be possible with HPF_2Y. If oxidative addition did occur, especially to the complex $PtH(PEt_3)_3{}^+BPh_4{}^-$ then loss of H_2 would yield $Pt(PF_2Y)(PEt_3)_3{}^+BPh_4{}^-$. Therefore the aim of this work was to study these reactions at low temperature with a view to synthesizing some more novel complexes containing the $Pt\text{-}PF_2Y$ group.

4.2 Results and Discussion

When the reactions of $PtX(PEt_3)_3{}^+BPh_4{}^-$ (X = H, Cl or I) with HPF_2Y (Y = S or Se) were studied at low temperature no reaction took place until $-60^{o}C$. After this a white precipitate appeared in the tubes. The ^{31}P n.m.r. spectra showed that $Pt\text{-}PF_2Y$ complexes remained in solution. From the parameters obtained these complexes were identified as $PtX(PF_2Y)(PEt_3)_2$ (X = H, Cl or I; Y = S or Se). At no stage was any other complex observed in solution. The white precipitate was identified as $HPEt_3{}^+BPh_4{}^-$ from C H analyses and i.r. studies.

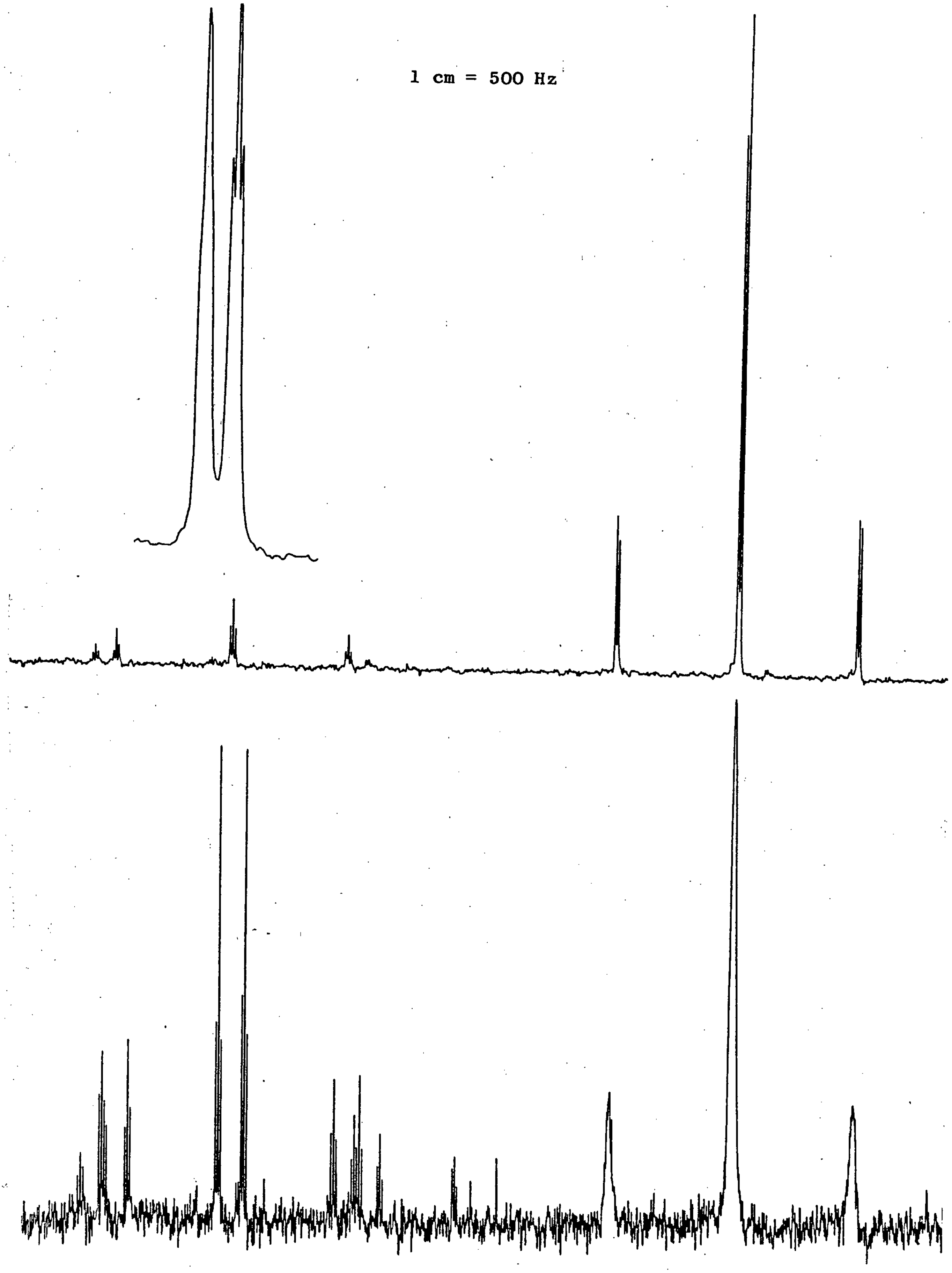
The results here were disappointing in that no "new" complexes were obtained. On the other hand it was shown that the complexes $PtH(PF_2Y)(PEt_3)_2$, which were observed as intermediates in the

Fig 4.1 ^{31}P n.m.r. spectrum of



$$\mathrm{H{-}Pt(PEt_3)_2{-}PF_2Se}$$

^{1}H decoupled above
^{1}H non-decoupled below



reactions discussed in Chapter 3, are in fact stable complexes (Fig. 4.1) and it is only the presence of HX in the solution which allows conversion to $PtX(PF_2Y)(PEt_3)_2$ (X = Cl, Br or I) to occur.

The reaction of $PtH(PEt_3)_3{}^+BPh_4{}^-$ with HPF_2Y would seem a good method of synthesising these hydride complexes. However, the by-product $HPEt_3{}^+BPh_4{}^-$ is slightly soluble in most solvents and so far a clean separation of the two products has not been achieved.

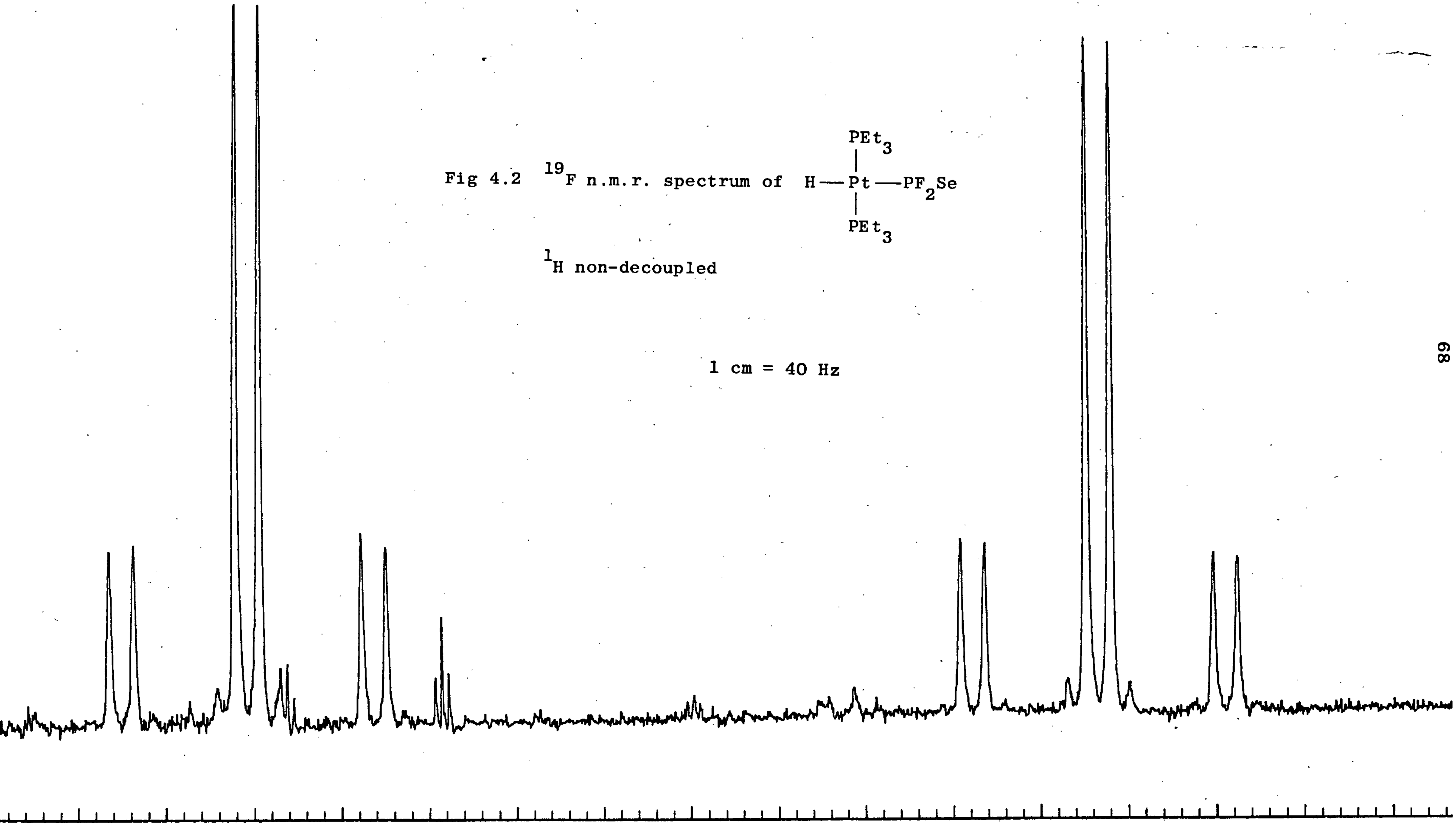
The isolation of one of the hydride complexes by perhaps using a different counterion would possibly enable a crystal structure to be obtained. From this some of the questions posed in Chapter 3 might be answered.

