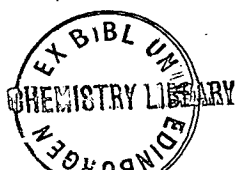


The Preparation and Properties of Some Difluorophosphites

George Maxwell Hunter

Presented for the Degree of
Doctor of Philosophy
University of Edinburgh
1981



I declare that the work described in this thesis is my own and where other results have been quoted acknowledgement has been made to the authors. Other than a small part of Appendix One (that relating to P_2F_4 /disulphide reactions), which was presented by myself as a dissertation as part of my Honours B.Sc. degree at Edinburgh University, the results presented in this thesis have not been submitted in any form for any other degree or professional qualification. At the time of submission only a preliminary communication of part of this work has been published. This publication is contained in Appendix Two of this thesis.

ACKNOWLEDGEMENTS

I would like to thank my supervisors Professor E.A.V. Ebsworth and Dr. D.W.H. Rankin for their advice and guidance in both experimental and theoretical matters relating to this work. I would also like to thank all other members of the inorganic research group for their assistance in carrying out this work and in particular Mr. S.G.D. Henderson, for his help with glassblowing and for supplying many of the silyl compounds used in this research, and Dr. S. Cradock for his help in recording and interpreting vibrational spectra. I am grateful to Mr. J. Miller, Dr. A. Boyd and Mr. L. Bell for recording n.m.r. spectra. I thank Mr. D. Thomas for recording mass spectra and Miss I. Simpson for recording photoelectron spectra. I thank the Science Research Council for provision of a Studentship. Finally I am indebted to Miss A. Erskine for her very careful and competent typing of this manuscript.

To my Mother and Father

I

CONTENTS

<u>Abstract</u>		1
<u>Chapter 1</u>	Introduction	3
	1.1 The synthesis of difluorophosphites.	3
	1.2 The reactions of difluorophosphites.	9
	1.3 The reactions of difluorophosphites with diborane.	10
	1.4 Transition metal complexes of difluorophosphites and of multi-PF ₂ compounds.	12
	1.5 N.M.R. spectra of difluorophosphines.	18
<u>Chapter 2</u>	The reaction of S(PF ₂) ₂ with Alcohols. The Synthesis and Characterisation of S(CH ₂ CH ₂ OPF ₂) ₂ and its use as a Multidentate Ligand.	25
	2.1 Results and Discussion.	26
	2.2 The mass spectrum of S(CH ₂ CH ₂ OPF ₂) ₂ .	28
	2.3 The ³¹ P, ¹⁹ F, ¹ H and ¹³ C n.m.r. spectra of S(CH ₂ CH ₂ OPF ₂) ₂ .	31
	2.4 The infra-red spectrum of S(CH ₂ CH ₂ OPF ₂) ₂ .	34
	2.5 The reaction of S(CH ₂ CH ₂ OPF ₂) ₂ with Mo(cycloheptatriene)(CO) ₃ and W(cycloheptatriene)- (CO) ₃ .	36
<u>Chapter 3</u>	The Reaction of S(PF ₂) ₂ with Orthophosphoric Acid and Derivatives of Orthophosphoric Acid. The Preparation and Characterisation of PO(OPF ₂) ₃ and PFO(OPF ₂) ₂ .	48
	3.1 The preparation and properties of PO(OPF ₂) ₃ and PFO(OPF ₂) ₂ .	50

3.2	The mass spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$.	51
3.3	The vibrational spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$.	55
3.4	The ^{31}P and ^{19}F n.m.r. spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$.	65
3.5	The reaction of $\text{PO}(\text{OH})_2\text{Ph}$ with $\text{S}(\text{PF}_2)_2$. The preparation of $\text{PO}(\text{OPF}_2)_2\text{Ph}$.	75
3.6	The reaction of $\text{PO}(\text{OH})\text{Ph}_2$ with $\text{S}(\text{PF}_2)_2$. The preparation of $\text{PO}(\text{OPF}_2)\text{Ph}_2$.	79
3.7	The reaction of $\text{PO}(\text{OPF}_2)_3$ with B_2H_6 .	79

Chapter 4

	The Reaction of $\text{S}(\text{PF}_2)_2$ with Phosphorous Acid and Derivatives of Phosphorous Acid. The Preparation and Characterisation of $\text{P}(\text{OPF}_2)_3$ and $\text{P}(\text{OMe})_2\text{OPF}_2$.	83
4.1	Results and Discussion.	83
4.2	The mass spectra of $\text{P}(\text{OMe})_2\text{OPF}_2$ and $\text{P}(\text{OPF}_2)_3$.	89
4.3	The vibrational spectra of $\text{P}(\text{OPF}_2)_3$ and $\text{P}(\text{OMe})_2\text{OPF}_2$.	93
4.4	The n.m.r. spectra of $\text{P}(\text{OPF}_2)_3$, $\text{P}(\text{OMe})_2\text{OPF}_2$ and $\text{P}(\text{OPh})_2\text{OPF}_2$.	95
4.5	The n.m.r. spectra of $\text{PHO}(\text{OPF}_2)_2$.	106
4.6	The photoelectron spectrum of $\text{P}(\text{OPF}_2)_3$.	110
4.7	The BH_3 adducts of $\text{P}(\text{OMe})_2\text{OPF}_2$.	110

Chapter 5

	The reaction of $\text{S}(\text{PF}_2)_2$ with Various Hydroxy Compounds and Diphenylphosphine Oxide.	118
5.1	Results and Discussion.	118
5.2	The reaction of $\text{S}(\text{PF}_2)_2$ with malonic and oxalic acid.	121

III

5.3	The reaction of $S(PF_2)_2$ with sulphuric acid.	122
5.4	The reaction of $S(PF_2)_2$ with telluric acid.	123
5.5	The reaction of $S(PF_2)_2$ with selenous acid.	124
5.6	The reaction of $S(PF_2)_2$ with hypophosphorous acid.	125
5.7	The reaction of $S(PF_2)_2$ with diphenylphosphine oxide.	126
<u>Chapter 6</u>	Conclusions and Future Work.	135
<u>Chapter 7</u>	Experimental	143
7.1	General.	143
7.2	Instrumentation.	146
7.3	Preparation of Reagents.	146
7.4	Experimental procedure related to Chapter 2.	147
7.5	Experimental procedure related to Chapter 3.	150
7.6	Experimental procedure related to Chapter 4.	152
7.7	Experimental procedure related to Chapter 5.	155
<u>Appendix 1</u>	Some Reactions of P_2F_4 .	158
<u>Appendix 2</u>	Published Material.	187
<u>References</u>		188
<u>Courses Attended</u>		193

ABSTRACT

The reactions of $S(PF_2)_2$ with alcohols, oxyacids and phosphites were investigated. The novel compounds $PO(OPF_2)_3$, $P(OPF_2)_3$, $PFO(OPF_2)_2$, $PHO(OPF_2)_2$, $P(OMe)_2OPF_2$, $P(OPh)_2OPF_2$, $POPh_2OPF_2$, $POPh(OPF_2)_2$, $S(CH_2CH_2OPF_2)_2$ and $(CH_2OPF_2)_2$ were prepared by this route. The ^{31}P , ^{19}F and 1H n.m.r. spectra of these compounds were recorded. The novel compounds $PO(OPF_2)_3$, $P(OPF_2)_3$, $PFO(OPF_2)_2$, $P(OMe)_2OPF_2$ and $S(CH_2CH_2OPF_2)_2$ were isolated and characterised by a variety of physical techniques including n.m.r. spectroscopy, infra-red spectroscopy, Raman spectroscopy, Mass spectrometry and melting point and vapour pressure determinations. From a study of the variable temperature vibrational spectra of $PO(OPF_2)_3$ it is suggested that there is some intermolecular interaction in the condensed phases of this compound. This interaction is proposed to involve the phosphoryl group. This proposition is supported by the absence of any similar intermolecular interaction in the condensed phases of the related compounds $P(OMe)_2OPF_2$ and $P(OPF_2)_3$.

Some chemical reactions of these novel species were investigated. The reaction of $P(OMe)_2OPF_2$ with diborane produced both the mono- and bis- BH_3 adducts. The reaction of $S(CH_2CH_2OPF_2)_2$ with molybdenum and tungsten cycloheptatriene tricarbonyl produced mainly polymeric species with small amounts of molecular species.

The reaction of $S(PF_2)_2$ with diphenylphosphine oxide produced a species proposed to be $POPh_2PF_2$ although some doubt exists as to its structure.

Some reactions of P_2F_4 were investigated. The photolytic reaction of P_2F_4 with $CDCl_3$ produced the novel species PF_2CCl_2D . P_2F_4 was shown to react with alkyl, aryl or fluoroalkyl disulphides by cleavage of both the phosphorus-phosphorus and sulphur-sulphur bonds. This reaction was used to prepare the novel species $PF_2S(p\text{-tolyl})$ and PF_2SEt .

CHAPTER 1

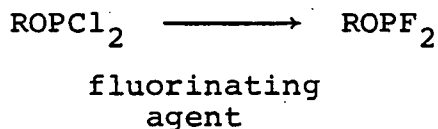
INTRODUCTION

The following sections describe some work which is relevant to that described in this thesis. In particular the synthesis of difluorophosphites, their reactions and their n.m.r. spectra are discussed. There is also a discussion of metal complexes with multi -PF₂ species which demonstrates the potential value of related species as ligands.

1.1 The Synthesis of Difluorophosphites

A large number of difluorophosphites are known and several general methods are now available for their synthesis. These are described below.

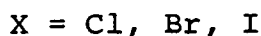
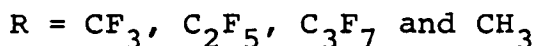
- (a) By fluorination of dichlorophosphites using SbF₃, AsF₃, NaF or KSO₃F as fluorinating agents⁽¹⁾.



R = alkyl or aryl

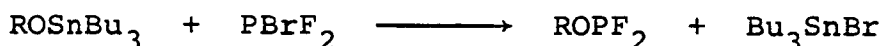
This method has been found to be suitable for the preparation of a large number of difluorophosphites. The reaction is however extremely exothermic and so would not be suitable for the synthesis of difluorophosphites of low thermal stability.

- (b) The synthesis of difluorophosphinecarboxylates by exchange reactions of silver carboxylates with difluorophosphinehalides⁽⁵⁾.



This reaction is rapid and a near quantitative yield of the difluorophosphine carboxylate is obtained. It is interesting to note that use was made of g.l.c for purification of the products.

- (c) By exchange reactions of PBrF_2 with tributyl tin oxides⁽⁶⁾



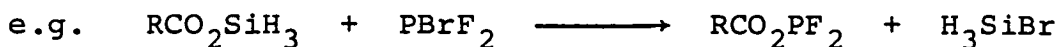
These reactions are rapid, near quantitative and mild. This method provides the best route to $\text{O}(\text{PF}_2)_2$ yet devised⁽⁷⁾ and an intermediate compound, $\text{Bu}_3\text{SnOPF}_2$ ⁽⁶⁾, has been observed.



Cromie⁽⁶⁾ found that reaction of PBrF_2 with $\text{O}(\text{SnBu}_3)_2$ in equimolar amounts produced the intermediate species, $\text{Bu}_3\text{SnOPF}_2$, which was isolated. He suggested that this species might be of use as a reagent for the synthesis of other difluorophosphites and has used it to prepare $\text{Me}_3\text{SiOPF}_2$ by the reaction shown below.



(d) By exchange reactions of PBrF_2 with silyl compounds^(8,9)



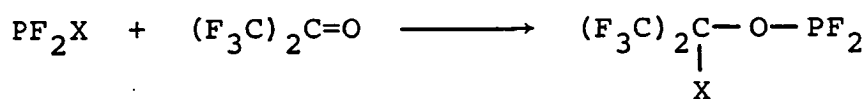
These reactions are currently under investigation by Huntley⁽⁹⁾ with a view to forming species such as RCOSPF_2 , RCOSePF_2 etc. from the thio or seleno acids and studying their bonding.

In the reaction between silylmonothioacetate and PBrF_2 , Huntley found that the reaction proceeded to produce difluorophosphino-monothioacetate. The $-\text{PF}_2$ group in difluorophosphino-monothioacetate was initially bonded to the monothioacetate group via the sulphur (when the reaction was carried out at low temperature) but rearranged to form a mixture of S and O bonded $-\text{PF}_2$ isomers, ca 20% and 80% respectively, at room temperature. It is interesting to note that Huntley has also observed this same ratio of S and O bonded $-\text{PF}_2$ isomers of difluorophosphino-monothioacetate, at room temperature, when this compound was formed by reaction of tributyltinmonothioacetate with PBrF_2 cf. reactions in section 1.1(c)). In the initial product the $-\text{PF}_2$ group was however bonded through the oxygen at low temperature.

This demonstrates that the initial reaction products of the reaction between silyl- or tributyltin- monthioacetates and PBrF_2 are controlled by kinetic rather than thermodynamic factors.

When Huntley carried out the reaction of PBrF_2 with silyl-selenoacetate the product, MeCOSePF_2 , was found to consist of both the O and Se bonded PF_2 isomers (ca. 33% and 67% respectively at -85°C). This reaction also produced elemental selenium and so was less amenable to study than the monothioacetate system.

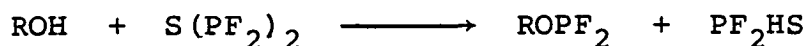
(e) The reaction of PF_2X with hexafluoroacetone^(26,11)



$\text{X} = \text{PF}_2, \text{Br}, \text{I}$

It would be of interest to know if this reaction could be extended to other ketones and types of X.

(f) By reaction of $\text{S}(\text{PF}_2)_2$ with Hydroxy Species^(6,13,14,15)



These reactions are rapid, employ mild conditions and result in high yields of product. Preliminary investigations were carried out by Cromie⁽⁶⁾ after Arnold⁽¹⁶⁾ had shown analogous reactions occurred with $\text{Se}(\text{PF}_2)_2$. These investigations were followed up as described in this thesis and R can be many different moieties. Stewart⁽¹³⁾ and Campbell⁽¹⁴⁾ also carried out work on these types of system and showed that MeSO_3H , Ph_3SiOH , $\text{HO}(\text{CH}_2)_3\text{OH}$ and $\text{HO}(\text{CH}_2)_6\text{OH}$ reacted as shown in the above equation. The novel species $\text{F}_2\text{PO}(\text{CH}_2)_3\text{OPF}_2$ and MeSO_3PF_2 were isolated and fully characterised.

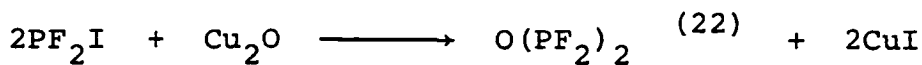
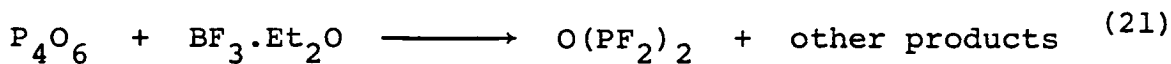
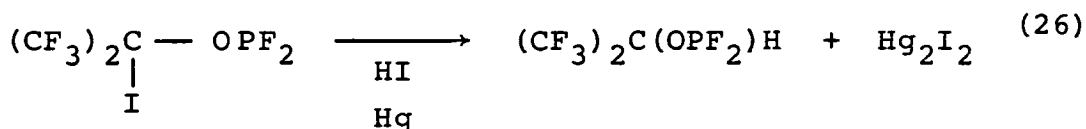
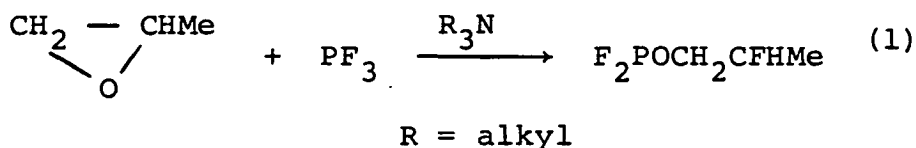
(g) By reaction of phosphites with $\text{S}(\text{PF}_2)_2$ as described in this work.



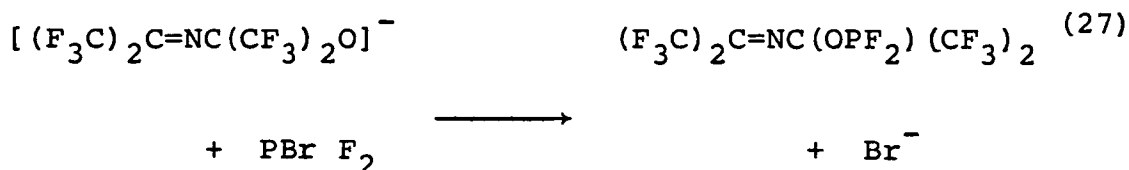
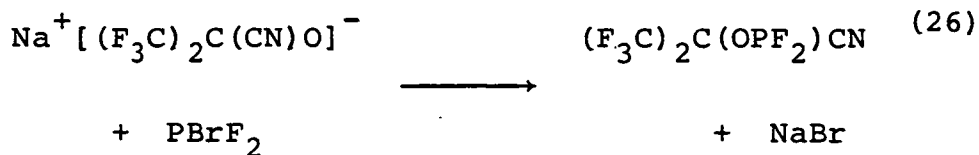
$\text{R} = \text{PF}_2, \text{Me}, \text{Ph}$

The above reactions represent several complementary methods for the formation of difluorophosphites and it should be possible to make most required species by one of these routes.

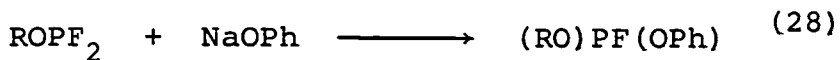
Some other methods for the synthesis of difluorophosphites are known and these are shown below. These are however much less general and in some cases apply to only one compound.



Two reactions have been shown to occur between PBrF_2 and the rather exotic anions shown in the equation below.



This would suggest that the reaction between oxyanions and PBrF_2 might be a general synthetic route to difluorophosphites. However the reaction between sodium phenoxide and alkyl difluorophosphites has been investigated and found to involve cleavage of the phosphorus-fluorine bond.

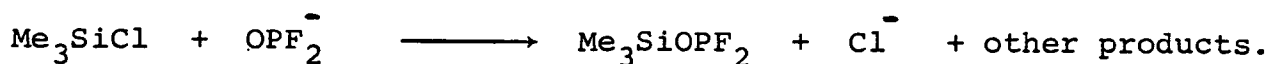


This suggests that competing reactions might occur in the reactions of oxyanions with PBrF_2 and these are unlikely to form a general synthetic route to difluorophosphites.

Some related work has been carried out by MacDonald⁽²⁹⁾ and Centofanti⁽²⁾ who used the reaction of PF_2HO with trimethylamine to generate the anion OPF_2^- .



MacDonald has used the reaction of OPF_2^- with Me_3SiCl to produce $\text{Me}_3\text{SiOPF}_2$ although the reaction also produced other species such as PF_3 and PF_5H^- .

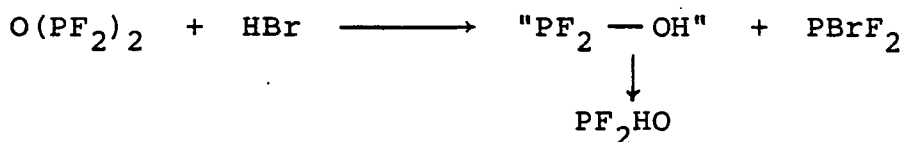


1.2 The Reactions of Difluorophosphites

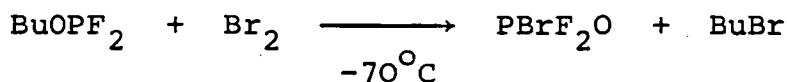
The chemistry of the difluorophosphites has not been extensively studied and remains to be fully investigated. Some reactions which have been reported are described below.

Difluorophosphites are hydrolysed by water and oxidised by air to phosphorus V. Cromie⁽⁶⁾ has reported that $\text{Bu}_3\text{SnOPF}_2$ hydrolyses/oxidises to produce $\text{O}(\text{PF}_2)\text{-OSnBu}_3$ as an initial product and that further reaction produces PF_2HO . The hydrolysis of RCO_2PF_2 has been reported⁽⁵⁾ to produce the anhydride, $(\text{RCO})_2\text{O}$ and $\text{O}(\text{PF}_2)_2$ initially, and then the acid, RCO_2H .

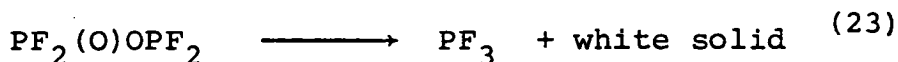
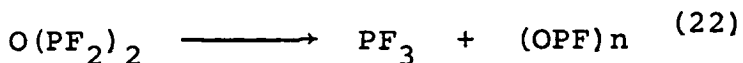
$\text{O}(\text{PF}_2)_2$ reacts with hydrogen bromide to form PF_2HO and PBrF_2 ⁽¹²⁾. This reaction is postulated to proceed via $\text{PF}_2(\text{OH})$ followed by rearrangement of this species to the four coordinate phosphorus form. The hydroxy isomer, $\text{PF}_2(\text{OH})$ is not known.



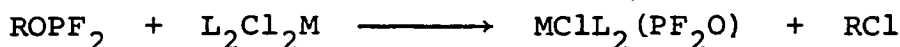
Alkyldifluorophosphites react with halogens⁽³¹⁾ resulting in cleavage of the carbon-oxygen bond under mild conditions.



Both $\text{O}(\text{PF}_2)_2$ and $\text{PF}_2(\text{O})(\text{OPF}_2)$ are reported to decompose at room temperature^(22,23). The decomposition of $\text{O}(\text{PF}_2)_2$ is enhanced by the presence of an adsorbent surface such as asbestos.



Difluorophosphites can act as Lewis bases and form complexes with BH_3 moieties (see next section). They also readily form complexes with transition metals by displacement of other ligands such as unsaturated organic molecules or carbon monoxide (see section 1.4). In contrast to this simple behaviour as Lewis bases alkyldifluorophosphites have been shown to react with some platinum and palladium chlorides with cleavage of the carbon-oxygen bond⁽¹⁸⁾.



M = Pt or Pd

R = alkyl

1.3 The Reactions of Difluorophosphites with Diborane

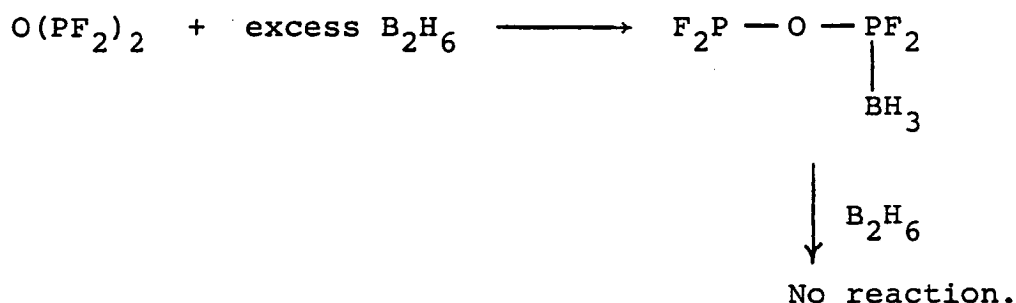
Difluorophosphites in common with other difluorophosphines readily form BH_3 adducts when reacted with diborane or borane carbonyl.



This reaction is rapid at room temperature for the simple difluorophosphites e.g. $MeSO_3PF_2$ ⁽¹⁴⁾ and $F_2PO(CH_2)_3OPF_2$ ⁽¹³⁾. However an equilibrium exists and these adducts, e.g. $PF_3 \cdot BH_3$, are in general extensively dissociated in the absence of excess diborane. In marked contrast to this the compound $PHF_2 \cdot BH_3$ is not dissociated to any measurable extent in the gas phase at room temperature⁽³³⁾. This was initially thought to be due to

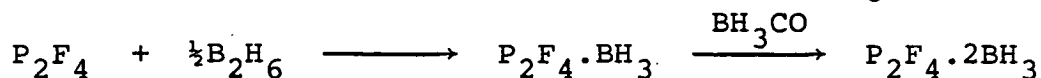
some form of internal hydrogen bonding, resulting in a very small pyramidal angle at the phosphorus although this now appears not to be the case and reasons for the stability of this complex are unclear⁽¹⁾.

In marked contrast to the simple difluorophosphites, $O(PF_2)_2$ forms only the mono adduct and not the bis adduct⁽²⁾.



This behaviour has been found for the related species $S(PF_2)_2$ and $Se(PF_2)_2$ ⁽³⁵⁾ and has been attributed to electron interchange via a π electron system resulting in a lowering of electron density on the free PF_2 group of the mono adduct. The compound $CH_2(PF_2)_2$ has been found to form the bis adduct⁽³⁶⁾ and this is presumably due to lack of a π electron system through which the electrons may interchange.

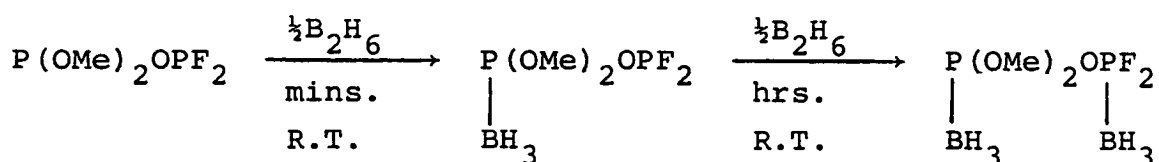
P_2F_4 has been found to form only the mono adduct readily with B_2H_6 ⁽¹²⁾ although treatment of $P_2F_4 \cdot BH_3$ with borane carbonyl results in the formation of the unstable bis BH_3 adduct⁽³⁸⁾.



The related species H_2PPF_2 and $(F_3C)_2PPF_2$ form only the mono BH_3 adduct⁽⁴⁾ with the BH_3 coordinated to the $-PF_2$ unit. The preference of these biphosphines to form only a mono, rather than a bis adduct is again presumably due to an electron interchange mechanism resulting in a lowering of the basicity of the free

phosphine unit of the mono BH_3 adduct. Compounds such as $\text{F}_2\text{PO}(\text{CH}_2)_3\text{OPF}_2$, in which the difluorophosphite groups are structurally isolated, readily form the bis BH_3 adducts⁽¹³⁾.

In this work it was found that $\text{P}(\text{OMe})_2\text{OPF}_2$, related to $\text{O}(\text{PF}_2)_2$ structurally, reacted initially to form the mono BH_3 adduct with diborane. This reaction was rapid at room temperature and was followed by a much slower reaction to form the bis BH_3 adduct.



Since $\text{O}(\text{PF}_2)_2 \cdot \text{BH}_3$ and $\text{F}_2\text{POP}(\text{OMe})_2 \cdot \text{BH}_3$ are very closely structurally related it is reasonable to assume that the lack of reaction of $\text{O}(\text{PF}_2)_2 \cdot \text{BH}_3$ with B_2H_6 and the slowness of reaction of $\text{F}_2\text{POP}(\text{OMe})_2 \cdot \text{BH}_3$ with B_2H_6 are due to similar reasons.

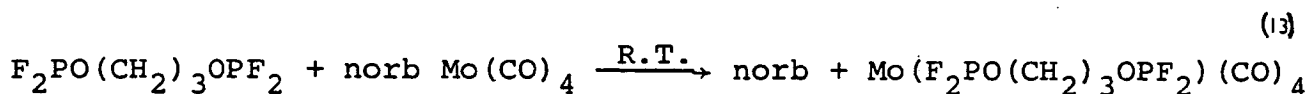
1.4 Transition Metal Complexes of Difluorophosphites and of Multi-PF₂ Compounds

There are a great many transition metal complexes of difluorophosphines and this subject has been reviewed by Nixon⁽¹⁾. Difluorophosphines have been compared with carbon monoxide as ligands particularly in their ability to stabilise transition metals in low oxidation states. The bonding in these complexes has been the subject of much discussion and appears to involve both dative σ bonding from the phosphorus to the metal and $d\pi-d\pi$ back bonding from metal to phosphorus. It is the latter form of bonding that has been suggested to stabilise the metal in a low oxidation state by withdrawal of electron density from

the metal although there is some controversy as to its importance. Nixon has concluded that the importance of σ and π contributions to the metal-phosphorus bond is unclear.

Difluorophosphites behave as other difluorophosphines in forming transition metal complexes. The two most useful methods for the formation of these complexes are the displacement of coordinated carbon monoxide or of coordinated organic molecules. The displacement of coordinated organic molecules by difluorophosphines usually occurs readily at room temperature, whereas the displacement of carbon monoxide usually requires photolysis or heating. One exception is $\text{Ni}(\text{CO})_4$ which generally reacts readily at room temperature with difluorophosphites.

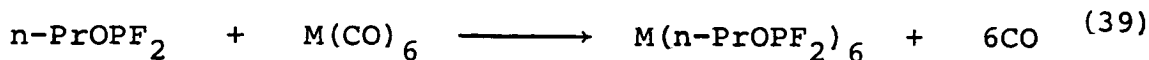
Some examples of reactions of simple difluorophosphites are shown below.



norb = norbornadiene



COD = cyclo octadiene



M = Cr, W, Mo

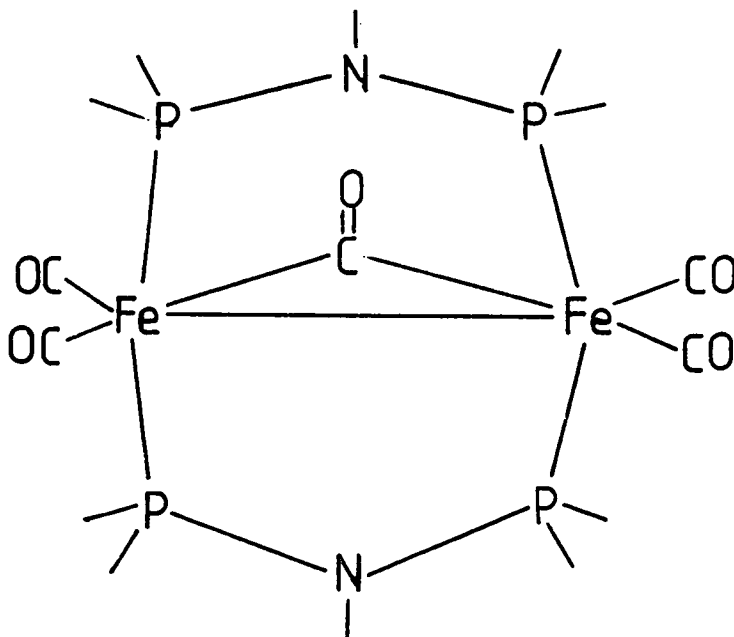
The following multi-PF₂ compounds have now been prepared.

$\text{O}(\text{PF}_2)_2$ (19,20,21,22,7), $\text{S}(\text{PF}_2)_2$ (63,11), $\text{Se}(\text{PF}_2)_2$ (35), $\text{Te}(\text{PF}_2)_2$ (35), $\text{H}_2\text{C}(\text{PF}_2)_2$ (36), $\text{P}(\text{PF}_2)_3$ (41,42), $\text{N}(\text{PF}_2)_3$ (43), P_2F_4 (22) and $\text{RN}(\text{PF}_2)_2$ R=H, alkyl (43,44). Other multi-PF₂ compounds are also known.

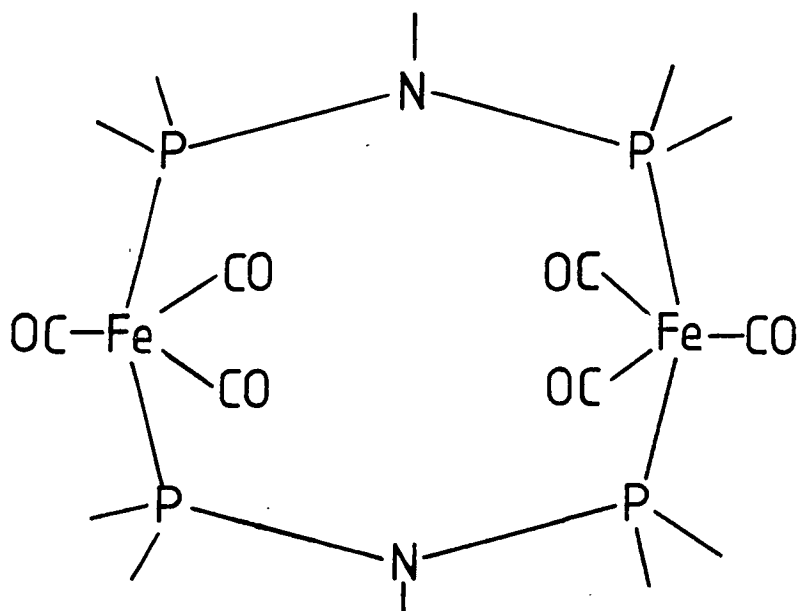
Although many of these compounds have been known for several years their use as ligands has not in general been studied. These are of particular importance as they form a group of multidentate ligands with ligand sites of similar properties to carbon monoxide, which obviously cannot be incorporated into a molecule to form multidentate ligands.

Of these multidentate ligands the two which have been most extensively studied are $\text{MeN}(\text{PF}_2)_2$, principally by King and Gimeno, and $\text{C}_6\text{H}_{10}(\text{PF}_2)_2$, principally by Morse.

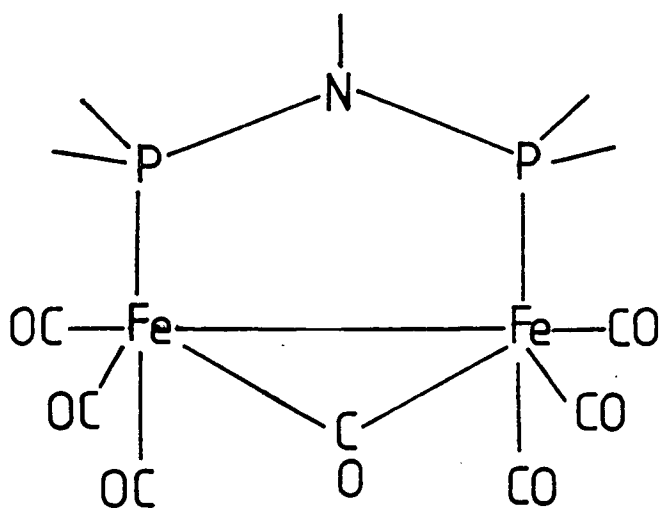
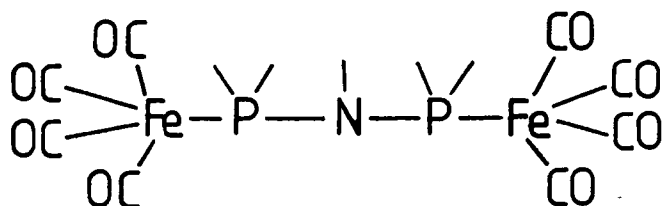
The reaction of $\text{RN}(\text{PF}_2)_2$, $\text{R} = \text{Me}$ or Et ^{(45,46) (47)}, with $\text{M}(\text{CO})_6$, $\text{M} = \text{Cr}, \text{W}, \text{Mo}$, proceeds under photolytic conditions or slowly at room temperature producing $\text{M}(\text{RN}(\text{PF}_2)_2)_3$ and shows that these ligands can act as chelating ligands and displace all carbon monoxide molecules to form monomeric adducts. The analogous reaction with iron carbonyls has been studied^(45,48) again initiated by photolysis or heating. The reaction of $\text{Fe}(\text{CO})_5$ can result in the formation of the simple monomer. $\text{Fe}(\text{MeN}(\text{PF}_2)_2)_2\text{CO}$ or, depending on conditions, the species in which the ligand is bridging as shown below.



Reaction of $\text{Fe}_3(\text{CO})_{12}$ can also produce the above compound by loss of carbon monoxide from the initial reaction product shown below.

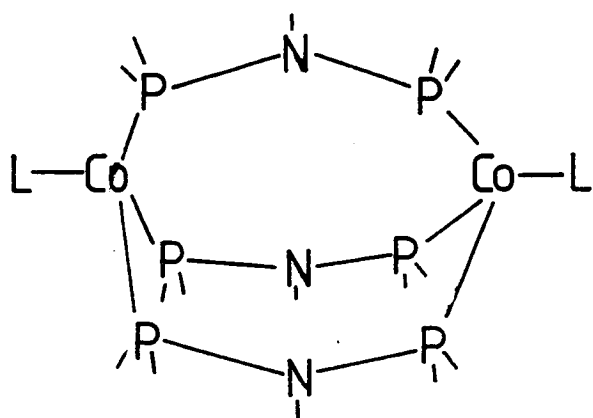


Reaction of $\text{Fe}_2(\text{CO})_9$ with $\text{MeN}(\text{PF}_2)_2$ results in the formation of two other complexes in which the ligand is again bridging two metal atoms. These complexes are shown below.



Reaction of nickel tetracarbonyl with $\text{MeN}(\text{PF}_2)_2$ can result in the formation of the simple monomeric species $\text{Ni}(\text{MeN}(\text{PF}_2)_2)_2$ under certain conditions. If conditions are varied then several other species can be formed in which the ligand is bridging.

The reactions of $\text{MeN}(\text{PF}_2)_2$ with $\text{Co}_2(\text{CO})_8$ have been studied^(49,50) and result in the formation of species with the structure shown below.



Again this ligand is showing a tendency to act as a bridging ligand but in one of these complexes it also acts as a monodentate ligand as well as a bidentate ligand.

Other examples which demonstrate the behaviour of this ligand are its reactions with cyclopentadienyl metal carbonyls⁽⁵¹⁾. In these reactions the cyclopentadiene remains attached to the metal complex.

The reaction of $\text{MeN}(\text{PF}_2)_2$ with $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{Cl}$, where $\text{M} = \text{Mo} \text{ or } \text{W}$, results in the displacement of one carbon monoxide from the metal, initially to form the complex $\{\text{C}_5\text{H}_5\text{M}(\text{CO})_2[\text{MeN}(\text{PF}_2)_2]\text{Cl}\}$, where the $\text{MeN}(\text{PF}_2)_2$ is acting as a monodentate ligand.

Further reaction produces the species $C_5H_5M[MeN(PF_2)_2]_2Cl$ where the ligands are acting in both a monodentate and a bidentate fashion.

The reaction of $C_5H_5Mn(CO)_3$ with $MeN(PF_2)_2$ is analogous to that with $C_5H_5M(CO)_3Cl$, first one carbon monoxide being displaced to form a complex with monodentate $MeN(PF_2)_2$, then displacement of two more carbon monoxide molecules to form the complex with both monodentate and bidentate $MeN(PF_2)_2$. Interestingly the reaction of $C_5H_5Fe(CO)_2Cl$ with $MeN(PF_2)_2$ produces two complexes by stepwise displacement of carbon monoxide by $MeN(PF_2)_2$, both containing only monodentate $MeN(PF_2)_2$. In contrast to these reactions, the reaction of $MeC_5H_4Mn(CO)_2C(OMe)Me$ with $MeN(PF_2)_2$ ⁽⁵²⁾ results in the displacement of both carbon monoxide molecules from the complex and the $MeN(PF_2)_2$ acts as bidentate chelating ligand.

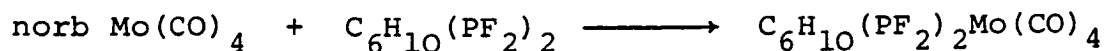
The reactions of $C_6H_{10}(PF_2)_2$ with metals have been studied.

This ligand is produced by the photolytic reaction of P_2F_4 with cyclohexene⁽⁵⁷⁾.



In this ligand the $-PF_2$ groups are trans to each other.

The reaction of $C_6H_{10}(PF_2)_2$ with $Ni(CO)_4$ resulted in the formation of $Ni(C_6H_{10}(PF_2)_2)_2$ ⁽⁵³⁾. Reaction of $C_6H_{10}(PF_2)_2$ with norbornadiene molybdenum tetracarbonyl⁽⁵⁴⁾ resulted in displacement of the norbornadiene by this ligand and the formation of a complex in which the ligand was again bidentate and chelating.



Reaction with $\text{Mo}(\text{CO})_6$ produced bridged species of general formula $\{\text{Mo}(\text{CO})_4[\text{C}_6\text{H}_{10}(\text{PF}_2)_2]\}_x$. The reaction of bistoluene molybdenum⁽⁵⁵⁾ with $\text{C}_6\text{H}_{10}(\text{PF}_2)_2$ produced $\text{Mo}(\text{C}_6\text{H}_{10}(\text{PF}_2)_2)_3$ showing that the formation of polymers in the previous reaction with $\text{Mo}(\text{CO})_6$ was a function of reaction conditions rather than an inability of this ligand to form the tris chelated species. Reaction of $\text{Fe}(\text{CO})_5$ or $\text{Mn}(\text{CO})_5\text{Br}$ with $\text{C}_6\text{H}_{10}(\text{PF}_2)_2$ resulted in the displacement of two or four carbonyls and the formation of complexes where the ligand was again bidentate and chelating.

Reactions of the related species $(\text{CH}_2\text{PF}_2)_2$ ⁽⁵⁶⁾ with $\text{Ni}(\text{CO})_4$ resulted in the formation of the polymer $[\text{Ni}(\text{F}_2\text{PCH}_2\text{CH}_2\text{PF}_2)_2]_x$ while reaction of this ligand with norbornadiene molybdenum tetracarbonyl produced $(\text{CH}_2\text{PF}_2)_2\text{Mo}(\text{CO})_4$ by displacement of the norbornadiene from the complex.

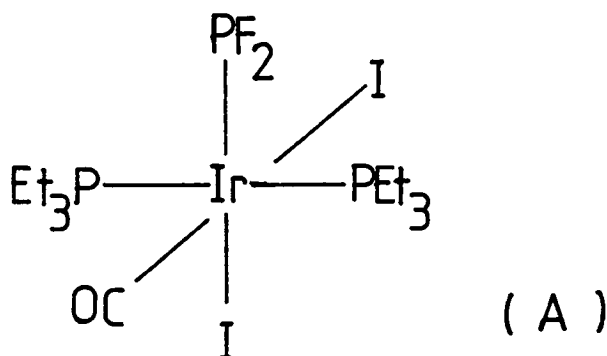
Clearly the products of reaction between these multi- PF_2 compounds and transition metal complexes are strongly dependent upon reaction conditions and on the metal complexes chosen for reaction. These reactions demonstrate the many ways in which these ligands may react and suggest that there is great scope for future work with other multi- PF_2 ligands such as those described in this thesis.