The main problem set by these complexes is the question of the method of bonding of the PF_2S group. Does this group contain a double or single P-S bond? It has been noted that as Cl is replaced by H trans to the PF_2S group then δP is shifted to high frequency and this has been explained as possibly being due to a greater negative charge being localised on the S and hence the PF_2S group may contain a single P-S bond. Solving the crystal structure of one of these hydride complexes would show if this theory is correct or not. Also in Chapter 3 it was proposed that as one exchanges a PF_2O for a PF_2S group then perhaps there was a greater tendency for P-Y to be a single bond. To further this argument then the solving of the structure of a Pt-PF_2Se complex would give some more answers. Any differences noted between a PF_2S and PF_2Se complex may also help explain why the selenium system shows a more complicated reaction mechanism. It would therefore seem that if crystals of the complex $PtH(PF_2Se)(PEt_3)_2$ could be obtained then many of the questions set could be answered.

Fig 4.2 ^{19}F n.m.r. spectrum of $H-\overset{\overset{PEt_3}{|}}{\underset{\underset{PEt_3}{|}}{Pt}}-PF_2Se$

^{1}H non-decoupled

1 cm = 40 Hz



CHAPTER 5

Experimental

5.1 Introduction

The techniques used in this project involved combining two areas of work covered by this research group in recent years.

In the past a lot of work has been carried out in fluorophosphine chemistry and many new and interesting compounds have been synthesised. At the same time other workers have carried out many reactions on transition metal complexes which have mainly been involved with studying oxidative addition reactions on Pt^{II} substrates using n.m.r. spectroscopy.

In the project the first stage involved making fluorophosphine and Pt starting materials. Then various reactions were studied using n.m.r. spectroscopy. If it appeared that a clean reaction was taking place then attempts were made to isolate the products.

Synthesis of the fluorophosphines was carried out using a standard pyrex glass vacuum line and all the fluorophosphines used were made from the basic starting material PF_2NMe_2. The Pt starting materials were made using standard methods given in the literature.

When attempts were made to isolate Pt.-PF_2 complexes a different type of vacuum line was used. This line allowed nitrogen or argon to be passed over the sample while solvents were added or taken out, or if required, solvents could be pumped off and the products dried under vacuum. This system, called a Schlenk line, allowed the complexes to be isolated while avoiding contact with air hence any decomposition in air was minimised until it was known whether the complexes were air stable or not. As it turned out all the complexes isolated were air stable which was in keeping with known transition metal fluorophosphine complexes. However, the Schlenk line still provides a very convenient way of attempting to work up a product, therefore most isolation attempts were carried out using the Schlenk line.

This chapter on the experimental techniques will therefore be divided into four parts: (1) The physical techniques used, eg i.r. and n.m.r; (2) The preparation of fluorophosphine starting materials; (3) Preparation of Pt starting materials; and (4) Preparation of Pt-PF_2 complexes.

5.2 The Physical Techniques

(a) The spectra

The ^{31}P n.m.r. spectra were recorded on a Jeol FX60Q spectrometer or on a Varian Associates XL-100 spectrometer while the ^{19}F spectra were recorded on the XL-100. The phosphorus chemical shifts were positive to high frequency of H_3PO_4 while the fluorine chemical shifts were positive to high frequency of CCl_3F.

(b) Setting up an n.m.r. experiment

Many of the results used in this thesis were obtained by studying reactions in n.m.r. tubes. The method of setting up these experiments was as follows: the n.m.r. tube was fitted with a B10 cone and the required amount of the Pt complex to be used was placed in the tube. The tube was then attached to the vacuum line and pumped for some time (~2-3 hrs) to allow the solid to dry.

The solvent was then condensed into the tube and the complex dissolved; the solvent was degassed and dried over molecular sieve before use. Once the complex had been dissolved the tube was kept frozen at -196°C and the required amount of fluorophosphine was measured on the line and condensed into the tube. The tube was then sealed off and kept at liquid nitrogen temperature until the spectra could be recorded. The tube was placed in the spectrometer without being allowed to warm up, usually at -90°C, and the reaction could then be studied at various stages up to room temperature.

5.3 Preparation of Fluorophosphine Starting Materials

The main compounds used were PF_2X (X = Cl, Br or I) and HPF_2Y (Y = S or Se). The PF_2X was prepared by simply reacting PF_2NMe_2 with a twofold excess of HX and collecting the product which was purified by passing it through a -96°C bath and then collecting it in a -120°C bath. The HPF_2Y preparation involved several stages which I shall describe in detail but firstly I shall describe the preparation of PF_2NMe_2.

(a) PF_2NMe_2

This compound was made from the chlorine analogue PCl_2NMe_2 which was first prepared by reacting PCl_3 with $HNMe_2$. The PCl_3 (200 ml) was placed in a 2 l. 3 necked flask which was fitted with two condensers at -78°C and a large mechanical stirrer. The $HNMe_2$ (235 ml) was blown into the flask by passing dry N_2 over the system. When all the $HNMe_2$ had been added a quick distillation gave the crude product. This was further distilled and the fraction at

149° - 151°C was the pure product PCl_2NMe_2.

The fluorination step was carried out by setting up a slurry of NaF(227 g) in 600 ml of tetramethyl sulpholane in a large flask. The PCl_2NMe_2 was added dropwise and after the addition was complete the mixture was heated to 50-60°C for 1 hour. The flask was kept under N_2 and fitted with an ice condenser to avoid loss of product. The product was then collected in a trap at -78°C and purified by first passing it through traps at -45, -78 and -196°C and then through -64, -96 into -196°C, the -96°C fraction being the pure PF_2NMe_2.

(b) PF_2X (X = Cl, Br or I)

This reaction was carried out in a 2 litre flask which was fitted with a cold finger. The flask was pumped on the vacuum line for 24 hrs then the PF_2NMe_2 (20 mmoles) was measured out in the flask. This was then transferred to a trap on the line and the HX (40 mmols) measured out. This was frozen down in the flask and the PF_2NMe_2 frozen down on top of it. The mixture was then allowed to warm giving off white fumes. The mixture was frozen down and allowed to warm up again several times to persuade the reaction to go to completion. The products were collected in -196°C and purified by passing the mixture through baths at -96°C which stopped any PF_2NMe_2 remaining and -120° which stopped the product PF_2X but allowed any PF_3 formed and any HX remaining to pass into the -196°C bath.

(c) HPF_2S

This was prepared by reacting $(PF_2)_2S$ with H_2S. The $(PF_2)_2S$ was prepared by reacting PF_2Br with $(Bu_3Sn)_2S$. The $(Bu_3Sn)_2S$ (10 mmols) was weighed out in a 500 ml flask fitted with a cold finger. This was then attached to the vacuum line and pumped out in order to de-gas the tin compound. The PF_2Br (20 mmols) was then condensed into the flask and the system allowed to warm to room temperature. The best yields were obtained if the two reactants were mixed in the liquid phase. The product was collected by pumping off all the volatile species left in the flask and collecting them at -196°C. The pure product was collected at -96°C and any PF_2Br passed into the -196°C bath.

The $(PF_2)_2S$ (8 mmol) was then measured into a 500 ml flask and the H_2S (16 mmol) condensed in. Allowing the mixture to warm to room temperature yielded HPF_2S. The pure product was collected at -120°C having passed the mixture through -96°C to stop any $(PF_2)_2S$ remaining. Any H_2S would carry on into -196°C.

(d) HPF_2Se

The HPF_2Se was prepared by reacting PF_2Br with H_2Se in the presence of Hg. 0.6 ml of Hg was placed in a 250 ml flask and PF_2Br (3.6 mmoles) and H_2Se (3.75 mmoles) were added. The system was allowed to warm to room temperature and shaken for two hours and then left for 24 hrs. The product was collected and purified by passing it through -78°C and -120°C baths. The HPF_2Se stopped in the -120°C bath.

5.4 Preparation of the Pt Starting Material

(a) cis $PtCl_2(PEt_3)_2$

This complex was made by reacting either $PtCl_2$ or K_2PtCl_4 with PEt_3. The K_2PtCl_4 (2 g) was dissolved in water and 1.4 ml of PEt_3 added. This mixture was left stirring for 1 hour which gave a mixture of cis and trans $PtCl_2(PEt_3)_2$. This mixture was collected and converted entirely to the cis isomer by suspending the mixture in hexane, adding one drop of PEt_3 and leaving the mixture stirring for several hours. The pure sample of cis $PtCl_2(PEt_3)_2$ could then be collected. For the $PtCl_2$ method the first stage was carried out in acetone otherwise the method was the same.

(b) t-$PtHCl(PEt_3)_2$

cis - $PtCl_2(PEt_3)_2$ (1.35 g) was suspended in 14 ml water and 0.3 ml of hydrazine hydrate was added. The mixture was refluxed for 1 hour during which time N_2 was evolved and an oily layer formed in the flask. On cooling this layer gave a yellow/white solid which was the impure product. This was purified using activated charcoal and a final recrystallisation from methanol.

(c) t-$PtHX(PEt_3)_2$ (X = Br or I)

These complexes were obtained by carrying out halogen exchange reactions on the chloride complex using LiBr or NaI. This was a general method and was used throughout the project for halogen exchange.

The Pt complex was dissolved in acetone and a solution of the alkali metal salt in acetone was added. For the Br system a large excess of LiBr was necessary to effect a complete exchange. The acetone was removed and the mixture washed with methylene chloride. This removed any alkali metal salts remaining. The product was collected and in the case of $PtHX(PEt_3)_2$ complexes they were recrystallised from methanol.

(d) $PtH(PEt_3)_3^+BPh_4^-$

A 1:1 ratio of $NaBPh_4$ and $PtHCl(PEt_3)_2$ was dissolved in methanol and an equimolar amount of PEt_3 added. This mixture was stirred for 10 min and a white precipitate was formed. This was collected and dried. The product was then washed with acetone to remove any NaCl remaining. The solution was then reduced ~5 ml and the product recrystallised by adding ether.

(e) $PtX(PEt_3)_3BPh_4^-$ (X = Cl or I)

The method used here was the same as for the hydride complex except that cis $PtCl_2(PEt_3)_2$ was used as the starting material. The iodide complex was prepared by carrying out a halogen exchange reaction on the chloride cation.

5.5 Preparation of Pt-PF_2 Complexes

(a) The PF_2 bridged complexes

The chloride complex was prepared by reacting $PtHCl(PEt_3)_2$ with PF_2Cl. The reaction was carried out in solution and the solvent, CH_2Cl_2, was dried over CaH_2 and freshly distilled before use.

The $PtHCl(PEt_3)_2$ (1 mmole) was weighed out into a Schlenk tube and then pumped dry on the vacuum line for 24 hrs. The solvent was then condensed in and the Pt complex dissolved. The system was then frozen at -196°C and the PF_2Cl (1 mmole) added. Best results were achieved if freshly prepared PF_2Cl was used. The system was then allowed to warm to room temperature and the solvent removed. This left a white gum which gave a white solid when washed with ether. Needle like crystals were obtained by recrystallisation from methanol.

The Br and I complexes were prepared by carrying out halogen exchange reactions on the chloride complexes.

Analysis:

	Expected		Found	
	%C	%H	%C	%H
Cl	23.50	4.93	23.44	4.82
Br	21.95	4.57	22.02	4.57
I	18.09	3.77	17.96	3.76

(b) The PF_2Y complexes

These complexes were prepared by reacting t-$PtHX(PEt_3)_2$ (X = Cl,Br,I) with HPF_2Y (Y = S or Se). The Pt complex was weighed into a Schlenk tube and the vessel pumped out. The complex was dissolved in CH_2Cl_2 then kept at -196°C when an equimolar amount of HPF_2Y was condensed in. The system was allowed to warm up and H_2 gas was evolved. Removing the solvent gave the product as a white powder. The crystallisation was carried out from benzene. The C,H analysis figures were obtained for the PF_2S complexes. However, the PF_2Se complexes never gave the expected values. This could be due to the mechanism which suggests that a more complicated reaction is occurring for the PF_2Se system. The n.m.r. spectra however show only the expected product to be present.

Analysis, Y = S

	Expected		Found	
	%C	%H	%C	%H
Cl	25.37	5.29	25.25	5.34
Br	23.53	4.84	23.35	4.90
I	21.85	4.55	21.96	4.65

APPENDIX I

Some reactions of Pt X $PF_2S(PEt_3)_2$
(X = Cl or I)

A.1 Introduction

The initial reason for synthesising the Pt-PF_2S complexes was to investigate the possibility of removing the S from the PF_2S group to leave a Pt-PF_2 group which might be used to prepare bridged complexes. Several examples are known in nickel chemistry where PPh_3 has been used to remove an S[36,37]; however when attempts were made with the Pt complexes no reaction took place.

Another interesting reaction which was reported was that when the $FeP(CF_3)_2S$ complexes were photolysed with u.v. light the $P(CF_3)_2S$ group became S-bonded to the metal[28]. This was also attempted for the Pt complexes without success.

However in the course of this work it was noted that by reacting the Cl-Pt-PF_2S complex with Na I the I-Pt-PF_2S complex was obtained. This suggested that the halogen may be labile enough to be replaced by several ligands and so in this chapter we report the results of reacting the complexes $PtX(PF_2S)(PEt_3)_2$ (X = Cl or I) with alkali metal salts and also with some bidentate ligands.

These exchange reactions were carried out by J.A.S. Duncan as part of his chemistry IV project[38] and a summary of the results is given in his project report. The work was done with my assistance and under the supervision of Prof E.A.V. Ebsworth. The results obtained are relevant to this project and it is felt that they merit discussion in this thesis.

A.2 Reactions with Alkali Metal Salts

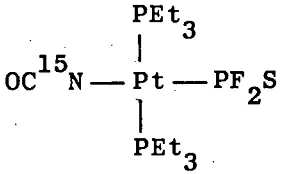
The salts used were NaNCO, $Ag^{15}NCO$, KNCS, KNCSe, NaCN and AgCN. The expected reaction was replacement of Cl by NCO, NCS, NCSe or CN groups. However, not all of the reactions behaved as expected.

(i) Reaction with NaNCO, $Ag^{15}NCO$

The reaction was carried out by mixing a solution of $PtCl(PF_2S)(PEt_3)_2$ in acetone with an equimolar amount of NaNCO which was also dissolved in acetone. A cloudy precipitate of NaCl was observed. The product was extracted and by examining the i.r. a band appeared at 2200 cm^{-1} which was assigned as being due to ν CN. This was a simple way of checking that a reaction had occurred.

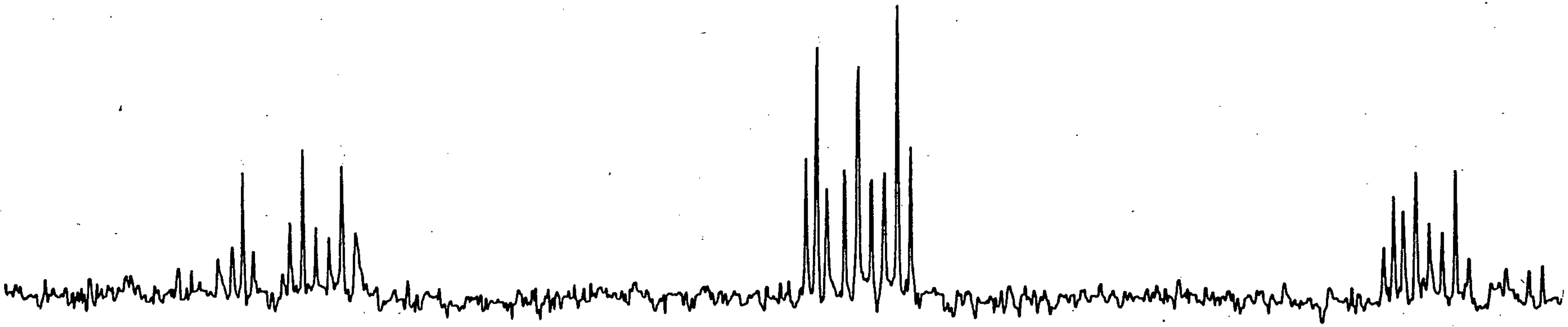
The product was also identified using ^{31}P ^{19}F n.m.r. techniques. The spectra obtained showed some interesting features. The ^{31}P spectra showed, at low frequency, the doublet of triplets expected for the PEt_3 part of a $PtX(PF_2S)(PEt_3)_2$ type complex. The chemical shifts and coupling constants were different from those obtained for the starting material, which suggested that X was NCO and not Cl. However when the high frequency area was examined there was no evidence for a PF_2 resonance.

This was not easy to understand since all the evidence pointed to the PF_2S group still being bound to the Pt. The only apparent explanation was that the NCO group was bound to the Pt through the N and that the quadrapolar relaxation of the nitrogen



$OC^{15}N{-}Pt(PEt_3)_2{-}PF_2S$

Fig A.1 ^{31}P n.m.r. spectrum of $OC^{15}N{-}Pt(PEt_3)_2{-}PF_2S$ showing the PF_2 resonance. Some $PtCl(PF_2S)(PEt_3)_2$ also present.



1 cm = 80 Hz

was causing the $\underline{P}F_2$ resonance to be lost. In an attempt to prove that this was the case the reaction was repeated using $Ag^{15}NCO$. It was found that complete exchange occurred much more readily if $PtI(PF_2S)(PEt_3)_2$ was used as the starting material. This was due to the relative solubilities of the various silver salts in acetone, i.e. $AgI < AgCl \sim AgNCO$. So the fact that AgI is less soluble than AgNCO provides a driving force for exchange to occur whereas for the Cl complex AgCl and AgNCO are of comparable solubility so the exchange reaction does not go to completion.