1.5 N.M.R. Spectra of Difluorophosphines

Since all difluorophosphines contain at least two spin $\frac{1}{2}$ nuclei of 100% abundance (^{31}P and ^{19}F) this topic has been the subject of considerable interest⁽¹⁾. ^{31}P and ^{19}F n.m.r. spectroscopy have been invaluable tools in the assignment of structure and several general trends can be noticed when

the spectra of the difluorophosphines are considered.

$^1J_{PF}$ for difluorophosphines is in the range 1000Hz to 1400 Hz⁽¹⁾ with PF_3 having the largest value reported. PF_3 also has the lowest chemical shift (+ve to high frequency) of the fluorophosphines with $\delta(P) = 100$ ppm. At the other extreme in this group of compounds are $Te(PF_2)_2$ with $\delta(P) = 295.8$ ppm⁽³⁵⁾ and the metal complex shown below with $\delta(P) = 364.8$ ppm⁽¹⁰⁾.



The n.m.r. parameters for a representative sample of difluorophosphines are given in Table 1.1 and it can be seen that there is considerable variation from compound to compound. It can be seen that $\delta(P)$ decreases for compounds of type $-X-PF_2$ in the order $X = Te > Se > S > O$.

The ^{31}P chemical shift and magnitude of $^1J_{PF}$ can also be used to confirm that the species is a fluorophosphine and not a compound with the phosphorus in some other oxidation state or with another coordination number. The values of $\delta(P)$ and $^1J_{PF}$ for PF_3 , OPF_3 , PF_5 and PF_6^- are given in Table 1.2 and it can be seen that both $\delta(P)$ and the magnitude of $^1J_{PF}$ decrease as the coordination number of the phosphorus increases. An exception to this general trend is found for the compounds F_2P-PMe_2 and $(S)F_2P-PMe_2$ ⁽⁴¹⁾ where the chemical shift of the F_2P unit differs as expected but the magnitude

Table 1.1 N.M.R. Parameters of Some Difluorophosphines

Compound	δ (P) /ppm	δ (F) /ppm	$^1J_{PF}$	Reference
Te(PF ₂) ₂	296	-73	1244	(63)
Se(PF ₂) ₂	247	-66	1305	(63)
S(PF ₂) ₂	219	-64	1303	(63)
O(PF ₂) ₂	111	-37	1365	(63)
F ₂ PI	242	-46	1340	(1)
F ₂ PBr	218	-40	1388	(1)
F ₂ PCl	176	-37	1390	(25)
MePF ₂	250	-93	1157	(1)
Me ₂ NPF ₂	143	-65	1197	(1)
MeOPF ₂	110	-53	1278	(60)
MeSPF ₂	237	-62	1261	(17)

Table 1.2 N.M.R. Parameters of Some Phosphorus-Fluorine
Compounds.

Compound	δ (P) /ppm	$^1J_{PF}$	Reference
PF ₃	104	1400	(1)
OPF ₃	-35	1055	(59)
PF ₅	-30	930	(25)
PF ₆ ⁻	-145	713	

of $^1J_{PF}$ differs in the opposite way to that expected (values are given in Table 1.3).

The ^{31}P chemical shift also changes when the difluorophosphine forms a BH_3 adduct or becomes coordinated to a transition metal. In general $\delta(P)$ of the BH_3 adduct is ca. 10 ppm to lower frequency than that of the free compound although a much larger shift in this direction of 115 ppm was found on forming the BH_3 adduct of the metal complex (A) shown overleaf.

It has been shown that there is no direct relationship between base strength in difluorophosphines and the magnitude of $^1J_{PB}$ in their borane adducts⁽¹⁷⁾.

The ^{31}P chemical shifts of difluorophosphine metal complexes are in general greater than those of the free ligand although this is variable.

Of particular interest to this research is the magnitude of the phosphorus-phosphorus coupling constant in difluorophosphines with another phosphorus moiety in the molecule. Some values of P-P coupling constants are given in Table 1.3 and it can be seen that $^1J_{PP}$ is generally several hundred hertz whereas $^2J_{POP}$ is in general at least an order of magnitude smaller for these difluorophosphines.

The magnitude of J_{PP} provides some assistance in assigning the structure of molecules. $^1J_{PP}$ can however vary in magnitude

Table 1.3 N.M.R. Parameters of Some Biphosphines and Related Compounds.

Compound	$\delta(P)/\text{ppm}$	$\delta(P')/\text{ppm}$	$^1J_{PP}/\text{Hz}$	$^2J_{PP}$	Reference
$O(PF_2)_2$	111	-	-	4	(1)
$P'(OPF_2)_3$	112	111	-	1	(58)
$P'O(OPF_2)_3$	108	-41	-	29	(58)
$PFO(OPF_2)_2$	107	-38	-	32	(58)
P_2F_4	227	-	229	-	(62)
$P'(SiH_3)_2PF_2$	289	-212	301	-	(37)
$P'(GeH_3)_2PF_2$	291	-192	295	-	(37)
$P'(Me)_2PF_2$	294	-54	250	-	(41)
$P'Me_2PF_2(S)$	132	-39	350	-	(41)
$P'(CF_3)_2PF_2$	236	0	234	-	(4)
$P'H_2PF_2$	292	-138	207	-	(4)

and sign greatly and so a small value of J_{pp} is not necessarily indicative of the absence of a PP bond. A large number of phosphorus-phosphorus coupling constants for a wide variety of compounds are given in a recent review by Finer and Harris⁽⁶⁹⁾.

Where the molecule under study contains more than one difluorophosphine group and these groups are linked by a very few bonds then a second order spectrum results due to coupling of magnetically inequivalent nuclei. This is the case for e.g. $RN(PF_2)_2$ and $S(PF_2)_2$. This situation also arises when two difluorophosphine moieties are coordinated to a transition metal. In general the n.m.r. spectra of such species have been analysed as examples of $[AX_2]_2$ type spin systems^(20,32,34).

The values of n.m.r. parameters for a range of difluorophosphites are given in Table 1.4 and it can be seen that there is remarkably little variation in these. The species $F_2POPF_2(O)$ has an abnormally high ^{31}P chemical shift⁽²³⁾ for the difluorophosphite group and this may be due to some sort of intermolecular exchange process with other species present.

Table 1.4 N.M.R. Parameters of Some Difluorophosphites

Compound	$\delta(P)$ /ppm [PF ₂ unit]	$\delta(F)$ /ppm [PF ₂ unit]	$^1J_{PF}$ [PF ₂ unit]	Reference
P ¹⁹ O(OPF ₂) ₃	108	-37	1385	(58)
P ¹⁹ F ₂ (O)(OPF ₂)	150	-38	1396	(23)
P ¹⁹ FO(OPF ₂) ₂	107	-37	1390	(58)
P ¹⁹ (OPF ₂) ₃	110	-37	1348	(58)
P ¹⁹ HO(OPF ₂) ₂	108	-40	1375	(58)
P ¹⁹ F(OPF ₂) ₂	111	-	1350	(8)
O(OPF ₂) ₂	111	-37	1365	(63)
MeOPF ₂	110	-53	1278	(1)
Bu ₃ SnOPF ₂	118	-23	1262	(6)
Me ₃ SiOPF ₂	112	-33	1299	(29)
EtOPF ₂	113	-50	1285	(6)
n-PrOPF ₂	112	-49	1288	(1)
i-PrOPF ₂	114	-47	1285	(6)
n-BuOPF ₂	112	-49	1288	(1)
i-BuOPF ₂	113	-48	1288	(6)
s-BuOPF ₂	113	-46	1288	(6)
t-BuOPF ₂	121	-41	1297	(6)
Ph ₃ SiOPF ₂	112	-	1326	(14)
F ₃ CCO ₂ PF ₂	-	-50	1389	(1)
MeCCO ₂ PF ₂	-	-54	1350	(1)
D ₃ CCO ₂ PF ₂	110	-	1280	(1)
CH ₂ CHCH ₂ OPF ₂	112	-49	1290	(1)
PhOPF ₂	110	-44	1326	(1)
MeSO ₃ PF ₂	112	-44	1380	(14)
(CCH ₂ OPF ₂) ₂	112	-	1297	(58)
N(CH ₂ CH ₂ OPF ₂) ₃	113	-	1294	(58)
S(CH ₂ CH ₂ OPF ₂) ₂	112	-48	1294	(58)
(CH ₂ OPF ₂) ₂	112	-49	1301	(1)
P(OMe) ₂ OPF ₂	105	-37	1321	(58)
P(OPh) ₂ OPF ₂	114	-38	1335	(58)
POPh(OPF ₂) ₂	111	-39	1363	(58)
POPh ₂ (OPF ₂)	114	-40	1358	(58)
F ₂ PO(CH ₂) ₃ OPF ₂	113	-49	1292	(13)
F ₂ PO(CH ₂) ₆ OPF ₂	113	-49	1289	(13)
F ₂ POC ₆ H ₄ OPF ₂	110	-45	1328	(1)
F ₂ POC(CF ₃) ₂ PF ₂	122	-41	1381	(40)
F ₂ POC(CF ₃) ₂ I	-	-47	1384	(40)
F ₂ POC(CF ₃) ₂ Br	-	-46	1384	(40)

CHAPTER 2

The Reaction of $S(PF_2)_2$ with Alcohols.

The Synthesis and Characterisation of $S(CH_2CH_2OPF_2)_2$
and its use as a Multidentate Ligand.

Introduction

This chapter describes the use of $S(PF_2)_2$ as a reagent in the synthesis of $-OPF_2$ compounds from the corresponding alcohols. This followed the observation made by Cromie and Rankin that a wide variety of alcohols reacted with $S(PF_2)_2$ according to the following equation.



Since many alcohols are known and there are a great number of multihydroxy species it was hoped that the above reaction could be used to make multi- OPF_2 compounds. These compounds might be of use as multidentate ligands.

In this chapter the synthesis of the novel compound $S(CH_2CH_2OPF_2)_2$ is described. It is to be hoped that the methods used in the synthesis of this compound will aid other workers in making and purifying related compounds which may have greater value as multidentate ligands. $S(CH_2CH_2OPF_2)_2$ itself was found to form mainly polymeric species when attempts were made to attach it to tungsten and molybdenum by displacement of cycloheptatriene from complexes of these metals. A monomeric species was however observed by n.m.r. spectroscopy and it is possible that this species could be produced in higher yield if the optimum reaction conditions could be determined. Section 2.1 below summarises the results of these experiments.

2.1 Results and Discussion

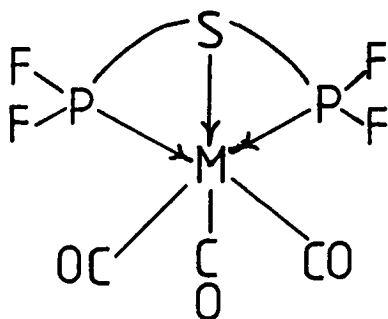
The work described in this chapter stems from preliminary, small scale reactions between $S(PF_2)_2$ and some alcohols. The alcohols chosen, all multifunctional, were $N(CH_2CH_2OH)_3$, $S(CH_2CH_2OH)_2$ and $(CCH_2OH)_2$. The reaction between $S(PF_2)_2$ and these alcohols was investigated using ^{31}P n.m.r. spectroscopy only. In all cases the n.m.r. spectra showed the presence of both the expected $-OPF_2$ compounds and PF_2HS reaction products. The n.m.r. parameters of these species are listed below.

	$N(CH_2CH_2OPF_2)_3$	$S(CH_2CH_2OPF_2)_2$	$(CCH_2OPF_2)_2$	PF_2HS
$\delta(P)/ppm$	112.9	111.5	111.7	67.6
$^1J_{PF}/Hz$	1294	1294	1297	1157

The n.m.r. parameters found were typical of those found in $-OPF_2$ compounds. The reaction with $S(PF_2)_2$ occurred quickly and cleanly at room temperature with both $S(CH_2CH_2OH)_2$ and $(CCH_2OH)_2$. However, the reaction of $S(PF_2)_2$ with $N(CH_2CH_2OH)_3$ produced yellow solids and PF_3 as side products. It was decided to follow up the more promising reaction of $S(CH_2CH_2OH)_2$ with $S(PF_2)_2$ and this reaction was carried out on a preparative scale as described in the experimental chapter. The reaction of $S(CH_2CH_2OH)_2$ with $S(PF_2)_2$ was carried out in the absence of solvent and $S(CH_2CH_2OPF_2)_2$ was produced in high purity and yield. This product, being of low volatility, was manipulated using standard inert atmosphere techniques and was characterised by mass spectrometry, ^{31}P , ^{19}F , 1H and ^{13}C n.m.r. spectroscopy and infra-red spectroscopy as described in Sections 2.2, 2.3 and 2.4 respectively. The results obtained from these techniques

supported the proposed structure and suggested that the compound was very pure. The reaction of $(\text{CCH}_2\text{OH})_2$ with $\text{S}(\text{PF}_2)_2$ was not investigated further although the novel compound produced, $(\text{CCH}_2\text{OPF}_2)_2$, would be an extremely interesting ligand as the $-\text{OPF}_2$ groups are separated by what would be expected to be a rigid linear chain of 4 carbon atoms. There is also the possibility that the acetylene group would act as a ligand and this species may be a bi-, tri- or quadridentate ligand.

The reactions between the newly prepared $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ and molybdenum cycloheptatrienetricarbonyl and its tungsten analogue were investigated. It was hoped that $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ would act as a tridentate ligand, coordinating via the sulphur and phosphorus atoms, and displacing the cycloheptatriene from the metal complex to produce the species show below.



The reactions attempted were initially carried out in n.m.r. tubes and the results are discussed fully in Section 2.5. To some extent the reactions were successful in that n.m.r. spectra consistent with those expected for compound I were observed. However the major reaction products of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ and molybdenum cycloheptatriene tricarbonyl and its tungsten analogue appeared to be insoluble, polymeric materials. In the case of the molybdenum adduct an attempt was made to scale the

reaction up and isolate the monomeric adduct. This met with a little success and better n.m.r. spectra were therefore obtained for the molybdenum adduct than for the related tungsten species. The ^{31}P and ^{19}F n.m.r. spectra of these metal complexes have been regarded as examples of an $[\text{AXY}]_2$ spin system. However the couplings of the inequivalent fluorine nuclei to the phosphorus atoms appears to be identical and so the ^{31}P spectra are as expected for the simpler $[\text{AX}_2]_2$ spin system. The reasons for the inequivalence of the geminal fluorines on the $-\text{PF}_2$ groups is discussed in Section 2.5. Using the assumptions given some n.m.r. parameters have been obtained for these complexes and these are given in Table 2.4.

It seemed unlikely that reasonable yields of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ metal adducts could be obtained in the time available. It was therefore decided to concentrate investigations on the reaction between $\text{S}(\text{PF}_2)_2$ and other hydroxy species as described in the following chapters.

2.2 The Mass Spectrum of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$

The mass spectrum of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ was recorded and is presented in Table 2.1. As the product was involatile and air sensitive a novel method of injecting the compound into the spectrometer was developed which is described in the experimental chapter. It would be imprudent to draw too many conclusions from the mass spectrum as some peaks may be artifacts of the manipulation procedure or caused by reaction of the compound with species present in the spectrometer.

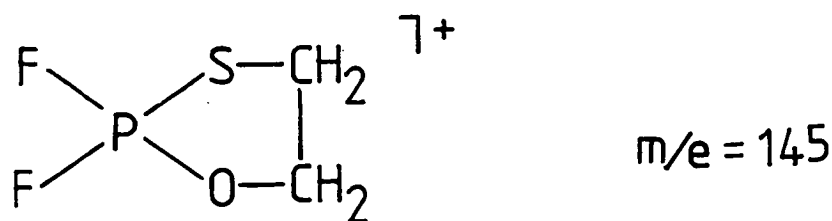
Table 2.1 The Mass Spectrum of S(CH₂CH₂OPF₂)₂

Peak/(m/e)	Relative Intensity/%	Assignment
258	18	[S(CH ₂ CH ₂ OPF ₂) ₂] ⁺
173	20	[F ₂ POCH ₂ CH ₂ SCH ₂ CH ₂] ⁺
145	100	[F ₂ POCH ₂ CH ₂ S] ⁺
119	11	[F ₂ POSH ₂] ⁺
113	6	[F ₂ POCH ₂ CH ₂] ⁺
99	9	[F ₂ POCH ₂] ⁺
87	7	[C ₄ H ₇ S] ⁺
73	59	[C ₃ H ₅ S] ⁺
69	46	[F ₂ P] ⁺
61	9	[C ₂ H ₅ S] ⁺
60	15	[C ₂ H ₄ S] ⁺
59	18	[C ₂ H ₃ S] ⁺
58	11	[C ₂ H ₂ S] ⁺
47	7	[CH ₃ S] ⁺ , [PO] ⁺
46	9	[CH ₂ S] ⁺
45	39	[CHS] ⁺
43	20	[C ₂ H ₃ O] ⁺
28	11	[C ₂ H ₄] ⁺ , [N ₂] ⁺ , [CO] ⁺
27	15	[C ₂ H ₃] ⁺
26	6	[C ₂ H ₂] ⁺

Metastable Peaks/(m/e)	Parent	Daughter
81.5	258	145
121.5	173	145
97.7	145	119
27.7	73	45
33.8	60	45

Notes: only peaks of intensity > 1/3 intensity of molecular ion were measured. Sample was injected through a septem into the system at 100°C. Ionising Voltage = 70 eV.

The outstanding feature of this spectrum is the strong peak at $m/e = 145$. This ion is linked by metastable peaks to peaks at $m/e = 173$ and 258. It therefore appears that the molecular ion (m/e 258) decomposes to this fragment directly (by loss of $\text{CH}_2\text{CH}_2\text{OPF}_2$) and indirectly (by loss of OPF_2 followed by loss of C_2H_4). This ion has been assigned as follows.



There are several reasons why this fragment should be particularly stable and easily formed and hence strong in the mass spectrum. These reasons are given below.

(a) The ion can be formed by an intramolecular cyclisation resulting in the formation of a five membered ring.

(b) The ion contains four coordinate phosphorus which can easily accommodate a positive charge.

(c) The ion can be formed by loss of $-\text{OPF}_2$ and C_2H_4 from the molecular ion. C_2H_4 is clearly a stable fragment and $-\text{OPF}_2$ has been shown to be lost easily from the related compounds $\text{PO}(\text{OPF}_2)_3$, $\text{PFO}(\text{OPF}_2)_2$ and $\text{P}(\text{OMe})_2\text{OPF}_2$ (see Sections 3.2 and 4.2).

In conclusion, the presence of both the molecular ion and ions linked to this via metastable peaks strongly support the proposed formulation for $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$.

2.3 The ^{31}P , ^{19}F , ^1H and ^{13}C n.m.r. Spectra of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$

The ^{31}P , ^{19}F , ^1H and ^{13}C n.m.r. spectra of $\text{S}(\text{C}'\text{H}'_2\text{CH}_2\text{OPF}_2)_2$ were recorded and parameters obtained are tabulated in Table 2.2. The individual n.m.r. spectra are discussed separately below.

(a) The ^{31}P n.m.r. Spectrum.

The ^{31}P n.m.r. spectrum of this compound was a simple triplet ($^1\text{J}_{\text{PF}}$), further split into triplets ($^3\text{J}_{\text{PH}}$) when proton coupling was retained.

(b) The ^{19}F n.m.r. Spectrum.

The ^{19}F n.m.r. spectrum was exceedingly simple, the fluorine showing coupling only to the adjacent phosphorus, and was a doublet ($^1\text{J}_{\text{PF}}$).

(c) The ^1H n.m.r. Spectrum of $\text{S}(\text{C}'\text{H}'_2\text{CH}_2\text{OPF}_2)_2$

This spectrum clearly shows two types of proton are present, each coupled to the other ($^3\text{J}_{\text{HH}'}$). The spectrum is shown in Figure 2.1 and consists of a triplet (labelled B) ($^3\text{J}_{\text{HH}'}$), due to the protons nearest to the sulphur atom, and a pseudoquartet (labelled A). This pseudoquartet is really a doublet ($^3\text{J}_{\text{PH}}$) of triplets ($^3\text{J}_{\text{HH}'}$) and this accidental coincidence in magnitude of $^3\text{J}_{\text{PH}}$ and $^3\text{J}_{\text{HH}'}$ has also been found in the related compounds $\text{CH}_2(\text{CH}_2\text{OPF}_2)_2$ and $(\text{CH}_2\text{CH}_2\text{CH}_2\text{OPF}_2)_2$.

(d) The ^{13}C n.m.r. Spectrum of $\text{S}(\text{C}'\text{H}'_2\text{CH}_2\text{OPF}_2)_2$

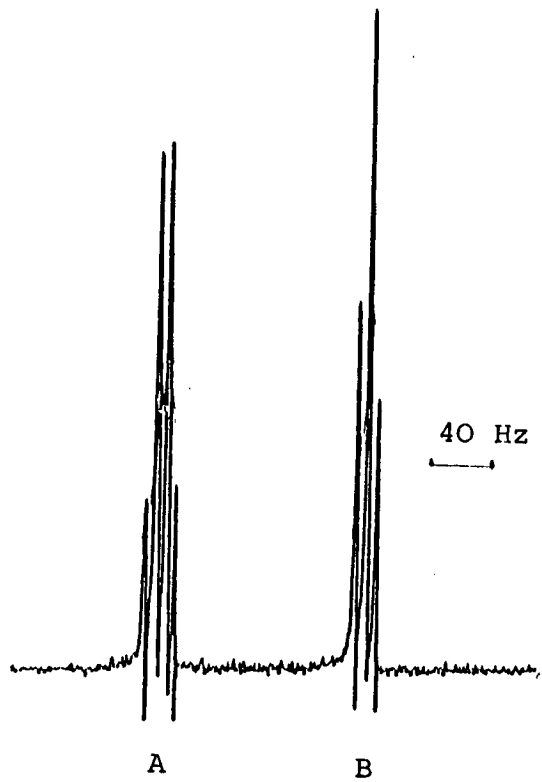
The ^{13}C , proton decoupled, n.m.r. spectrum of $\text{S}(\text{C}'\text{H}'_2\text{CH}_2\text{OPF}_2)_2$ was recorded and is shown in Figure 2.1. This spectrum is clearly very simple. There are two types of carbon and both are coupled to phosphorus, resulting in the splitting of all lines into doublets. Strangely, $^2\text{J}_{\text{PC}}$ and $^3\text{J}_{\text{PC}}$ are of

Table 2.2 The N.M.R. Parameters of $S(C'H'_2CH_2OPF_2)_2$

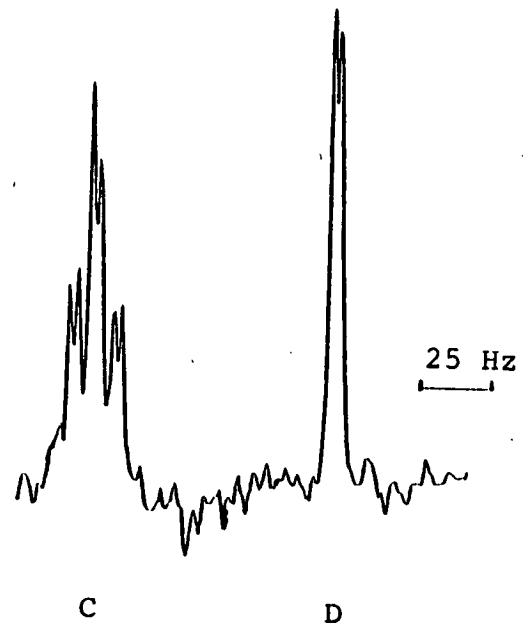
$^1J_{PF}$	1294 Hz
$J_{HH'}$	7.3 Hz
J_{CP}	3.2 Hz
$J_{C'P}$	2.6 Hz
J_{CF}	9.5 Hz
J_{HP}	7.3 Hz
$\delta(H)$	2.81 ppm
$\delta(H')$	4.19 ppm
$\delta(C)$	62.1 ppm
$\delta(C')$	32.4 ppm
$\delta(P)$	111.5 ppm
$\delta(F)$	-48.3 ppm

Solvent = $CDCl_3$

¹H



¹³C



approximately equal magnitude; again this was found for the related compounds $\text{CH}_2(\text{CH}_2\text{OPF}_2)_2$ and $(\text{CH}_2\text{CH}_2\text{CH}_2\text{OPF}_2)_2$, and these may be of opposite sign. The spectrum therefore consists of a triplet (${}^3J_{\text{CF}}$) of doublets (${}^2J_{\text{CP}}$) (labelled C) and a doublet (${}^3J_{\text{C,P}}$) (labelled D). It is interesting to note that ${}^3J_{\text{CF}}$ is very much larger than ${}^2J_{\text{CP}}$ and to compare this with ${}^3J_{\text{PF}}$ and ${}^2J_{\text{PP}}$ for $\text{P}(\text{OPF}_2)_3$ where ${}^3J_{\text{PF}}$ is very much larger than ${}^2J_{\text{PP}}$ (see Table 4.6).

If all the n.m.r. spectra recorded are considered, then they provide very strong evidence for the proposed structure of this compound. These spectra also provide evidence for high purity of this compound as any likely impurities would be expected to be detected if present in any significant amounts. In Table 2.2 the most striking feature is the magnitude of ${}^1J_{\text{PF}}$ when compared with the other coupling constants recorded there. ${}^1J_{\text{PF}}$ is typically of this magnitude and variations in it can be indicative of the coordination about the phosphorus atom as mentioned in Chapter 1.

2.4 The Infra-Red Spectrum of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$

The infra-red spectrum of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ was recorded in the liquid phase and details of this and the assignments made are given in Table 2.3. These assignments are only tentative and have been made by comparison with the spectra of related compounds. These assignments are likely to be unreliable as the concept of group frequencies is unlikely to be valid for this molecule and certainly for ν_{PO} , ν_{PF} and ν_{CO} where substantial mixing may occur as these vibrations involve similar masses and are likely to be of similar symmetry.

Table 2.3 The Infra-Red Spectrum of S(CH₂CH₂OPF₂)₂

Peak Position/cm ⁻¹		Assignment
2970	m	
2910	m	ν _{C-H}
1465	m	
1425	m	
1405	m	
1295	m	ν _{C-C} and δ _{C-H}
1240	w	
1200	m	ν _{C-O}
1050	s	
1005	s	ν _{P-O}
965	s	
895	w	
805	s	ν _{P-F}
760	s	
540	m	

Notes: Spectrum was not recorded below 400 cm⁻¹

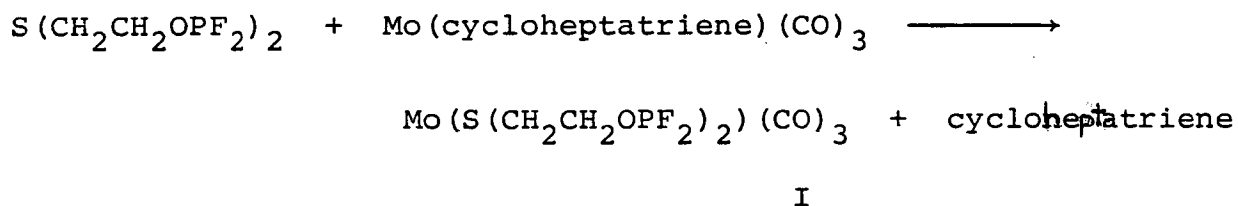
Sample was liquid and at R.T.

w = weak, s = strong, m = medium

The infra-red spectrum should be of use as a "finger print" to check purity in subsequent preparations of this compound.

2.5 The Reaction of S(CH₂CH₂OPF₂)₂ with Mo(cycloheptatriene)(CO)₃ and W(cycloheptatriene)(CO)₃

The reaction of S(CH₂CH₂OPF₂)₂ with Mo(cycloheptatriene)(CO)₃ and its tungsten analogue was investigated. It was hoped that S(CH₂CH₂OPF₂)₂ would act as a tridentate ligand (coordinating via the sulphur and phosphorus atoms) and displace the cycloheptatriene from the metal complex. The expected reaction can be summarised by the equation below.



The reaction was followed by ³¹P and ¹⁹F n.m.r. spectroscopy which suggested that compound I and its tungsten analogue were formed. However large amounts of insoluble, presumably polymeric, material were formed. The formation of polymeric material is not surprising when the reaction is considered. Each S(CH₂CH₂OPF₂)₂ molecule could coordinate to three metals which would each be attached to two other S(CH₂CH₂OPF₂)₂ molecules thus forming polymers.

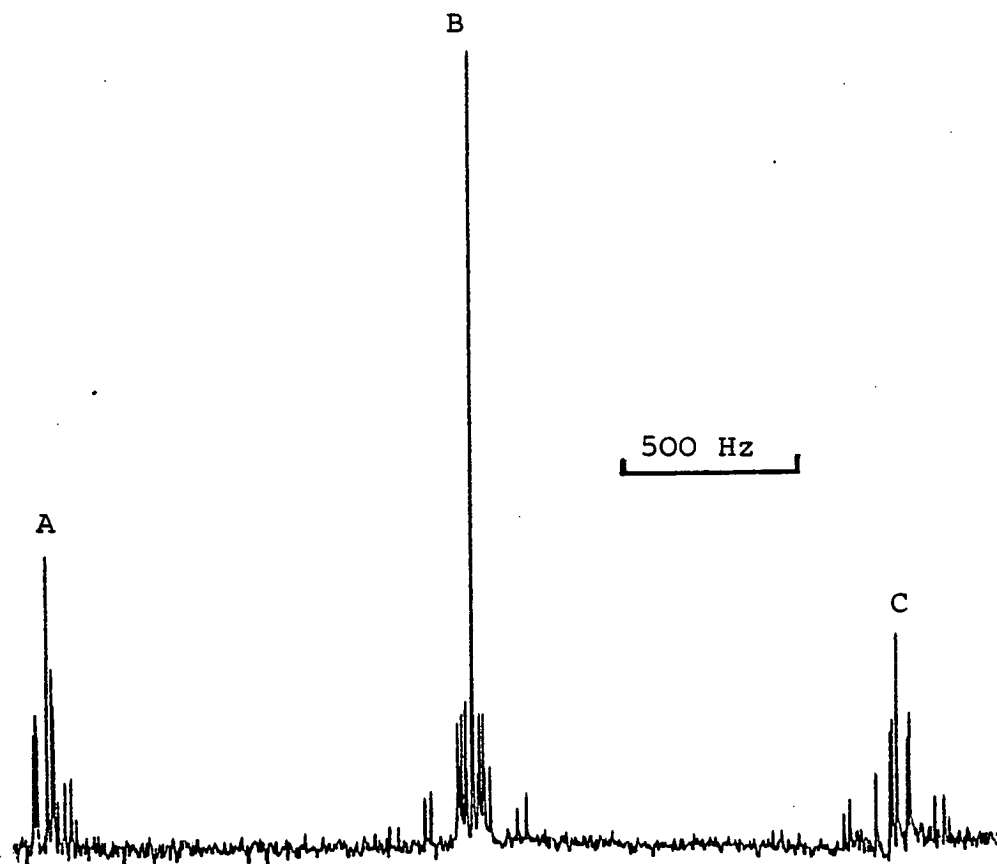
The results for the reaction of Mo(CO)₃(cycloheptatriene) with S(CH₂CH₂OPF₂)₂ are discussed first as some attempt was made to purify species I whereas its tungsten analogue was

observed by n.m.r. spectroscopy only in the crude reaction mixture.

(a) The reaction of $S(CH_2CH_2OPF_2)_2$ with $Mo(cycloheptatriene)(CO)_3$

This reaction was carried out on a small scale initially and observed by ^{31}P n.m.r. spectroscopy. The formation of large amounts of solid suggested that mainly polymers were formed. However ^{31}P n.m.r. spectroscopy showed that a species was present in solution with n.m.r. parameters which were consistent with those expected for species I. The reaction was then attempted under conditions of higher dilution and on a larger scale as described in the experimental chapter. This attempt met with very little success and again mainly polymeric materials were formed. A relatively pure sample of what appears to be compound I was however obtained. There was only a very small amount of this material and good n.m.r. spectra were obtained only after many accumulations using fourier transform techniques. The ^{31}P and ^{19}F n.m.r. spectra of this species are shown in Figs. 2.2 and 2.3 respectively. N.m.r. parameters obtained from these spectra are given in Table 2.4 along with those for the related tungsten species mentioned later in this section. The ^{31}P n.m.r. spectrum of this compound consists of what appears to be a $q_n [AX_2]_2$ type pattern, symmetrical about the centre. The separation of the most intense outer peaks from the central peak should be $^1J_{PF} + ^3J_{PF}$. Since $^3J_{PF}$ should be small compared to $^1J_{PF}$ this separation approximates to $^1J_{PF}$ and is the value of $^1J_{PF}$ given in Table 2.4.

Fig. 2.2 The ^{31}P n.m.r. Spectrum of $\text{Mo}(\text{CO})_3\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$



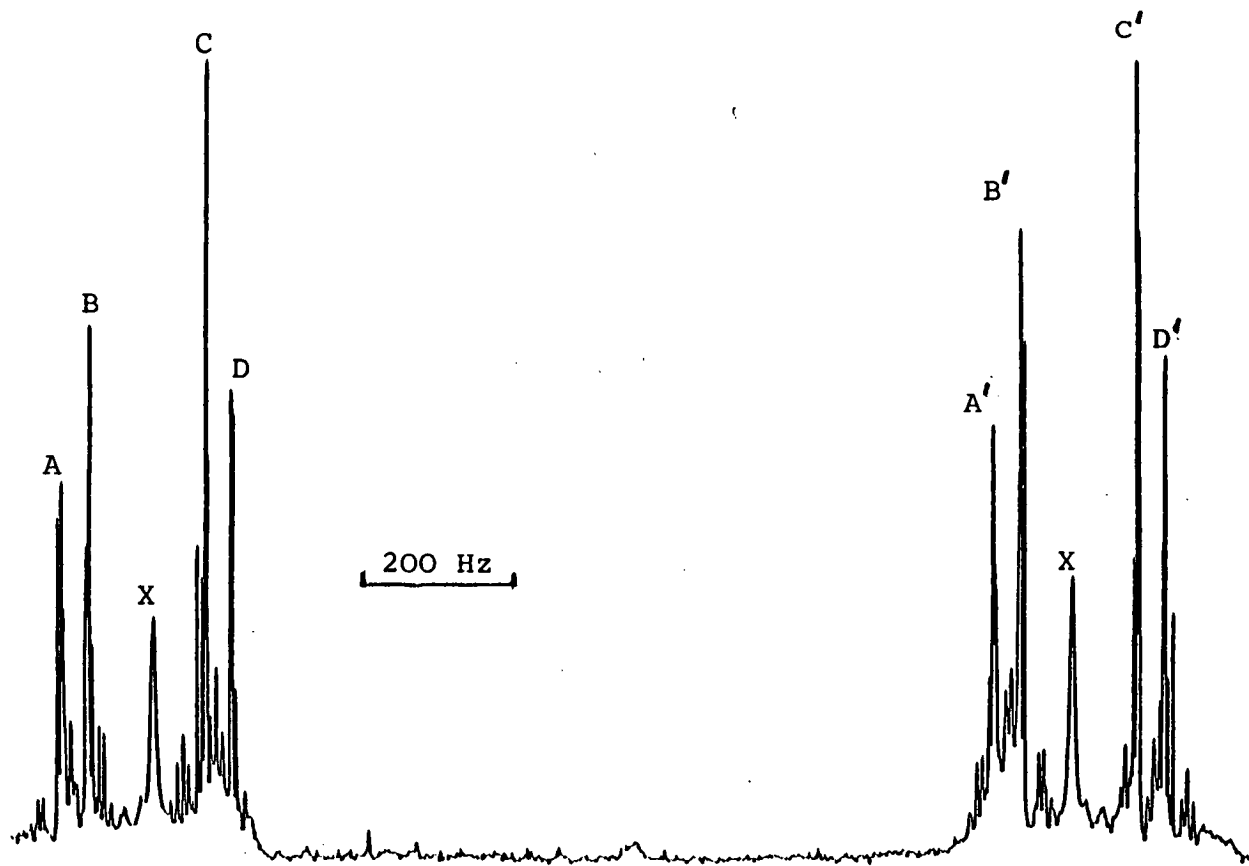
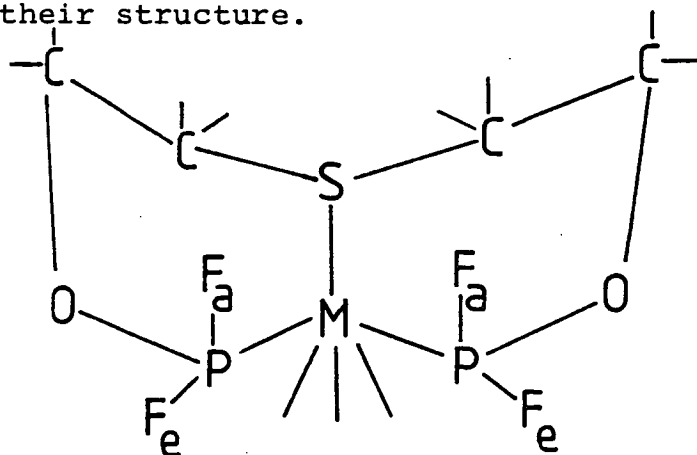


Table 2.4 N.M.R. Parameters of $S(CH_2CH_2OPF_2)_2$ adducts of $W(CO)_3$ and $Mo(CO)_3$

Metal	Mo	W
$\delta(F)$ /ppm	-15	-16
$\delta(P)$ /ppm	165	137
$^1J_{PF}$ /Hz	1236	1217
$^2J_{FF}$ /Hz	37	33
Difference in chemical shift/ppm of F and F'	2	2
Separation of broad lines (labelled X in Figs.) /Hz	1218	1200
$^1J_{PW}$ /Hz	-	444

The peaks which were symmetrical about the central peak of this pattern were measured and are shown in Fig. 2.4. The few peaks which did not fit into this pattern were presumably due to traces of other species which were not assigned but were obviously present in only small amounts. The ^{19}F n.m.r. spectrum of this species is much more complex and in its gross structure approximates to that expected for an $[\text{AXY}]_2$ spin system but could well be as complex as an ABWXYZ spin system. From Fig. 2.3 it can be seen that the ^{19}F n.m.r. spectrum of this complex approximates to a doublet ($^1J_{\text{PF}}$) of AB patterns i.e. an $[\text{AXY}]_2$ spin system. The two AB patterns are labelled ABCD and A'B'C'D'. The separation of the AB patterns i.e. AA', BB', CC' and DD' is 1236 Hz which is as expected from $^1J_{\text{PF}}$ measured from the ^{31}P n.m.r. spectrum. The separation of lines AB, CD, A'B', and C'D', due presumably to geminal FF coupling, is 37 Hz and the difference in chemical shifts of the two fluorine atoms is approximately 2 ppm. The other major feature of this spectrum is the broad lines among the AB patterns (labelled X). These are symmetrical about the centre of the AB patterns and are separated from each other by 1218 Hz. These lines may be part of a more complex second order pattern. It is of interest to compare the n.m.r. parameters of this species with those of $\text{PRO}(\text{OPF}_2)_2$ (R = F, Ph or ^1H , section 4.5). $^2J_{\text{FF}}$ is approximately double that found in these species. The chemical shift difference for geminal fluorines in complex I is much larger than that found in the compounds of type $\text{PRO}(\text{OPF}_2)_2$ suggesting that the fluorines in complex I are in very much more extreme chemical environments.

The chemical inequivalence of the geminal fluorines in this complex may be explained if the probable structure of this complex is considered. If the ligand is bound to the metal via the two phosphorus atoms and the sulphur atom as expected then the structure contains two six membered rings as shown below. These rings are similar to cyclohexane rings in their structure.

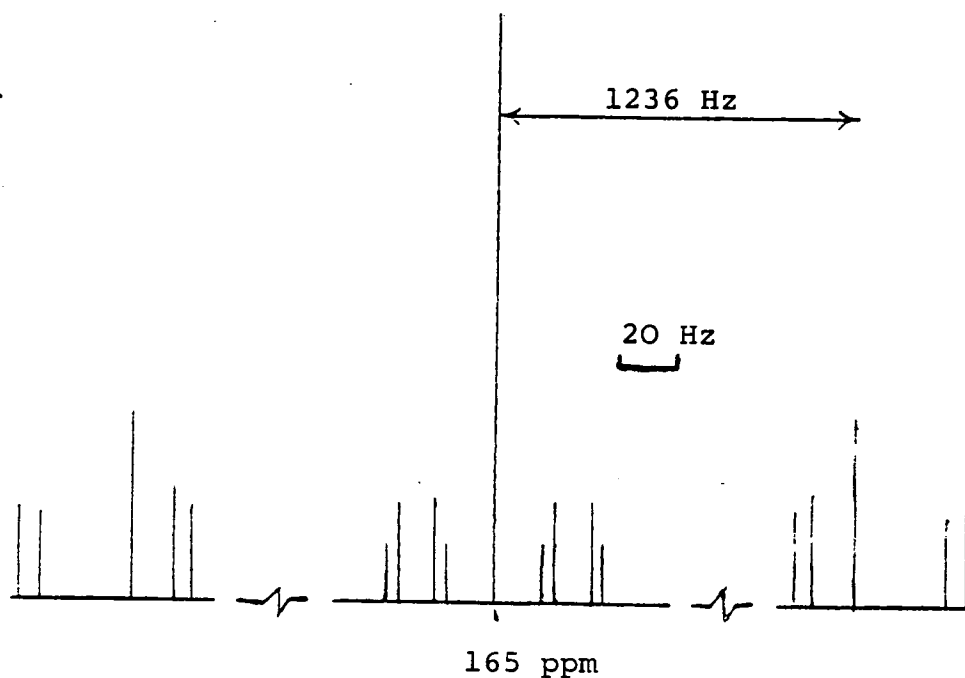


The fluorines would be expected to occupy roughly axial and equatorial positions with respect to the ring and interconversion might be expected to be slowed by the presence of two inter-linked rings which would have to interconvert simultaneously.