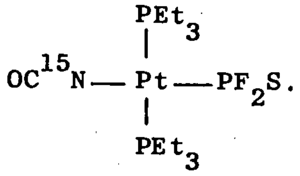
When the ^{31}P spectrum of the product of this reaction was studied the PF_2 part was observed and showed an additional doublet coupling (Fig A.1) which must be due to ^{15}N trans to the PF_2S group. The PEt_3 region also shows an additional coupling (Fig A.2) which can be observed on the high resolution spectra as being ~4.4 Hz. This would appear to confirm that the NCO group is bound through the nitrogen.

The ^{19}F spectra confirm the results predicted from the phosphorus data. The unlabelled sample showed the expected doublet of triplets all with Pt satellites. When the labelled sample was examined the spectrum showed a doublet of quartets (Fig A.3). This could be explained if the values for $^3J(F^{15}N)$ and $^3J(FP)$ were approximately equal then overlap of the lines would occur, giving the quartet instead of the expected doublet of triplets.

(ii) Reaction with KNCS

It was not unexpected that the NCO ligand should bond to the Pt through the nitrogen since a Pt-O bond is not usually very strong. However the Pt-S bond is known to be considerably stronger

Fig A.2 ^{31}P n.m.r. spectrum of



$$OC^{15}N—\overset{PEt_3}{\underset{PEt_3}{Pt}}—PF_2S.$$

High resolution spectrum showing the cis coupling ^{15}N.

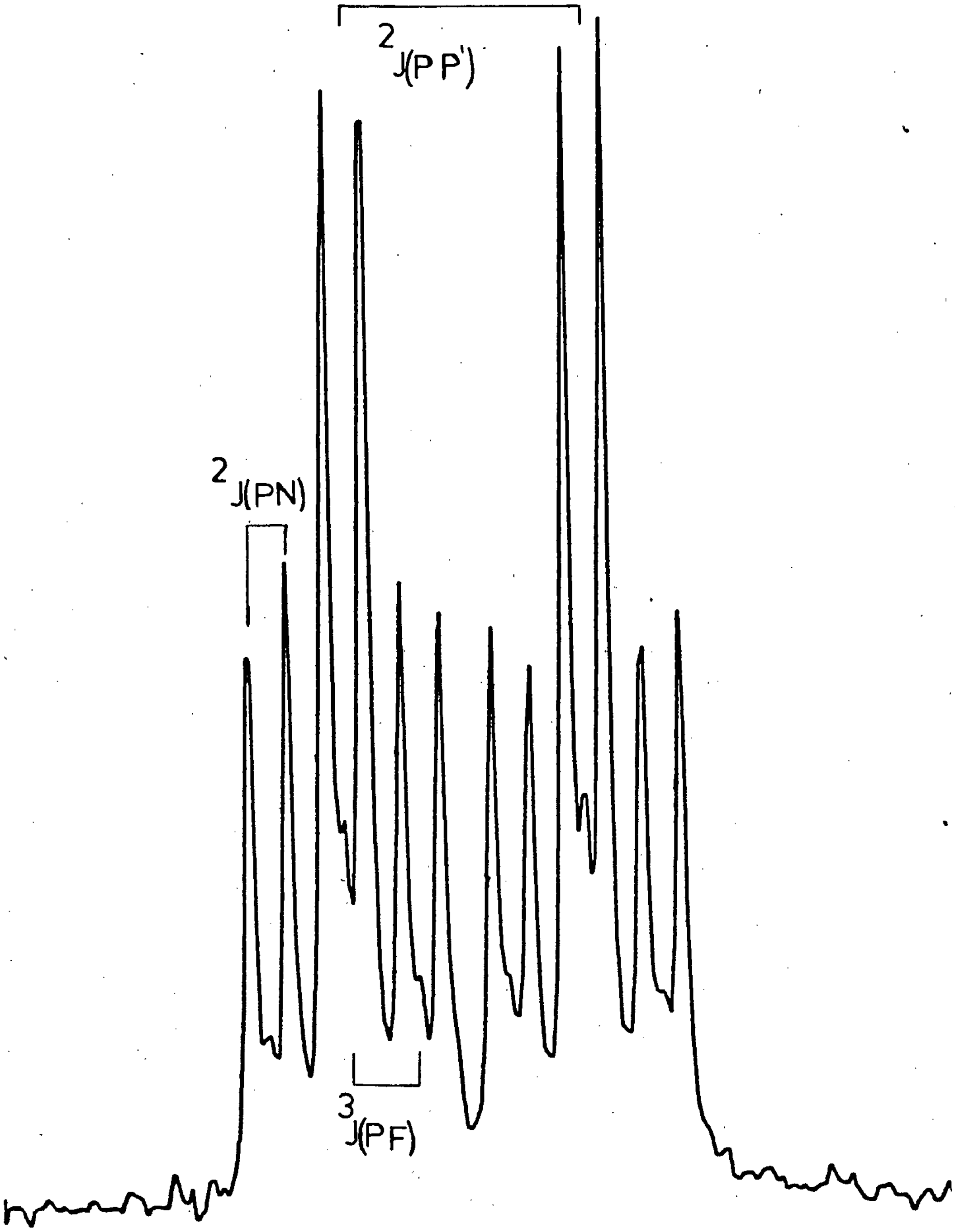
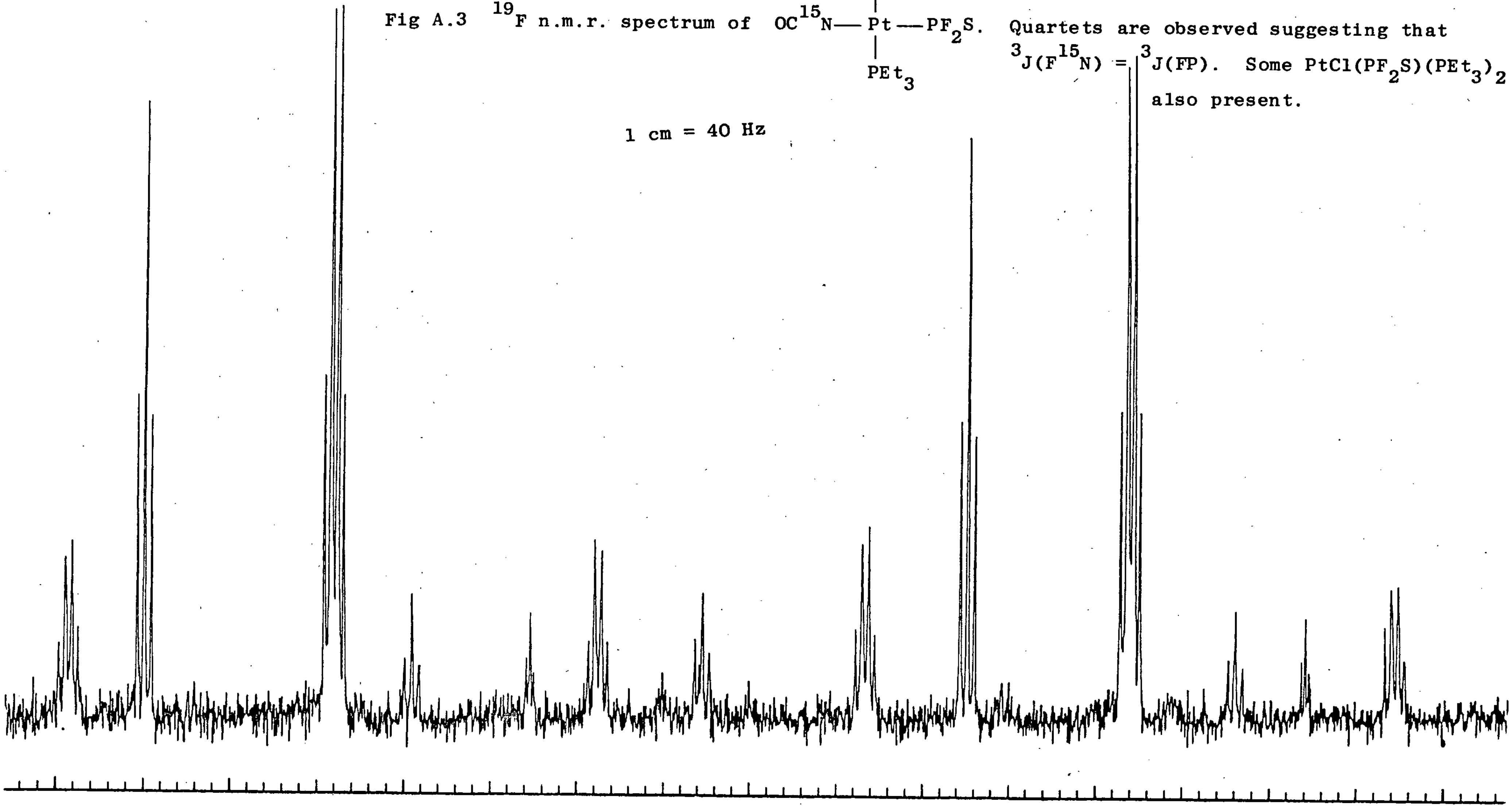


Fig A.3 ^{19}F n.m.r. spectrum of $OC^{15}N-\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}-PF_2S$. Quartets are observed suggesting that $^{3}J(F^{15}N) = {}^{3}J(FP)$. Some $PtCl(PF_2S)(PEt_3)_2$ also present.