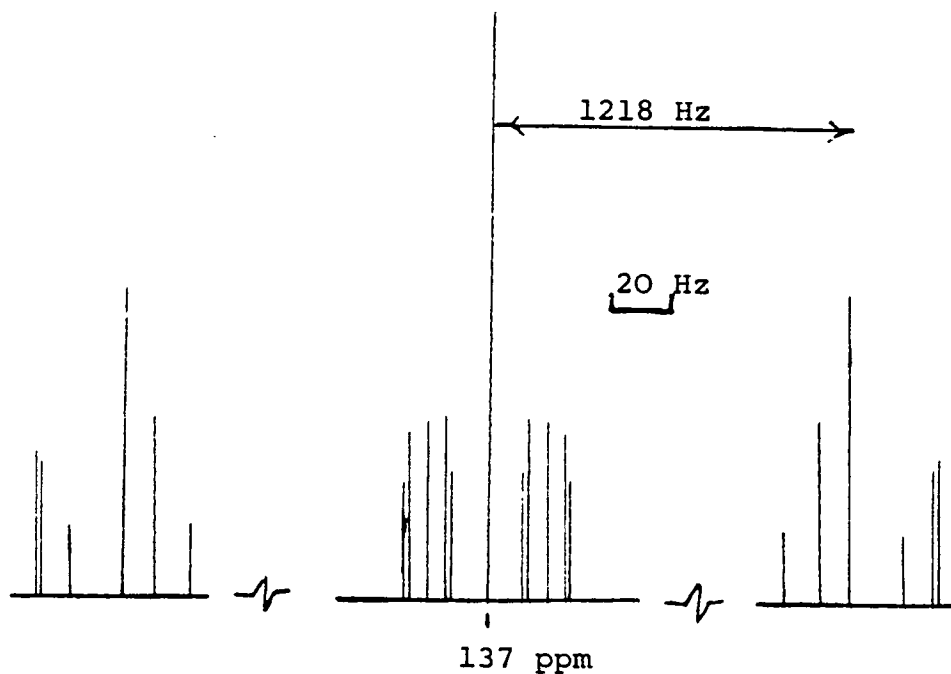
These rings could also be in different configurations with respect to each other and so all four fluorines might be chemically inequivalent. These factors could explain the complexity of the ^{19}F n.m.r. spectra and its approximation to an $[\text{AXY}]_2$ spin system. The phosphorus atoms appear to be accidentally equally coupled to each geminal fluorine resulting in a pattern in the ^{31}P n.m.r. spectrum which is of an $[\text{AX}_2]_2$ type. It is interesting to note that the chemically inequivalent geminal fluorines of the compounds $\text{PRO}(\text{OPF}_2)_2$ ($\text{R} = \text{H}, \text{F}, \text{Ph}$) couple to other parts of the molecule as if equivalent.

Fig. 2.4 Diagram of the AX_2X_2 Patterns found in the ^{31}P n.m.r. Spectra of the Mo and W Adducts of $\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$

Mo Species



W Species



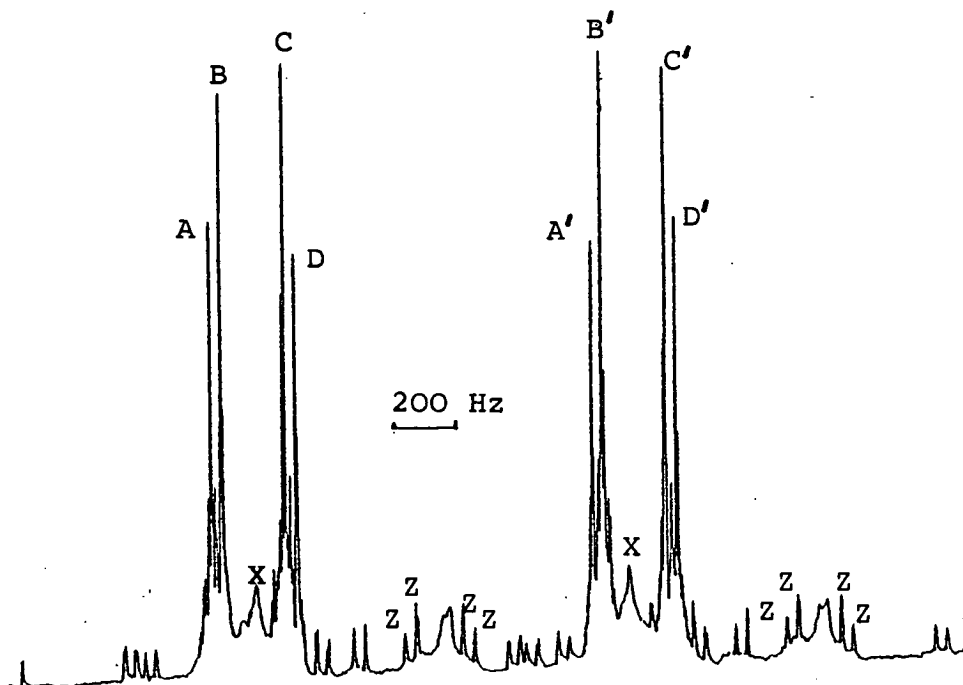
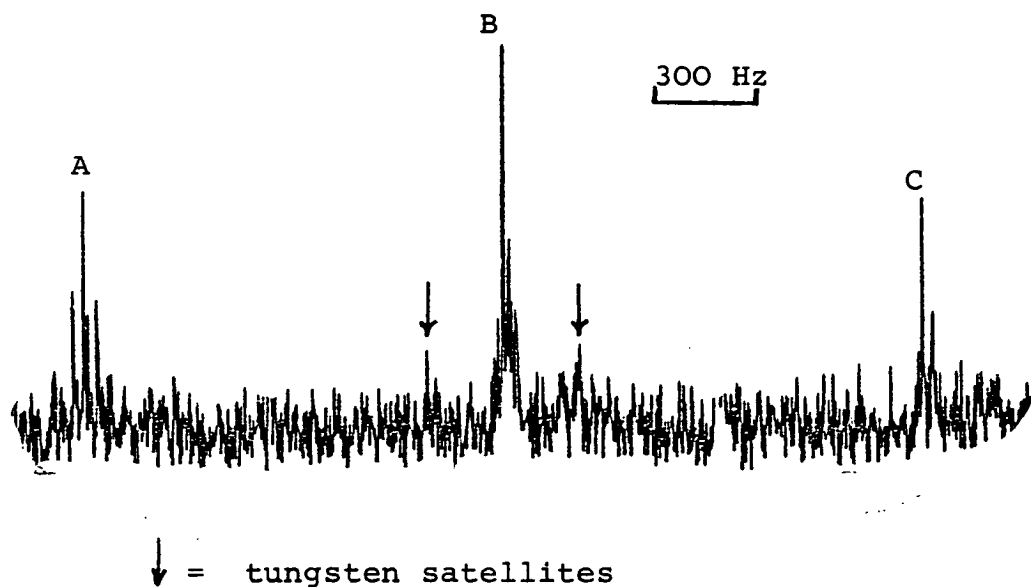
Also observed W satellites 222 Hz to either side of the main peak.

Further suggestion that these n.m.r. spectra have been correctly assigned comes from the observation that a related species was observed in n.m.r. spectra of the reaction mixture of $S(CH_2CH_2OPF_2)_2$ and $W(\text{cycloheptatriene})(CO)_3$ as described in the following part of this section.

(b) The Reaction between $S(CH_2CH_2OPF_2)_2$ and $W(CO)_3(\text{cycloheptatriene})$

This reaction was carried out on a small scale in a sealed n.m.r. tube and was followed by ^{31}P and ^{19}F n.m.r. spectroscopy as described in the experimental chapter. The reaction produced large amounts of solid material (presumably a polymeric species). The ^{31}P and ^{19}F n.m.r. spectra showed that one major product was present in solution. These spectra are shown in Fig. 2.5 and the major species present has been assigned as $W(S(CH_2CH_2OPF_2)_2)(CO)_3$, i.e. the tungsten analogue of the species described in the preceding part of this section. The overall features of the n.m.r. spectra of this compound are similar to those of the molybdenum analogue and the spectra have been analysed similarly. The ^{31}P spectrum shows a pattern which is of an $[AX_2]_2$ type; this is shown schematically in Fig. 2.4. This pattern shows a strong resemblance to that obtained for the molybdenum analogue. In addition peaks were found which have been assigned to those produced by coupling to ^{183}W , spin $\frac{1}{2}$, 14% abundance. These would be expected to be ca. 8% intensity relative to the main peaks which is as found. This value of $^1J_{PW}$ is given in Table 2.4 and is somewhat larger than those found in the related species $W(CO)_5PF_3$ and $W(CO)_4(PF_3)_2$

Fig. 2.5 The ^{31}P and ^{19}F n.m.r. Spectra of impure $\text{W}(\text{CO})_3\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$

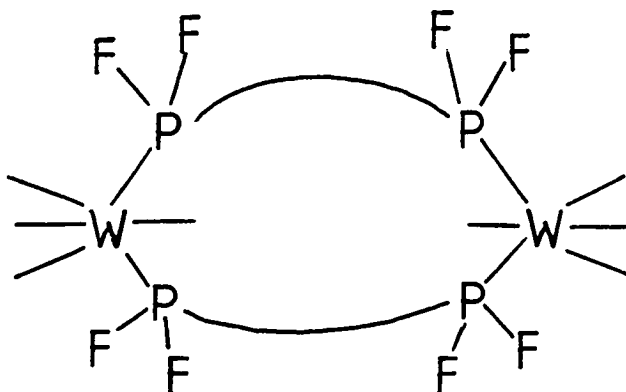


of 260 ± 10 Hz⁽⁴⁷⁾. Similarly ${}^2J_{WF}$ would be expected to be ca 30 Hz and these were not observed in the ${}^{19}\text{F}$ spectrum, probably due to overlapping signals and the complexity of the spectrum. The ${}^{19}\text{F}$ n.m.r. spectrum shows a species to be present which produces a spectrum similar to that observed for $\text{Mo}(\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2)(\text{CO})_3$ and this has been labelled by analogy in Fig. 2.5. In addition to the pattern expected, there are several other species present but due to their complexity most of these have not been assigned. One other species was however observed in the ${}^{19}\text{F}$ n.m.r. spectrum which was similar to the previously described species but present in much smaller amounts. Its n.m.r. parameters are described below. This species (labelled Z, Fig. 2.5) is clearly a doublet of AB patterns. The n.m.r. parameters extracted from this pattern are given below, assuming the AB coupling to be due to geminal FF coupling and the separation of the AB patterns to be ${}^1J_{PF}$ as for the previously mentioned species.

$\delta(\text{F})/\text{ppm}$	23
${}^1J_{PF}/\text{Hz}$	1235
${}^2J_{FF}/\text{Hz}$	35
differance in chemical shift of F and F'	2

The broad lines among these AB patterns clearly do not fit into a symmetrical pattern with them and are presumably due to some other species. There are also some other parts which on first glance appear to form a symmetrical pattern with

those of the AB pattern. On close inspection this was found not to be the case and these peaks have not been assigned. Presumably this other AB pattern and the other peaks observed are due to other complexes of $S(CH_2CH_2OPF_2)_2$ which may be of the type shown below or other condensed species.



At this stage it was decided to leave the study of these complexes in order that the more fruitful studies described in the following chapters could be carried out in the limited time available. The studies described in this chapter have however shown that there is scope for use of compounds such as $S(CH_2CH_2OPF_2)_2$ as multidentate ligands and that these may be preparatively useful if purification techniques can be developed.

CHAPTER 3

The Reaction of $S(PF_2)_2$ with Orthophosphoric Acid
and Derivatives of Orthophosphoric Acid.

The Preparation and Characterisation of
 $PO(OPF_2)_3$ and $PFO(OPF_2)_2$

Introduction

Following the successful preparation of $-OPF_2$ compounds by the reaction of alcohols with $S(PF_2)_2$ it was decided to try the reaction with other hydroxy compounds. Phosphoric acid and some of its derivatives was the next group of hydroxy compounds chosen for reaction with $S(PF_2)_2$. These hydroxy compounds were chosen since they were very stable, well known, and readily commercially available. Some of these reagents had several hydroxy groups per molecule and so the products of reaction with $S(PF_2)_2$ were expected to contain several $-PF_2$ groups and be potential multi-dentate ligands. The $-PF_2$ derivatives of these phosphorus compounds would also be expected to be of interest from the point of view of their ^{31}P and ^{19}F n.m.r. spectra.

Some organic derivatives of orthophosphoric acid were studied initially as these compounds were not hygroscopic, unlike orthophosphoric acid itself which is deliquescent and presented great handling difficulties as moisture had to be rigorously excluded. After successful reaction of the organic derivatives of orthophosphoric acid to form $-OPF_2$ compounds the reaction of orthophosphoric acid and fluorophosphoric acid were also studied. All reactions of $S(PF_2)_2$ with orthophosphoric

acid and its derivatives were studied on a small scale initially and followed by ^{31}P and ^{19}F n.m.r. spectroscopy. In some cases the reaction was then scaled up to a preparative or semi preparative level after the feasibility of the reaction as a synthetic route had been established by the small scale experiments. Since many hydroxy derivatives of phosphorus are known only a selected few compounds were chosen for reaction with $\text{S}(\text{PF}_2)_2$ in order that reactions of other compounds with $\text{S}(\text{PF}_2)_2$ could be studied in the time available.

The results of the experiments involving reaction of orthophosphoric acid and its derivatives with $\text{S}(\text{PF}_2)_2$ and preparation of the novel compounds produced are given in Section 3.1 below.

The sections following deal with the interpretation of the data obtained from a range of physical techniques. Sections 3.2, 3.3 and 3.4 deal with the mass spectra, n.m.r. spectra and vibrational spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$. These molecules have been compared with related compounds, particularly PF_3O and $\text{PF}_2\text{O}(\text{OPF}_2)$. Sections 3.5 and 3.6 deal with the n.m.r. spectra of $\text{PO}(\text{OPF}_2)\text{Ph}_2$ and $\text{PO}(\text{OPF}_2)_2\text{Ph}$ respectively. These two compounds were not isolated and n.m.r. spectra are the sole evidence for their existence and proposed structure. In Section 3.7 the reaction of $\text{PO}(\text{OPF}_2)_3$ with B_2H_6 as followed by ^{31}P and ^{19}F n.m.r. spectroscopy is described. Experimental procedures are described in Chapter 7.

Results and Discussion

3.1 Preparation and Properties of PO(OPF₂)₃ and PFO(OPF₂)₂

The following reaction was found to occur.



This reaction was found to be general for all n and R tried.

Compounds reacted are given in the table of n and R below.

n	R
3	-
2	Ph or F
1	Ph

The reaction was found to proceed in high yield and rapidly at room temperature. In all cases excess of S(PF₂)₂ was used in order to remove any traces of moisture present.

The novel compounds PO(OPF₂)₂Ph, PO(OPF₂)Ph₂, PO(OPF₂)₃ and PFO(OPF₂)₂ were characterised by ¹⁹F and ³¹P n.m.r. spectroscopy. The last two compounds were isolated using standard high vacuum techniques and characterised more comprehensively using vibrational spectroscopy and mass spectrometry in addition to n.m.r. spectroscopy. No attempt was made to isolate PO(OPF₂)Ph₂ and fairly pure PO(OPF₂)₂Ph was produced by simply pumping off the more volatile HPF₂S and S(PF₂)₂ from the reaction mixture.

In the case of PFO(OPF₂)₂ some PO(OPF₂)₃ was present as an impurity due to the presence of some orthophosphoric acid in the commercial fluorophosphoric acid. The presence of PO(OPF₂)₃ did not prove to be a great barrier to the characterisation of

PFO(OPF₂)₂ as the spectroscopic properties of the former compound were already known.

Both PO(OPF₂)₃ and PFO(OPF₂)₂ were found to be clear colourless liquids at room temperature. The physical properties of PO(OPF₂)₃ were measured and are given below.

M.Pt. = -19°C

V.P. (0°C) = 0.1 cm Hg

These properties and the observation that the compound crystallises readily to give rod like micro crystals suggest a significant intermolecular interaction in the condensed phases which is discussed further in Section 3.3.

3.2 The Mass Spectra of PO(OPF₂)₃ and PFO(OPF₂)₂

The mass spectra of PO(OPF₂)₃ and PFO(OPF₂)₂ were recorded and are tabulated in Tables 3.1 and 3.2. The metastable peaks observed are also recorded in those tables along with assigned parent and daughter ions.

These spectra must be viewed with a degree of caution as some peaks may be due to impurities produced by decomposition or reaction with water, oxygen or other species present in the spectrometer. Some products which may be expected to be produced by reaction of the samples in the instrument are PF₂HO, PF₃ and O(PF₂)₂. O(PF₂)₂ and PF₃ may also be expected to be produced as true fragments. Some PF₂HO was observed, but this was present in low abundance, indicating that there had been a little hydrolysis in the instrument. The sample of PFO(OPF₂)₂ was known to contain some PO(OPF₂)₃ as an impurity, and peaks due to this were observed.



Table 3.1 The Mass Spectrum of $\text{PO}(\text{OPF}_2)_3$

m/e	Relative (70 eV)	Abundance (11 eV)	Assignments
302	3	9	$[\text{PO}(\text{OPF}_2)_3]^+$
217	24	68	$[\text{PO}(\text{OPF}_2)_2]^+$
154	16	100	$[\text{O}(\text{PF}_2)_2]^+$
151	12	-	$[\text{F}_3\text{O}_2\text{P}_2]^+$
150	4	14	$[\text{F}_3\text{P}_2]^+$
148	4	18	$[\text{F}_2\text{O}_4\text{P}_2]^+$
135	8	-	$[\text{F}_3\text{OP}_2]^+$
129	10	-	$[\text{FO}_3\text{P}_2]^+$
88	10	27	$[\text{F}_3\text{P}]^+$
86	4	-	$[\text{PF}_2\text{HO}]^+$
85	4	-	$[\text{F}_2\text{PO}]^+$
69	100	41	$[\text{F}_2\text{P}]^+$
66	4	-	$[\text{FOP}]^+$
50	8	-	$[\text{FP}]^+$
47	24	-	$[\text{OP}]^+$
28	4	-	$[\text{N}_2]^+$

Metastable Peaks:-

m/e	Parent	Daughter
155.9	302	217
105.1	217	151
76.7	217	129
31.5	151	69
16.4	135	47

Notes: (a) Only peaks of intensity > intensity of molecular ion recorded except metastable peaks.

(b) Sample was entered as a gas.

Table 3.2 The Mass Spectrum of PFO(OPF₂)₂

m/e	Relative Abundance	Assignment
302	0.4	[PO(OPF ₂) ₃] ⁺
236	9	[PFO(OPF ₂) ₂] ⁺
217	3	[PO(OPF ₂) ₂] ⁺
170	7	[F ₄ O ₂ P ₂] ⁺
154	10	[O(PF ₂) ₂] ⁺
151	78	[F ₃ O ₂ P ₂] ⁺
135	4	[F ₃ OP ₂] ⁺
132	4	[F ₂ O ₂ P ₂] ⁺
129	5	[FO ₃ P ₂] ⁺
88	5	[F ₃ P] ⁺
86	6	[PF ₂ HO] ⁺
85	8	[F ₂ PO] ⁺
79	3	[O ₃ P] ⁺
69	100	[F ₂ P] ⁺
66	7	[FOP] ⁺
50	5	[FP] ⁺
47	15	[OP] ⁺
32	10	[O ₂] ⁺
28	44	[N ₂] ⁺

Metastable Peaks:

m/e	Parent	Daughter
96.6	236	151
76.7	217	129

Notes: Only peaks above 3% relative abundance measured other than those at m/e = 302 and metastables.

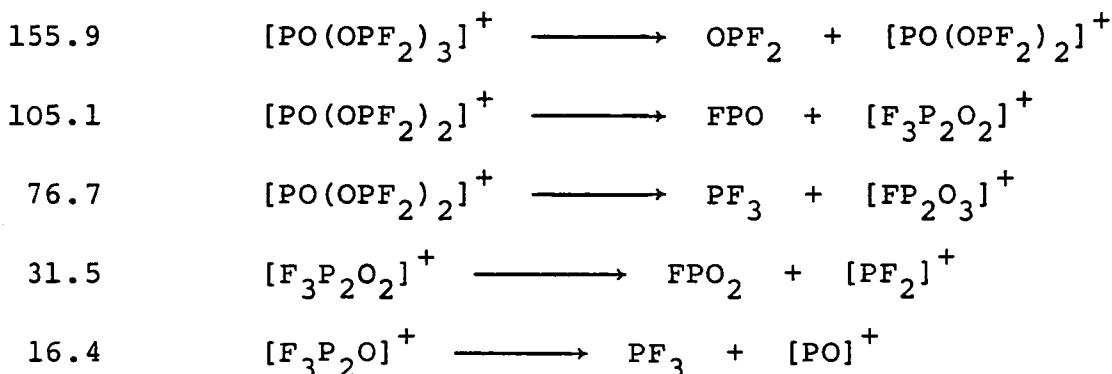
Ionising voltage = 70 eV

Sample was entered as a liquid.

Both samples show ions in common, indicating similar fragmentation modes. Some metastable peaks were observed in each spectrum and from these the following fragmentation routes were deduced.

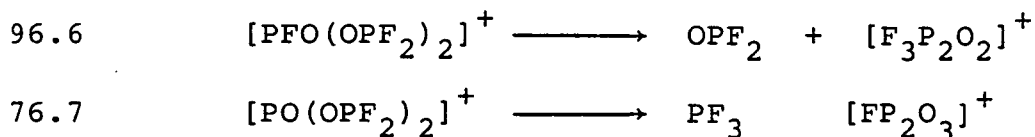
(a) for PO(OPF₂)₃

Metastable Peak



(b) for PFO(OPF₂)₂

Metastable Peak



In both spectra the most abundant ion was that of $[\text{PF}_2]^+$ as is found for most $-\text{PF}_2$ compounds. When the spectrum of $\text{PO}(\text{OPF}_2)_3$ was recorded at a lower ionising voltage the abundance of the molecular ion increased dramatically, as did that of the fragment ion $[\text{PO}(\text{OPF}_2)_2]^+$ (formed by loss of OPF_2).

This indicates that the fragmentation of the molecular ion proceeds to a large degree via loss of OPF_2 . Both compounds produce metastable peaks showing loss of OPF_2 to be a mode of fragmentation for the molecular ions. Further, the relative abundances of the molecular ions for the compounds $\text{PO}(\text{OPF}_2)_3$,

$\text{PFO}(\text{OPF}_2)_2$ and $\text{PF}_2\text{O}(\text{OPF}_2)$ are 3, 9 and 50%* respectively. This is in agreement with the idea that loss of OPF_2 was a major fragmentation route and that the more OPF_2 moieties present the more easily the molecular ion would break up.

In conclusion, the mass spectra support the suggested structures, and suggest that the molecular ion fragments primarily by loss of OPF_2 .

* corrected to relative abundance (w.r.t. to the most intense ion at 100% from %age of the total ionisation⁽²³⁾).

3.3 The Vibrational Spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$

(a) $\text{PO}(\text{OPF}_2)_3$

The infra red spectrum of this compound was recorded in the gas, liquid and solid phases. The raman spectrum was recorded in the liquid and solid phases. The compound readily crystallised on annealing the amorphous solid and so two sets of data were obtained in the solid state (amorphous and crystalline). The vibrational spectra are tabulated in Table 3.3.

The analysis of the vibrational spectra of this compound is difficult for three major reasons. Firstly, the conformation of the molecule is not known. The oxygen atoms will almost certainly be approximately tetrahedrally arranged around the central phosphorus atom. However, the overall symmetry of the molecule is dependent upon the orientation of the PF_2 groups. The PF_2 groups can be positioned in such a way that the molecule may belong to the point groups C_{3v} , C_3 , C_s or C_1 .

Table 3.3 Vibrational Spectra of PO(OPF₂)₃

GAS (ambt)	LIQUID (ambt)		AMORPH SOLID (-196°C)		CRYSTAL (-196°C)		ASSIGNMENT
	I.R.	I.R. Raman	I.R.	Raman	I.R.	Raman	
1345 m	1321 s	1314 m p	1298 m	1295 w	1258 s	1255 s	v(P = O)
1042 (sh+) w			1050 (sh+)		1057 s		}v(POP asym) impurity/hydroly product
988 vs	977 br s (916 w)		990 br s		1021 s		
867 vs	843 br s	860 vs p 841 s dp	835 br s	870 s 820 s	877 m 844 s 825 s 808 vs	853 s 808 s	v(PF)
	746 (sh+)m	735 m dp	743 w		743 w 734 m		v(POP sym)
728 m	710 m	661 s p	716 w 670 (sh+)w	725 m 665 vs	726 m	728 m	
529 m			535 m		616 m 611 m 507 m 499 s	613 s 505 m	bends and deformations
469 (sh+)w	509 m 474 (sh+)w	415 m dp	515 w 457 w 410 w	410 w	487 m 414 w 406 m 359 w 324 vw 296 vw	416 m 359 m 325 m 296 m 264 m	
399 vw			370 vw				
	not observed below 400cm ⁻¹ (K.Br. plates)	220 m dp spectrum poor quality due to decomposition of sample in laser beam (form of white solid) not recorded below 120cm ⁻¹		spectrum of poor quality not recorded below 250cm ⁻¹		broad hump ca 500cm ⁻¹ wide, centered at ca 700cm ⁻¹ "fluorescence?"	

sh = shoulder, arrow indicates on which peak.
w = weak, m = medium, s = strong
vs = very strong
br = broad
p = polarised
dp = depolarised
amb = ambient
peak positions are in cm⁻¹.

In any case there is likely to be fairly free rotation about PO bonds and so all these conformers may be present and may interconvert fairly readily. Secondly, the molecule contains fourteen atoms and so has thirty-six normal vibrational modes. Of these, there are thirteen stretching modes and twenty-three bending modes. Since many of the bending modes would be expected to be of similar energy and symmetry it is highly unlikely that they could be reliably assigned. Finally, the atoms are of comparable mass and mixing of vibrations may therefore occur. The concept of group frequencies is therefore not very helpful. Nevertheless, by comparison of the vibrational data, for related but simpler molecules, it is possible to assign the stretching frequencies with a reasonable degree of certainty.

In assigning these stretching frequencies use was made of the rule of thumb that the more highly symmetric stretches are stronger in the Raman spectra than in the infra red spectra and vice versa for the less highly symmetric stretches. Also a symmetric vibration gives rise to a polarised or partially polarised Raman line while a non-symmetric vibration produces a depolarised Raman line.

By considering initially the infra-red spectrum of the gaseous sample and the Raman spectrum of the liquid sample the following assignments were made.

The P=O stretch was expected to occur at approximately 1300 cm^{-1} and to be polarised in the Raman spectrum. This was therefore easily assigned. By comparison with the spectra of other PF_2 compounds the PF stretching frequencies were expected to occur around 800 cm^{-1} . These were expected to consist of both

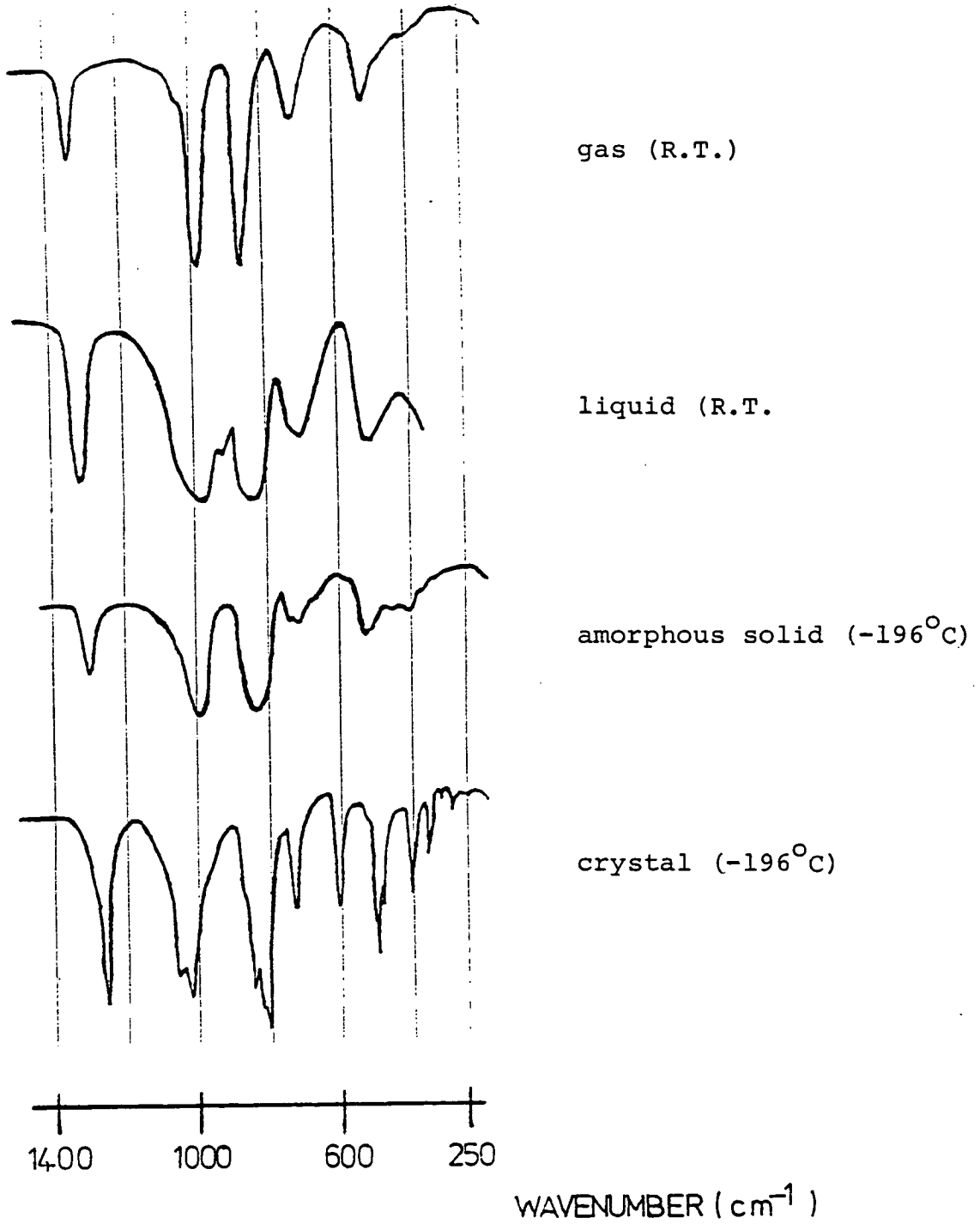
antisymmetric and symmetric stretches (for C_{3v} symmetry one would expect to get stretches of symmetry $a_1 + a_2 + e + e$) leading to both polarised and depolarised bands in the Raman spectrum as was found. Having assigned these stretches, only the PO stretches remained.

The PO stretches would be expected to combine to give POP antisymmetric and POP symmetric stretches. Further, these stretches may combine depending on the symmetry of the molecule. For example, if the overall symmetry was C_{3v} then the three POP symmetric (or POP antisymmetric) stretches would form POP symmetric (or POP antisymmetric) stretches one of which had a_1 symmetry and the other two e symmetry. If, however, the P-O stretches are simply considered as POP symmetric and POP antisymmetric, by comparison with $O(PF_2)_2$ ⁽²²⁾, the former would be expected to occur at approximately 680 cm^{-1} and the latter at approximately 980 cm^{-1} . The symmetric stretch would be expected to be strong and strongly polarised in the Raman of the liquid and vice versa for the antisymmetric stretch. The bands at ca. 700 cm^{-1} and ca. 1000 cm^{-1} were therefore assigned to POP symmetric and POP antisymmetric stretching frequencies respectively.

The infra-red spectra of $PO(OPF_2)_3$ in the gas, liquid and amorphous solid phases are composed of rather broad bands as shown in Fig. 3.1. On forming the crystalline solid by annealing the amorphous solid the bands sharpen and increase in number as expected.

The most striking feature observed in the vibrational spectra was the dependence of the phosphoryl stretching frequency on the

Fig. 3.1 I.R. Spectra of $\text{PO}(\text{OPF}_2)_3$



phase of the sample. The phosphoryl stretching frequency decreased progressively on condensing the sample from gas, through liquid to crystalline solid. The overall change was 90 cm^{-1} and is unlikely to be due to non-specific packing effects as the phosphoryl stretching frequency decreased by 40 cm^{-1} on annealing the amorphous solid. This suggests that there is some intermolecular interaction involving the phosphoryl group. The crystals formed were observed to be rod like by Barrow⁽⁶⁴⁾ on attempting to determine the low temperature crystal structure. Unfortunately the rod like micro crystals could not be grown into one single crystal and the attempt to determine the structure was abandoned. The observation that the crystals were rod like suggests some sort of interaction in which the molecules have formed long chains with little branching. It is only possible to guess at the nature of this intermolecular interaction without knowing the crystal structure. It is however likely to be one of two possible interactions:

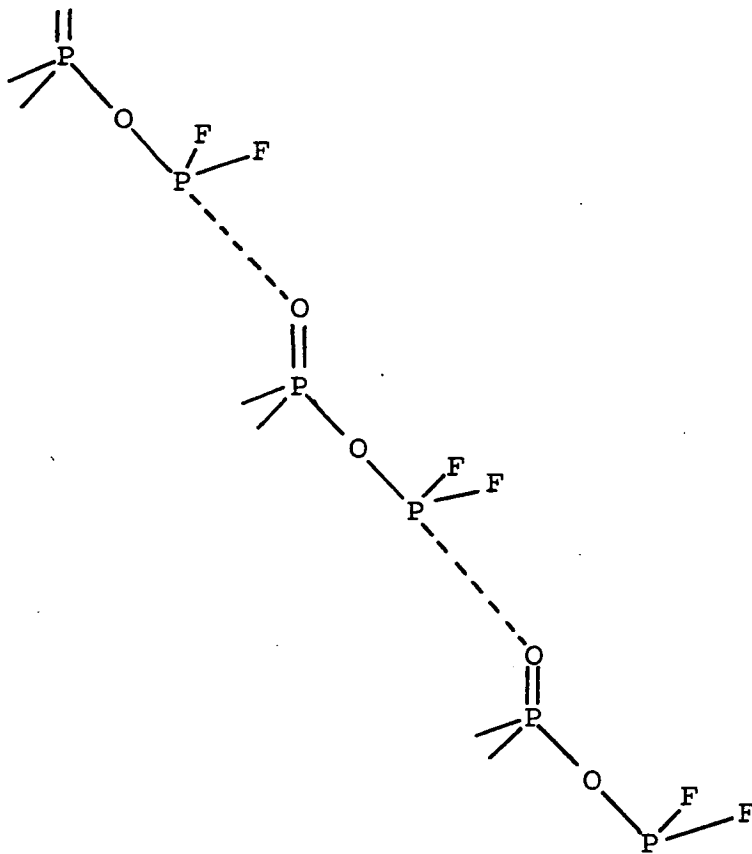
(a) The oxygen of the phosphoryl group may be interacting with the phosphorus of a difluorophosphine group on a neighbouring molecule. This would lead to a structure of type A in Fig. 3.2.

(b) The interaction may be purely between the oxygen and phosphorus in the phosphoryl groups of neighbouring molecules leading to a structure of the form labelled B in Fig. 3.2.

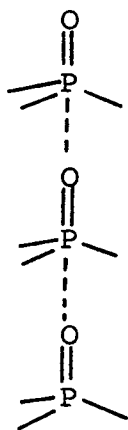
Some suggestion that structure A is more likely comes from the crystal structures of POX_3 ($\text{X} = \text{Br}$ and Cl)⁽⁶⁵⁾. These form rod like crystals in which the molecules interact to form

Fig. 3.2 Possible types of interaction between molecules of $\text{PO}(\text{OPF}_2)_3$ in the crystal.

Type A



Type B



chains linked by the oxygens of the phosphoryl group and one halogen of each molecule.

In any case this interaction has the effect of raising the melting point and lowering the vapour pressure of this compound from that which would be expected for a molecule containing only one oxygen more than $P(OPF_2)_3$ (see Chapter 4).

Compound	M.Pt.	V.P. ($^{\circ}C$)/cm Hg
$PO(OPF_2)_3$	-19	0.1
$P(OPF_2)_3$	-108 ± 2	2.0

It is of interest to compare the melting points of the phosphorus trihalides with those of the phosphoryl trihalides⁽⁶⁷⁾.

Compound	M.Pt./ $^{\circ}C$	Compound	M.Pt./ $^{\circ}C$
PBr_3	- 40	$POBr_3$	56
PCl_3	-112	$POCl_3$	2
PF_3	-151.5	POF_3	-68

The difference in melting points of PX_3 from POX_3 ($X = \text{halogen}$) is approximately 90 to $100^{\circ}C$ which is very similar to the difference in melting point between $P(OPF_2)_3$ and $PO(OPF_2)_3$. This suggests that there is some interaction in the compounds POX_3 and $PO(OPF_2)_3$ which is similar. Since $POBr_3$ and $POCl_3$ have been shown to interact in the solid phase as shown in Fig.3.2 (type A) this is further evidence for some related interaction in $PO(OPF_2)_3$ as was suggested earlier in this section.

The Infra-Red Spectrum of Gaseous PFO(OPF₂)₂

The infra-red spectrum of PFO(OPF₂)₂ was recorded in the gas phase only. The compound was slightly impure with PO(OPF₂)₃ but this would be expected to have no effect on band positions of this species in the infra-red of the compound in the gas phase. The presence of this impurity would however be expected to cause some change in the properties of the compound i.e. its M.Pt. and perhaps interaction in the solid phase. Therefore a full study of the vibrational spectra in several phases was considered to be pointless as molecular interaction of the impurity may affect the spectra. In the gas phase the two different molecules should not interact so bands due to the impurity could be recognised by comparison with standard spectra of pure PO(OPF₂)₃.

The spectrum of PFO(OPF₂)₂ was very similar to that of PO(OPF₂)₃ and so was easily assigned. The spectrum of PFO(OPF₂)₂ contained one extra band which was assigned to the P(V)-F stretch as in Table 3.4.

It was noted that the phosphoryl stretch of PFO(OPF₂)₂ occurred at a higher frequency than that of PO(OPF₂)₃. This prompted a comparison with the phosphoryl stretch of PF₂O(OPF₂) and PF₃O. It was observed that the phosphoryl stretch increased in frequency on increasing the number of fluorines attached to the phosphorus of the phosphoryl group for the compounds of general formula POF_(n)(OPF₂)_(3-n) as shown below.

n	0	1	2	3
vp = O/cm ⁻¹	1345	1365	1384	1415
reference	-	-	(23)	(68)

Note: all samples were run as gases.

Table 3.4 The I.R. Spectrum of gaseous $\text{PFO}(\text{OPF}_2)_2$

Absorption/ cm^{-1}	Assignment
1365 s	$\nu\text{P} = \text{O}$
1005 vs	νPOP asym.
930 vs	$\nu\text{P}^{\text{V}}\text{-F}$
865 vs	$\nu\text{P}^{\text{III}}\text{-F}$
725 s	νPOP sym.
530 m	PF_2 scissors

Note: v = very, s = strong, m = medium

Spectrum not recorded below 400 cm^{-1}

3.4 The ^{31}P and ^{19}F n.m.r. Spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$

(1) The ^{31}P and ^{19}F n.m.r. Spectra of $\text{PO}(\text{OPF}_2)_3$

The ^{31}P and ^{19}F n.m.r. spectra of $\text{PO}(\text{OPF}_2)_3$ were recorded and are shown in Figures 3.3 and 3.4 respectively. The n.m.r. parameters extracted from these spectra are tabulated in Table 3.5 along with those of some related compounds for comparison.

This spin system is of interest as the molecule contains ten spin $\frac{1}{2}$ nuclei and provides an example of a molecule containing both phosphorus V and phosphorus III. The molecule contains three PF_2 groups and so would be expected to show second order spectra associated with these groups coupling to each other.

When observed at a resolution of only a few hertz the ^{31}P and ^{19}F n.m.r. spectra appear deceptively simple. The ^{31}P n.m.r. spectrum is shown in Fig. 3.3. There are two distinct phosphorus signals. The lines due to the difluorophosphino moieties (labelled A, B, C, D, E and F) are essentially a triplet (ca. $^1J_{\text{PF}}$) of doublets ($^2J_{\text{PP}'}$). On closer inspection this pattern is seen to be more complex, each "line" being a multiplet. "Lines" A and B are indential in structure and are mirror images of E and F about the centre of the pattern. "Lines" C and D are identical in structure. Therefore the fine structure of only two lines need be shown to define the pattern and that of lines A and C is shown in Fig. 3.3.

The tabulated value of $^1J_{\text{PF}}$, given in Table 3.5, is really the separation of lines A and C which is $^1J_{\text{PF}} + 2^5J_{\text{PF}}$.