1 cm = 40 Hz



and for NCS the possibility exists that the ligand may bond through the sulphur.

When the reaction was carried out the i.r. spectrum showed a band at 2077 cm^{-1} which suggested that exchange had taken place. The ^{31}P spectrum showed the expected pattern in the PEt_3 region but again there was no signal in the PF_2 region.

It would appear that this is again due to the quadrupolar relaxation effect of the N and that the NCS group is bound to the Pt through the nitrogen. This is somewhat surprising as Pt usually prefers to bond to sulphur as opposed to nitrogen.

The ^{19}F spectra and C,H analysis figures seem to confirm that the complex formed was $Pt(NCS)(PF_2S)(PEt_3)_2$. A sample of ^{15}NCS was not available so it can only be assumed that the NCS is behaving the same way as the NCO but this seems likely from the evidence presented.

(iii) Reaction with KNCSe

The reaction was carried out as before and again the i.r. spectrum showed a band at 2075 cm^{-1} which suggested that exchange had taken place. However when the ^{31}P spectrum was obtained several products appeared to be present. The peaks all overlapped and no assignment could be made. The ^{19}F spectra, on the other hand, showed that several complexes were present but here the different signals could be distinguished.

The main species present showed the doublet of triplets pattern with Pt satellites which would be expected of a $PtX(PF_2S)(PEt_3)_2$

complex. The parameters were different from those of starting material and it would seem reasonable to assign the species as $Pt(NCSe)(PF_2S)(PEt_3)_2$. The ^{31}P spectra showed very few peaks in the PF_2 region, therefore it is proposed that the NCSe is bound to the Pt through the nitrogen. One other complex present was shown to be starting material while another two $PtX(PF_2S)(PEt_3)_2$ type complexes were also observed. One of these complexes was assigned as $Pt(CN)(PF_2S)(PEt_3)_2$ from the data obtained from the reaction of $PtClPF_2S(PEt_3)_2$ with Na CN, which will be discussed in the next section.

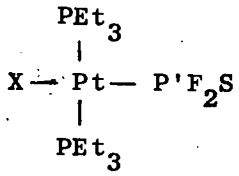
This would imply that decomposition is occurring in solution. This is not surprising since NCSe is not such a good ligand as NCO or NCS and loss of Se is possible. The identity of the fourth complex present is not known although the possibility remains that it is the complex $Pt(SeCN)(PF_2S)(PEt_3)_2$ where the NCSe group is bound to the Pt through the selenium. However better defined ^{31}P spectra would be required before any positive identification could be made.

The C, H and N analysis figures obtained were reasonably accurate for $Pt(NCSe)(PF_2S)(PEt_3)_2$ and the complex behaved as expected in the solid phase. It was only when it was dissolved in $CDCl_3$ for the n.m.r. work that decomposition seemed to occur. This seems to suggest that the complex is stable as a solid and that it is in solution that slow decomposition occurs to give $Pt(CN)(PF_2S)(PEt_3)_2$.

(iv) Reaction with NaCN

As with the NCSe reaction the i.r. and analysis results obtained have suggested that a clean exchange had taken place. However the ^{31}P spectra were inconclusive. Here again the ^{19}F

Table A.1 ^{31}P and ^{19}F n.m.r. data for



$$X - \overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}} - P'F_2S$$

(X = Cl, I, OCN, SCN, SeCN, CN)

X	Cl	I	OCN	SCN	SeCN	CN
δP	18.9	8.6	18.6	17.6	NR	NR
δP'	132.7	133	127.9	NO	NR	NR
$^{1}J(PtP)$	2346	2305	2324	2312	NR	NR
$^{1}J(PtP')$	5322	5217	NO	NO	NR	NR
$^{2}J(PP)$	24	22	27	27	NR	NR
$^{3}J(PF)$	9.8	9.8	9.8	8.5	8.7	6.2
$^{1}J(PF)$	1162	1184	1147	1150	1152	1176
$^{2}J(P^{15}N)$	-	-	81	-	-	-
δF	-5.7	-5.1	-7.6	-7.8	-7.9	-11.7
$^{2}J(PtF)$	792	772	759	773	780	1023
$^{3}J(F^{15}N)$	-	-	10	-	-	-

Chemical shifts are in ppm, coupling constants in Hz

NR not resolved
NO not observed

spectra were more useful. The main species present gave the expected doublet of triplets with Pt satellites and this was assigned as being due to $Pt(CN)(PF_2S)(PEt_3)_2$. There was one other fluorine containing species present and it also showed the pattern expected for a $PtX(PF_2S)(PEt_3)_2$ complex. However the identity of this complex cannot be determined from the data obtained.

As with the NCSe system it appears as if the complex $Pt(CN)(PF_2S)(PEt_3)_2$ while being stable in the solid phase is slightly unstable in solution.

For this system it was hoped to carry out the reaction using $AgC^{15}N$. However when the reaction was attempted using AgCN it was found that not enough AgCN went into solution to allow exchange to take place. No suitable solvent could be found to carry out the reaction successfully.

A.3 Reaction with Bidentate Ligands

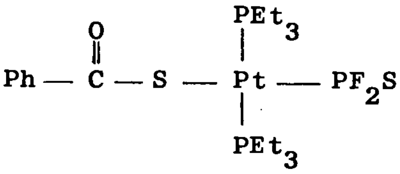
The work in this section gave a direct comparison of the relative strengths of Pt-O and Pt-S bonds. Reactions with several bidentate ligands were attempted, namely acetate, monothiobenzoate, dithiocarbonate, dithiophosphonate.

For the acetate system no reaction took place, which is of no surprise since Pt-O bonds are usually weak[39] and it might be expected that the platinum would prefer to bond to a halogen. However for the other systems studied a reaction took place.

(i) Reaction with NaSCOPh

The reaction was carried out in the same way as those with the alkali metal salts. In this case a precipitate of NaCl was formed which was removed and the product isolated. The i.r. showed three characteristic bands at 1615 cm^{-1}, 1575 cm^{-1} and 910 cm^{-1}. The positions of these bonds suggest that the SCOPh group has bound to the Pt through the sulphur. This can be deduced from the observation that the CS stretch has shifted to lower frequency[40] than would be expected in the free ligand (νCS = 960 cm^{-1} in NaSCOPh)[41]. The C and H analysis figures also supported the idea that SCOPh had replaced Cl on the Pt.

The ^{31}P and ^{19}F n.m.r. spectra showed patterns expected for a $PtX(PF_2S)(PEt_3)_2$ type complex and the chemical shifts and coupling constants differed from those of the starting material. From all this evidence it is proposed that the complex isolated was



$$Ph-\overset{\overset{O}{\|}}{C}-S-\underset{\underset{PEt_3}{|}}{\overset{\overset{PEt_3}{|}}{Pt}}-PF_2S$$

(ii) Reaction with NaS_2PMe_2

This reaction was carried out in the ratio 1:1 and then with a four-fold excess of NaS_2PMe_2. In neither case were the results very clear.

In the 1:1 reaction the ^{19}F spectra (Fig A.4) showed a complex second order pattern while the ^{31}P spectra (Fig A.5) showed a triplet of quintets at low frequency. The PF_2 region showed a strong

Fig A.4 ^{19}F n.m.r. spectrum recorded for the 1:1 reaction of $PtCl(PF_2S)(PEt_3)_2$ with NaS_2PMe_2

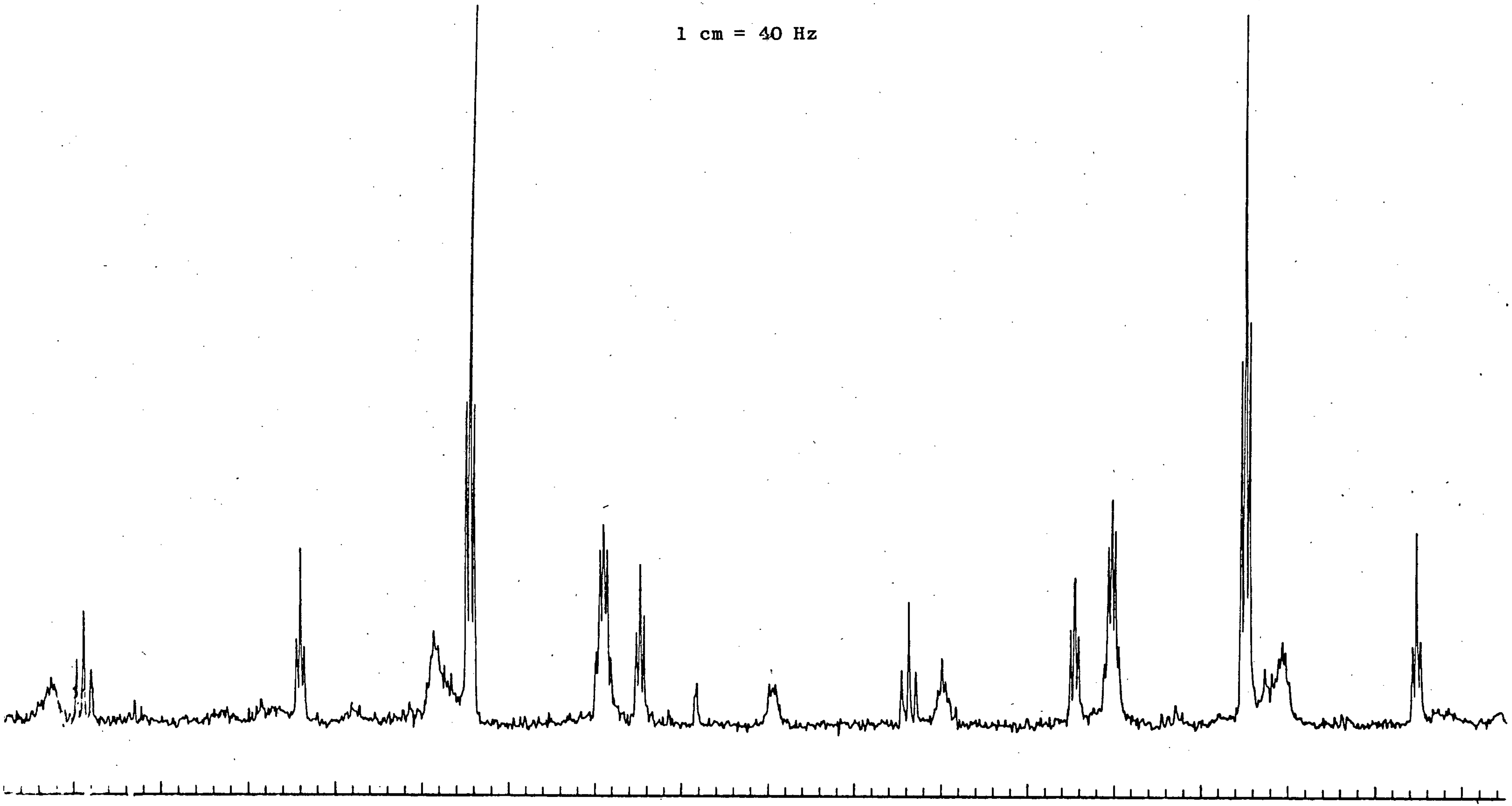
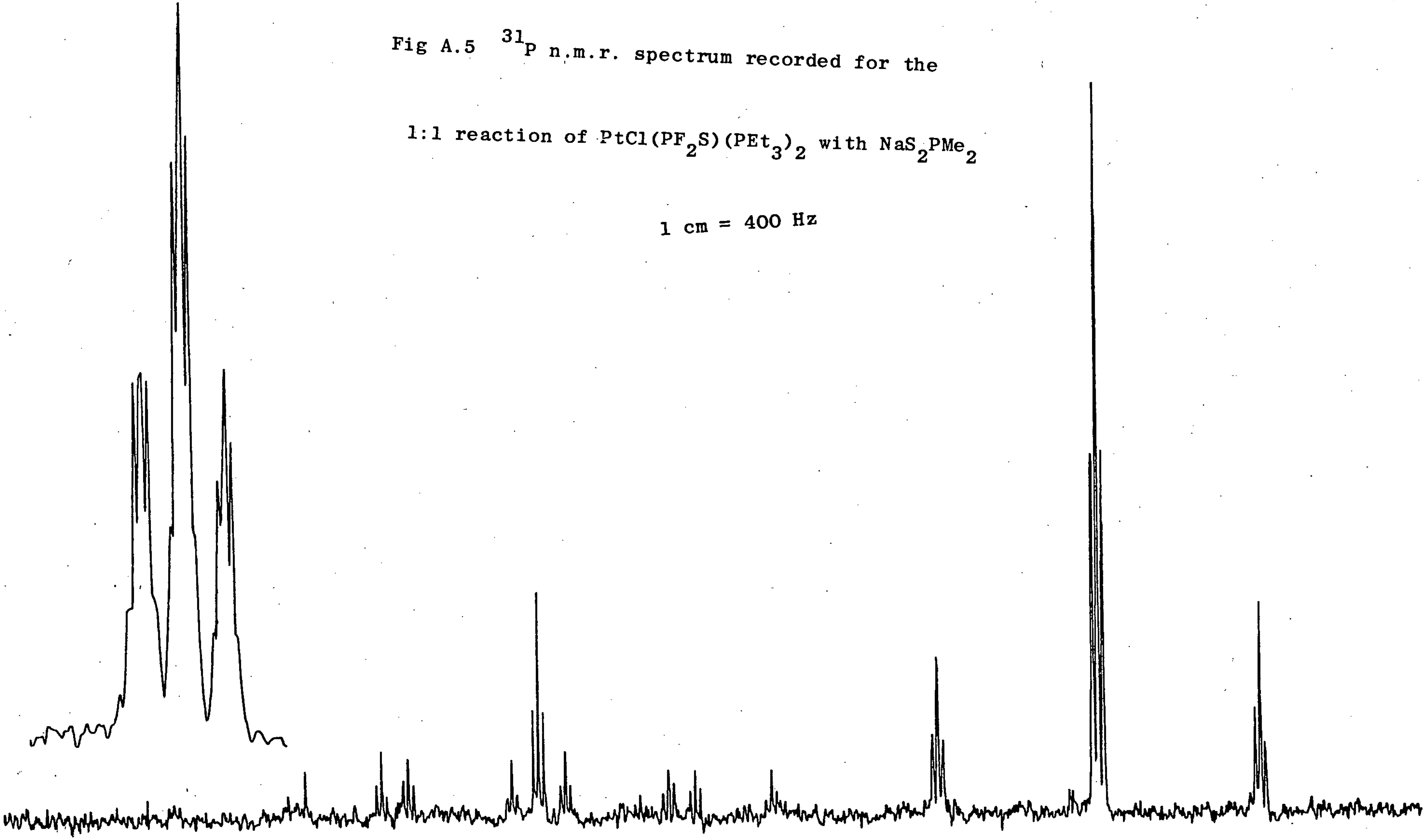


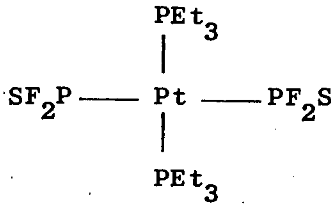
Fig A.5 ^{31}P n.m.r. spectrum recorded for the

1:1 reaction of $PtCl(PF_2S)(PEt_3)_2$ with NaS_2PMe_2

1 cm = 400 Hz



triplet with four less intense triplets on either side of the main resonance. This again could be a second order pattern. The PEt_3 region suggest that there is coupling to two PF_2S groups and the PF_2 region shows triplets which suggest that two PEt_3 groups are bound to the Pt. From this information it seems feasible that the complex formed was



$$\begin{array}{ccccc} & & PEt_3 & & \\ & & | & & \\ SF_2P & — & Pt & — & PF_2S \\ & & | & & \\ & & PEt_3 & & \end{array}$$

$\delta P = 10.6$ ppm $\delta P'$ 174.1 ppm

There is no obvious reason why the complex should be observed yet it remains one possible explanation of the complex spectra obtained.

When the reaction was carried out using a four-fold excess of NaS_2PMe_2 the spectra obtained were even more complicated. The ^{31}P spectra (Fig A.6) showed three distinct resonances. The PEt_3 region gave a complex multiplet with a large $^1J(PtP)$ coupling. The PF_2 part showed a doublet which suggested a PF group, each line was split into a quartet. The third resonance was in the S_2PMe_2 region and again this was complex. The ^{19}F spectra indicated that two complexes were present. Both gave a doublet with Pt satellites, $\delta F = -26.8$ ppm, -14, 2 ppm; $^1J(PF)$ 1123 Hz, 1193 Hz; $^2J(PtF) = 720$ Hz, 749 Hz. There was no fine structure on these peaks which would indicate the presence of PEt_3 groups bound to the Pt.