Fig. 3.3 ^{31}P n.m.r. Spectrum of $\text{PO}(\text{OPF}_2)_3$

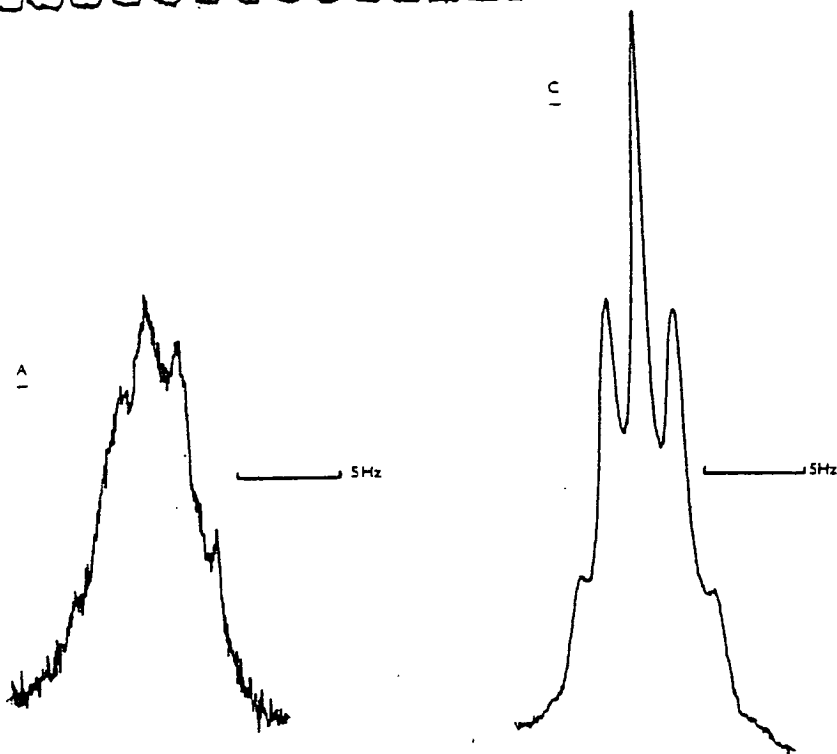
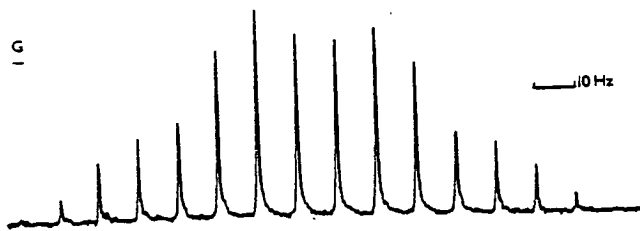
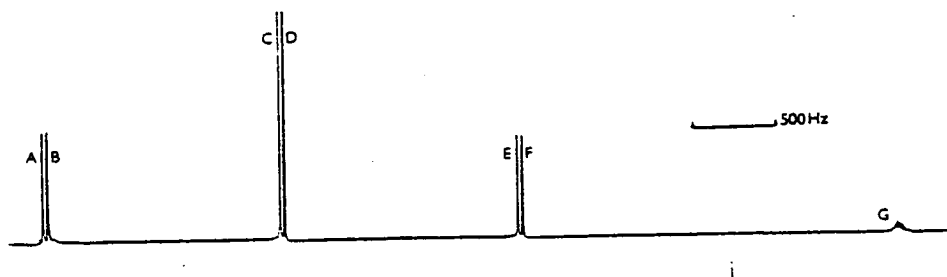


Fig. 3.4 ^{19}F n.m.r. spectrum of $\text{PO}(\text{OPF}_2)_3$

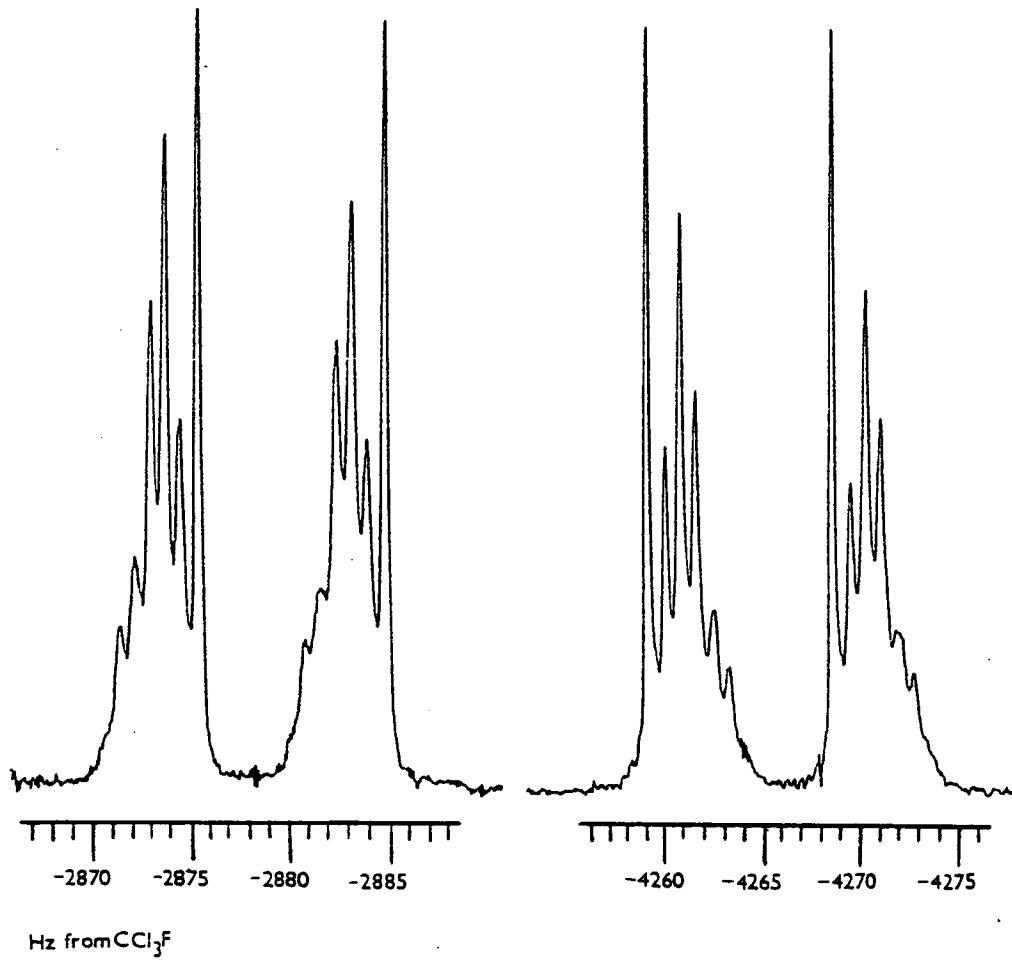


Table 3.5 ^{31}P and ^{19}F n.m.r. Parameters of $\text{PO}(\text{OPF}_2)_3$, $\text{POF}(\text{OPF}_2)_2$ and some Related Compounds

Compound	$\text{P}'\text{OF}'_3$	$\text{OP}'\text{F}'_2\text{OPF}_2$	$\text{OP}'\text{F}'(\text{OPF}_2)_2$	$\text{PO}(\text{OPF}_2)_3$
$\delta(\text{P}')/\text{ppm}$	-35.5	10*	-37.5	-40.8
$\delta(\text{P})/\text{ppm}$	-	150*	106.8	107.9
$\delta(\text{F}')/\text{ppm}$	-94	-80.0	-66.2	-
$\delta(\text{F})/\text{ppm}$	-	-38.3	-37.2	-37.5
$^1\text{J}_{\text{P}'\text{F}'}/\text{Hz}$	1055	1032.5	1024.9	-
$^1\text{J}_{\text{PF}'}/\text{Hz}$	-	1396.4	1390 ^a	1385 ^a
$^2\text{J}_{\text{PP}'}/\text{Hz}$	-	n.o.	32.5	28.9
$^3\text{J}_{\text{P}'\text{F}'}/\text{Hz}$	-	n.o.	9.4	9.5
$^3\text{J}_{\text{PF}'}/\text{Hz}$	-	n.o.	n.o.	-
$^4\text{J}_{\text{FF}'}/\text{Hz}$	-	n.o.	n.o.	-
$^2\text{J}_{\text{FF}'}/\text{Hz}$ (of PF_2 group)	-	-	21	-
difference in chemical shift of/ppm geminal fluorines	-	-	0.17	-
Solvent			CDCl_3	CDCl_3
Reference	(59,66)	(23)		

Notes: (a) approximate value of $^1\text{J}_{\text{PF}'}$, see text

* see text, corrected from reference P_4O_6 to H_3PO_4 by subtraction of 113 ppm.

${}^5J_{PF}$ would be expected to be small and so this separation approximates to ${}^1J_{PF}$.

The signal due to the phosphorus of the phosphoryl group (labelled G) was truly first order and consists of a quartet (${}^2J_{PP'}$) of septets (${}^3J_{P'F}$). However, ${}^3J_{P'F}$ is approximately one third the magnitude of ${}^2J_{PP'}$ and so some lines overlap and only sixteen lines are seen. The intensity pattern which would be predicted is

1:6:15:21:21:21:22:21:21:22:21:21:21:15:6:1

This intensity pattern was not exactly the same as that found due to imperfect overlap of lines.

The ${}^{19}F$ n.m.r. spectrum of $PO(OPF_2)_3$ (shown in Fig. 3.4) was also second order, but again was deceptively simple at low resolution. It appeared to be a doublet (${}^1J_{PF}$) of doublets (${}^3J_{P'F}$) as expected for this molecule. No attempt was made to analyse the second order parts of these spectra as they were not very well resolved and $(AX_2)_3$ systems are very complex.

(II) The ${}^{31}P$ and ${}^{19}F$ n.m.r. Spectra of $PFO(OPF_2)_2$

The ${}^{31}P$ and ${}^{19}F$ n.m.r. spectra of $PFO(OPF_2)_2$ were recorded and are shown in Figures 3.5 and 3.6 respectively. The n.m.r. parameters for this molecule are tabulated in Table 3.5 along with those of $PO(OPF_2)_3$ and two related compounds.

As already mentioned the compound contained some $PO(OPF_2)_3$ as an impurity and peaks due to this are labelled in the spectra shown.

The ${}^{31}P$ and ${}^{19}F$ n.m.r. spectra of this molecule are complex. In this molecule the geminal fluorines in difluorophosphino

Fig. 3.5 The ^{31}P n.m.r. Spectrum of $\text{PFO}(\text{OPF}_2)_2$
(Peaks labelled * due to $\text{PO}(\text{OPF}_2)_3$ impurity)

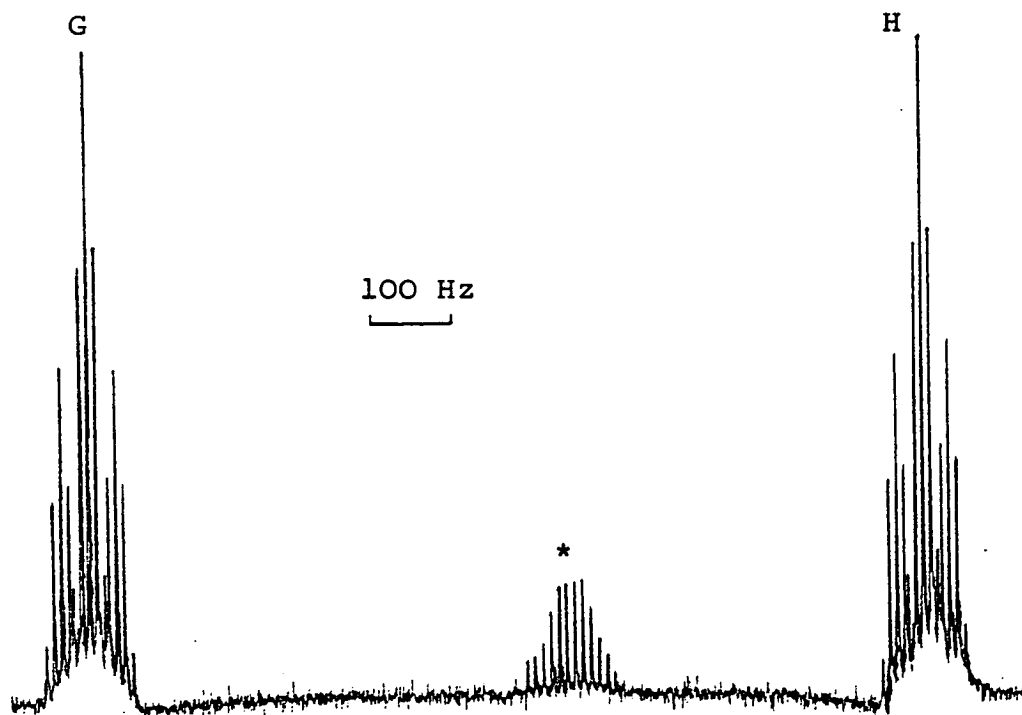
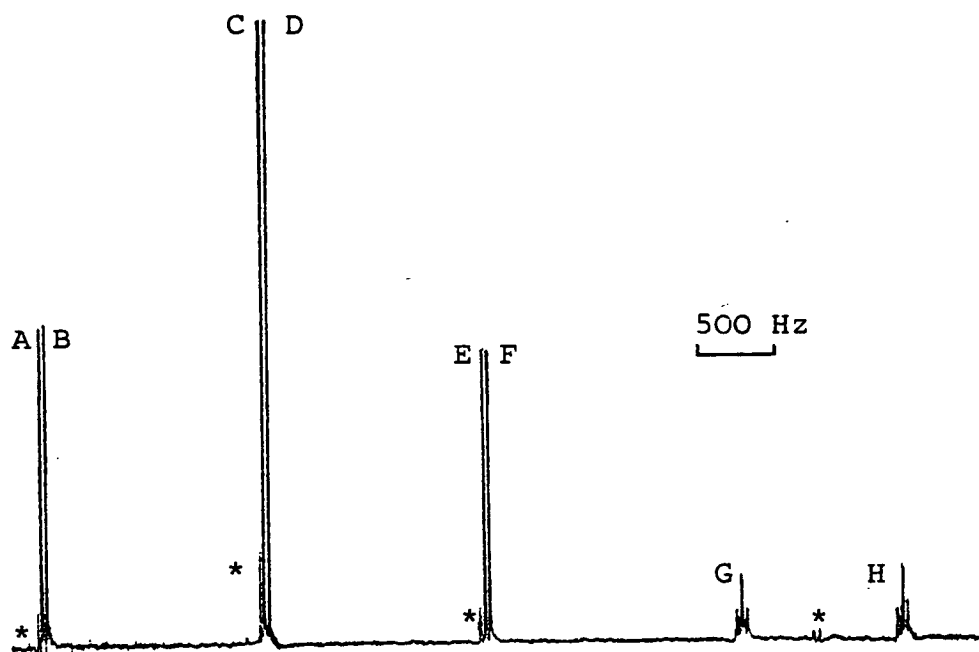
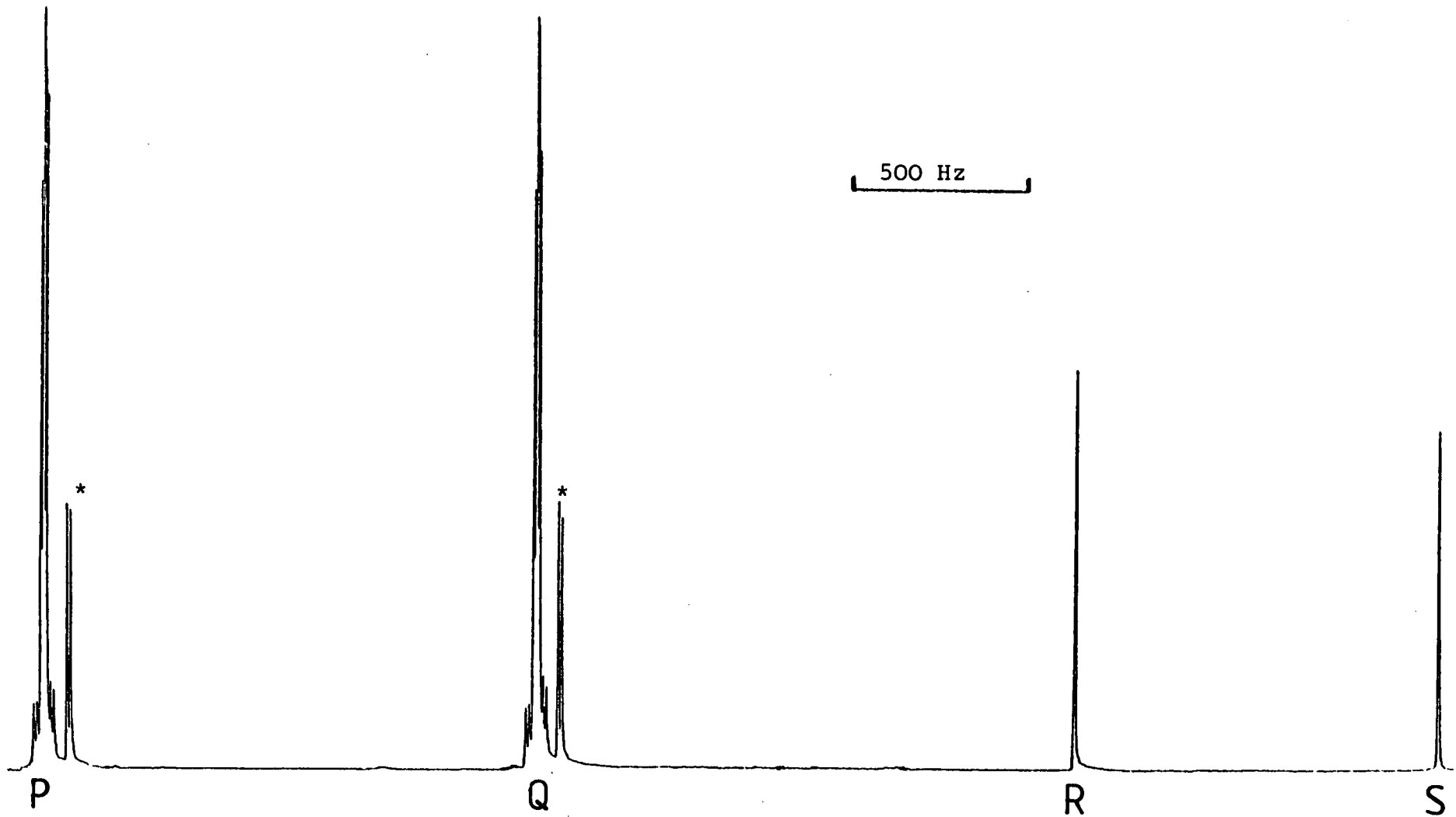


Fig. 3.6 ^{19}F n.m.r. Spectrum of $\text{PFO}(\text{OPF}_2)_2$

(Peaks labelled * due to $\text{PO}(\text{OPF}_2)_3$ impurity)



groups are inequivalent due to the prochiral centre at the phosphorus of the phosphoryl group. Therefore, not only are there two types of chemically different phosphorus but there are three types of chemically inequivalent fluorine atoms.

The presence of two $-PF_2$ groups would also be expected to lead to second order spectra similar to those obtained for $PO(OPF_2)_3$. However, the second order patterns due to interaction of the PF_2 groups were not clearly resolved in the spectra obtained and are not discussed further.

The ^{31}P n.m.r. spectrum of $P'FO(OPF_2)_2$ (Fig. 3.5) is as expected for this molecule. The phosphoryl group gives rise to a doublet (labelled G and H) ($^1J_{P',F}$) of triplets ($^2J_{PP'}$) of quintets ($^3J_{P',F}$). The signals due to the phosphorus of the PF_2 groups (labelled A, B, C, D, E and F) consisted of a triplet ($^1J_{PF}$) of doublets ($^2J_{PP}$).

The ^{19}F n.m.r. spectrum of $PFO(OPF_2)_2$ (shown in Fig. 3.6) consists of a complex pattern due to the fluorines of the PF_2 groups (labelled P and Q). This pattern consisted of a doublet ($^1J_{PF}$) of doublets ($^3J_{PF}$) of AB patterns. The AB patterns were due to coupling ($^2J_{FF}$) between the slightly inequivalent fluorines on the PF_2 group. These patterns were analysed by standard methods⁽⁷⁰⁾ and the parameters obtained are listed in Table 3.5.

One extra line was observed in the ^{19}F spectra among each AB pattern and this may have been due to another conformer or an impurity.

The ^{19}F n.m.r. spectrum also showed a simple doublet ($^1J_{P',F'}$) due to the fluorine directly attached to the phosphoryl

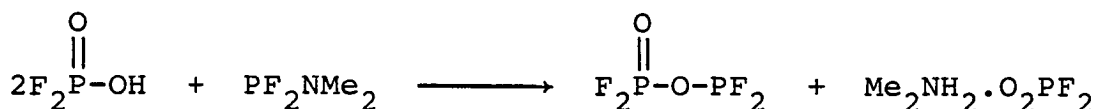
group (labelled R and S). This doublet showed no other splitting.

The n.m.r. spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$ obtained are consistent with the proposed structures and suggest a high level of purity in the former compound. It is interesting to compare the n.m.r. parameters of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$ with each other and with those of the related compounds $\text{PF}_2\text{O}(\text{OPF}_2)$ and PF_3O . These four compounds form a series with the general formula $\text{P}'\text{F}'(n)\text{O}(\text{OPF}_2)(3-n)$ where $n = 0, 1, 2$ or 3 . The parameters for these four compounds are given in Table 3.5. These parameters may well be expected to vary as n varies. Surprisingly most of these parameters are almost invariant, particularly $\delta(\text{P})$, $\delta(\text{F})$ and $^1\text{J}_{\text{PF}}$. The only parameter in which a clear trend can be seen is $\delta(\text{F}')$ which moves to a progressively lower frequency as n increases. Noticably $^1\text{J}_{\text{P}^{\text{III}}\text{F}}$ is larger than $^1\text{J}_{\text{P}}\text{V}_{\text{F}}$ as is normally found. Clearly the parameters of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$ are consistent with those expected by comparison with PF_3O and $\text{PF}_2\text{O}(\text{OPF}_2)$ and so the structures are certainly as assigned. In particular there seems little likelihood of an isomer with a P-P bond as this would be expected to result in a much larger PP coupling of several hundred hertz magnitude⁽⁶⁹⁾: also this would require a $\text{F}_2\text{P}(\text{O})$ -group to be present which would be expected to have much lower chemical shift and $^1\text{J}_{\text{PF}}$ of the same order as $^1\text{J}_{\text{P}'\text{F}'}$, which was not found.

It is interesting to note that neither $^2\text{J}_{\text{PP}'}$, nor $^3\text{J}_{\text{P}'\text{F}'}$ were observed by Chalton and Cavell in the n.m.r. spectra of $\text{PF}_2\text{O}(\text{OPF}_2)$ and they have suggested that this may be due to rapid rotation about the POP unit or some other rapid averaging

process. By comparison with the related compounds $\text{PFO}(\text{OPF}_2)$ and $\text{PO}(\text{OPF}_2)_3$ it would be expected that $\text{PF}_2\text{O}(\text{OPF}_2)_2$ would show substantial coupling between the PF_2 group and the phosphoryl phosphorus. It therefore seems likely that $^2J_{\text{PP}}$ and $^3J_{\text{PF}}$ were not observed in the n.m.r. spectra of this molecule due to some sort of rapid intermolecular exchange process. This seems likely as $\text{PF}_2\text{O}(\text{OPF}_2)$ is reported to be rather unstable and decomposition products could participate in such a scrambling process.

$\text{O}(\text{PF}_2)_2$ has been reported to decompose readily in the presence of an adsorbent surface such as asbestos⁽²²⁾ and it is likely that a similar process would occur for $\text{PF}_2\text{O}(\text{OPF}_2)$. Since the synthetic route used by Charton and Cavell for the preparation of $\text{PF}_2\text{O}(\text{OPF}_2)$ involved the production of a solid it is possible that this solid is one cause for the reported instability of this compound particularly in the reaction mixture. The decomposition of $\text{PF}_2\text{O}(\text{OPF}_2)$ results in the formation of PF_3 and an unidentified white solid. It is likely that this white solid acts as an adsorbent surface enhancing the decomposition of this compound and so the decomposition may be auto catalytic in nature.



It would therefore be worthwhile investigating the reaction of difluorophosphoric acid with $\text{S}(\text{PF}_2)_2$ which would be expected to occur as shown below by analogy with the reaction of phosphoric and fluorophosphoric acid with $\text{S}(\text{PF}_2)_2$. This reaction would not generate any solid material to enhance the

decomposition of the product and so should be superior to that used by Charton and Cavell.



This reaction should occur under mild conditions and could be carried out at reduced temperature in a sealed n.m.r. tube. After reaction it should be possible to observe the species present by ^{31}P and ^{19}F n.m.r. to see if $^2\text{J}_{\text{PP}}$ and $^3\text{J}_{\text{PF}}$ could be detected.

It is also notable that no coupling was observed even at -90°C between the PF_2 group and the phosphoryl phosphorus in $\text{PO}(\text{OPF}_2)_2$ as mentioned in Section 3.6. This suggests that there may be a phenomenon peculiar to the compounds $\text{PO}(\text{OPF}_2)_2$ ($\text{R} = \text{Ph}$ or F) which results in loss of coupling between the two phosphorus atoms. It would be worthwhile investigating this further by studying other molecules of type $\text{PO}(\text{OPF}_2)_2$. The nature of this possible phenomenon is not clear but could involve an intermolecular exchange process.

3.5 The Reaction of $\text{PO}(\text{OH})_2\text{Ph}$ with $\text{S}(\text{PF}_2)_2$. The Preparation of $\text{PO}(\text{OPF}_2)_2\text{Ph}$.

The reaction of $\text{PO}(\text{OH})_2\text{Ph}$ with $\text{S}(\text{PF}_2)_2$ was investigated. This reaction was carried out initially in a sealed n.m.r. tube and followed by ^{31}P and ^{19}F n.m.r. spectroscopy. The reaction produced $\text{PO}(\text{OPF}_2)_2\text{Ph}$ and PF_2HS but difficulty was experienced in obtaining good n.m.r. spectra of $\text{PO}(\text{OPF}_2)_2\text{Ph}$. For this reason it was decided to prepare $\text{PO}(\text{OPF}_2)_2\text{Ph}$ and attempt to purify it. The reaction was then carried out in

an ampoule fitted with an n.m.r. tube. After the reaction had occurred the volatile components were removed onto a vacuum line and solvent added to the product in the n.m.r. tube before sealing this off and recording the n.m.r. spectra (see Experimental Section). This procedure, though crude, resulted in the preparation of a fairly pure sample of $\text{PO}(\text{OPF}_2)_2\text{Ph}$ with only very small amounts of PF_2HS present.

The ^{31}P and ^{19}F n.m.r. spectra of $\text{PO}(\text{OPF}_2)_2\text{Ph}$ were then recorded and parameters obtained are given in Table 3.6. The ^{31}P n.m.r. spectrum showed that there were two chemically different phosphorus groups present as expected for $\text{PO}(\text{OPF}_2)_2\text{Ph}$. The phosphoryl phosphorus produced a triplet ($^2\text{J}_{\text{PP}}$) of quintets ($^3\text{J}_{\text{PF}}$). The phosphorus of the PF_2 groups produced signals consisting of triplets ($^1\text{J}_{\text{PF}}$) of doublets ($^2\text{J}_{\text{PP}}$). These lines were not observed at higher resolution but would be expected to be second order due to coupling between the magnetically inequivalent PF_2 groups. c.f. $\text{PO}(\text{OPF}_2)_3$.

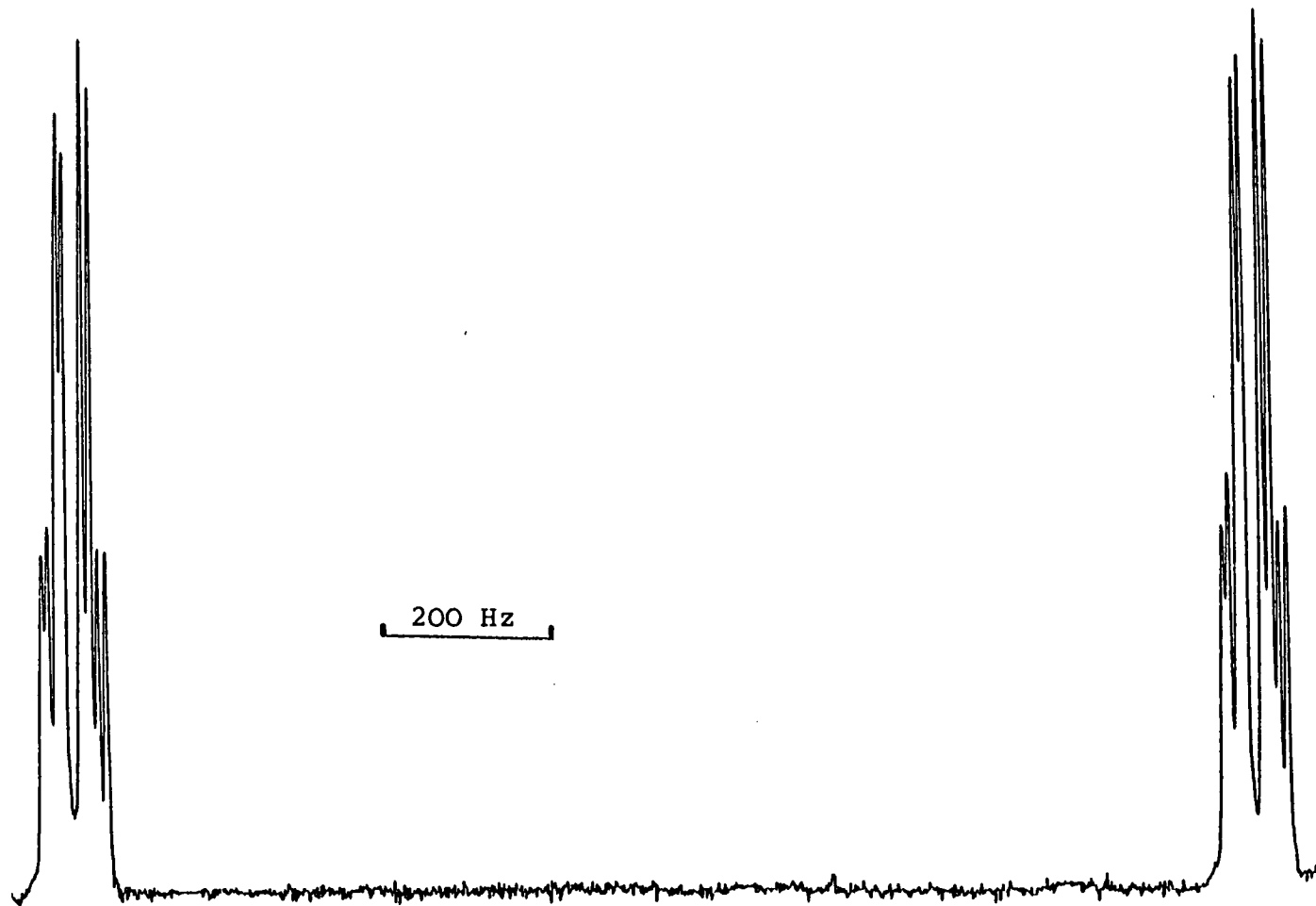
The ^{19}F n.m.r. spectrum of this molecule was of interest as there is a prochiral centre on the phosphoryl phosphorus. The geminal fluorines of the PF_2 groups are therefore chemically inequivalent and $^2\text{J}_{\text{FF}}$ was observed. The fluorine n.m.r. spectrum therefore consisted of a doublet ($^1\text{J}_{\text{PF}}$) of doublets ($^3\text{J}_{\text{PF}}$) of AB patterns (due to $^2\text{J}_{\text{FF}}$). This is shown in Fig. 3.7. The AB pattern was analysed by standard methods⁽⁷⁰⁾ and the parameters obtained are given in Table 3.6. The n.m.r. parameters of this molecule were compared with those of POPh_3 , $\text{PO}(\text{OPF}_2)_3$ and $\text{PO}(\text{OPF}_2)_2\text{Ph}_2$ and are discussed in Section 3.6 below.

Table 3.6 ^{31}P and ^{19}F n.m.r. Parameters of $\text{PO}(\text{OPF}_2)_2\text{Ph}_2$,
 $\text{PO}(\text{OPF}_2)_2\text{Ph}$, $\text{PO}(\text{OPF}_2)_3$ and POPh_3 .

Compound	$\text{P}'\text{OPh}_3$	$\text{P}'\text{O}(\text{OPF}_2)\text{Ph}_2$	$\text{P}'\text{O}(\text{OPF}_2)_2\text{Ph}$	$\text{P}'\text{O}(\text{OPF}_2)_3$
$\delta(\text{P})/\text{ppm}$	-	113.7	110.7	107.9
$\delta(\text{P}')/\text{ppm}$	29	30.4	1.4	-40.8
$\delta(\text{F})/\text{ppm}$	-	-39.7	-38.6*	-37.5
$^1\text{J}_{\text{PF}}/\text{Hz}$	-	1358	1363	1385
$^2\text{J}_{\text{PP}}/\text{Hz}$	-	n.o.	17.8	28.9
$^3\text{J}_{\text{PF}}/\text{Hz}$	-	n.o.	7.5	9.5
$^2\text{J}_{\text{FF}}/\text{Hz}$	-	-	19	-
difference in chemical shift of geminal fluorines /ppm	-	-	0.46	-
Solvent		CD_2Cl_2	CDCl_3	CDCl_3

Notes: * Average chemical shift of geminal fluorines.

Fig. 3.7 ^{19}F n.m.r. Spectrum of $\text{PO}(\text{OPF}_2)_2\text{Ph}$



3.6 The Reaction of PO(OH)Ph₂ with S(PF₂)₂. The Preparation of PO(OPF₂)Ph₂.

The reaction of PO(OH)Ph₂ with S(PF₂)₂ was carried out in a sealed n.m.r. tube and followed by ³¹P and ¹⁹F n.m.r. spectroscopy. As expected, PO(OPF₂)Ph₂ and PF₂HS were produced. The ³¹P n.m.r. spectrum of PO(OPF₂)Ph₂ showed two types of phosphorus but no interaction between them. Thus, only a triplet (¹J_{PF}) and a singlet were observed. The ¹⁹F n.m.r. spectrum of this compound was a doublet (¹J_{PF}). ²J_{PP} and ³J_{PF} would be expected to be observed in this compound by comparison with the related species shown in Table 3.6. This suggests that some exchange process is taking place and this is further suggested by the observation that the lines in the ³¹P spectrum of this compound sharpened but did not split on recording the spectrum at -80°C rather than at room temperature. Presumably this exchange process is rapid even at -80°C. The signal due to the phosphoryl phosphorus was particularly broad at R.T., being ca. 50 Hz width at half height. This was reduced to at least a third of this width at -80°C.

3.7 The Reaction of PO(OPF₂)₃ with B₂H₆

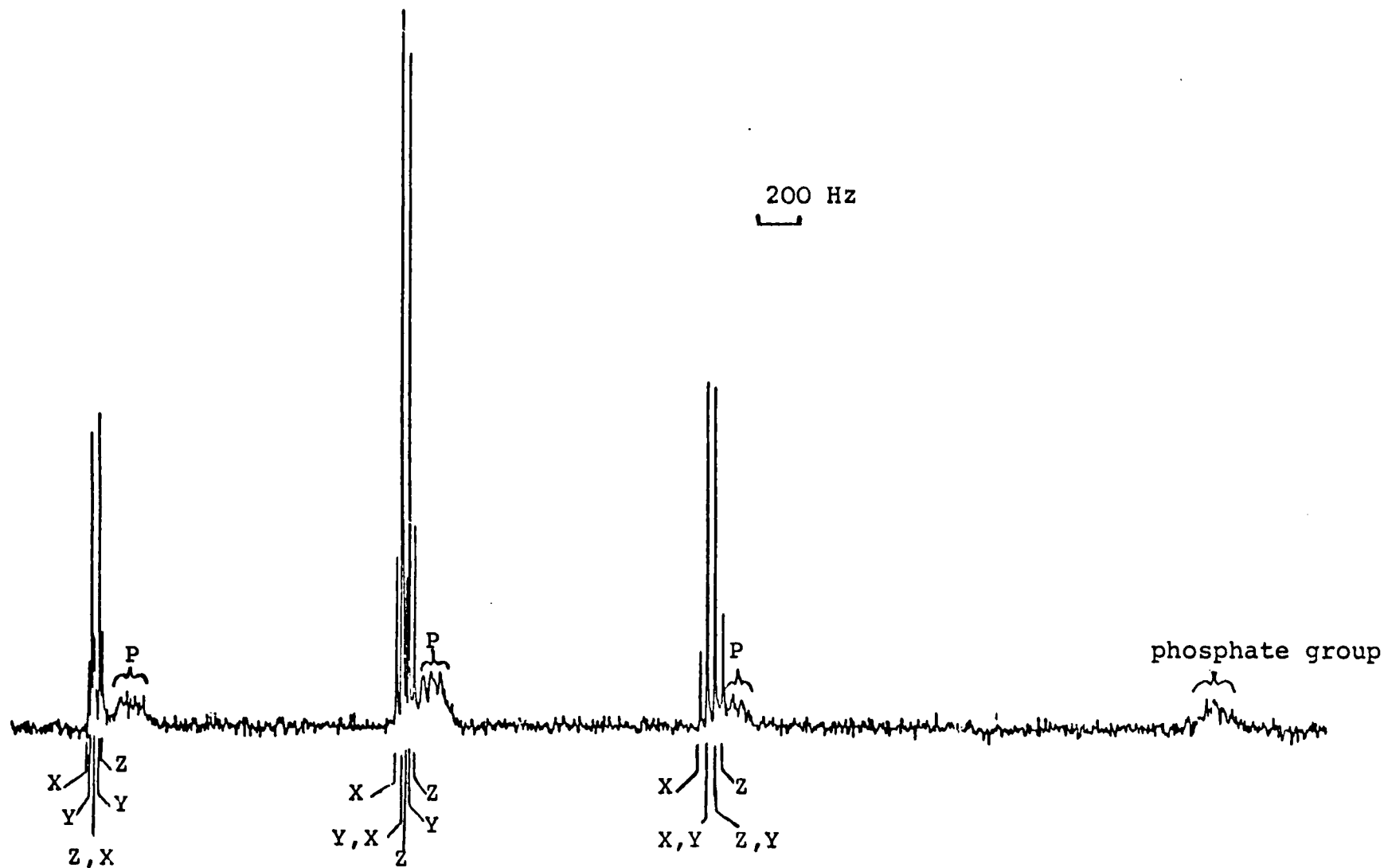
This reaction was carried out in a sealed n.m.r. tube and followed by ³¹P and ¹⁹F spectroscopy. The reaction was carried out in the presence of a large excess of diborane and it was hoped that the mono, bis and tris BH₃ adducts would be observed. The reaction was followed by ³¹P n.m.r. spectroscopy over a period of several hours and it could be seen that the mono, bis and tris adducts were indeed formed. Good n.m.r. spectra were very difficult to obtain due to the complexity

of the spectra of the species present in the mixture. For this reason only the signals due to the free $-PF_2$ groups of the mono and bis adducts, along with those of the free compound were clearly resolved in the n.m.r. spectra. The signals due to the $-PF_2.BH_3$ moieties of the mono, bis and tris adducts overlapped and were broad due to coupling with and relaxation effects of the boron. The signals due to the phosphoryl phosphorus nuclei of these species also overlapped and so were not resolved. It was observed that three related species were present. These all exhibited triplets ($^1J_{PF}$) of doublets ($^2J_{PP}$) in the ^{31}P spectrum and their n.m.r. parameters are given below.

Species	$\delta(P)/ppm$	$^1J_{PF}/Hz$	$^2J_{PP}/Hz$	Assignment
X	108.0	1386	28	$PO(OPF_2)_3$
Y	106.8	1396	34	$PO(OPF_2)_3.BH_3$
Z	105.9	1406	40	$PO(OPF_2)_3.2BH_3$

The ^{31}P n.m.r. spectrum of this mixture after 20 minutes at R.T. is shown in Fig. 3.8. On standing at room temperature signals due to $PO(OPF_2)_3$ decreased in size and those due to the mono and bis adduct increased. After fifty minutes at room temperature all $PO(OPF_2)_3$ had disappeared and the n.m.r. spectrum indicated that there was more mono than bis adduct. After 21 hours at room temperature there was more bis than mono adduct and it was hoped that if left at room temperature the species present would be converted totally to the tris adduct. Unfortunately this did not occur. On standing at room temperature a solid was formed and the n.m.r. spectra indicated that $PF_2H.BH_3$

Fig. 3.8 The ^{31}P n.m.r. Spectrum of $\text{B}_2\text{H}_6/\text{PO}(\text{OPF}_2)_3$ Reaction Mixture



P = signals due to $-\text{PF}_2\cdot\text{BH}_3$ groups

had been formed. This had the following n.m.r. parameters:

$$\begin{aligned}\delta(\text{P}) &= 170.5 \text{ ppm} \\ \delta(\text{F}) &= -96.0 \text{ ppm} \\ {}^1J_{\text{PB}} &= 48 \text{ Hz} \\ {}^1J_{\text{PF}} &= 1160 \text{ Hz} \\ {}^2J_{\text{FH}} &= 2 {}^3J_{\text{FH}} = 14 \text{ Hz}\end{aligned}$$

It is clear that the PF_2 units have gained a hydrogen. The only source of this is diborane itself, which must therefore be left without a proton. One possible reaction is shown below.



An attempt was made to isolate the white solid produced but this was found to be pyrophoric and was clearly not simply boron phosphate but may be a related species.

It is also possible that the hydrogen necessary for the formation of PF_2H was produced by a reaction in which diborane formed higher boranes although there is no evidence from n.m.r. spectroscopy that higher boranes were formed.

CHAPTER 4

The Reaction of $S(PF_2)_2$ with Phosphorous Acid
and Derivatives of Phosphorous Acid.

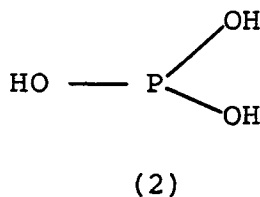
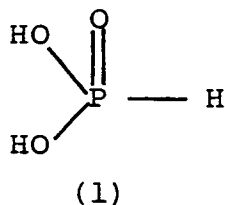
The Preparation and Characterisation of $P(OPF_2)_3$ and $P(OMe)_2OPF_2$.

Introduction

After preparing $PO(OPF_2)_3$ by the reaction of orthophosphoric acid with $S(PF_2)_2$, as described in the preceding chapter, it was decided to investigate the reaction of $S(PF_2)_2$ with other oxyacids of phosphorus and related compounds. It was hoped that this would provide a route to some novel $-PF_2$ derivatives. Also the $-PF_2$ derivatives of phosphorous acid and of other phosphorus III compounds would be interesting for comparison with those of phosphorus V discussed in Chapter 3. This investigation did meet with success and several novel $-PF_2$ derivatives were synthesised as discussed in Section 4.1 below. The reaction of diborane with some of these novel compounds was investigated and this is discussed in Section 4.1 and 4.7. Sections 4.2 to 4.6 describe the n.m.r., vibrational, P.E. and mass spectra for some of the novel compounds produced, reference being made to these sections in Section 4.1.

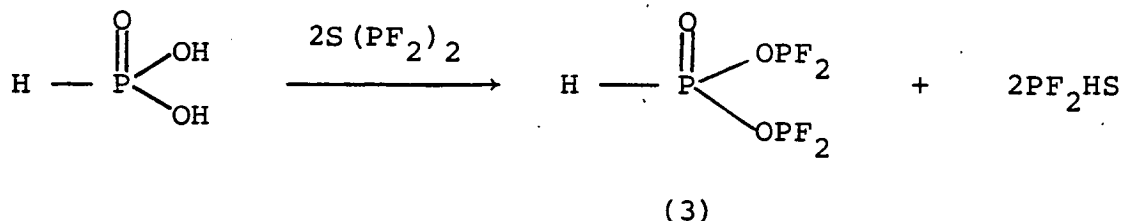
4.1 Results and Discussion

The reaction of $S(PF_2)_2$ with phosphorous acid was of particular interest as this acid is thought to have two tautomeric forms as shown below⁽⁶⁶⁾.



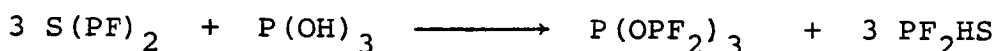
This equilibrium lies heavily on the side of species (1) and no species (2) is observed in the n.m.r. spectrum of this compound. The equilibrium is however rapid at room temperature as can be seen by the rapid incorporation of deuterium into the molecule and formation of a P-D bond when the acid is dissolved in D₂O.

It has been established in Chapters 2 and 3 of this thesis that S(PF₂)₂ readily reacts with hydroxy groups to form -OPF₂ groups and PF₂HS. Two products are therefore possible if S(PF₂)₂ reacts with the hydroxy groups of phosphorous acid depending on whether the acid reacts as compound 1 or compound 2. S(PF₂)₂ has also been shown to react with other active hydrogens⁽¹⁵⁾ and so there is the possibility of reaction with the hydrogen bound directly to the phosphorus in compound 1. Phosphorous acid exists predominantly in form 1⁽⁶⁶⁾ and so it was not surprising that the following reaction was observed.

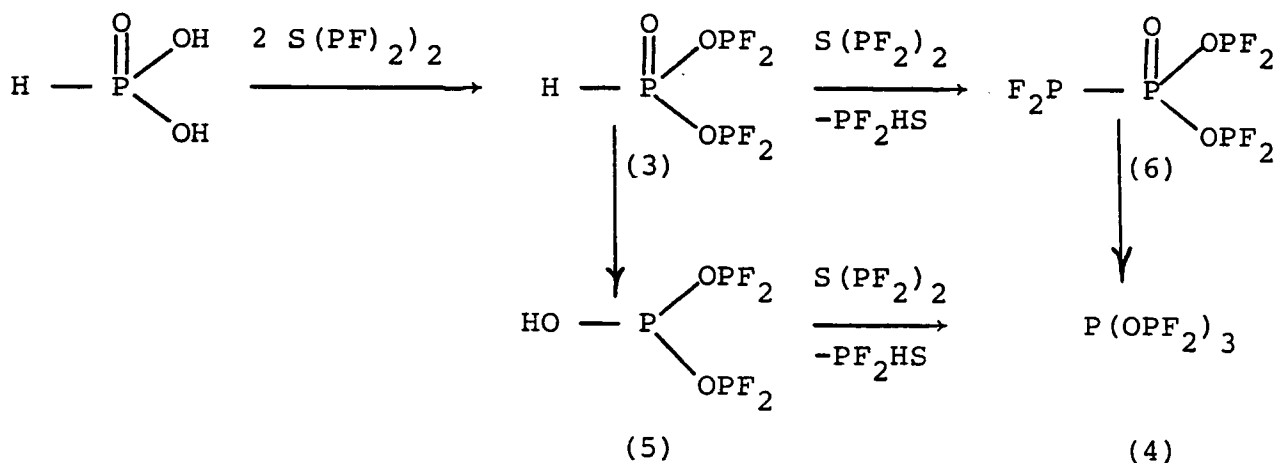


Compound (3) was not isolated for reasons discussed later but was characterised in situ by ³¹P, ¹⁹F and ¹H n.m.r. spectroscopy. The n.m.r. spectra of this molecule are discussed in Section 4.5 and parameters are given in Table 4.8.

The reaction of phosphorous acid with S(PF₂)₂ was observed to proceed further and compound (3) reacted with excess S(PF₂)₂ to yield compound (4), formally derived by reaction of S(PF₂)₂ with phosphorous acid in form (2) as shown below.



The above equation describes the overall reaction and this occurs rapidly at room temperature, being complete after approximately five minutes. During this time however the intermediate, species (3), can be observed. The reaction is clearly stepwise as species (3) could be trapped at low temperature. The precise mechanism of reaction between $S(PF_2)_2$ and phosphorous acid is therefore not clear but two reasonable mechanisms are shown below.



Since neither species (5) nor species (6) was observed in the reaction mixtures it is impossible to say which reaction route was followed.

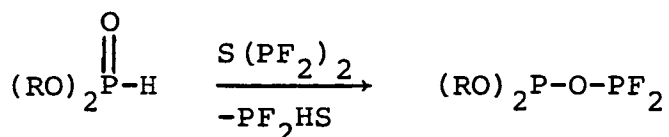
It was found to be impossible to isolate compound (3) by careful reaction of phosphorous acid with $S(PF_2)_2$. Two methods were used to attempt to produce pure species (3) (and these are described below). The first method attempted was that of warming a mixture of phosphorous acid and $S(PF_2)_2$ in $CDCl_3$ or CD_2Cl_2 while observing by ^{31}P n.m.r. spectra at various temperatures. In this case both species (3) and species (4) were observed to form and at no temperature was species (3) only formed. This lack of ability to observe selective reaction may

be due to the insolubility of phosphorous acid in the solvents used. The phosphorous acid would therefore be much less reactive at low temperatures where selective reaction might be expected to occur if the reactants could mix properly. At the higher temperatures necessary for the heterogeneous reaction between $S(PF_2)_2$ and phosphorous acid to occur it is likely that complete reaction would occur.

The second method attempted to produce pure compound (3) involved reaction of exactly two equivalents of $S(PF_2)_2$ with one equivalent of phosphorous acid. This was not successful as mainly compound (4) was formed, some solid being left in the mixture. The best method found for generating species (3) was to take a mixture of phosphorous acid and excess $S(PF_2)_2$ with $CDCl_3$ in a sealed n.m.r. tube and to warm this quickly to room temperature until all effervescence ceased. The n.m.r. tube was then observed at low temperature (ca. $-60^\circ C$) and contained a reasonable amount of species (3) along with some species (4).

Compound 4, $P(OPF_2)_3$, was isolated and characterised by vibrational, ^{31}P and ^{19}F n.m.r. and P.E. spectroscopy and mass spectrometry as described in Sections 4.3, 4.4, 4.6 and 4.2 respectively. All these techniques confirmed the structure as given.

After observing the reaction of phosphorous acid with $S(PF_2)_2$ it was decided to attempt to extend the reaction to dialkyl and diaryl phosphites. An analogous reaction was found to occur for dimethyl and diphenyl phosphite which can be summarised as below.



R = Me or Ph

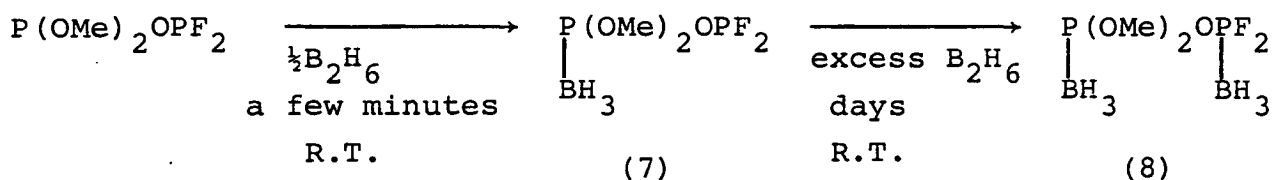
The reaction was carried out only with dimethyl and diphenyl phosphite but there is no reason to suggest that it is not general for all dialkyl and diaryl phosphites and so it may provide a general route to a novel range of $-\text{PF}_2$ derivatives. In the case of dimethyl phosphite the reaction was carried out on a preparative scale and the product isolated and characterised by mass spectrometry, vibrational spectroscopy and ^{31}P , ^{19}F , ^{13}C and ^1H n.m.r. spectroscopy as described in section 4.2, 4.3 and 4.4 respectively. Evidence for the structure of $\text{P}(\text{OMe})_2\text{OPF}_2$ comes from all these techniques and is discussed in the relevant sections. It is clear however that there is not a phosphoryl group present and that the two phosphorus atoms are linked via an oxygen atom and not directly bound to each other. In the case of the reaction between diphenyl phosphite and $\text{S}(\text{PF}_2)_2$ the product, $\text{P}(\text{OPh})_2\text{OPF}_2$ was not isolated, due to lack of time, and was characterised by ^{31}P and ^{19}F n.m.r. spectroscopy only. It is clear by comparing the n.m.r. parameters of $\text{P}(\text{OPh})_2\text{OPF}_2$ with those of $\text{P}(\text{OMe})_2\text{OPF}_2$ that the compounds are very similar (see Table 4.7) and must be structurally related.

The melting points and vapour pressures of $\text{P}(\text{OPF}_2)_3$ and $\text{P}(\text{OMe})_2\text{OPF}_2$ were determined and are tabulated below.

Compound	M.Pt./ $^{\circ}\text{C}$	V.P./mm Hg at 0°C
$\text{P}(\text{OPF}_2)_3$	-108 (2)	20
$\text{P}(\text{OMe})_2\text{OPF}_2$	-144 (2)	9

It is interesting to note that neither compound crystallised on annealing and neither had a sharp melting point, c.f. $\text{PO}(\text{OPF}_2)_3$ which crystallised readily and had a sharp melting point. The M.Pts. of $\text{P}(\text{OPF}_2)_3$ and $\text{P}(\text{OMe})_2\text{OPF}_2$ are also very much lower than that of $\text{PO}(\text{OPF}_2)_3$. These facts are consistent with the idea that the phosphites have no specific intermolecular interaction whereas the phosphate is thought to have a specific intermolecular interaction (see sections 3.1 and 3.3).

Having produced the novel compound $\text{P}(\text{OMe})_2\text{OPF}_2$ in a pure state it was decided to investigate its reaction with diborane. This reaction was of interest as phosphites are known to form BH_3 adducts⁽¹⁾ but $\text{O}(\text{PF}_2)_2$ forms only a mono adduct, not a bis adduct⁽²⁾. The reaction between $\text{P}(\text{OMe})_2\text{OPF}_2$ and B_2H_6 was found to be stepwise as shown below.



The novel compounds (7) and (8) were characterised in situ by ^{31}P , ^{19}F , ^1H and ^{11}B n.m.r. spectroscopy as described in section 4.7. This reaction is rather surprising when that of $\text{O}(\text{PF}_2)_2$ with diborane is considered. The mono adduct was however formed much more readily than the bis adduct, implying that the basicity of the $-\text{PF}_2$ group in compound (8) is very much less than the basicity of the $-\text{PF}_2$ phosphorus in the free compound, $\text{P}(\text{OMe})_2\text{OPF}_2$. This is presumably due to withdrawal of electron density from the free phosphite

phosphorus to the phosphorus coordinated to the BH_3 group via a π electron system as discussed in section 1.

4.2 The Mass Spectra of $\text{P}(\text{OMe})_2\text{OPF}_2$ and $\text{P}(\text{OPF}_2)_3$

The mass spectra of $\text{P}(\text{OPF}_2)_3$ and $\text{P}(\text{OMe})_2\text{OPF}_2$ were recorded and are presented in Tables 4.1 and 4.2 respectively. The mass spectra of these compounds support the proposed formulae in that all fragments can be accounted for and molecular ions were observed. The spectra should again be viewed with some caution as some hydrolysis and oxidation would be expected to occur in the spectrometer resulting in spurious ions in the mass spectra associated with the impurities produced by these reactions.

Details of the spectra of $\text{P}(\text{OPF}_2)_3$ and $\text{P}(\text{OMe})_2\text{OPF}_2$ are discussed separately below.

(a) The mass spectrum of $\text{P}(\text{OPF}_2)_3$

The largest peak observed in the spectrum was that due to $[\text{PF}_2]^+$ as is generally found for $-\text{PF}_2$ compounds. The strong peak at $m/e = 201$ is linked by a metastable peak to the molecular ion and is formed by loss of OPF_2 . It therefore appears that loss of OPF_2 is a major fragmentation route for this compound as was found for $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$ in section 3.2. The spectrum shows several other fragments which are common to the mass spectra of $\text{PO}(\text{OPF}_2)_3$ and $\text{PFO}(\text{OPF}_2)_2$. In particular $[\text{PF}_2]^+$, $[\text{PO}]^+$, $[\text{O}(\text{PF}_2)_2]^+$ and $[\text{F}_3\text{P}_2\text{O}]^+$ seem strong in all spectra of these compounds suggesting some common modes of fragmentation.

Table 4.1 Mass Spectrum of $(F_2PO)_3P$

Peak/(m/e)	Relative Abundance/%	Assignment
286	11	$[(F_2PO)_3P]^+$
201	61	$[(F_2PO)_2P]^+$
154	22	$[F_2POPF_2]^+$
135	61	$[F_2POPF]^+$
113	13	$[P_2O_2F]^+$
86	17	$[HPF_2O]^+$
85	9	$[OPF_2]^+$
69	100	$[PF_2]^+$
67	9	$[HPOF]^+$
66	11	$[OPF]^+$
50	11	$[PF]^+$
47	66	$[PO]^+$
28	8	$[N_2]^+$

Metastable Peaks		Parent	Daughter
143.3	weak	286	201
90.7	weak	201	135
63.5	weak	201	113
16.4	weak	135	47
16.2	weak	154	50

Note: Sample was run as a gas.

Ionising voltage = 70 eV.

Table 4.2 Mass Spectrum of (MeO)₂POPF₂

Peak/(m/e)	Relative Abundance	Assignment
178	3	$[(\text{MeO})_2\text{POPF}_2]^+$
147	6	$[\text{MeOPOPF}_2]^+$
97	2	$[\text{MeOPOF}]^+$
94	2	$[\text{MePO}_3]^+$
93	100	$[(\text{MeO})_2\text{P}]^+$
81	34	$[\text{MeOPF}]^+$
69	12	$[\text{F}_2\text{P}]^+$
63	18	$[\text{MeOPH}]^+$
62	4	$[\text{MeOP}]^+, [\text{P}_2]^+$
47	22	$[\text{PO}]^+$
45	3	$[\text{C}_2\text{H}_5\text{O}]^+$
31	3	$[\text{P}]^+, [\text{MeO}]^+$
29	3	$[\text{HCO}]^+, [\text{C}_2\text{H}_5]^+$
28	7	$[\text{CO}]^+, [\text{N}_2]^+$
15	12	$[\text{Me}]^+$

Metastable Peak	Parent	Daughter
48.6 strong	178	93
42.7 weak	93	63
44.6 strong	147	81
27.3 weak	81	47
23.8 weak	93	47

Note: Sample was injected as a liquid.

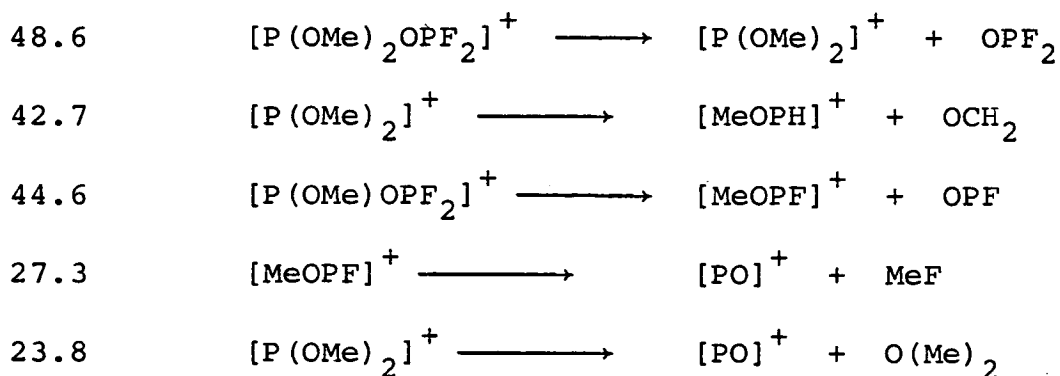
Only peaks above 2% were recorded apart from metastables.

Ionising voltage = 70 eV.

(b) The mass spectrum of P(OMe)₂OPF₂

The spectrum is dominated by the large peak at m/e = 93 due to P(OMe)₂ formed by loss of OPF₂ from the molecular ion as proved by the presence of a metastable ion (m/e = 48.6). Notably the only ions observed which contain only phosphorus and either fluorine or oxygen atoms are [PO]⁺ and [PF₂]⁺ which were found to be strong in the spectra of the related compounds PO(OPF₂)₃, P(OPF₂)₃ and PFO(OPF₂)₂. The metastable peaks observed in the mass spectrum of P(OMe)₂ are given below and in Table 4.2.

Metastable



It can be seen that this molecule also has modes of fragmentation which involve the formation of the very stable species OMe₂ and MeF.

In conclusion, the mass spectra of P(OPF₂)₃ and P(OMe)₂OPF₂ support the proposed structures and show similar fragmentation modes to those of the related compounds PO(OPF₂)₃ and PFO(OPF₂)₂.

4.3 The Vibrational Spectra of $P(OPF_2)_3$ and $P(OMe)_2OPF_2$

The vibrational spectra of $P(OPF_2)_3$ and $P(OMe)_2OPF_2$ were recorded in several phases and are tabulated in Tables 4.3 and 4.4 respectively along with assignments. Neither compound was found to anneal and it appears that neither compound readily forms crystals. This is consistent with the discussion of intermolecular interaction in the related molecules $PO(OPF_2)_3$ and $P(OPF_2)_3$ mentioned in section 3.1 and 3.3. A similar difficulty has been found in assigning the spectra of $P(OPF_2)_3$ and $P(OMe)_2OPF_2$ to that found for $PO(OPF_2)_3$ and $PFO(OPF_2)_2$ and discussed extensively in section 3.3. The spectra of $P(OPF_2)_3$ and $P(OMe)_2OPF_2$ are discussed separately in the following part of this section.

(a) The vibrational spectra of $P(OPF_2)_3$

The infra red spectrum of this compound was recorded in the gas and solid phases. The Raman spectrum was recorded in the liquid and solid phases. As already mentioned the compound did not anneal and this suggests no strong intermolecular interactions in the solid phase. The spectrum was complex and has been assigned tentatively as in Table 4.3. These assignments are not very reliable as the concept of group frequencies is not very helpful since many of the atoms are of similar mass and mixing of vibrational modes may occur. The spectra might be expected to be similar to those of $PO(OPF_2)_3$ but without the phosphoryl stretch at ca. 1400 cm^{-1} but they are much more complex. No phosphoryl stretch is seen and this is consistent with the proposed structure. Infra red and Raman bands have been assigned by comparison with the related compounds $PO(OPF_2)_3$

Table 4.3 Vibrational Spectra of P(OPF₂)₃

GAS I.R.	LIQUID		SOLID		Assignment
	Raman		I.R.	Raman	
1018 s	1017 w dp	1004 m	1001 w 966 w	ν _{POP} asym	
910 vs	900 w dp	902 s	916 w 896 w		
830 vs	847 s p 817 dp	848 m 791 vs	845 m 806 m 786 m 770 w	ν _{P-F}	
740 w 675 m 650 m	737 w p 657 vs p	740 w 701 m 683 w 657 w 630 m	706 w 689 w 650 s 630 s	ν _{POP} sym	
515 m	523 m dp	530 w 513 m	526 m 514 w	Deformations	
450 m	446 w p	466 w 448 w	463 w	Deformations	
360 vw 320 w	396 m p 326 w dp 261 w dp 206 m dp	401 w 381 w 360 w 339 w 318 w	403 m 277 w 216 m	Deformations	

Note: v = very, s = strong, w = weak, m = medium,
 p = polarised, dp = depolarised.
 Peak positions are in cm⁻¹.

and $\text{PFO}(\text{OPF}_2)_2$ but the complexity of the spectra would suggest that considerable mixing has occurred.

(b) The vibrational spectra of $\text{P}(\text{OMe})_2\text{OPF}_2$

The infra red spectra of this molecule were recorded in the gas and solid phases. The Raman spectrum was recorded in the liquid phase only. Assignments of bands in these spectra are recorded in Table 4.4. These spectra are even more complex than those of $\text{P}(\text{OPF}_2)_3$ and the presence of C-H deformations and C-O stretches complicates matters further. In this case the only bands which are unequivocally assigned are the C-H stretches at ca. 3000 cm^{-1} . The band at ca. 1465 cm^{-1} has been assigned to a C-H deformation rather than a phosphoryl stretch which could be expected to occur at a lower frequency, around 1400 cm^{-1} . A phosphoryl stretch would be expected if the molecule existed as either $\text{PO}(\text{OMe})_2\text{PF}_2$ or $\text{PF}_2\text{O}(\text{P}(\text{OMe})_2)$ to any extent. The absence of this band suggests that the molecule does not exist in either of these forms to any appreciable extent but as $\text{P}(\text{OMe})_2\text{OPF}_2$ as formulated.

4.4 The n.m.r. Spectra of $\text{P}(\text{OPF}_2)_3$, $\text{P}(\text{OMe})_2\text{OPF}_2$ and $\text{P}(\text{OPh})_2\text{OPF}_2$

The spectra of these molecules are interesting as there are several spin $\frac{1}{2}$ nuclei in each molecule. It is the n.m.r. spectra which provide the strongest evidence for structure and bonding in these molecules and ^{31}P n.m.r. spectra have been particularly useful. The ^{31}P and ^{19}F n.m.r. spectra have been recorded for all three compounds and ^1H and ^{13}C n.m.r. spectra have also been recorded for $\text{P}(\text{OMe})_2\text{OPF}_2$. The spectra of $\text{P}(\text{OMe})_2\text{OPF}_2$ and $\text{P}(\text{OPh})_2\text{OPF}_2$ are discussed separately.

Table 4.4 Vibrational Spectra of (MeO)₂POPF₂

INFRA-RED		RAMAN		Assignment
Gas	Solid (amorph)	Liquid		
3010 m	3007 w	2882 m p		ν C-H
2960 m	2895 w	2827 m p		
2920 w	2881 m			
2855 m	2824 w			
1467 w	1465 m 1255 w	1460 m dp		C-H deformations
1185 m	1187 s			νP-O-P and νC-O
1040 vs	1050 s	1060 m p		
940 vs	1015 vs 930 vs	1025 w p		
825 vs	808 vs	820 m dp		νP-F
770 s	775 vs	770 vs p		
700 w	700 w	706 m p		
600 m	600 s	600 w ^(a)		
520 w	525 m	518 m ^(a)		
440 w	470 w	490 w ^(a)		
	430 w	440 w ^(a)		
	410 w	380 w ^(a)		
	400 w	278 w ^(a)		
	370 m			
	330 w			

Notes: (a) polarisability data not reliable
 m = medium, s = strong, w = weak,
 p = polarised, dp = depolarised.
 Peak positions are in cm⁻¹.

(a) The ^{31}P and ^{19}F n.m.r. spectra of $\text{P}(\text{OPF}_2)_3$

The ^{31}P and ^{19}F n.m.r. spectra of $\text{P}(\text{OPF}_2)_3$ were recorded and the parameters are tabulated in Table 4.5 and compared in Table 4.6 with those of some related compounds. The ^{31}P spectrum is shown in Fig. 4.1 and the detail of the central region is shown in Fig. 4.2. The ^{31}P spectrum shows two types of phosphorus to be present. The signal due to the phosphorus of the PF_2 groups is a large triplet ($^1\text{J}_{\text{PF}}$) (A, B and C, Fig. 4.1) further split into doublets ($^2\text{J}_{\text{PP}}$) and then into a complex second order pattern (due to coupling of magnetically inequivalent PF_2 groups). The signal due to the central phosphorus is a septet ($^3\text{J}_{\text{PF}}$) (labelled D in Fig. 4.1) of quartets ($^2\text{J}_{\text{PP}}$). From Fig. 4.2 it can be seen that $^2\text{J}_{\text{PP}}$ is very temperature dependent and values of this are tabulated in Table 4.5. This dependence of $^2\text{J}_{\text{PP}}$ on temperature may be due to changes of conformation with temperature. The other parameters can be seen to be somewhat temperature dependent also and this sort of effect has been found in the related compounds $\text{NH}(\text{PF}_2)_2$, $\text{NR}(\text{PF}_2)_2$, $\text{Se}(\text{PF}_2)_2$ and $\text{S}(\text{PF}_2)_2$ in which $^2\text{J}_{\text{PP}}$ has been found to be temperature dependent^(63,16).

The ^{19}F spectrum (shown in Fig. 4.3) is essentially a doublet ($^1\text{J}_{\text{PF}}$) of doublets ($^3\text{J}_{\text{PF}}$) of multiplets as was found for the related compound $\text{PO}(\text{OPF}_2)_3$. Again no attempt was made to analyse the second order spectrum due to its complexity and values of $^1\text{J}_{\text{PF}}$ given for this compound are really $^1\text{J}_{\text{PF}} + 2\ ^5\text{J}_{\text{PF}}$ but approximate to $^1\text{J}_{\text{PF}}$ as $^5\text{J}_{\text{PF}}$ should be small.

Table 4.6 gives the n.m.r. parameters for a series of compounds with the general formula $\text{P}'\text{F}'(n)(\text{OPF}_2)_{(3-n)}$ and several trends can be seen. The most striking point is that all ^{31}P chemical shifts are very similar indicating that all phosphorus atoms are in very similar chemical environments and

Table 4.5 N.M.R. Parameters of P' (OPF₂)₃

Temperature/°C	-58	R.T.	+68
δP /ppm	111.60	112.25	112.49
$\delta P'$ /ppm	110.83	110.04	109.84
δF /ppm	Not Studied	-37.3	Not Studied
$^1J_{PF}$ /Hz	Not Studied ^(a)	1349 [*]	Not Studied ^(a)
$^2J_{PP}$ /Hz	2.68 (5)	0.84 (3)	<0.1
$^3J_{PF}$ /Hz	19.20 (5)	17.86 (4)	17.44 (5)

Notes: Solvent CDCl₃

* See Text

(a) Spectra recorded on only narrow spectral width.

Table 4.6 The N.M.R. Parameters of Compounds with General
Formula $F'_n P' (OPF_2)_{3-n}$

	<u>PF₃</u>	<u>O(PF₂)₂</u>	<u>PF(OPF₂)₂</u>	<u>P(OPF₂)₃</u>
$\delta P'$	104	111	111	110
δP	-	111	111	112
$\delta F'$	-54	-37	n.r.	-
δF	-	-37	n.r.	-37.4
$^1 J_{P', F'}$	1400	1365	1314	-
$^1 J_{PF}$	-	1365	1350	1348*
$^2 J_{PP'}$	-	4	2.2	ca. 1 Hz (temp dep)
$^3 J_{P', F}$	-	14	15.5	17.6
$^3 J_{PF'}$	-	14	12	-
Reference	(1)	(1,63)	(8)	

Notes: * See text

n.r. = not recorded.

Chemical shifts are in ppm, coupling constants are in Hz.

Fig. 4.1

The ^{31}P n.m.r. Spectrum of $\text{P}(\text{OPE}_2)_3$

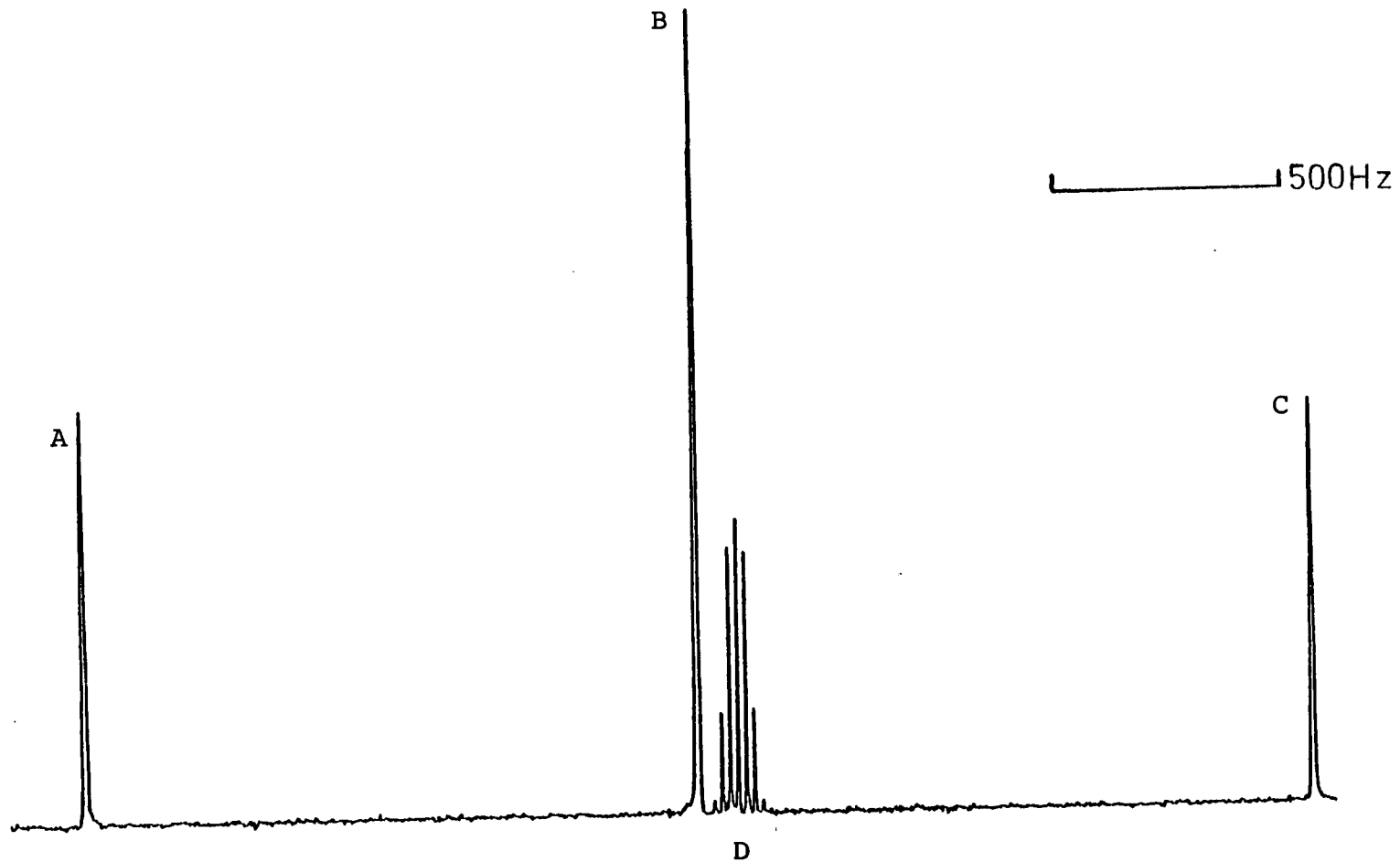


Fig. 4.2 Central Region of ^{31}P n.m.r. Spectrum of $\text{P}(\text{OPF}_2)_3$
(area marked by Labels B and D in Fig. 4.1)

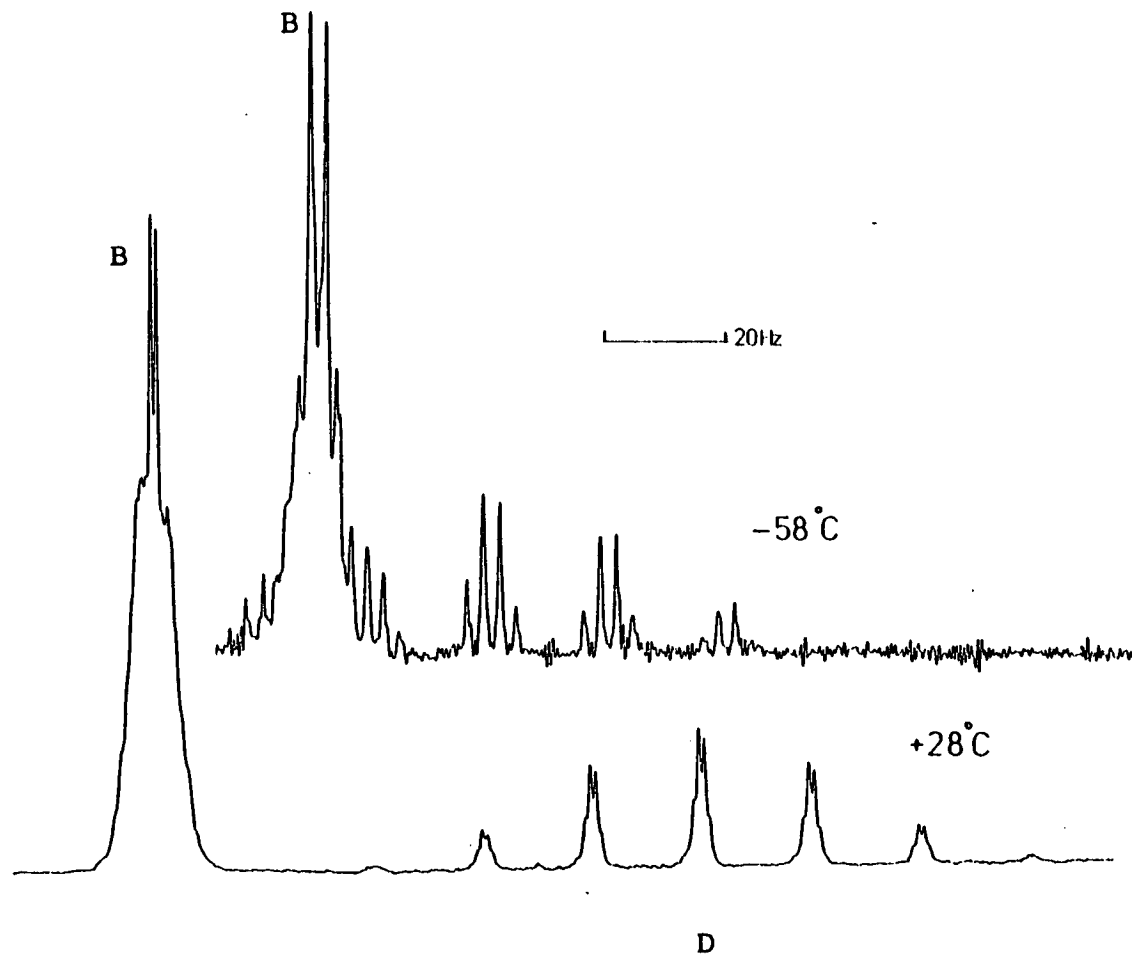
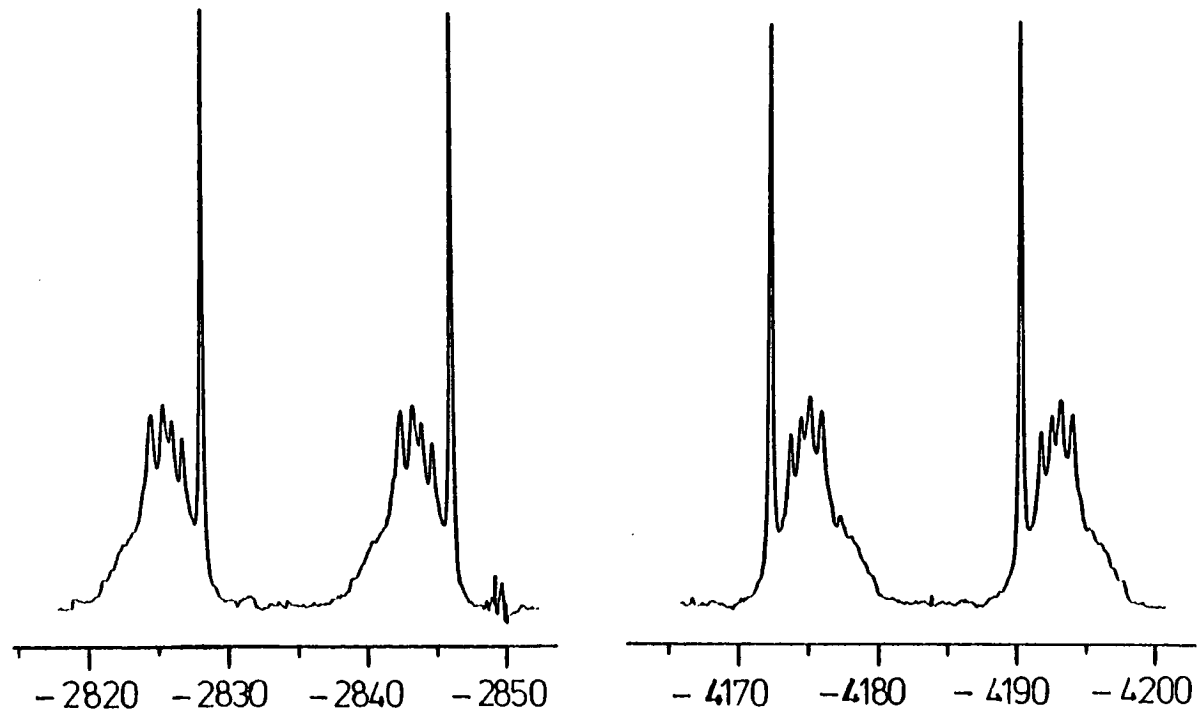


Fig. 4.3 ^{19}F n.m.r. Spectrum of $\text{P}(\text{OPF}_2)_3$



Hz from CCl_3F

that the $-\text{OPF}_2$ groups have similar electronic effects to those of fluorine.

$^1J_{\text{P}'\text{F}'}$ and $^1J_{\text{PF}}$ increase as n increases while $^3J_{\text{P}'\text{F}'}$ decreases very slightly. The reasons for these trends are not obvious as several factors are involved in determining coupling constants. It is however useful to collect the parameters for these compounds together as they then provide evidence for the compounds being structurally similar. This is particularly important for $\text{PF}(\text{OPF}_2)_2$ which was observed by Bett⁽⁸⁾ but not fully characterised. However from the way the parameters of this compound fit into the table it can be seen that this species has been correctly identified.

(b) The N.M.R. Spectra of $\text{P}(\text{OMe})_2\text{OPF}_2$ and $\text{P}(\text{OPh})_2\text{OPF}_2$

The ^{31}P , ^{19}F , ^1H and ^{13}C n.m.r. spectra of $\text{P}(\text{OMe})_2\text{OPF}_2$ were recorded. The n.m.r. parameters are given in Table 4.7 along with those of $\text{P}(\text{OPh})_2\text{OPF}_2$ (discussed later in this section). The ^{31}P , proton decoupled, n.m.r. spectrum of $\text{P}(\text{OMe})_2\text{OPF}_2$ is shown in Fig. 4.4. This spectrum can be seen to consist of a large triplet ($^1J_{\text{PF}}$) (labelled A, B, C) of doublets ($^2J_{\text{PP}}$) and a small triplet ($^3J_{\text{PF}}$) of doublets ($^2J_{\text{PP}}$) (labelled D). The ^{19}F n.m.r. spectrum is a doublet ($^1J_{\text{PF}}$) of doublets ($^3J_{\text{PF}}$) and when observed at very high resolution a further splitting of ca. 0.2 Hz which may be $^6J_{\text{HF}}$ was observed.

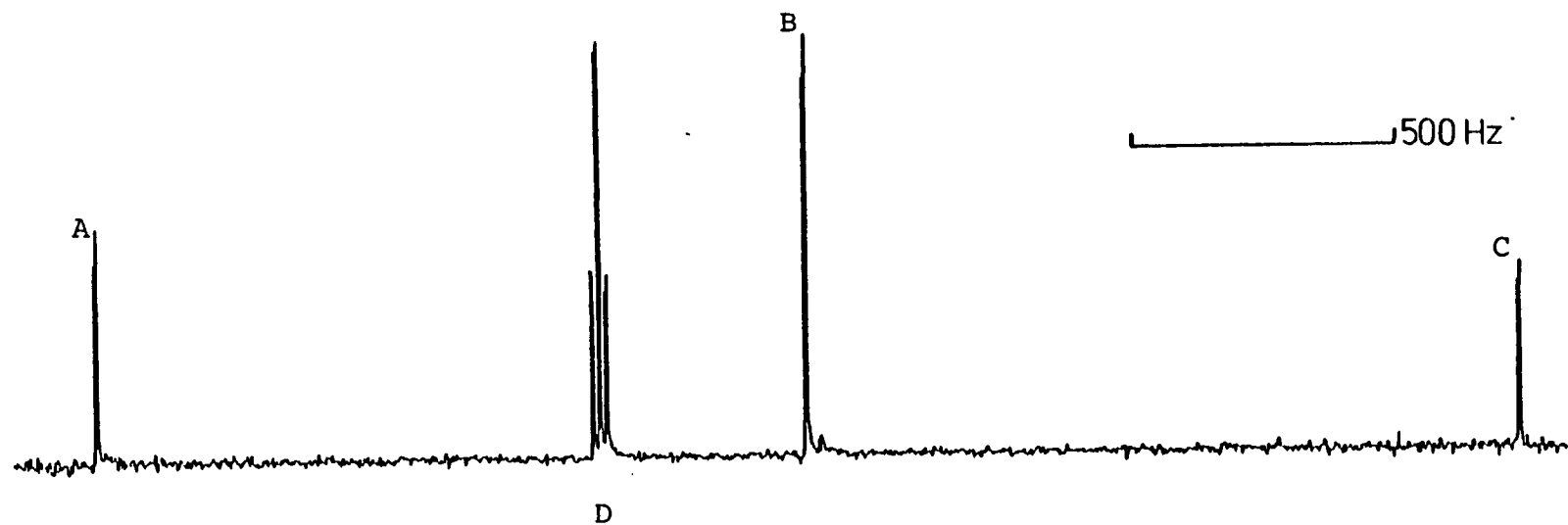
The ^1H spectrum was a doublet ($^3J_{\text{PH}}$) with no further splitting being resolved. The ^{13}C spectrum was also a simple doublet ($^2J_{\text{PC}}$). The parameters are consistent with the proposed structure, notably $^2J_{\text{PP}}$ and $^3J_{\text{PF}}$ are of similar magnitude to those of $\text{P}(\text{OPF}_2)_3$ and other related compounds listed in Table 4.6.