Until better defined spectra can be obtained the structure of

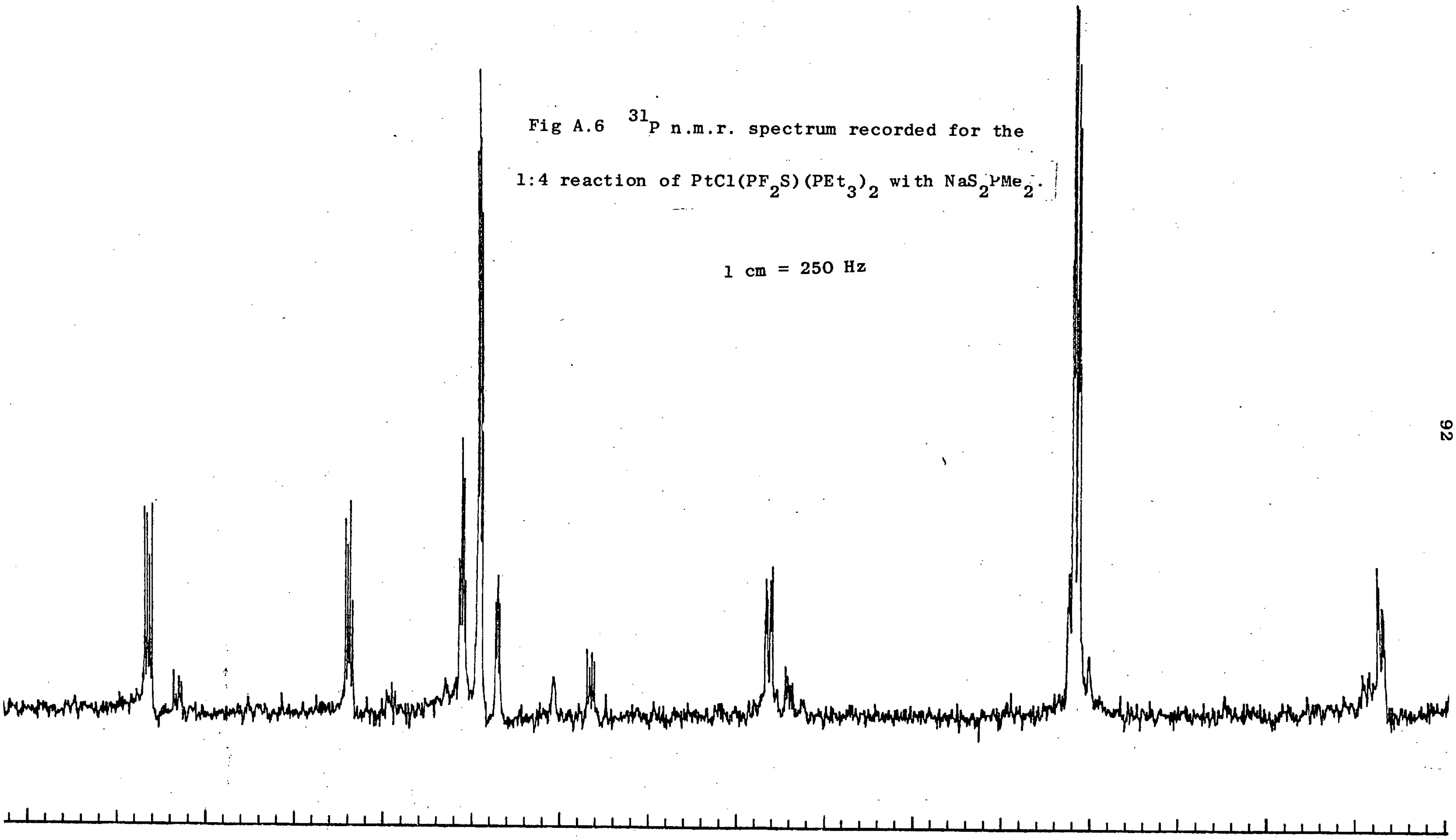


Fig A.6 ^{31}P n.m.r. spectrum recorded for the 1:4 reaction of $PtCl(PF_2S)(PEt_3)_2$ with NaS_2PMe_2.

1 cm = 250 Hz

this complex must remain unsolved. However the spectra were very interesting and further attempts are being made to solve the structure of these complexes.

(iii) Reactions with NaS_2CNEt_2

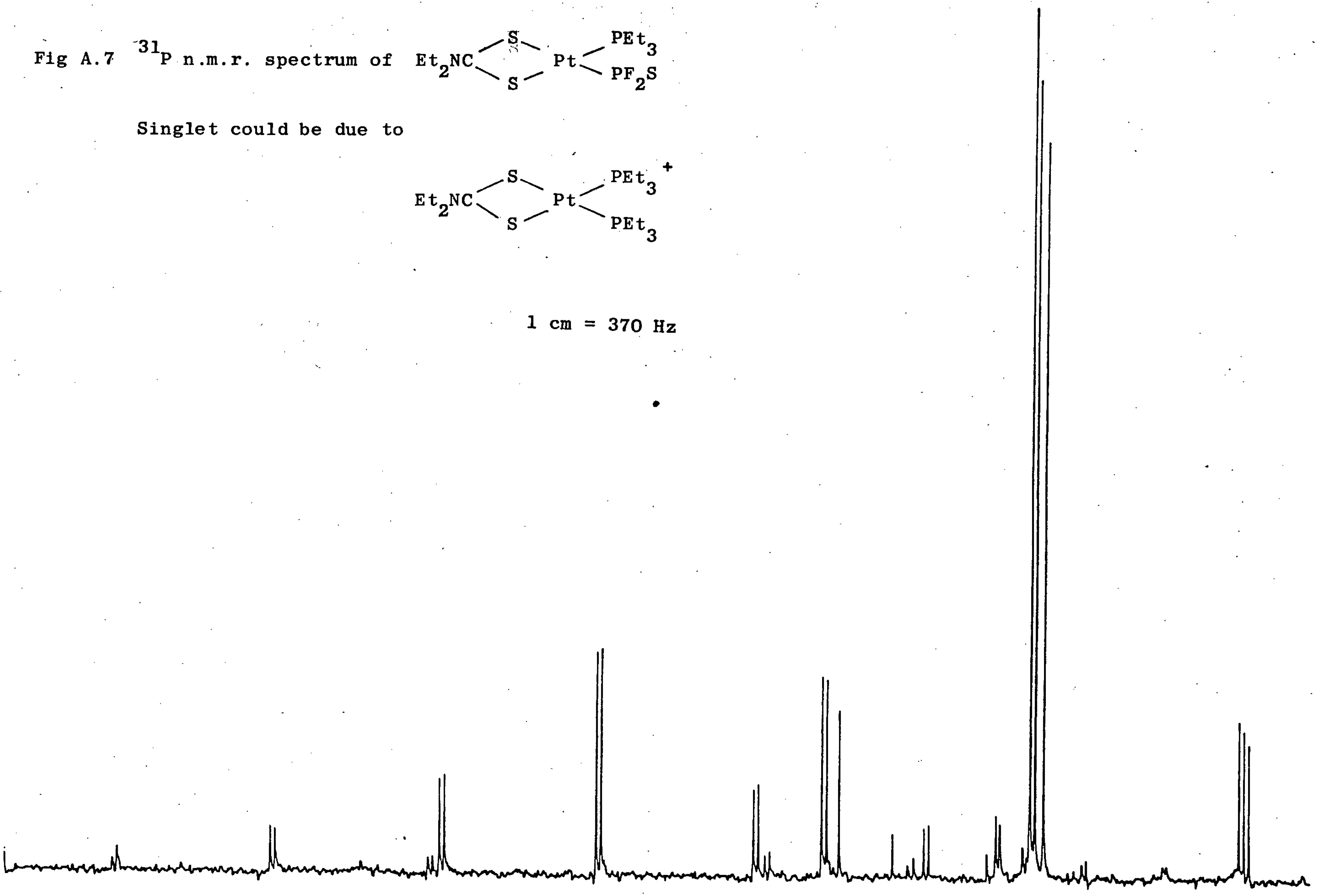
Dithiocarbamate was chosen because it is a much stronger nucleophile than dithiophosphinate and it was thought that it would show a greater tendency to bond to the platinum.

The reaction was carried out as before and again a white precipitate of NaCl was observed. As the reaction proceeded there was also a distinct smell of PEt_3 from the flask, indicating that perhaps the S_2CNEt_2 group had displaced a phosphine.

The i.r. evidence suggested that this was the case as only one band was observed in the region 1000 $\pm$70 cm^{-1} (at 1030 cm^{-1})[42]. Theory predicts[43] that if the S_2CNEt_2 has bound bidentate then only one band will be observed whereas if the bonding was monodentate two bands would be observed.

The ^{31}P spectra (Fig A.7) gave conclusive proof that a PEt_3 group had been replaced. The spectra showed a triplet ($^1J(PF)$) of doublets ($^2J(PP)$) to high frequency which shows the presence of only one PEt_3 group cis to the PF_2S group. The PEt_3 resonance showed a doublet with Pt satellites which suggests that $^3J(PF) \sim 0$. The ^{19}F spectra confirm these observations (the n.m.r. parameters are given in Table A.2).

Fig A.7 ^{31}P n.m.r. spectrum of

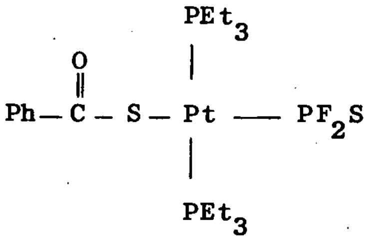


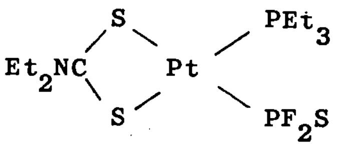
Singlet could be due to

1 cm = 370 Hz

Table A.2

^{31}P and ^{19}F n.m.r. data for the products obtained from the reactions with bidentate ligands





δP	13.1	8.8
δP'	161.5	144.7
$^{1}J(PtP)$	2373	3151
$^{1}J(PtP')$	NR	4884
$^{2}J(PP)$	26.9	36.6
$^{1}J(PF)$	1189	1196
$^{3}J(PF)$	6.1	0.0
δF	-8.4	-13.1
$^{2}J(PtF)$	640	711

NR Not resolved

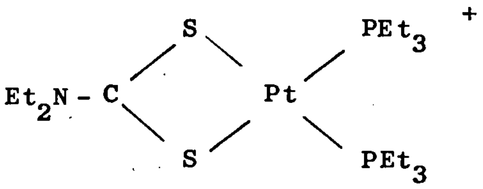
Chemical shifts are given in ppm and coupling constants in Hz

The products for the reactions with S_2PMe_2 have still to be assigned a structure, however the n.m.r. parameters obtained were

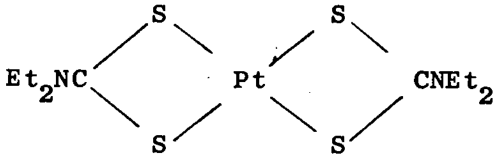
^{31}P spectra septet P = 9 ppm $^{1}J(PtP) = 3420$
triplet of quartets P = 80 ppm, triplet = 90 Hz
doublet of quartets P = 123 ppm, doublet = 1142 Hz

^{19}F spectra two species δF = -14.2 ppm, $^{2}J(PtF) = 749$ Hz
δF = 24.9 ppm, $^{2}J(PtF) = 720$ Hz

A singlet with Pt satellites was also observed in the ^{31}P spectra, (δP = 5.4 ppm $^{1}J(PtP)$ = 3096 Hz) which does not correspond to any of the known Pt-PEt_3 complexes. The possibility here is that the S_2CNEt_2 group initially displaces the Cl and bonds monodentate to the Pt. The other S can now attack the Pt removing either a PEt_3 or a PF_2S^- group (Fig A.8). It would seem reasonable that the singlet could be due to the complex formed when a PF_2S^- group is displaced.