Table 4.7 N.M.R. Parameters of P(OMe)₂OPF₂ and P(OPh)₂OPF₂

compd.	(MeO) ₂ P'OPF ₂	(PhO) ₂ P'OPF ₂
δ (H)	3.62	Not Studied
δ (C)	49.76	Not Studied
δ (P)	104.84	114.1
δ (P')	120.70	121.3
δ (F)	-36.86	-38.18
² J _{P',C}	7.1	Not Studied
¹ J _{PF}	1321.5	1335
³ J _{P',F}	12.7	11.7
² J _{P',P}	4.5 (4)	1.5
³ J _{P',H}	10.4	Not Studied
Solvent	CDCl ₃ Possible ⁶ J _{HF} = 0.2 Hz	CD ₂ Cl ₂

Note: Chemical shifts are in ppm, coupling constants are in Hz.

Fig. 4.4 ^{19}F n.m.r. Spectrum of $\text{P}(\text{OMe})_2\text{OPF}_2$



$P(OPh)_2OPF_2$ was not isolated but was formed by reaction of $S(PF_2)_2$ and diphenylphosphite in a sealed n.m.r. tube and was characterised in situ by ^{31}P and ^{19}F n.m.r. spectroscopy. The ^{31}P and ^{19}F , proton decoupled, n.m.r. spectra were essentially the same as those of $P(OMe)_2OPF_2$, the magnitudes of coupling constants and chemical shifts varying only very slightly. The n.m.r. parameters of $P(OPh)_2OPF_2$ are given in Table 4.7 and from their similarity to those of $P(OMe)_2OPF_2$ a similar structure can be inferred for both these compounds.

4.5 The N.M.R. Spectra of $PHO(OPF)_2$

This compound was not isolated but was observed at reduced temperature as a product of the reaction between phosphorous acid and $S(PF_2)_2$ as mentioned in section 4.1 and the experimental chapter.

The compound was observed by 1H , ^{31}P and ^{19}F n.m.r. spectroscopy and the parameters obtained are presented in Table 4.8.

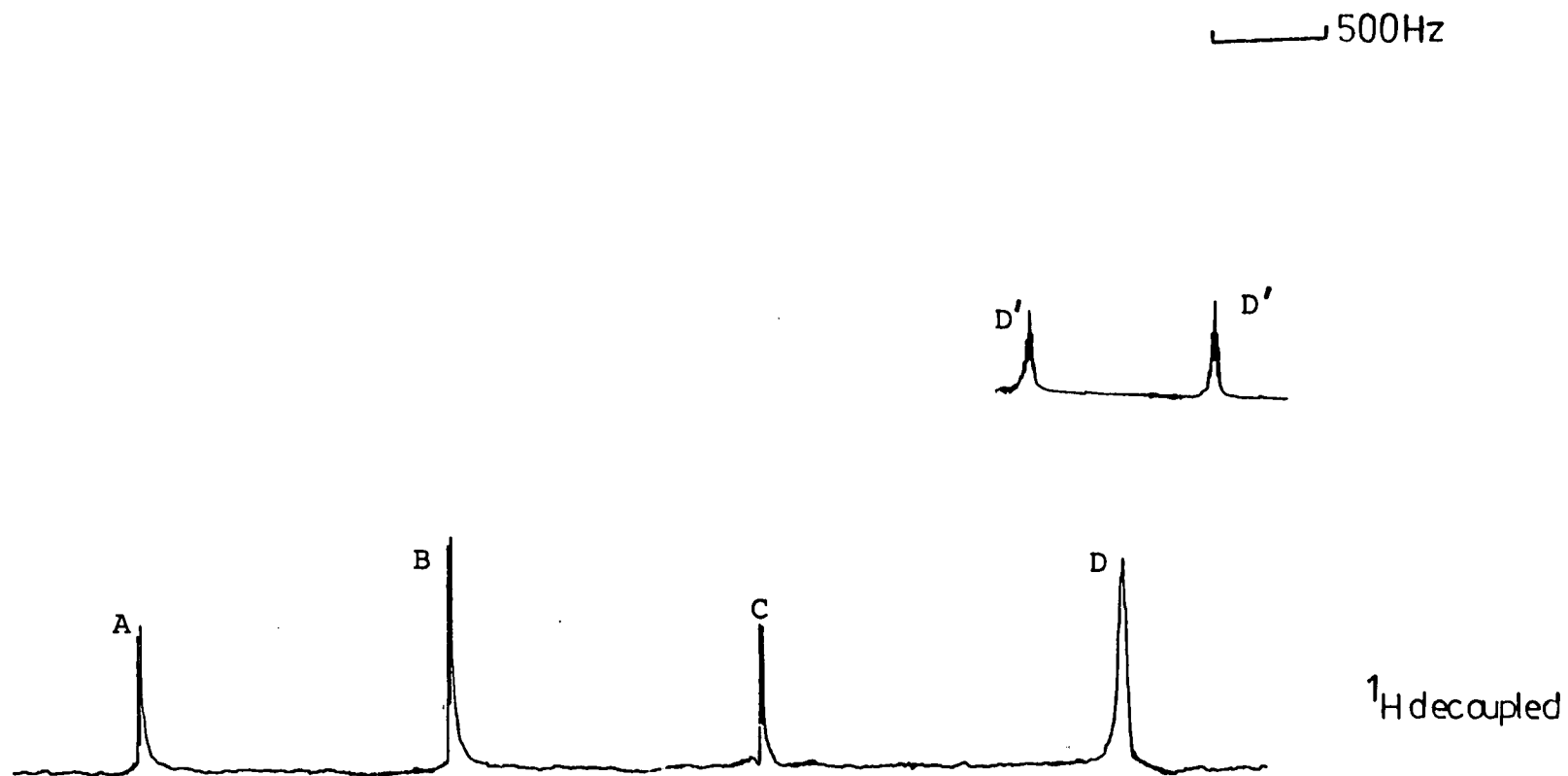
The 1H spectrum of this compound consisted of a doublet ($^1J_{PH}$) of 803 Hz magnitude which is typical for $^1J_{PH}$ in four coordinate $P(V)$. The ^{31}P spectrum, shown in Fig. 4.5, was made up of two patterns. The first due to the phosphorus of the PF_2 groups consisted of a triplet ($^1J_{PF}$) (labelled A, B and C) of doublets ($^2J_{PP}$) unaffected by proton decoupling. The second resonance was a multiplet (labelled D) which was poorly resolved but was split into a doublet (labelled D') when proton coupling was introduced. This was clearly due to the phosphoryl phosphorus nucleus. The n.m.r. parameters agree well with

Table 4.8 N.M.R. Parameters of P'HO(OPF₂)₂

δ (H)	7.47
δ (P)	108
δ (P')	-13
δ (F) *	-39.8
difference in chemical shift /ppm of geminal F's	0.88
$^1J_{PF}$	1375
$^2J_{PP'}$	13
$^3J_{P'F}$	12
$^1J_{PH}$	803
$^2J_{FF'}$	17.5

* average chemical shift of geminal fluorines in the -PF₂ groups
Chemical shifts are in ppm, coupling constants are in Hz.

Fig. 4.5 ^{31}P n.m.r. Spectrum of $\text{PHO}(\text{OPF}_2)_2$



those expected for a compound related to $\text{PO}(\text{OPF}_2)_3$ (Table 3.5) and little doubt exists as to the structure of this species. It is interesting to note that $^2J_{\text{PP}'}$ and $^3J_{\text{P}'\text{F}}$ are of very similar magnitude for $\text{PHO}(\text{OPF}_2)_2$ whereas $^2J_{\text{PP}}$ is almost three times $^3J_{\text{PF}}$ in $\text{PO}(\text{OPF}_2)_3$.

The ^{19}F n.m.r. spectrum of $\text{PHO}(\text{OPF}_2)_2$ is of particular interest as this compound has a prochiral centre at the phosphoryl phosphorus atom and therefore the chemical shifts of geminal fluorines on the $-\text{PF}_2$ groups differ and $^2J_{\text{FF}}$ is observed and results in an AB pattern. The ^{19}F n.m.r. spectrum of $\text{PHO}(\text{OPF}_2)_2$ is therefore a doublet ($^1J_{\text{PF}}$) of doublets ($^3J_{\text{PF}}$) of AB patterns (due to $^2J_{\text{FF}}$). The AB pattern was analysed by standard means⁽⁷⁰⁾ and n.m.r. parameters obtained are given in Table 4.8. It is, however, interesting to compare the geminal FF coupling observed in $\text{PFO}(\text{OPF}_2)_2$ (table 3.5), $\text{POPh}(\text{OPF}_2)_2$ (Table 3.6) and $\text{PHO}(\text{OPF}_2)_2$. These are summarised below.

For $\text{POR}(\text{OPF}_2)_2$

R =	F	Ph	H
$^2J_{\text{FF}}/\text{Hz}$	21	19	17.5
difference in geminal ^{19}F chemical shift /ppm	0.17	0.46	0.88

It is clear that $^2J_{\text{FF}}$ is very similar for all three compounds. The chemical shift difference for geminal fluorines is very much larger for $\text{PHO}(\text{OPF}_2)_3$ and $\text{POPh}(\text{OPF}_2)_2$ than for $\text{PFO}(\text{OPF}_2)_2$ and this may be due to some intramolecular hydrogen bonding which could

occur to some extent in the first two compounds but not in $\text{PFO}(\text{OPF}_2)_2$, and would be expected to alter the chemical shifts of the fluorines.

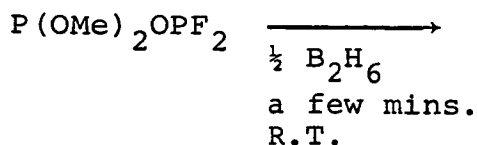
4.6 The Photoelectron Spectrum of $\text{P}(\text{OPF}_2)_3$

The He(I) P.E. spectrum of $\text{P}(\text{OPF}_2)_3$ was recorded and is shown in Fig. 4.6, and peak positions are given in Table 4.9 along with data for the related compound $\text{O}(\text{PF}_2)_2$ (16,35). The spectrum of $\text{P}(\text{OPF}_2)_3$ is essentially very similar to that of $\text{O}(\text{PF}_2)_2$ except that there is one extra band at ca. 10.5 eV. This would be expected as the two compounds are similar in structure and the extra band is presumably due to the lone pair of the central phosphorus atom in $\text{P}(\text{OPF}_2)_3$. There is some dispute as to the assignment of the P.E. spectrum of $\text{O}(\text{PF}_2)_2$, particularly as to which bands are due to P lone pairs and O lone pairs (16,35). In a molecule as complicated as $\text{P}(\text{OPF}_2)_3$ it is unlikely that any definite assignments can be made and the assignments in Table 4.9 should therefore be viewed with caution.

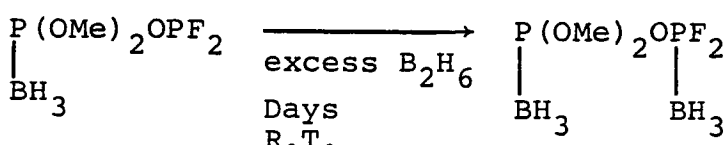
4.7 The BH_3 Adducts of $\text{P}(\text{OMe})_2\text{OPF}_2$

The reaction between diborane and $\text{P}(\text{OMe})_2\text{OPF}_2$ was followed by ^{31}P , ^{19}F , ^1H and ^{11}B n.m.r. spectroscopy, the reaction taking place in a sealed n.m.r. tube. It was clear from the n.m.r. spectra that two different adducts could be formed depending on the amount of diborane used and the time of reaction.

The observed reactions can be summarised as below.



(7)



(8)

Fig. 4.6 The Photoelectron Spectrum of $P(OPF_2)_3$

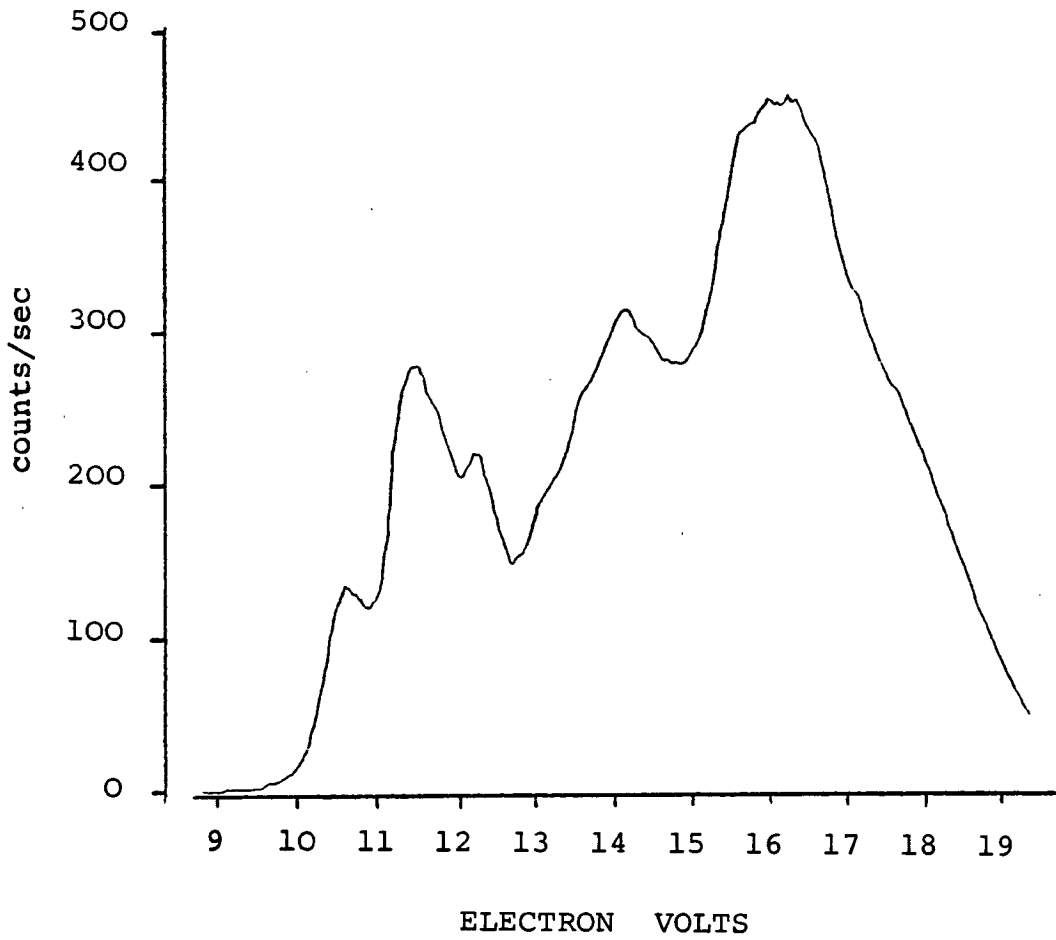


Table 4.9 The Photoelectron Spectra of P(OPF₂)₃ and O(PF₂)₂

Vertical Ionisation Potential/eV		Assignment
O(PF ₂) ₂	P'(OPF ₂) ₃	
	10.55 ^(a)	P' Lone pair
11.2	11.57 ^(a)	O Lone pair
12.4	12.28 ^(a)	P Lone pair
14.2	14.13 ^(a)	P-O bonding
ca. 16.5	ca. 16 ^(a)	F Lone pairs
17-19		P-F bonding

Ref: (35,16)

Note: (a) the assignments of these bands are very tentative.
 e.g. the 3 oxygen lone pairs could combine to form a₁ + e bands. The assignments should only be regarded as possibilities.

The structure of (7), formed quickly at room temperature as described in the experimental section, was confirmed by ^{11}B , ^{31}P , ^{19}F and ^1H n.m.r. spectroscopy. The n.m.r. parameters of the compound are given in Table 4.10. The ^{11}B n.m.r. spectrum of this adduct was simple and consisted of a doublet ($^1\text{J}_{\text{PB}}$) of quartets ($^1\text{J}_{\text{BH}}$). The ^1H n.m.r. spectrum showed two types of proton to be present. The methyl protons resulted in a doublet ($^3\text{J}_{\text{PH}}$). The protons of the BH_3 group produced a doublet ($^2\text{J}_{\text{PH}}$) of equal intensity quartets ($^1\text{J}_{\text{BH}}$). The signals due to the protons of the BH_3 group were greatly broadened by quadrupolar relaxation due to the boron.

The ^{31}P n.m.r. spectrum of this adduct is shown in Fig. 4.7 and should be contrasted with that of the free compound, $\text{P}(\text{OMe})_2\text{OPF}_2$ (Fig. 4.4). As can be seen in Fig. 4.7 there is a triplet (A, B and C) ($^1\text{J}_{\text{PF}}$) of doublets ($^2\text{J}_{\text{PP}}$) due to the free $-\text{PF}_2$ group. This $-\text{PF}_2$ group is obviously not complexed to a $-\text{BH}_3$ unit as there is no coupling to boron or broadening due to quadrupolar relaxation. The lines due to the other phosphorus are on the other hand broad (labelled D) and split into equal intensity quartets ($^1\text{J}_{\text{PB}}$) of doublet ($^2\text{J}_{\text{PP}}$). The ^{19}F n.m.r. spectrum of compound (7) is a simple doublet ($^1\text{J}_{\text{PF}}$).

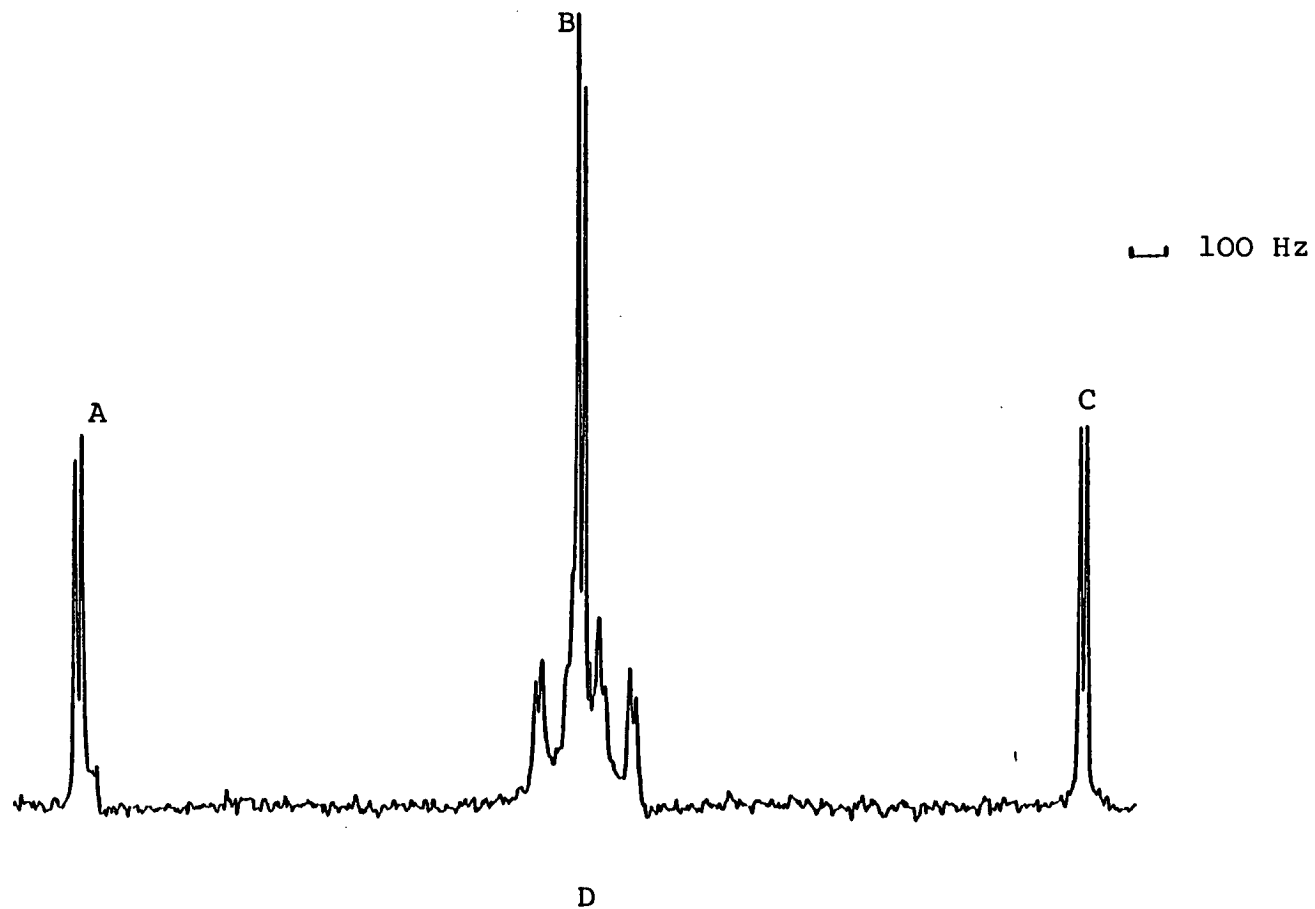
The bis adduct, compound (8), is an extremely interesting species from the point of view of its n.m.r. spectra and no fewer than eighteen n.m.r. parameters were extracted from these. These parameters are given in Table 4.10. The ^{11}B n.m.r. spectra consisted of two quartets ($^1\text{J}_{\text{BH}}$) of doublets ($^2\text{J}_{\text{PB}}$) clearly establishing the presence of two types of BH_3 group. The ^1H spectrum was obscured to a large extent by the presence of excess

Table 4.10 N.M.R. Parameters of BH_3 adducts of $\text{P}(\text{OMe})_2\text{OPF}_2$

Compd.	$\begin{array}{c} (\text{MeO})_2\text{P} - \text{O} - \text{PF}_2 \\ \qquad \qquad \\ \text{B}'\text{H}'_3 \qquad \text{B}''\text{H}''_3 \end{array}$	$\begin{array}{c} (\text{MeO})_2\text{POPF}_2 \\ \\ \text{BH}_3 \end{array}$
$\delta(\text{P})$	100.69	111.3
$\delta(\text{P}')$	116.27	111.0
$\delta(\text{F})$	-52	-38.75
$\delta(\text{B}')$	-61.8	-61.1
$\delta(\text{B}'')$	-62.3	-
$\delta(\text{H})$	3.91	3.83
$\delta(\text{H}')$	0.63	0.6
$\delta(\text{H}'')$	0.75	-
$^1J_{\text{PF}}$	1342	1366
$^2J_{\text{PH}''}$	20	-
$^2J_{\text{P}'\text{H}'}$	19	18
$^3J_{\text{P}'\text{H}}$	12	11.5
$^2J_{\text{PP}'}$	44	16 (2)
$^1J_{\text{B}'\text{H}'}$	97	99
$^1J_{\text{B}''\text{H}''}$	104	-
$^3J_{\text{FH}''}$	16.6	-
$^1J_{\text{PB}''}$	56	-
$^1J_{\text{P}'\text{B}'}$	73	86

Note: Chemical shifts are in ppm, coupling constants are in Hz.

Fig. 4.7 The ^{31}P n.m.r. Spectrum of $\text{P}(\text{OMe})_2\text{OPF}_2$
 BH_3



diborane but this problem was overcome by observing the ^1H spectrum with ^{11}B decoupled. Under these conditions the adduct showed three types of proton: (a) The methyl groups which produced doublets ($^3\text{J}_{\text{PH}}$), (b) The $-\text{BH}_3$ group on the $-\text{PF}_2$ phosphorus which produced a doublet ($^2\text{J}_{\text{PH}}$) of triplets ($^3\text{J}_{\text{FH}}$), (c) The $-\text{BH}_3$ group attached to the other phosphorus produced a simple doublet ($^2\text{J}_{\text{PH}}$). The ^{19}F n.m.r. spectrum consisted of a doublet ($^1\text{J}_{\text{PF}}$) of quartets ($^3\text{J}_{\text{FH}}$).

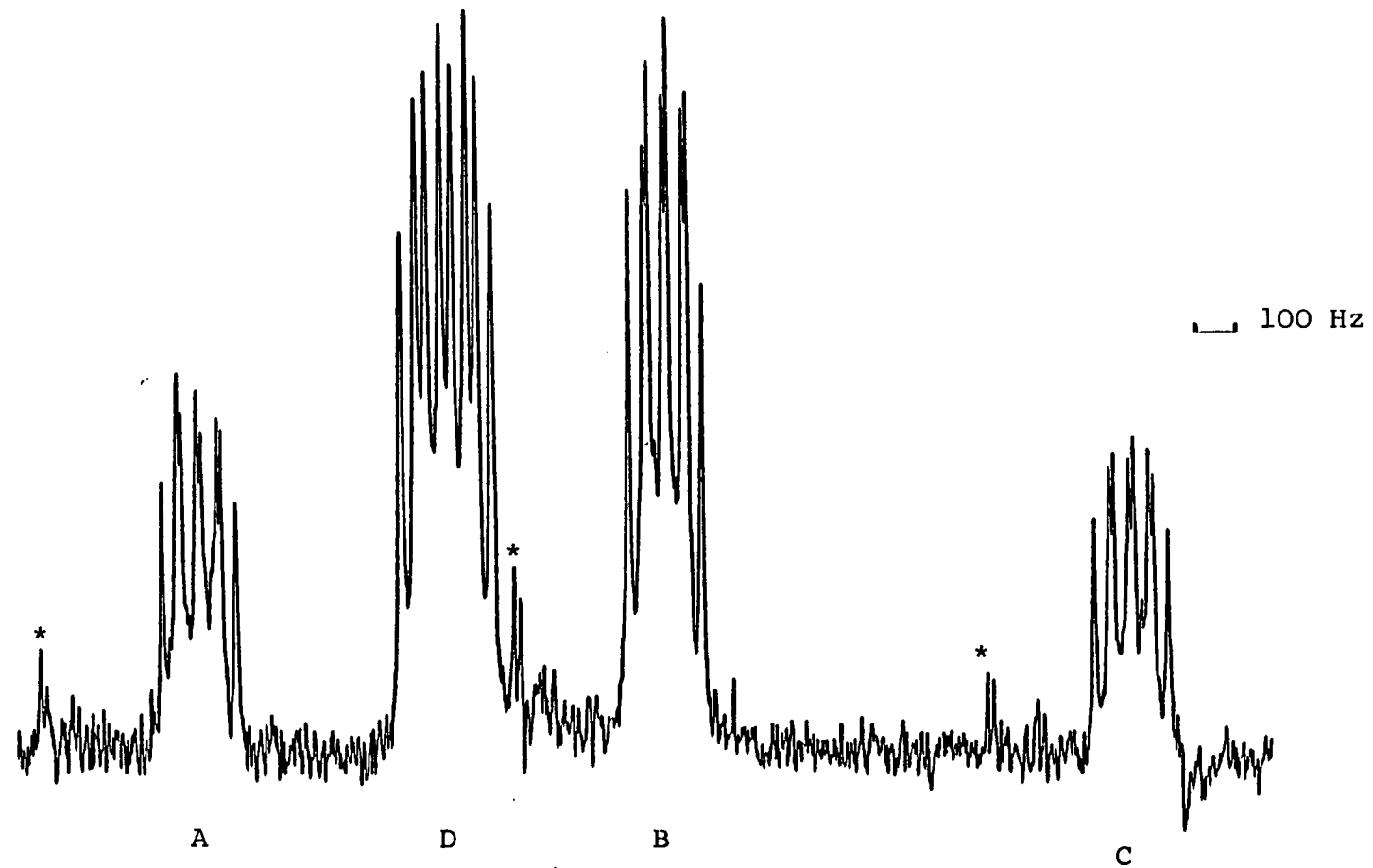
The ^{31}P n.m.r. spectrum of compound (8) is shown in Fig. 4.8 and clearly shows two different phosphorus groups. The first is a triplet (labelled A, B and C) ($^1\text{J}_{\text{PF}}$) of equal intensity quartets ($^1\text{J}_{\text{PB}}$) of doublets ($^2\text{J}_{\text{PP}}$) and is due to the PF_2 group. The other phosphorus signal (labelled D) is a doublet ($^2\text{J}_{\text{PP}}$) of equal intensity quartets ($^1\text{J}_{\text{PB}}$). Peaks labelled * are due to traces of the mono adduct, compound (7).

The n.m.r. parameters of the borane adducts of $\text{P}(\text{OME})_2\text{OPF}_2$ are as expected for the structures given and compare reasonably well with those of $\text{MeOPF}_2\cdot\text{BH}_3$ and $\text{MeSPF}_2\cdot\text{BH}_3$ given below. ⁽¹⁷⁾

Compound	$\delta(\text{P})/\text{ppm}$	$\delta(\text{B})/\text{ppm}$	$^1\text{J}_{\text{PB}}$	$^1\text{J}_{\text{PF}}$
$\text{MeOPF}_2\cdot\text{BH}_3$	93.7	-65.0	69.3	1280
$\text{MeSPF}_2\cdot\text{BH}_3$	164.9	-58.1	41.4	1235

The reaction of $\text{P}(\text{OPF}_2)_3$ with B_2H_6 was investigated. This resulted in extensive decomposition of $\text{P}(\text{OPF}_2)_3$. The major reaction products were $\text{O}(\text{PF}_2)_2$ and an unidentified yellow solid.

Fig. 4.8 The ^{31}P n.m.r. Spectrum of $\text{P}(\text{OMe})_2\text{OPF}_2$
 BH_3 BH_3



CHAPTER 5

The Reaction of S(PF₂)₂ with Various Hydroxy Compounds
and Diphenyl Phosphine Oxide

Introduction

This chapter describes the reaction of S(PF₂)₂ with several types of hydroxy species and with diphenylphosphine oxide. These reactions were carried out in order to gauge the scope of the reaction between hydroxy species and S(PF₂)₂ for synthetic purposes. These reactions were carried out simultaneously with those described in Chapters 2, 3 and 4. However, unlike the reactions described in these preceding Chapters many of these investigations are not complete and would benefit from further study. Although to some extent incomplete, it is hoped that the results of these investigations may be of help to future workers in this field.

These reactions were carried out in sealed n.m.r. tubes and were followed by n.m.r. spectroscopy. Since the only evidence for the reactions described was obtained from visual inspection and n.m.r. spectra of the reaction mixtures these results must be less conclusive than those given in previous Chapters where other physical techniques were employed.

5.1 Results and Discussion

The preceding three chapters show that, in the absence of competing reactions, hydroxy compounds react according to the following equation:

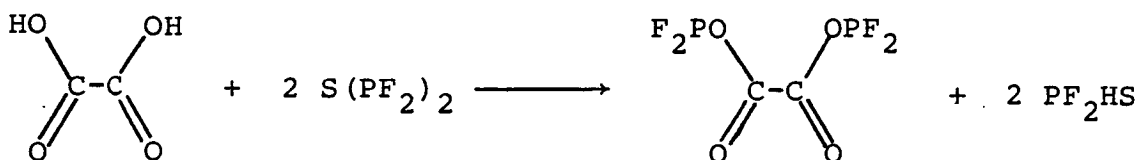


It was also shown that phosphites may react as follows:



It is therefore tempting to assume that other related species will react similarly with $\text{S}(\text{PF}_2)_2$ and that where a pure hydroxy species can be obtained that this can be converted to the corresponding $-\text{OPF}_2$ derivative. The following results show that this is not the case. Other factors must be considered such as reaction rates and competing reactions. The reaction of $\text{S}(\text{PF}_2)_2$ with groups of related compounds is summarised in the following part of this section.

The reaction of $\text{S}(\text{PF}_2)_2$ with boric acid ($\text{B}(\text{OH})_3$) and sulphamic acid ($\text{NH}_2\text{SO}_3\text{H}$) was investigated using ^{31}P n.m.r. spectroscopy. In neither case was any reaction found even after several days at room temperature. Details of the experimental conditions are given in the experimental chapter. It is possible that the lack of reaction is due to the great stability of these solids and their lack of solubility in the solvent system used which was limited to solvents such as CDCl_3 and CD_2Cl_2 which do not react with fluorophosphines. The reaction of $\text{S}(\text{PF}_2)_2$ with two dicarboxylic acids, malonic acid and oxalic acid, was investigated. These reactions were followed by ^{31}P and ^{19}F n.m.r. spectroscopy and the expected reactions were found to occur. The reaction is given for oxalic acid below.



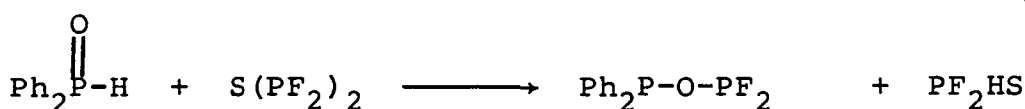
The analogous reaction occurred for malonic acid. Details of these reactions and the n.m.r. parameters of $(\text{CO}_2\text{PF}_2)_2$ and $\text{CH}_2(\text{CO}_2\text{PF}_2)_2$ are given in Section 5.2. The most surprising feature of these reactions was their slowness, taking a matter of a day to go to completion. This is in sharp contrast to the reaction of $\text{S}(\text{PF}_2)_2$ with alcohols, phosphoric acid and phosphorous acid, described in preceding chapters, which occurred in a matter of minutes under similar reaction conditions. It is possible that hydrogen bonding, resulting in insolubility of the acids, is a major factor in determining reaction rate. The $-\text{PF}_2$ derivatives obtained appeared stable at room temperature in solution and it would be worth attempting to isolate these compounds and characterise them further (e.g. by ^{13}C n.m.r. and infra red spectroscopy and mass spectrometry). Unfortunately time was not available to do this in this study.

To investigate the reaction of $\text{S}(\text{PF}_2)_2$ with oxy acids of other elements the reactions with sulphuric acid, telluric acid and selenous acid were investigated using ^{31}P n.m.r. spectroscopy. The results are discussed in detail in Sections 5.3, 5.4 and 5.5 respectively. The results suggest that major side reactions occurred in all these reactions and that oxidation of the phosphorus moieties occurred. These three reactions appear to be of little synthetic value.

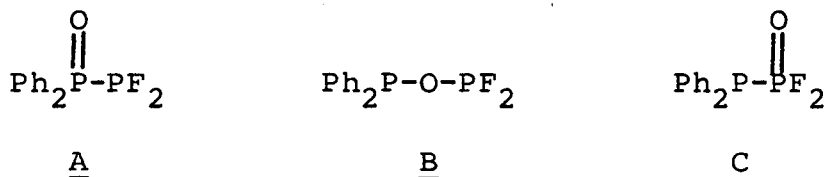
Since phosphorous acid (H_3PO_3) reacted cleanly with $\text{S}(\text{PF}_2)_2$, as described in Chapter 4, it was decided to investigate the reaction of hypophosphorous acid (H_3PO_2) with $\text{S}(\text{PF}_2)_2$. It was hoped that this reaction would produce $\text{PH}(\text{OPF}_2)_2$: however, $\text{O}(\text{PF}_2)_2$ and a yellow solid were the major products, as described

in Section 5.6, and this reaction appears to have little synthetic value.

The reaction of diphenylphosphine oxide with $S(PF_2)_2$ was investigated. It was hoped that the reaction shown in the equation below would occur by analogy with that of $S(PF_2)_2$ with dialkylphosphites (see Chapter 4). It was hoped that either Ph_2POPF_2 or a structural isomer of this compound would be obtained.



The possible structural isomers which could be obtained are shown below.



The reaction was carried out on a preparative scale and a compound was obtained which appears to be isomer A rather than B or C. Details of this reaction, n.m.r. parameters of the product, and reasons for assigning its structure as shown are given in Section 5.7.

5.2 The Reaction of $S(PF_2)_2$ with Malonic and Oxalic Acid

These reactions were carried out in sealed n.m.r. tubes using $CDCl_3$ as solvent. The reactions were followed by ^{31}P and ^{19}F n.m.r. spectroscopy. In both cases the reactions were slow and were complete after one day at room temperature. In both cases the reaction mixtures were slightly yellow, but

no solid was present. $\text{CH}_2(\text{CO}_2\text{PF}_2)_2$ and $(\text{CO}_2\text{PF}_2)_2$ produced by reaction of $\text{S}(\text{PF}_2)_2$ with malonic and oxalic acid respectively had similar n.m.r. parameters and spectra. Each species exhibited a triplet ($^1J_{\text{PF}}$) in the ^{31}P n.m.r. spectrum and a doublet ($^1J_{\text{PF}}$) in the ^{19}F n.m.r. spectrum as expected. The n.m.r. parameters are similar to those found for MeCO_2PF_2 and related compounds (see Table 1.1) as expected and are given below.

Species	$\delta(\text{P})/\text{ppm}$	$\delta(\text{F})/\text{ppm}$	$^1J_{\text{PF}}/\text{Hz}$
$(\text{CO}_2\text{PF}_2)_2$	120.3	-49.2	1383
$\text{CH}_2(\text{CO}_2\text{PF}_2)_2$	122.1	-52.0	1362

These n.m.r. spectra provide strong evidence for the suggested structures of these products. This system would however benefit from further investigation, particularly by ^{13}C n.m.r. spectroscopy, which was not possible in this study due to lack of time. Cromie has previously investigated the reaction of simple carboxylic acids such as acetic acid and found them to react similarly with $\text{S}(\text{PF}_2)_2$ ⁽⁶⁾.

5.3 The Reaction of Sulphuric acid with $\text{S}(\text{PF}_2)_2$

The reaction of sulphuric acid with $\text{S}(\text{PF}_2)_2$ was investigated by ^{31}P n.m.r. spectroscopy. The reaction was carried out in a sealed n.m.r. tube as described in the experimental section. It was clear from the ^{31}P n.m.r. spectrum that the species which would be formed by simple reaction of the hydroxy groups in H_2SO_4 with $\text{S}(\text{PF}_2)_2$ was not

the only product. This product, $\text{SO}_2(\text{OPF}_2)_2$ would be expected to have a ^{31}P n.m.r. spectrum similar to that of other known $-\text{OPF}_2$ compounds, i.e. a triplet ($^1J_{\text{PF}}$) with $\delta(\text{P}) \approx 110$ ppm. This reaction occurred rapidly at room temperature, taking no more than a few minutes, and in addition to PF_2HS four major products were observed in the ^{31}P n.m.r. spectrum. These were all triplets ($^1J_{\text{PF}}$) and their n.m.r. parameters are given below.

Species	$\delta(\text{P})/\text{ppm}$	$^1J_{\text{PF}}/\text{Hz}$	
A	110.5	1355	Large amounts
B	30.0	1160	Small amounts
C	-5.4	1127	" "
D	-39.0	1094	" "

It is possible that species A was the expected product, $\text{SO}_2(\text{OPF}_2)_2$: however there is no conclusive evidence for this and there were clearly three other species present in the reaction mixture. From the magnitude of $^1J_{\text{PF}}$ (see Chapter 1) these three species are probably four coordinate phosphorus compounds and it would appear that extensive oxidation has occurred. It is however possible that if this reaction were carried out on a preparative scale that $\text{SO}_2(\text{OPF}_2)_2$ could be isolated if this species is present.

5.4 The Reaction of Telluric Acid with $\text{S}(\text{PF}_2)_2$

The reaction of telluric acid with $\text{S}(\text{PF}_2)_2$ was investigated. This reaction was carried out in a sealed n.m.r. tube and followed by ^{31}P n.m.r. spectroscopy. The reaction was slow,

requiring a day at room temperature for complete reaction to occur, as indicated by the disappearance of solid $\text{Te}(\text{OH})_6$ and formation of a bright yellow solution. It does not appear that one simple reaction occurred and the n.m.r. parameters of the three major species, other than PF_2HS , are given below. These three species produced triplets in the ^{31}P n.m.r. spectrum.

Species	$\delta(\text{P})/\text{ppm}$	$^1\text{J}_{\text{PF}}/\text{Hz}$	
A	110.3	1358	Large amounts
B	-5.4	1127	Large amounts
C	33.2	1335	Small amounts

No satellite peaks were observed due to coupling to ^{125}Te , spin $\frac{1}{2}$, 7% abundance. Clearly species A could be the expected product, having roughly the n.m.r. parameters expected for $\text{Te}(\text{OPF}_2)_6$. Species B was also observed in the $\text{H}_2\text{SO}_4/\text{S}(\text{PF}_2)_2$ system (see Section 5.3) and may be PF_2HO or a related species. It was again clear that no simple reaction was occurring and further investigation would be necessary to determine the precise reactions occurring. These investigations could not be carried out in the limited time available for this work.

5.5 The Reaction of Selenous Acid (H_2SeO_3) with $\text{S}(\text{PF}_2)_2$

This reaction was carried out in a sealed n.m.r. tube and was only studied very briefly by ^{31}P n.m.r. spectroscopy as it appeared to have little if any synthetic value.

The reaction occurred with great vigour and a red solid (presumably selenium) was formed quickly and in large amounts

at room temperature. The n.m.r. tube in which the reaction was taking place became very hot to touch. The major reaction products, as judged by ^{31}P n.m.r. spectroscopy, were PF_3 , PF_2HS and three other species which were triplets ($^1J_{\text{PF}}$) by ^{31}P n.m.r. spectroscopy with parameters given below.

Species	$\delta(\text{P})/\text{ppm}$	$^1J_{\text{PF}}/\text{Hz}$
A	81.1	1213
B	55.2	1315
C	-20.6	977

The identity of the species tabulated above is not clear but, from the magnitude of $^1J_{\text{PF}}$, it seems likely that A and B are of type PF_2X and that compound C is a phosphorane (PF_2X_3 type). In any case it is clear that a vigorous, uncontrolled reaction has occurred and that this is likely to be of little synthetic value, particularly if carried out in the absence of solvent when it should be even more vigorous. As little time was available it was decided to abandon the study of this reaction in favour of the more promising reactions described elsewhere in this text.

5.6 The Reaction of Hypophosphorous Acid (H_3PO_2) with $\text{S}(\text{PF}_2)_2$

The reaction of hypophosphorous acid with $\text{S}(\text{PF}_2)_2$ was investigated in the hope that a reaction, analogous to that found with $\text{S}(\text{PF}_2)_2$ and phosphorous acid (Chapter 4), would occur forming $\text{PH}(\text{OPF}_2)_2$. This compound would be of particular interest as the fluorines on each $-\text{PF}_2$ group would be inequivalent and display geminal FF coupling due to the

prochiral centre at the central phosphorus. This assumes that all phosphorus atoms are three coordinate but there is also the possibility that this compound would be a structural isomer of that suggested. These structural isomers would also display geminal FF coupling.

However, when H_3PO_2 and $\text{S}(\text{PF}_2)_2$ were mixed in a sealed n.m.r. tube at room temperature a yellow/orange solid formed rapidly and the only species observed in the ^{31}P n.m.r. spectrum, other than PF_2HS and $\text{S}(\text{PF}_2)_2$, was $\text{O}(\text{PF}_2)_2$. Attempts to observe this reaction at reduced temperature resulted in a similar reaction being observed and it was decided not to investigate this system further due to lack of time.

5.7 The Reaction of Diphenylphosphine Oxide with $\text{S}(\text{PF}_2)_2$

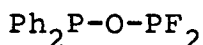
This reaction was carried out on a preparative scale after preliminary investigations using n.m.r. spectroscopy had indicated that it might be synthetically valuable. The reaction was carried out in a vessel in which the solid product could be isolated after removal of the volatile fractions ($\text{S}(\text{PF}_2)_2$ and PF_2HS), as described in the experimental section. The major product of reaction, other than PF_2HS , was a white microcrystalline solid which was handled using standard inert atmosphere techniques. Attempts were made to purify this solid using solvent extraction and some success was had but the compound was never obtained in a totally pure state. The major evidence for the structure of this product therefore comes from ^{31}P and ^{19}F n.m.r. spectroscopy.

An analogous reaction to that found for the dimethylphosphite/S(PF₂)₂ system (see Chapter 4) was expected and this can be summarised by the equation below.



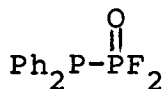
(A)

or



(B)

or



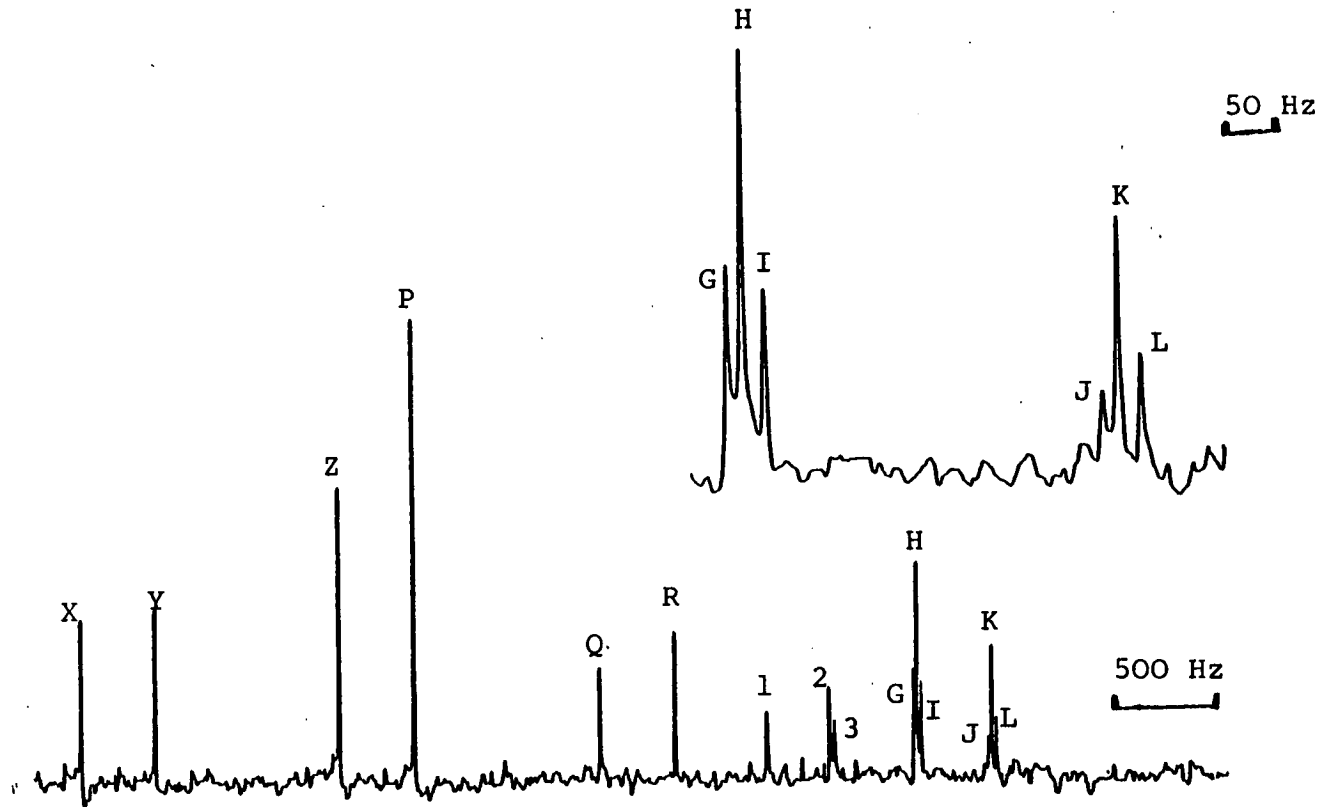
(C)

The n.m.r. spectra suggest that a compound whose n.m.r. parameters are roughly compatible with those expected for isomer A was the product formed. There is however some doubt as to the structure and formulation of this product and detailed arguments for making this assignment follow.

The species concerned exhibited a ³¹P n.m.r. spectrum shown in Figure 5.1. Peaks labelled 1, 2 and 3 are due to impurities and are discussed later in this section. As can be seen from Figure 5.1, the ³¹P n.m.r. spectrum consists of two parts. There is a triplet of doublets (labelled X, Y, Z, P, Q and R). The triplet splitting has a magnitude of 1274 Hz (i.e. XZ, YP, ZQ and PR). The doublet splitting is 366 Hz in magnitude (i.e. XY, PZ and QR). There is a doublet of three lines (labelled G, H, I, J, K and L), the two groups (i.e. G, H, I and J, K, L) appear to be identical in structure

Fig. 5.1

^{31}P n.m.r. Spectrum of $\text{Ph}_2\overset{\text{O}}{\parallel}\text{P}\text{PF}_2$



and an expansion of this region is shown in Fig. 5.1. The separation of line G from line H and of line J from line K is 15.6 Hz. The separation of line H from line I and of line K from line L is 21.7 Hz. The doublet splitting (i.e. GJ, HK and IL) is 366 Hz. It is clear that the doublet splitting in both multiplets is the same and must be a PP coupling. The magnitude of this PP coupling would suggest that it is $^1J_{PP}$ rather than $^2J_{POP}$ which is normally very much smaller (see discussion of PP couplings in Chapter 1). The large triplet splitting must be due to $^1J_{PF}$ and suggest that the unit exhibiting this coupling is a PF_2X group, and from the doublet splitting X appears to be phosphorus. If this is the case then the compound would seem to be isomer A. It should be noted that the observed chemical shifts are not entirely consistent with this. The triplet of doublets (X, Y, Z, P, Q, R) has a phosphorus chemical shift of 114.0 ppm. This is the chemical shift expected for a F_2P-O- compound (see Table 1.1) and would suggest that the species is isomer B. Isomer A would be expected to have a chemical shift of ca. 290 ppm by analogy with the related species F_2PPX_2 (X = GeH_3 or SiH_3).

Little can be deduced from the chemical shift of the other unit, $\delta(P) = -2.3$, (labelled G, H, I, J, K, L) as Ph_2P-O and $Ph_2P(O)-$ compounds may be expected to come in approximately the same region of the phosphorus spectrum.

The reason for the presence of several lines for this unit is not clear and is discussed further later.

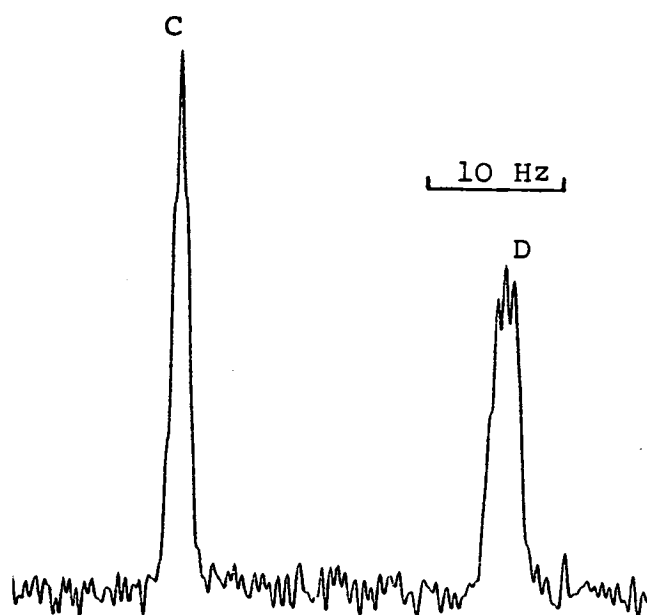
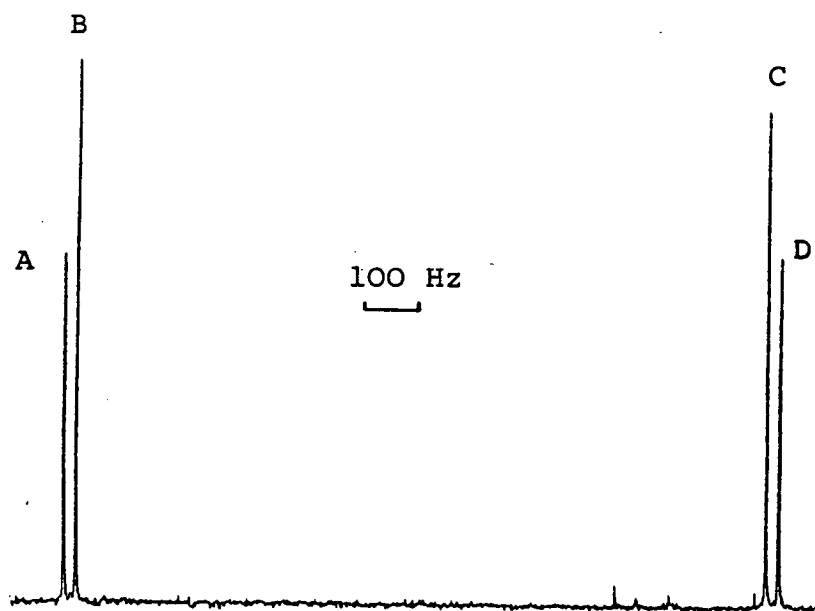
It was hoped that the ^{19}F n.m.r. spectrum would shed some light on this rather complex situation. The ^{19}F n.m.r. spectrum is shown in Figure 5.2 and is again more complex than expected. At low resolution the spectrum appears to consist of a doublet of doublets (labelled A, B, C and D). The larger doublet separation (AC and BD) is 1275 Hz and is clearly consistent with the larger triplet found in the ^{31}P n.m.r. spectrum confirming the presence of a PF_2^- compound. The smaller doublet separation is 23 Hz and the reasons for this splitting are discussed later. The fluorine chemical shift is -35.6 ppm but is of little use in assigning structure as ^{19}F chemical shifts do not appear to correlate clearly with structure.

On closer inspection of the ^{19}F spectrum it can be seen to consist of, not a simple doublet of doublets, but a pattern symmetrical about the centre where the outside lines have fine structure and are broader than the inside lines. (Shown in the bottom part of Fig. 5.1 for the low frequency "pair" of lines.

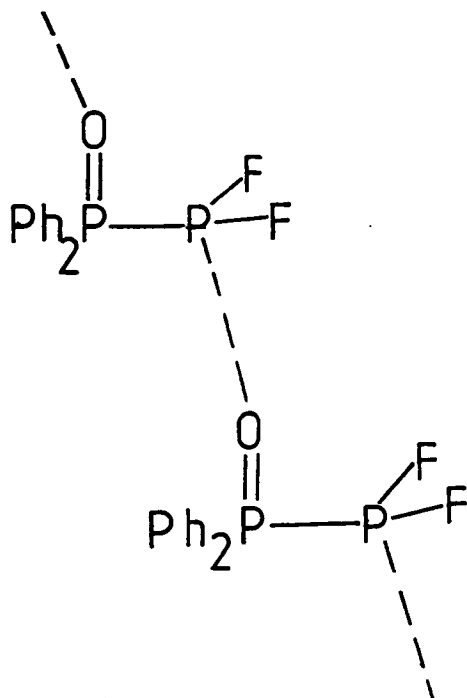
It is clear that some explanation must be found for this phenomenon but before this is discussed it should be noted that isomer C is ruled out completely as the $-\text{PF}_2(\text{O})$ unit would have $\delta(\text{P})$ much nearer to 0 ppm than 114 ppm and a very much smaller value for $^1\text{J}_{\text{PF}}$ (see Chapter 1).

The effects causing the multiplet structure of the phosphorus signals assigned to the $\text{Ph}_2\text{P}-\text{O}$ unit and the complex pattern in the ^{19}F spectrum could be chemical in nature and involve an interaction of the type suggested for $\text{PO}(\text{OPF}_2)_3$ in

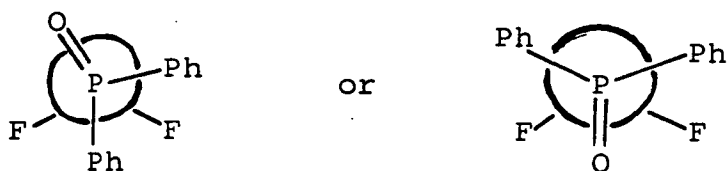
Fig. 5.2 The ^{19}F n.m.r. Spectrum of $\text{Ph}_2\text{P}(\text{O})\text{PF}_2$



Chapter 3, i.e. the phosphoryl oxygen could be interacting with the phosphorus of the PF₂ group as shown below.



There is also the possibility of inter and/or intramolecular hydrogen bonding from the phenyl protons to the PF₂ fluorine atoms. A further complicating factor is that Ph₂P(O)PF₂ could be in more than one conformation ignoring hydrogen bonding effects as shown below.



It is also possible to formulate several isomers by rotation of the planar phenyl groups in this molecule about the C-P bonds. It is also possible that an equilibrium might exist between conformers A, B and C which is rapid but lies heavily to the side of A.

If all these possible effects are considered then the presence of several peaks where only a doublet is expected in the ^{31}P spectrum for the $\text{Ph}_2\text{P-O-}$ unit may be explained as being due to more than one isomer/conformer. The absence of $^3\text{J}_{\text{PF}}$ may be linked in some way to the complex pattern observed in the ^{19}F n.m.r. spectrum. It is realised that this system requires further investigation but this was not possible in the time available and it is to be hoped that this will be investigated further by other workers. It may be of more use if the reaction between $\text{S}(\text{PF}_2)_2$ and $\text{Me}_2\text{P}(\text{O})\text{H}$ and/or $(\text{F}_3\text{C})_2\text{POH}$ were investigated as these systems should be more amenable to investigation by n.m.r. spectroscopy than the phenyl analogue. These systems could be studied more thoroughly using ^{13}C and ^1H n.m.r. in addition to ^{31}P and ^{19}F n.m.r. spectroscopy and many more couplings should be observable. The trifluoromethyl system might well produce a volatile species which could be handled using vacuum line techniques rather than inert atmosphere techniques. This would have great advantages in that water could be more rigorously excluded and purification could be carried out using fractional condensation.

In conclusion, the results, when viewed overall, suggest that the following reaction has occurred.



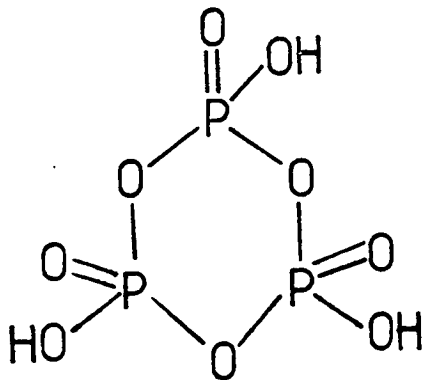
Further work is however necessary for this to be substantiated.

Peaks labelled 1, 2 and 3 in the ^{31}P n.m.r. spectrum (Fig. 5.1) are due to impurities as was shown by attempted purification of the species. Peaks 1 and 3 disappeared and peak 2 (due to PPh_2HO) increased in intensity. The increase in the amount of diphenyl phosphine oxide indicates that some hydrolysis had taken place during attempted purification.

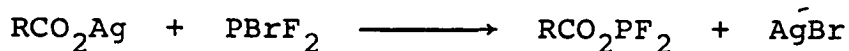
The results obtained in this Chapter probably leave more questions unanswered than solved and should provide the basis for future study. The scope for future investigations is discussed in the next Chapter - Conclusions and Future Work.

There is no reason to believe that pyrophosphoric acid and hypophosphoric acid would not react with $S(PF_2)_2$ to form compounds (1) and (2) by analogy with the orthophosphoric acid/ $S(PF_2)_2$ and phosphorous acid/ $S(PF_2)_2$ reactions. Compounds (1) and (2) would have particularly interesting ^{31}P and ^{19}F n.m.r. spectra and it would be interesting to compare $^1J_{PF}$ and $^2J_{POP}$ and other coupling constants in these molecules with each other and with those of related species such as $PO(OPF_2)_3$ and $P(OPF_2)_3$. Compounds (1) and (2) would also contain prochiral centres at the phosphoryl phosphorus atoms and so the geminal fluorines in the $-PF_2$ groups would be chemically inequivalent and values of $^2J_{FF}$ should be obtainable.

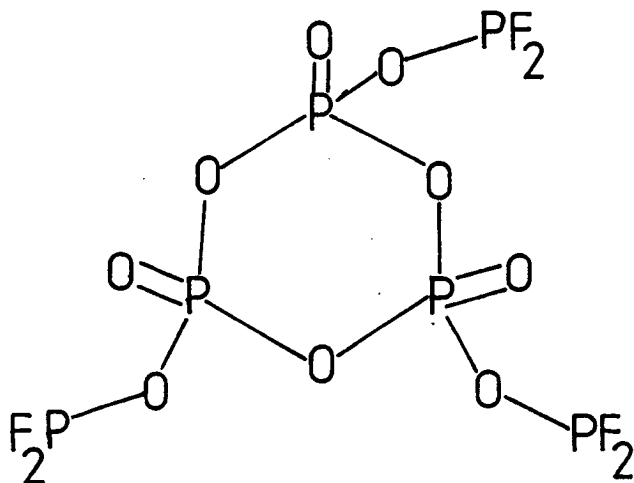
There are some other oxyacids of phosphorus which can be obtained only in dilute aqueous solution or as their salts. Clearly these compounds would not be suitable for reaction with $S(PF_2)_2$ as were the pure oxyacids and some other synthetic route would have to be employed if their $-PF_2$ derivatives were to be made. One such acid which can only be obtained in dilute solution or as its salt is the cyclic acid shown below.



It would be worth investigating the reaction of the silver salt of the above acid with PBrF_2 . This reaction might be expected to produce the PF_2 derivative by analogy with the PBrF_2 /silver carboxylate reaction (see section 1.1).



It should therefore be possible to produce the extremely interesting species shown below.

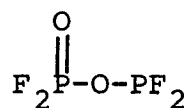
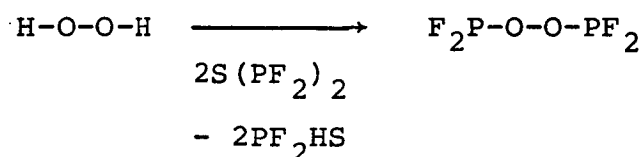


This species would be extremely interesting from the point of view of ^{31}P and ^{19}F n.m.r. spectroscopy, particularly as there is the possibility of several different conformational and structural isomers due to the presence of the ring. It should also be possible to form $-\text{PF}_2$ derivatives of other such condensed oxyacids of phosphorus by this route and there is great scope for future work.

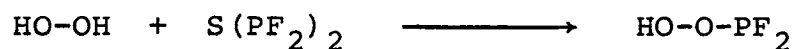
As mentioned in section 3.4(II) it would be worth investigating the reaction of difluorophosphoric acid with $\text{S}(\text{PF}_2)_2$ to see if a sample of $\text{PF}_2\text{O}(\text{OPF}_2)$ could be obtained in which $^2\text{J}_{\text{PP}}$ and $^3\text{J}_{\text{PF}}$ could be detected. These couplings were not observed in the ^{31}P and ^{19}F n.m.r. spectra of the sample prepared by Charton and Cavell but would be expected to be observable by comparison with the related species given in

Table 3.5. The absence of these couplings may be due to some intermolecular scrambling process caused by the presence of impurities which might not be present if the compound was prepared by another synthetic route. Another reaction which would be worth studying would be that of $S(PF_2)_2$ with hydrogen peroxide. This might produce $PF_2O(OPF_2)$ or the isomer with a peroxy bridge (perhaps observable at low temperature by n.m.r. spectroscopy).

i.e.

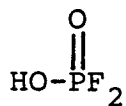


There is also the possibility that an equimolar mixture of hydrogen peroxide and $S(PF_2)_2$ would react as follows:



(3)

or

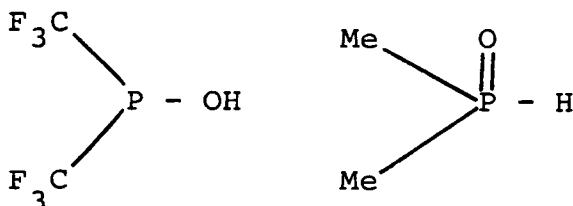


(4)

It is also possible that species (3) might be observable at

This system needs further study for the identity of species (A) to be confirmed (see section 5.7) and it would also be worth investigating the reaction of $(F_3C)_2POH$ and Me_2POH with $S(PF_2)_2$.

$(F_3C)_2POH$ and Me_2POH , although closely related, exist in quite different structural forms as shown below.



It is therefore possible that reaction of these compounds with $S(PF_2)_2$ would produce compounds which also existed in different structural forms



There is also the possibility of an equilibrium between these isomeric forms and this line of research is potentially very interesting and rewarding.

The reaction of $S(PF_2)_2$ with the various phosphorus compounds mentioned in this section could lead to the formation of many novel species and lead to a significant advancement in this field of chemistry. In particular the use of possible products as ligands could be investigated and their n.m.r. parameters would be of great interest.

There are many other hydroxy species which could be reacted with $S(PF_2)_2$ in the hope of forming the $-PF_2$ derivative and a few are mentioned below.

The volatile acid, pentafluorotelluric acid (F_5TeOH)⁽⁷¹⁾, might well react with $S(PF_2)_2$ to yield the very interesting species F_5TeOPF_2 which would also be expected to be volatile. F_3CSO_3H might also react with $S(PF_2)_2$ to produce $F_3CSO_3PF_2$ which would be expected to be much more volatile than $MeSO_3PF_2$ produced by Campbell by the analogous $MeSO_3H/S(PF_2)_2$ reaction (see section 1.1). The reaction of nitric acid with $S(PF_2)_2$ would be worthy of study. Nitric acid is however extensively autoionised in its liquid state and it might be necessary for the reaction to be carried out in the gas-phase to avoid competing reactions which might occur in the presence of ionic species.

Reactions of carboxylic acids mentioned in section 5.2 clearly need further investigation and many $-PF_2$ derivatives could be formed by this route. It would be particularly interesting to react formic acid with $S(PF_2)_2$ in the hope of forming HCO_2PF_2 .

In Chapter 2 the reaction of $S(PF_2)_2$ with alcohols was shown to be synthetically useful and clearly this reaction could be used for the synthesis of many $-OPF_2$ compounds. As mentioned in Chapter 1, Stewart has used this reaction to prepare both $F_2PO(CH_2)_3OPF_2$ and $F_2PO(CH_2)_6OPF_2$ and it would be possible to make a series of compounds of general formula $F_2PO(CH_2)_nOPF_2$. The use of these compounds as bidentate ligands could be investigated and some sort of systematic variation in their

properties would be expected as n varies.

In conclusion, there is great scope for future work based on the results of experiments presented in Chapters 2 to 5 and many novel and interesting chemical species could be produced.

CHAPTER 7

EXPERIMENTAL

7.1 General

The difluorophosphites described in this work are all air and water sensitive compounds and all experimental procedures used had to take this factor into account. There are many methods of manipulating air sensitive compounds⁽³⁾, e.g. vacuum line, schlenk line and glove box techniques, and the method chosen depended on the physical properties of the compounds being handled or prepared. Vacuum line techniques are ideal for the manipulation of volatile air sensitive compounds but are not applicable to involatile compounds. Similarly inert atmosphere techniques cannot easily be used to handle compounds which are of high volatility but are essential for the manipulation of low volatility air sensitive compounds.

In this work it was often necessary to use a combination of techniques e.g. to react the involatile phosphoric acid with the volatile $S(PF)_2$ and to handle the products which differed in volatility considerably.

Infra red spectra of gaseous samples were recorded using a glass cell fitted with CsI or KBr windows. Infra red spectra of liquid samples were recorded as a film between KBr plates contained in an air tight holder. Low temperature infra red spectra were recorded using standard apparatus and CsI windows⁽³⁾. Gaseous samples were admitted into the mass spectrometer from ampoules after first purging the system

with trimethylsilylchloride or silyl bromide to remove water from the system. Liquids were injected into the mass spectrometer through a rubber septum. The sample being contained in a microsyringe inside a sealed nitrogen filled polyethylene bag until injected by piercing the bag and septum simultaneously. Raman spectra of liquids were recorded with the compound sealed in a thin walled pyrex glass ampoule. N.m.r. spectra were recorded in sealed 5 or 10 mm pyrex glass n.m.r. tubes containing a suitable deuterated solvent with or without an internal standard such as T.M.S. Reference compounds used for n.m.r. spectra are given in Table 7.1.

Photoelectron spectra were recorded by admitting the sample to the evacuated system from an ampoule fitted with a sovirel tap.

Melting points were determined using an ampoule fitted with a glass coated iron plunger. The sample was first admitted via a sovirel tap and condensed at the bottom of the ampoule. The plunger was then rested on the solid while holding the system at -196°C . The ampoule was then surrounded by a bath of solvent (acetone or pentane) pre cooled to a suitable temperature by the addition of liquid nitrogen. The bath was then warmed slowly by the addition of solvent at room temperature while recording the temperature using an electronic thermometer. The melting of the solid was evident by the collapse of the plunger and the temperature was then noted.

Table 7.1 Reference Compounds Used for n.m.r. Spectroscopy

Nucleus	Compound	Resonance
^1H	SiMe_4	59.7 (FX60Q)
		100.1 (XL100)
		360.0 (WH360)
^{11}B	$\text{B}(\text{OMe})_3$	115.5 (WH360)
^{19}F	CFCl_3	94.1 (XL100)
^{31}P	H_3PO_4 (85% aqueous soln.)	24.2 (FX60Q)
		40.5 (XL100)

7.2 Instrumentation

Infra-red spectra were recorded in the range 4000 - 200 cm^{-1} using a Perkin Elmer 577 grating spectrometer.

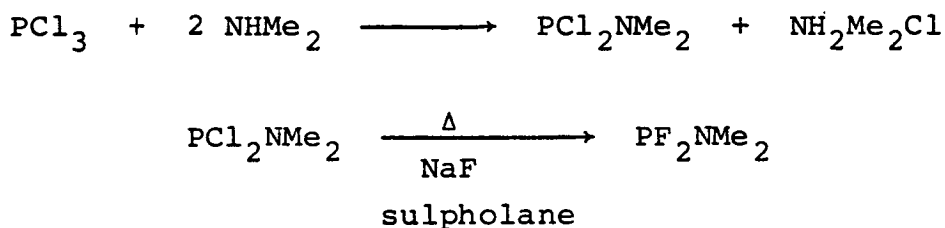
Raman spectra were obtained using a Cary 83 spectrometer with 488 nm argon-ion excitation. Mass spectra were recorded using an AEI MS902 spectrometer.

N.m.r. spectra were recorded using a JEOL FX60Q spectrometer (for ^{31}P or ^1H spectra), a VARIAN XL100 spectrometer (for ^{31}P , ^{19}F , ^1H spectra), a BRUKER WH360 spectrometer (for ^1H , ^{13}C and ^{11}B spectra) or a VARIAN HA100 spectrometer (for ^1H spectra).

Photoelectron spectra were recorded on a Perkin-Elmer PS16 spectrometer having He(1) excitation (21.22 eV).

7.3 Preparation of Reagents

The basic starting material for all difluorophosphines used was PF_2NMe_2 . This reagent was synthesised by standard means according to the following reaction scheme⁽⁷²⁾.

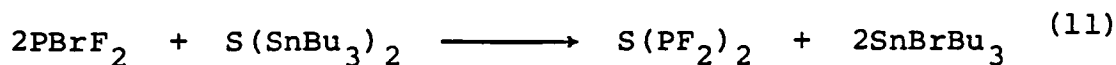
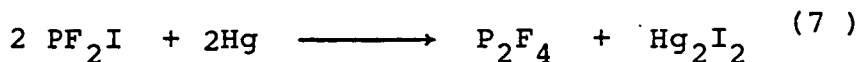


The PF_2NMe_2 so prepared was then used to make PF_2I or PF_2Br as follows⁽⁷²⁾.



X = Br or I

These difluorophosphinohalides were then used to prepare $S(PF_2)_2$ or P_2F_4 as follows.



Methods of preparation of other reagents are summarised in Table 7.2.

7.4 Experimental Details Relating to Chapter 2

7.4.1 The Reaction of $S(PF_2)_2$ with $(CCH_2OH)_2$

$(CCH_2OH)_2$ (0.1 mmol) and $S(PF_2)_2$ (0.25 mmol) were reacted at room temperature in a sealed 5 mm n.m.r. tube containing $CDCl_3$ as solvent. Reaction was rapid at room temperature, being complete within 15 seconds, and was accompanied by effervescence. The reaction was observed by ^{31}P n.m.r. spectroscopy.

7.4.2 The Reaction of $S(PF_2)_2$ with $N(CH_2CH_2OH)_3$

$N(CH_2CH_2OH)_3$ (0.09 mmol) and $S(PF_2)_2$ (0.33 mmol) were reacted at room temperature in a sealed 5 mm n.m.r. tube containing $CDCl_3$ as solvent. The reaction occurred rapidly at room temperature, being essentially complete by the time the ^{31}P n.m.r. spectrum was recorded (a few minutes) and was accompanied by the formation of an unidentified yellow solid.

Table 7.2 The Preparation of Reagents

Reagent	Method	Reference
B_2H_6	$KBH_4 + H_3PO_4$	74
P_2Me_4	$P_2Me_4S_2 + Fe$	75
$P_2Me_4S_2$	$SPCl_3 + MeMgI$	75
Si_2Me_6	$SiClMe_3 + Na/K$ alloy	76
$S(SnBu_3)_2$	$SnBu_3Cl + Na_2S$	77
$PPh_2(OH)$	$PPh_2H +$ dry air	78
$M(\text{cycloheptatriene})-(CO)_3$	$M(CO)_6 +$ cycloheptatriene	79
(M = W or Mo)		
SEt_2	$EtSH +$ iodine	80

7.4.3

$S(PF_2)_2$ (4 mmol) was condensed into a 40 ml glass ampoule containing $S(CH_2CH_2OH)_2$ (1.7 mmol) and the reagents were warmed to room temperature for 45 minutes. The volatile products were then removed onto a vacuum line while the mixture was held at $-78^\circ C$. The remaining $S(CH_2CH_2OPF_2)_2$ was then distilled in vacuo at room temperature into another ampoule which was sealed. An 80% yield (1.4 mmol) of $S(CH_2CH_2OPF_2)_2$ was obtained based on $S(CH_2CH_2OH)_2$ used.

The product, $S(CH_2CH_2OPF_2)_2$, was a mobile colourless liquid at room temperature and was subsequently manipulated by syringe in an inert atmosphere.

7.4.4 The Reaction of $S(CH_2CH_2OPF_2)_2$ with $Mo(CO)_3$ (cycloheptatriene).

This reaction was originally carried out in a sealed 5 mm n.m.r. tube using $S(CH_2CH_2OPF_2)_2$ (0.10 mmol) and $Mo(CO)_3$ cycloheptatriene (0.10 mmol) with $CDCl_3$ as solvent. The reaction occurred over a period of ca. 5 minutes at room temperature and produced large amounts of insoluble orange material. This insoluble material was presumed to be polymeric material. This material would be expected to form less readily if the reagents were mixed under more dilute conditions and so the reaction was repeated. In this experiment a solution of $S(CH_2CH_2OPF_2)_2$ (0.3 mmol in 5 ml CH_2Cl_2) and a solution of $Mo(CO)_3$ cycloheptatriene (0.3 mmol in 5 ml CH_2Cl_2) were added dropwise by syringe to a flask containing 10 ml CH_2Cl_2 over a period of ca. 15 minutes

in an inert atmosphere. The reaction mixture was then filtered and evaporated using schlenk techniques. Again considerable amounts of insoluble solids were produced but a small sample of an orange material was obtained. This was dissolved in CDCl_3 and its ^{31}P n.m.r. spectra recorded.

7.4.5

$\text{S}(\text{CH}_2\text{CH}_2\text{OPF}_2)_2$ (0.06 mmol) was reacted with $\text{W}(\text{CO})_3$ cycloheptatriene (0.06 mmol) in a sealed 5 mm n.m.r. tube containing CDCl_3 as solvent. The reaction occurred over a period of ca. 10 minutes at room temperature and was accompanied by the formation of large amounts of insoluble red material.

7.5 Experimental Details Relating to Chapter 3

7.5.1 The Preparation of $\text{PO}(\text{OPF}_2)_3$

$\text{S}(\text{PF}_2)_2$ (16.5 mmol) was condensed into a 250 ml glass ampoule containing 100% H_3PO_4 (4.5 mmol). The mixture was then warmed to room temperature and reaction was evident by effervescence and disappearance of solid material. After 30 minutes at room temperature the volatile products were removed onto a vacuum line and the $\text{PO}(\text{OPF}_2)_3$ produced was purified by fractional condensation in vacuo. The fractional condensation was carried out in two stages, first through a -96°C bath to remove any products of very high volatility, then through a -45°C trap. The product,

was involatile at -45°C and a 95% yield (4.3 mmol) was obtained. The product, a clear liquid at -45°C , was characterised by vibrational spectroscopy, n.m.r. spectroscopy and mass spectrometry.

7.5.2 The Preparation of $\text{PFO}(\text{OPF}_2)_2$

$\text{S}(\text{PF}_2)_2$ (5 mmol) was condensed into an 40 ml glass ampoule containing $\text{PFO}(\text{OH})_2$ (1.5 mmol). The mixture was then allowed to warm to room temperature for 20 minutes after which the volatile products were removed onto a vacuum line for purification by fractional condensation. The $\text{PFO}(\text{OPF}_2)_2$ was obtained by fractional condensation of the mixture through a -78°C trap at which temperature this compound was involatile. An 87% (1.3 mmol) yield of $\text{PFO}(\text{OPF}_2)_2$ was obtained and this compound was characterised by n.m.r. spectroscopy, mass spectrometry and infra red spectroscopy. The product was slightly contaminated with $\text{PO}(\text{OPF}_2)_3$ which was present due to a phosphoric acid contaminant in the fluorophosphoric acid.

7.5.3 The Preparation of $\text{PO}(\text{OPF}_2)_2\text{Ph}$

This reaction was carried out in a 20 ml ampoule fitted with a 5 mm glass n.m.r. tube.

$\text{S}(\text{PF}_2)_2$ (0.5 mmol) was condensed into this ampoule which contained $\text{PO}(\text{OH})_2\text{Ph}$ (0.2 mmol) and the mixture was warmed to room temperature for 15 minutes. The volatile products were then removed onto a vacuum line and the involatile product, $\text{PO}(\text{OPF}_2)_2\text{Ph}$, was sealed into the n.m.r. tube after the addition of CDCl_3 .

7.5.4 The Reaction of PO(OH)Ph₂ with S(PF₂)₂

PO(OH)Ph₂ (0.05 mmol) was reacted with S(PF₂)₂ (0.11 mmol) in a sealed 5 mm n.m.r. tube containing CDCl₃ as solvent. The reaction was rapid at room temperature, being complete within one minute, and was accompanied by effervescence and disappearance of solid material.

7.5.5 The Reaction of PO(OPF₂)₃ with B₂H₆

A mixture of PO(OPF₂)₃ (0.18 mmol) and B₂H₆ (0.6 mmol) contained in a sealed 5 mm n.m.r. tube with CDCl₃ as solvent was warmed to room temperature and the ensuing reaction was followed over a period of several days by ³¹P n.m.r. spectroscopy as described in Section 3.7.

The mixture became less mobile on standing at room temperature and became pale yellow and gelatinous after a day at room temperature. After a few days at room temperature the volatile components of the mixture were removed onto a vacuum line leaving a brilliant white powder. This solid was found to be pyrophoric when exposed to air and its characterisation was not completed as time did not permit.

7.6 Experimental Details Relating to Chapter 4

7.6.1 The Preparation of P(OPF₂)₃ and PO(OPF₂)₂H

(a) The Preparation of P(OPF₂)₃

S(PF₂)₂ (10 mmol) was condensed into a 250 ml glass ampoule containing phosphorous acid (2.0 mmol). The mixture

was then warmed to room temperature and reaction was evident by disappearance of solid and effervescence. After 4½ hours at room temperature the volatile products were removed onto a vacuum line and the product was purified by fractional condensation.

The fractional condensation was carried out in two stages. The mixture was first fractionally condensed using a -96°C bath to remove products of high volatility. The final fractionation was carried out using a -64°C bath at which temperature $\text{P}(\text{OPF}_2)_3$ was involatile. A 95% (1.9 mmol) yield of $\text{P}(\text{OPF}_2)_3$ was obtained.

(b) The Preparation of $\text{PHO}(\text{OPF}_2)_2$

Phosphorous acid (0.17 mmol) was reacted with $\text{S}(\text{PF}_2)_2$ (0.40 mmol) in a sealed 5 mm n.m.r. tube containing CDCl_3 . The reaction was carried out by allowing the mixture to warm to room temperature for a few seconds until effervescence ceased and all solid material had disappeared. The mixture was then cooled and the n.m.r. spectra were recorded at -60°C .

7.6.2 The Preparation of $\text{P}(\text{OMe})_2\text{OPF}_2$

$\text{S}(\text{PF}_2)_2$ (3 mmol) was condensed into a 250 ml glass ampoule containing dimethylphosphite (2.0 mmol) and the mixture was warmed to room temperature for 1½ hours. The volatile products were then removed onto a vacuum line and purified by fractional condensation. The volatile products

were first fractionally condensed by passing through a trap held at -78°C and collecting the more volatile products at -196°C . The fraction stopping at -78°C was then further fractionally condensed by passing through a trap held at -46°C to a -196°C trap. The $\text{P}(\text{OMe})_2\text{OPF}_2$ obtained was involatile at -46°C and an 85% (1.7 mmol) yield was obtained.

7.6.3 The reaction of $\text{S}(\text{PF}_2)_2$ with Diphenylphosphite

$\text{S}(\text{PF}_2)_2$ (0.15 mmol) was reacted with $\text{PhO}(\text{OPh})_2$ (0.1 mmol) in a sealed 5 mm n.m.r. tube containing CD_2Cl_2 as solvent. The reaction was carried out at room temperature and was complete by the time the ^{31}P n.m.r. spectrum was recorded (ca. 6 minutes).

7.6.4 The Reaction of $\text{P}(\text{OMe})_2\text{OPF}_2$ with B_2H_6

(a) $\text{P}(\text{OMe})_2\text{OPF}_2$ (0.08 mmol) was reacted at room temperature with B_2H_6 (0.04 mmol) in a sealed 5 mm n.m.r. tube containing CDCl_3 as solvent. The reaction was observed by ^{31}P n.m.r. spectroscopy initially and was complete after ca. 10 minutes at room temperature. The major reaction product was the mono BH_3 adduct.

(b) $\text{P}(\text{OMe})_2\text{OPF}_2$ (0.1 mmol) was reacted with B_2H_6 (0.2 mmol) in a sealed 5 mm n.m.r. tube containing CDCl_3 as solvent. Again the reaction was followed initially by ^{31}P n.m.r. spectroscopy. The mono BH_3 adduct again formed rapidly at room temperature, this reaction being complete

after 10 minutes at room temperature. A much slower reaction then occurred to form the bis-BH₃ adduct, this reaction required several hours at room temperature and was essentially complete after 36 hours.

7.7 Experimental Details Relating to Chapter 5

7.7.1 The Reaction of S(PF₂)₂ with Malonic Acid or Oxalic Acid

S(PF₂)₂ (0.25 mmol) was reacted with the acid (0.1 mmol) in a sealed 5 mm n.m.r. tube containing CDCl₃ as solvent. The reaction was slow at room temperature and a pale yellow solution was formed after 19 hours at room temperature. At this time all solid acid had disappeared.

7.7.2 The Reaction of S(PF₂)₂ with Sulphuric Acid

H₂SO₄ (0.52 mmol) was reacted with S(PF₂)₂ (1.2 mmol) in a sealed 5 mm n.m.r. tube containing CDCl₃ as solvent. The reaction was rapid and was essentially complete by the time the ³¹P n.m.r. spectrum was recorded (ca. 5 minutes).

7.7.3 The Reaction of S(PF₂)₂ with Telluric Acid

Te(OH)₆ (0.05 mmol) was reacted with S(PF₂)₂ (0.4 mmol) in a sealed 5 mm n.m.r. tube containing CDCl₃ as solvent. The reaction was slow at room temperature and after 24 hours at room temperature only a small amount of solid telluric acid remained (ca. less than 5%) and a clear yellow solution had formed.