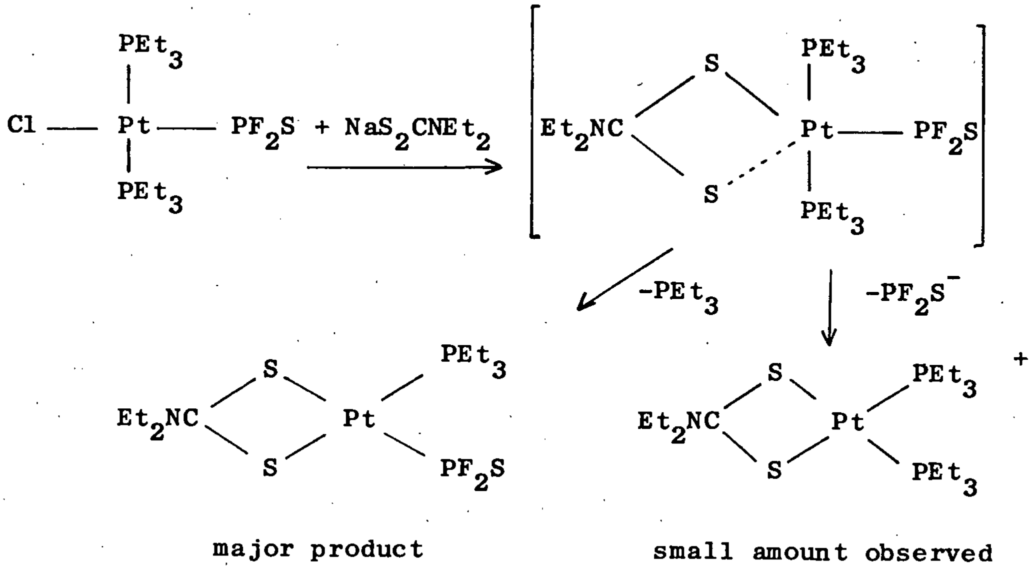


When a four-fold excess of NaS_2CNEt_2 was reacted with $PtCl(PF_2S)(PEt_3)_2$ the complex isolated showed no signal in the ^{31}P spectrum. This would suggest that all the ligands have been replaced by dithiocarbamate group to give



If this was the case then it seems more than likely that the singlet observed in the 1:1 reaction was $[Pt(S_2CNEt_2)(PEt_3)_2]^+$.

Fig A.8 Possible Reaction Mechanism



The complex $[Pt(S_2CNEt_2)(PEt_3)_2]^+$ is a known complex but to date the ^{31}P n.m.r. parameters have not been quoted.

As with the reaction with NaS_2PMe_2 this system requires a little more work and the questions which remain unanswered could be solved, i.e. the identity of the product from the 1:4 reaction could be identified as being $Pt(S_2CNEt_2)_2$ with some certainty since this is also a known complex. Also the complex $[Pt(S_2CNEt_2)(PEt_3)_2]^+$ could be separated from the 1:1 reaction mixture to give a pure sample of $Pt(S_2CNEt_2)(PF_2S)(PEt_3)$.

APPENDIX II: Some ^{31}P n.m.r. data for various Pt complexes used as starting materials

Introduction

Although the complexes used as starting materials are well characterised species, the ^{31}P n.m.r. spectra have not been reported. The data used were recorded via double resonance work and as such the values for $^{1}J(PtP)$ were not as accurate as they might be.

Since much of the work carried out by this research group involves studying reactions of platinum complexes using ^{31}P n.m.r. spectroscopy it was felt that the directly observed values for δP and $^{1}J(PtP)$ should be obtained. Also, many of the studies carried out involved obtaining ^{31}P spectra over a range of temperatures so some idea of how δP and $^{1}J(PtP)$ vary with temperature was required. Two solvents, CD_2Cl_2 and $C_6D_5CD_3$, were used to see if changing the solvent had any effect.

This appendix does not attempt to rationalise the variations observed, it is merely a collection of data which will provide a valuable reference for future research workers.

Results

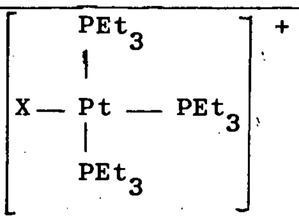
When the $^{1}J(PtP)$ values were plotted against temperature a straight line graph was obtained. The results have therefore been summarised in Tables I and II where the values for δP and $^{1}J(PtP)$ are given for $0^{o}C$ and the variation with temperature is noted for both figures.

TABLE I

Complex	CD_2Cl_2 δP	CD_2Cl_2 $^1J(PtP)$	Toluene δP	Toluene $^1J(PtP)$	Variation of $^1J(PtP)$ with T	Variation of δP with T
$PtHCl(PEt_3)_2$	22.9	2695	22.4	2720	0.6 ΔT	0.0 ΔT
$PtHBr(PEt_3)_2$	21.6	2675	21.1	2690	0.6 ΔT	0.0 ΔT
$PtHI(PEt_3)_2$	19.3	2630	19.0	2650	0.6 ΔT	0.0 ΔT
cis $PtCl_2(PEt_3)_2$	9.2	3505	insoluble		0.1 ΔT	$-5x10^{-3}$ ΔT
cis $PtBr_2(PEt_3)_2$	9.4	3475	insoluble		0.1 ΔT	$-1x10^{-2}$ ΔT
cis $PtI_2(PEt_3)_2$	7.0	3373	insoluble		0.1 ΔT	$-2x10^{-2}$ ΔT
t-$PtCl_2(PEt_3)_2$	12.4	2390	11.8	2420	0.4 ΔT	$-5x10^{-3}$ $ΔT^*$
t-$PtBr_2(PEt_3)_2$	7.6	2320	7.2	2345	0.4 ΔT	$-5x10^{-3}$ $ΔT^*$
t-$PtI_2(PEt_3)_2$	0.3	2255	0.0	2275	0.4 ΔT	0.0 ΔT
$Pr_4N^+(Cl_3PtPEt_3)^-$	1.8	3690	insoluble		0.5 ΔT	$-1.3x10^{-2}$ ΔT
$Pr_4N^+(Br_3PtPEt_3)^-$	1.5	3565	insoluble		0.5 ΔT	$-1.3x10^{-2}$ ΔT
$Pr_4N^+(I_3$ $tPEt_3)^-$	1.6	3415	insoluble		0.5 ΔT	$-2.0x10^{-2}$ ΔT

Values given were recorded at 0°C
Chemical shifts are given in ppm
Coupling constants are given in Hz
* $-3x10^{-3}$ ΔT in $C_6D_5CD_3$

TABLE II ^{31}P data for



$$\left[X-\overset{PEt_3}{\underset{PEt_3}{Pt}}-PEt_3\right]^+ BPh_4^-$$

(X = H, Cl, Br or I)

X	δP	$^1J(PtP)$	$δP^1$	$^1J(PtP')$	Variation with T δP	Variation with T $^1J(PtP)$	Variation with T δP'	Variation with T $^1J(PtP')$
H	16.2	2515	13.0	2025	$1x10^{-2}$ ΔT	0.2 ΔT	$0.5x10^{-3}$	0.3 ΔT
Cl	18.3	2250	9.3	3483	$-1.3x10^{-2}$ΔT	0.15ΔT	$-1.5x10^{-2}$	0.08 ΔT
Br	14.3	2240	10.3	3478	$-1.3x10^{-2}$ΔT	0.15ΔT	$-2.0x10^{-2}$	0.08 ΔT
I	9.1	2240	6.8	3380	$0.7x10^{-3}$ΔT	0.15ΔT	$-2.0x10^{-2}$	0.10 ΔT

This data was recorded in CD_2Cl_2, the complexes being insoluble in toluene.
Values given are those for T = 0°C

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List of Courses Attended

Multiple resonance n.m.r. spectroscopy	Dr W. McFarlane
Cage and Cluster Compounds	Dr T.A. Stephenson
Optical properties of Transition Metal Complexes	Dr T.A. Stephenson
Chemistry at its most colourful	ICI
Flare systems	B.P.
University of Strathclyde Inorganic Club conferences	(3 years)
Departmental and group seminars	