7.7.4 The Reaction of $S(PF_2)_2$ with Selenous Acid

$S(PF_2)_2$ (0.4 mmol) was reacted with H_2SeO_3 (0.2 mmol) in a sealed 5 mm n.m.r. tube containing $CDCl_3$ as solvent. The reaction was rapid and vigorous at room temperature being complete within ten minutes. The reaction proceeded with the formation of large amounts of red solids (presumably selenium) and the evolution of heat.

7.7.5 The Reaction of $S(PF_2)_2$ with Hypophosphorous Acid

H_3PO_2 (0.05 mmol) was reacted with $S(PF_2)_2$ (0.4 mmol) in a sealed 5 mm n.m.r. tube containing $CDCl_3$ as solvent. The reaction was rapid at room temperature and was accompanied by the formation of an orange solid.

7.7.6 The Reaction of Diphenylphosphine oxide with $S(PF_2)_2$

This reaction was carried out in a pyrex glass ampoule fitted with a cold finger. The cold finger had a constricted section in order that it could be sealed off and the cold finger plus contents removed to an inert atmosphere.

$S(PF_2)_2$ (9 mmol) was condensed into the 200 ml ampoule which contained diphenylphosphine oxide (3.4 mmol). The reaction mixture was then warmed to room temperature and reaction was evident by effervescence and disappearance of solid material leaving a clear colourless solution. The mixture was then left at room temperature for 15 minutes with agitation. The volatile components were then removed onto a vacuum line very slowly such that the white solid product remained at the base of the cold finger. The cold finger was then sealed at the constriction and the

white product removed for manipulation in an inert atmosphere.

The white product was seen to consist largely of microcrystalline material but was contaminated with a small amount of yellow liquid. Attempts were then made to purify this solid by extraction into ether and filtration. This process was repeated using n-pentane. The product obtained was free from the yellow oil but contained some diphenylphosphine oxide (presumably formed by hydrolysis). By examination of its ^{31}P and ^{19}F n.m.r. spectra the product was seen to be reasonably pure (see section 5.7) and was assigned as $\text{Ph}_2\text{P}(\text{O})\text{PF}_2$. The yield of this material was not determined as a large amount of this material was lost during the manipulation procedure.

7.7.7 The Reaction of $\text{S}(\text{PF}_2)_2$ with Sulphamic Acid

Sulphamic acid (0.1 mmol) and $\text{S}(\text{PF}_2)_2$ (0.25 mmol) were mixed in a sealed 5 mm n.m.r. tube containing CDCl_3 as solvent. The reaction mixture was held at room temperature for 50 hours during which time no reaction was evident from ^{31}P n.m.r. spectra recorded.

7.7.8 The Reaction of $\text{S}(\text{PF}_2)_2$ with Boric Acid

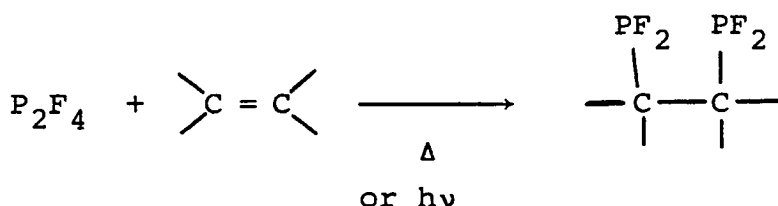
Boric acid (0.1 mmol) was mixed with $\text{S}(\text{PF}_2)_2$ (0.4 mmol) in a sealed 5 mm n.m.r. tube containing CDCl_3 as solvent. No reaction was observed by ^{31}P n.m.r. spectroscopy after 27 hours at room temperature.

APPENDIX 1

Some Reactions of Tetrafluorodiphosphine

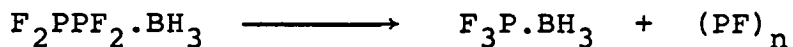
Introduction

Most reactions of tetrafluorodiphosphine reported proceed with cleavage of the phosphorus-phosphorus bond which is very chemically reactive. The extreme reactivity of the phosphorus-phosphorus bond probably accounts for the lack of success in the attempted preparation of tetrafluorodiphosphine by fluorination of tetraiododiphosphine (81). Tetrafluorodiphosphine has been shown to react with alkenes in the following manner (57).



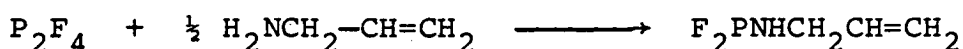
This reaction occurs at elevated temperatures ($\sim 300^\circ\text{C}$) or when irradiated with ultraviolet light (3000 \AA). Under these conditions tetrafluorodiphosphine has been shown to produce PF_2 radicals (42,82). It therefore appears that these reactions are radical reactions. The reaction of tetrafluorodiphosphine with perfluoroalkenes occurs similarly but more slowly and in lower yields as the degree of fluorination is increased (57,61). This indicates the preference for an electronegative site of reaction.

Tetrafluorodiphosphine reacts smoothly with diborane to form the 1:1 adduct⁽¹²⁾, which slowly decomposes with cleavage of the phosphorus-phosphorus bond.



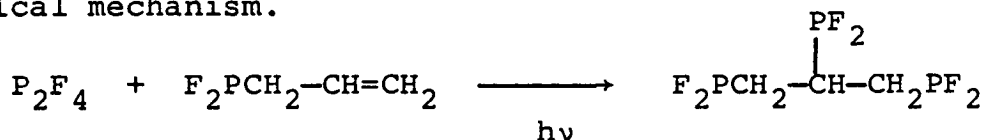
Tetrafluorodiphosphine appears to be a stronger base towards borane⁽³⁾ than is trifluorophosphine⁽¹²⁾. The 1:2 borane adduct can also be prepared by reaction of $\text{P}_2\text{F}_4 \cdot \text{BH}_3$ with borane carbonyl⁽³⁸⁾, however this adduct is very unstable towards decomposition and dissociation.

Tetrafluorodiphosphine reacts with allylamine as follows⁽⁴⁰⁾.



and with N,N dimethylallylamine to form an unidentified brown solid.

Both reactions appear to proceed via a non-radical mechanism. cf. The following mechanism which proceeds via a radical mechanism.



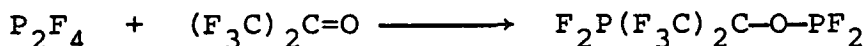
Tetrafluorodiphosphine is very air sensitive and its reaction with oxygen can be used to prepare $\text{O}(\text{PF}_2)_2$ in reasonably good yields⁽¹⁹⁾.



The phosphorus-phosphorus bond of tetrafluorodiphosphine is also cleared by the action of Brønsted-Lowry acids⁽¹²⁾.



Tetrafluorodiphosphine has also been found to react with diselenides⁽³⁰⁾ and hexafluoroacetone⁽¹¹⁾ as follows.



The reaction of tetrafluorodiphosphine with $(\text{F}_3\text{C})_2\text{PPH}_2$ and $(\text{F}_3\text{C})_2\text{AsPH}_2$ produces $(\text{F}_3\text{C})_2\text{PPF}_2$ and $(\text{F}_3\text{C})_2\text{AsPF}_2$ respectively along with F_2PPH_2 ⁽⁷³⁾.

As can be seen from the above discussion tetrafluorodiphosphine is potentially a very useful reagent for the synthesis of difluorophosphines. It was hoped to use tetrafluorodiphosphine to make novel difluorophosphines. To this end numerous reactions of tetrafluorodiphosphine with a wide variety of reagents were studied. These reactions were not however found to be of synthetic value and the results are discussed in the following sections of this appendix.

A.1 Results and Conclusions

The reactions of P_2F_4 with a wide variety of reagents were investigated and experimental details are given in section A.2. While many of these reactions have not been investigated as fully as possible due to lack of time the results give a general impression of how P_2F_4 reacts with many compounds. It is hoped that these results will be of use to future workers in this field by indicating potentially fruitful areas of research and at the same time indicating areas of research which are unlikely to produce any useful results.

The reactions investigated fall into four categories and are dealt with as such in the following sections.

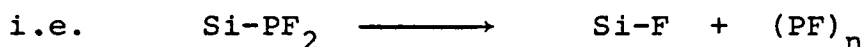
- (a) The reaction of P_2F_4 with silyl and Germyl reagents.
- (b) The reaction of P_2F_4 with chlorides of boron, phosphorus and sulphur.
- (c) The reactions of P_2F_4 with phosphorus and hydrogen chalconides.
- (d) The reaction of P_2F_4 with P_2Me_4 .

A.1.1 The Reaction of P_2F_4 with Silyl and Germyl Reagents

- (a) The Reaction of P_2F_4 with Silyl reagents.

The reactions of P_2F_4 with SiH_3NMe_2 , SiF_3NMe_2 , SiH_3I , SiH_3Br , SiH_3F , Si_2Me_6 , $N(SiH_3)_3$, $Hg(SiMe_3)_2$, and $S(SiH_3)_2$ were investigated. Si_2H_6 , Si_2Me_6 , SiH_3F and $N(SiH_3)_3$ were found to be inert towards P_2F_4 . In the other cases reaction

proceeded with cleavage of the silicon-halogen, silicon-nitrogen and silicon-sulphur bonds. The silyl or trifluoro-silyl groups remained intact and a silicon fluorine bond was formed. In no case was the Si-PF₂ species produced although it is possible that this species was an intermediate in the reaction.



This is consistent with the observed formation of an orange solid which may have been (PF)_n polymer.

In the reaction mixtures of P₂F₄ with SiH₃NMe₂, SiF₃NMe₂, S(SiH₃)₂, Hg(SiMe₃)₂ and SiH₃I a species with the following n.m.r. spectra was observed. This species was also observed in the reaction mixture of P₂F₄ with sulphamic acid. It is postulated that this species is P(PF₂)₂I and that the iodine has been derived from PF₂I present as a slight impurity in the P₂F₄. The ³¹P and ¹⁹F n.m.r. spectra at low resolution were as follows.

The ³¹P n.m.r. spectrum consisted of a triplet of doublets

$$\begin{aligned} \delta(\text{P}) &= 270 \text{ ppm} \\ {}^1J_{\text{PF}} &= 1210 \text{ Hz (triplet)} \\ {}^1J_{\text{PP}} &= 325 \text{ Hz (doublet)} \end{aligned}$$

The lines associated with this multiplet showed some fine structure which was not clearly resolved but which would be expected for signals associated with the PF₂ group in P(PF₂)₂I due to interaction of the two PF₂ groups. The ³¹P spectrum of this multiplet is shown in Figure A.1. A second multiplet

was also observed in the ^{31}P n.m.r. spectrum which was weak and poorly resolved but appeared to consist of a triplet of quintets.

$$\begin{aligned}\delta(\text{P}) &= 32 \text{ ppm} \\ {}^1\text{J}_{\text{PP}} &= 325 \text{ Hz (triplet)} \\ {}^2\text{J}_{\text{PF}} &= 64 \text{ Hz (quintets)}\end{aligned}$$

This is assigned to the central phosphorus of $\text{P}(\text{PF}_2)_2\text{I}$.

The ^{19}F n.m.r. spectrum of this species consisted of a doublet of doublets

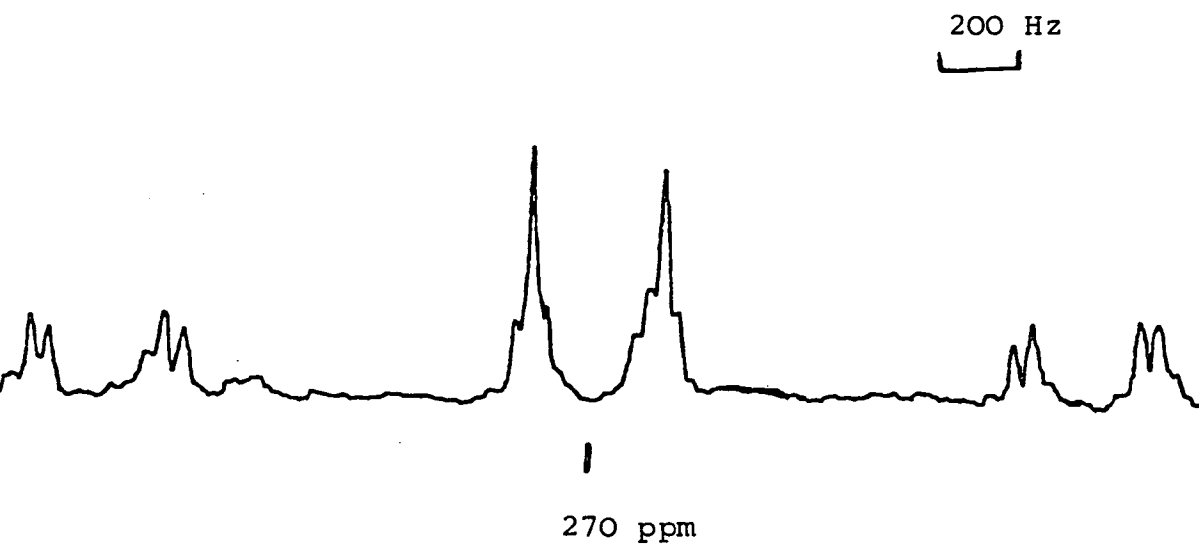
$$\begin{aligned}\delta(\text{F}) &= -90 \text{ ppm} \\ {}^1\text{J}_{\text{PF}} &= 1213 \text{ Hz (doublet)} \\ {}^2\text{J}_{\text{PF}} &= 63 \text{ Hz (doublet)}\end{aligned}$$

Again this spectrum had fine structure associated with it as would be expected. This pattern is shown in Figure A.1. This species was observed to be stable at room temperature in the P_2F_4 /sulphamic acid, $\text{S}(\text{SiH}_3)_2$, and $\text{Hg}(\text{SiMe}_3)_2$ mixtures. In the other reaction mixtures it was observed only at reduced temperature and disappeared on warming to room temperature. In all cases this species was present only in small amounts and isolation was not possible.

In the reaction mixtures of P_2F_4 with $\text{S}(\text{SiH}_3)_2$, $\text{Hg}(\text{SiMe}_3)_2$, SiF_3NMe_2 and SiH_3I another complex species was observed in the ^{19}F n.m.r. spectrum. The identity of this species is not clear but is clearly due to a PF_2 group.

Figure A.1 N.m.r. spectra of the $-PF_2$ group in the species assigned $P(PF_2)_2I$

^{31}P n.m.r.



^{19}F n.m.r.

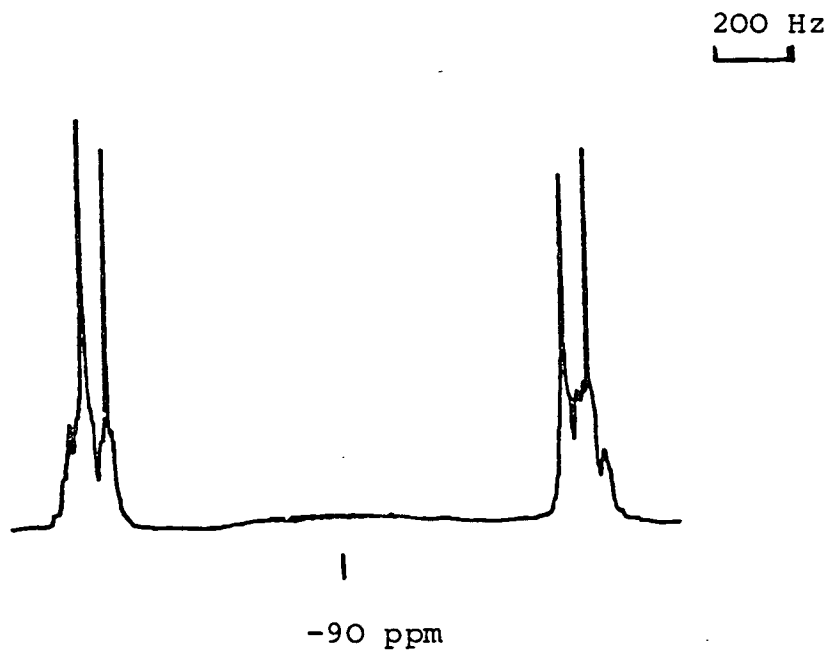
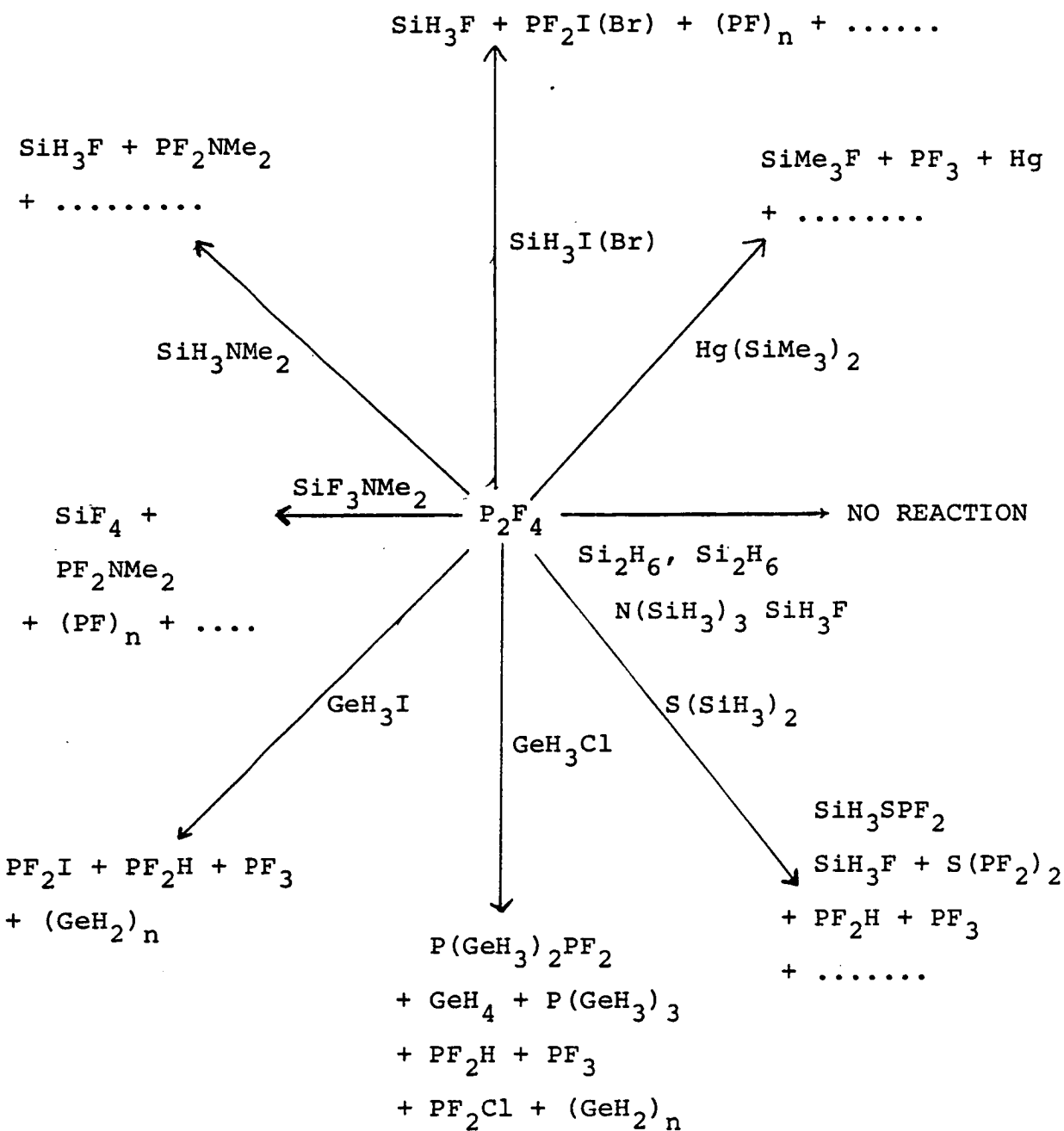
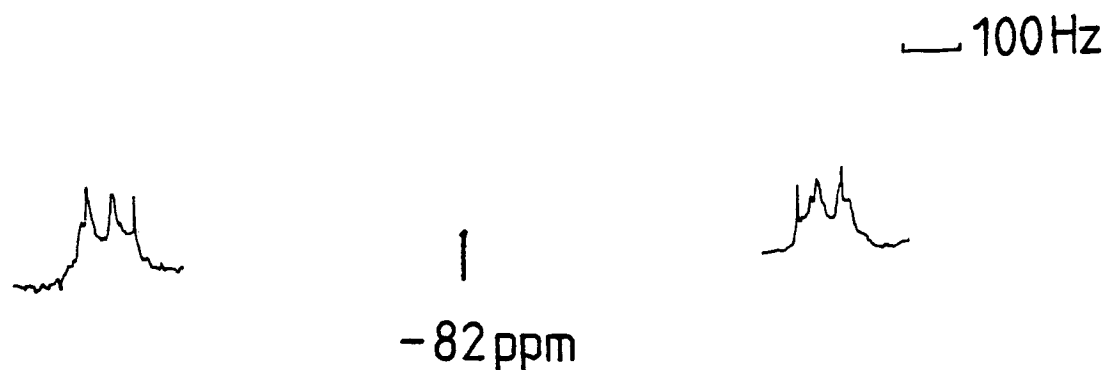


Figure A.2 The Reactions of P_2F_4 with Silyl and Germyl Reagents



The pattern produced in the ^{19}F n.m.r. spectrum consisted of a doublet of multiplets symmetrical about the centre and this pattern is shown below.



The species producing this pattern is clearly not simple and it is hoped that its identity may be determined by future workers in this field.

It is clear that the observed reactions of P_2F_4 with silyl reagents are not simple and may involve some very complex intermediates. These reactions are summarised in Figure A.2 although further study would be necessary for the reactions to be understood fully. Time was not available for this further work to be carried out.

(b) The Reaction of P_2F_4 with Germyl Compounds

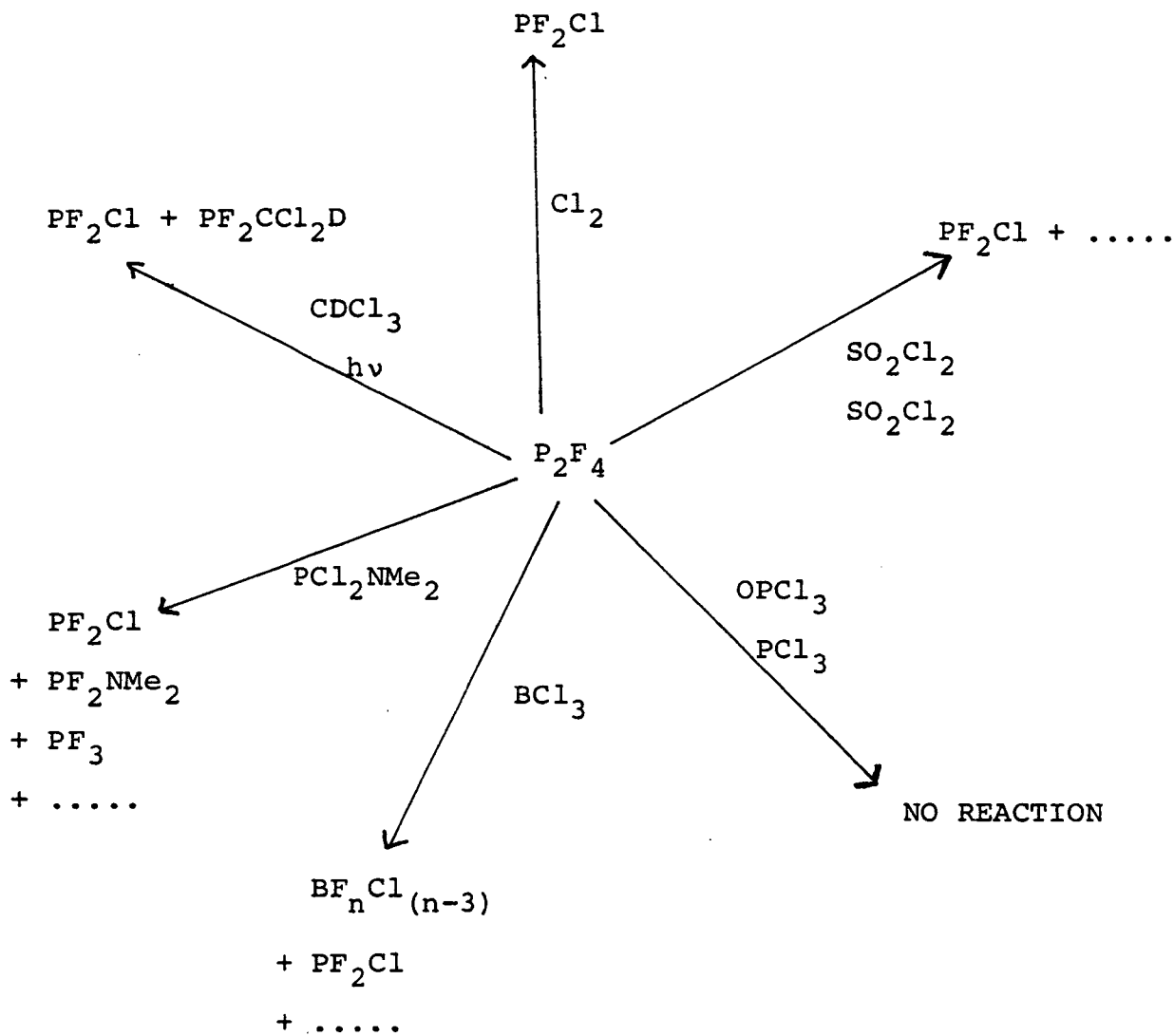
The reactions of P_2F_4 with GeH_3I and GeH_3Cl were investigated and the results are summarised in Figure A.2.

These reactions were in general very much slower than those of the related silyl compounds. In both cases brown solids were produced and these are likely to be $(\text{GeH}_2)_n$ polymer which can be formed readily by germyl compounds. Clearly there is a tendency for these germyl halides to simultaneously halogenate and protonate P_2F_4 to form PF_2Cl or PF_2I and PF_2H . These reactions are however very much more complex and PF_3 is formed in both cases. In the case of the $\text{GeH}_3\text{I}/\text{P}_2\text{F}_4$ reaction $(\text{GeH}_3)_2\text{PPF}_2$, GeH_4 and $\text{P}(\text{GeH}_3)_3$ were also formed. The mechanism of formation of these complex species cannot be determined with the limited amount of data available.

A.1.2 The Reaction of P_2F_4 with Chlorides of Boron, Phosphorus, and Sulphur.

The reactions of P_2F_4 with BCl_3 , PCl_2NMe_2 , SO_2Cl_2 , SOCl_2 , POCl_3 , PCl_3 , Cl_2 and CDCl_3 were investigated. The results of these experiments are summarised in Figure A.3 and experimental details are given in Section A.3. POCl_3 and PCl_3 were found to be inert towards P_2F_4 at room temperature as was CDCl_3 . CDCl_3 however reacted with P_2F_4 under ultra violet radiation to form $\text{PF}_2\text{CCl}_2\text{D}$ and PF_2Cl . The other reagents reacted with P_2F_4 cleaving the P-P bond and forming PF_2Cl , although the identity of other species produced is unclear as is the stoichiometry of the reactions.

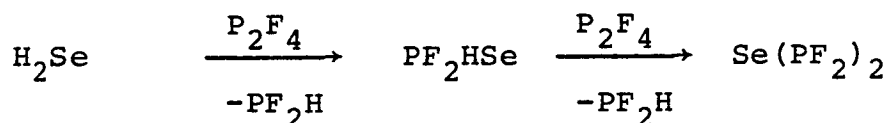
Figure A.3 The Reaction of P_2F_4 with Chlorides of Boron, Phosphorus and Sulphur



A.1.3 The Reaction of P₂F₄ with Phosphorus and Hydrogen
Chalconides

The reactions of P₂F₄ with H₂S, H₂Se, PF₂HS, PF₂HSe, and R₂S₂ (R = Me, Et, CF₃, p-tolyl) were investigated. These reactions are summarised in Figure A.4 and experimental details are given in Section A.2.

It is clear that P₂F₄ reacts with disulphides to form RSPF₂ by cleavage of the S-S and P-P bonds and formation of an S-P bond. The reaction of H₂Se with P₂F₄ produced Se(PF₂)₂, PF₂HSe and PF₂H. PF₂HSe was found to react with P₂F₄ to form Se(PF₂)₂ and PF₂H. This suggests that the reaction of P₂F₄ with H₂Se proceeds via PF₂HSe as shown below.



In the related reaction of H₂S with P₂F₄ the reaction was found to produce PF₂HS but not S(PF₂)₂ and this is in agreement with the observation that PF₂HS does not react with P₂F₄. The reaction can therefore be summarised as follows:

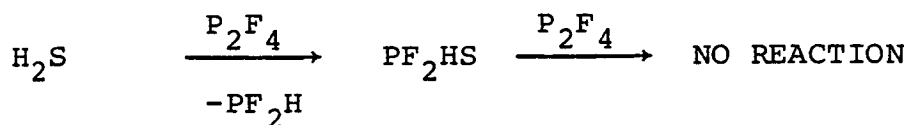
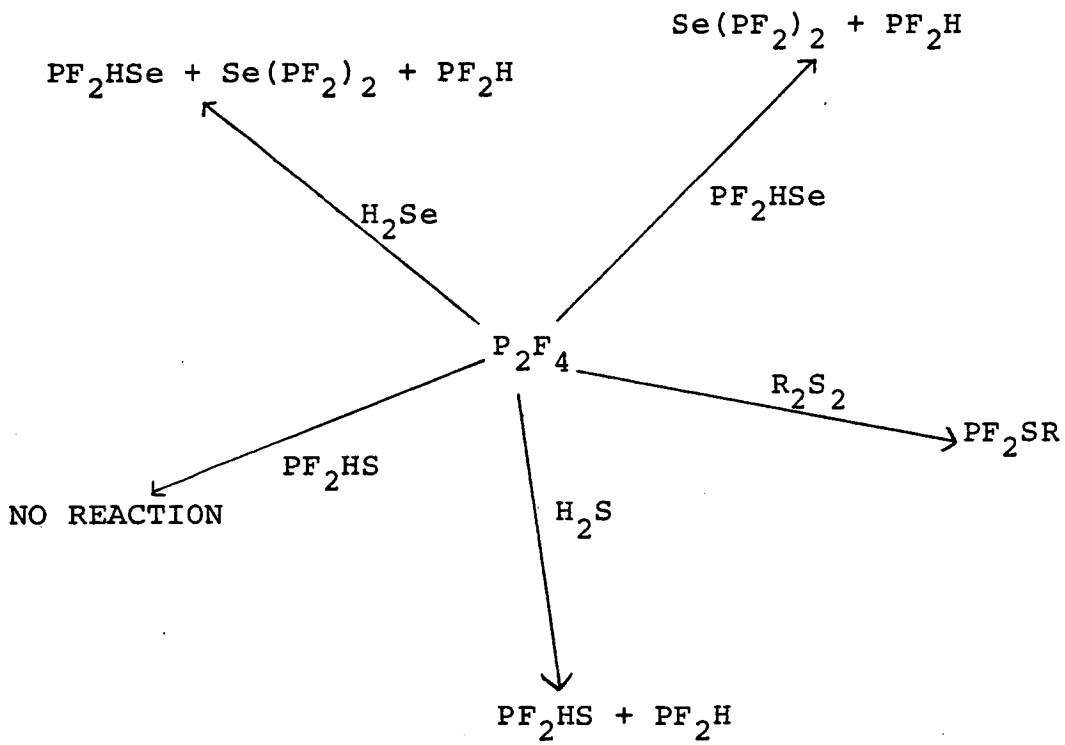


Figure A.4 The Reactions of P_2F_4 with Phosphorus and Hydrogen Chalcogenides

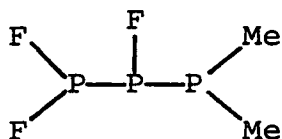


A.1.4 The Reaction of P_2F_4 with P_2Me_4

The decomposition of P_2F_4 to PF_3 and $(PF)_n$ appears to be catalysed by P_2Me_4 .



In addition small amounts of PF_6^- , a phosphorane and a compound which may have the structure shown below are formed.



A very small amount of PF_2PMe_2 was also observed suggesting that the following reaction may have occurred to some extent.



The experimental details are given in Section A.2.22 and considering the complexity of the species observed it is impossible to propose a reaction mechanism for this clearly complex process.

A.1.5 Conclusion

In conclusion it is clear from the work described in the introduction and the reaction of P_2F_4 with disulphides, H_2Se , PF_2HSe , H_2S , Cl_2 and $CDCl_3$ that P_2F_4 has great potential as a reagent for the synthesis of novel PF_2 compounds.

However, in the reactions studied in which novel PF_2 compounds might have been expected to be produced, particularly those with silyl and germyl species, much more complex reactions occurred. These often produced complex phosphorus containing species but only in small amounts and the reactions were not synthetically promising.

A.2 Experimental Procedure

In almost all cases the reactions studied were carried out in sealed 5 mm n.m.r. tubes. The solvent and quantities of reagents used are given in Table A1 along with nuclei for which n.m.r. spectra were recorded. N.m.r. parameters of species mentioned in this section but whose n.m.r. parameters are not quoted in the text are given in Table A2.

In general the reactions were followed from the melting point of the solvent to room temperature in stages of ca. 10°C in the hope of obtaining a controlled chemical reaction under the mildest possible conditions. If reaction was not observed on the mixture being warmed to room temperature then the mixture was held at room temperature for up to a week with periodic examination of the n.m.r. spectra. In some cases photolysis of the reaction mixture was carried out by placing the n.m.r. tube in close proximity to an ultra violet light.

In a very few cases the reactions were carried out on a semi preparative scale and infrared spectroscopy was used to identify the products.

A.2.1 The reaction of P_2F_4 with alkyl, aryl and fluoroalkyl disulphides

This reaction was carried out with S_2Et_2 , $S_2(CF_3)_2$, S_2Me_2 and $S_2(p\text{-tolyl})_2$. In all cases the reaction appears to be simple, involving cleavage of both the PP and SS bonds

Table A.1 Composition of Reaction Mixtures and N.M.R. Spectra Recorded

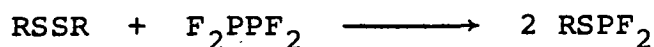
Reagent	Quantity/mmol	P ₂ F ₄ /mmol	Solvent	³¹ P	¹⁹ F	¹ H
S ₂ Et ₂	0.2	0.2	1	*	*	
S ₂ Me ₂	0.2	0.2	1	*	*	
S ₂ (CF ₃) ₂	0.2	0.2	1	*	*	
S ₂ (p-tolyl) ₂	0.2	0.2	1	*	*	
Cl ₂	0.2	0.2	1	*	*	
SO ₂ Cl ₂	0.2	0.2	3	*	*	
SO ₂ Cl ₂	0.15	0.07	2	*	*	
SOCl ₂	0.2	0.2	3	*	*	
PCl ₃	0.2	0.2	3	*		
OPCl ₃	0.2	0.2	1	*		
BCl ₃	0.2	0.2	3	*	*	
PCl ₂ NMe ₂	0.2	0.2	2	*		
H ₂ Se	0.2	0.2	1	*	*	
PF ₂ HSe	0.1	0.1	3	*		
H ₂ S	0.2	0.2	1	*		
PF ₂ HS	0.2	0.2	1	*		
CDCl ₃	solvent	0.2	1	*	*	
SiH ₃ Br	0.2	0.2	3	*	*	
SiH ₃ I	0.2	0.2	3	*	*	
SiH ₃ F	0.2	0.2	3	*		
SiH ₃ NMe ₂	0.2	0.2	3	*	*	*
SiF ₃ NMe ₂	0.2	0.2	3	*	*	
Hg(SiMe ₃) ₂	0.2	0.2	3	*	*	
Si ₂ H ₆	0.2	0.2	1	*	*	*
Si ₂ Me ₆	0.2	0.2	4	*		*
N(SiH ₃) ₃	0.2	0.2	2	*		
S(SiH ₃) ₂	0.2	0.2	1	*	*	
GeH ₃ Cl	0.2	0.2	3	*	*	*
GeH ₃ I	0.2	0.2	3	*	*	*
P ₂ Me ₄	0.2	0.2	2	*	*	*
NH ₂ SO ₃ H	0.2	0.2	3	*		

Solvents: (1) CDCl₃ (2) CD₂Cl₂/CH₂Cl₂
 (3) d⁸ toluene/C₇H₈ (4) d⁶ benzene/benzene

Table A.2 Observed N.M.R. Parameters of Species Present in Reaction Mixtures

Compound	$\delta(P)/\text{ppm}$	$\delta(F)/\text{ppm}$	$\delta(H)/\text{ppm}$	
PF_2Cl	175	-38		$^1J_{\text{PF}} = 1374 \text{ Hz}$
PF_2Br	218	-40		$^1J_{\text{PF}} = 1362 \text{ Hz}$
PF_2I	240	-47		$^1J_{\text{PF}} = 1338 \text{ Hz}$
PF_3	104	-34		$^1J_{\text{PF}} = 1401 \text{ Hz}$
PF_2H	223	-116		$^1J_{\text{PF}} = 1130 \text{ Hz}$ $^1J_{\text{PH}} = 185 \text{ Hz}$ $^2J_{\text{FH}} = 42 \text{ Hz}$
P_2F_4	225	-113		
PF_2SMe	233	-71	2	$^1J_{\text{PF}} = 1261 \text{ Hz}$ $^3J_{\text{PH}} = 8 \text{ Hz}$ $^4J_{\text{FH}} = 2 \text{ Hz}$
$\text{PF}_2\text{S}(p\text{-tolyl})$	222	-66		$^1J_{\text{PF}} = 1272 \text{ Hz}$
$\text{PF}_2\text{SCF}_3'$	212	-69, -29		$^1J_{\text{PF}} = 1307 \text{ Hz}$ $^3J_{\text{PF}'} = 25 \text{ Hz}$ $^4J_{\text{FF}'} = 5.1 \text{ Hz}$
PF_2SEt	236	-69		$^1J_{\text{PF}} = 1261 \text{ Hz}$
PF_2NMe_2	146	-63	2	$^1J_{\text{PF}} = 1198 \text{ Hz}$
PCl_2NMe_2	164			
$\text{PF}_2\text{P}'(\text{GeH}_3)_2$	291.5, -192.8	-83	4	$^1J_{\text{PF}} = 1217 \text{ Hz}$ $J_{\text{P}'\text{F}} = 69 \text{ Hz}$ $^1J_{\text{P}'\text{P}} = 296 \text{ Hz}$ $^2J_{\text{PH}} = 16.5 \text{ Hz}$ $^4J_{\text{FH}} = 3 \text{ Hz}$ $^3J_{\text{PF}} = 11 \text{ Hz}$
$\text{O}(\text{PF}_2)_2$	111	-37		
$\text{Se}(\text{PF}_2)_2$	249	-64		
PF_2HSe	77	-42		$^1J_{\text{PF}} = 1194 \text{ Hz}$ $^1J_{\text{PH}} = 700 \text{ Hz}$ $^2J_{\text{FH}} = 91 \text{ Hz}$
PF_2HS	68	-46		$^1J_{\text{PF}} = 1157 \text{ Hz}$ $^1J_{\text{PH}} = 737 \text{ Hz}$
PCl_3	218			
OPCl_3	4			

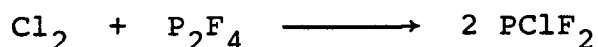
and formation of an SP bond. The reactions appeared complete or at least well advanced after several hours at room temperature and may be summarised by the following equation.



This reaction produced the known compounds MeSPF₂ and F₃CSPF₂ and the novel compounds EtSPF₂ and p-tolyl SPF₂. In all cases the phosphorus III isomer was obtained rather than the phosphorus V isomer.

A.2.2 The reaction of P₂F₄ with chlorine

This reaction was found to be complete at -60°C, PClF₂ being the sole product. The reaction can be summarised as follows.



A.2.3 The reaction of P₂F₄ with sulphuryl chloride

When a 1:1 mixture of sulphuryl chloride and P₂F₄ was mixed, the reaction was found to be complete at -90°C, ³¹P and ¹⁹F n.m.r. spectroscopy indicated that PClF₂ had been formed. Another possible product is SO₂. The reaction may therefore be:



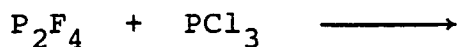
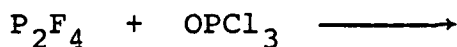
When this reaction was carried out with a two to one ratio of P_2F_4 to SO_2Cl_2 the reaction was shown to produce $PClF_2$ along with PF_3 and $O(PF_2)_2$. This reaction would therefore seem to be more complex than that above and its exact nature is not clear. It appears that sulphuryl chloride acts initially as a chlorinating agent and then, in the presence of excess P_2F_4 , as an oxidising agent.

A.2.4 The reaction of P_2F_4 with thionyl chloride

This reaction was found to occur rapidly above $-80^\circ C$, leading to the formation of $O(PF_2)_2$ and $PClF_2$. A little PF_3 was also formed. Without further information about the sulphur containing species produced the nature of the reaction must remain unclear. It is however clear that the thionyl chloride is acting as both a chlorinating agent and an oxidising agent towards P_2F_4 as did sulphuryl chloride.

A.2.5 The "reaction" of P_2F_4 with PCl_3 and $OPCl_3$

Neither PCl_3 nor $OPCl_3$ was observed to react with P_2F_4 even after several hours at room temperature.



NO REACTION

A.2.6 The reaction of P₂F₄ with BCl₃

This reaction was found to occur quickly at room temperature to produce PClF₂ and a mixture of boron chlorofluorides. The reaction can be summarised as follows.

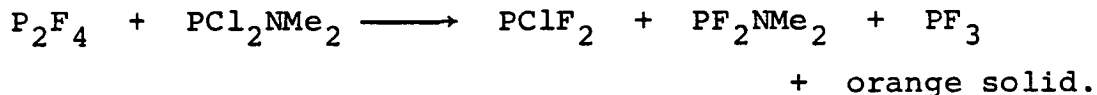


$$n = 1, 2 \text{ or } 3$$

This reaction was carried out in a sealed n.m.r. tube and also on a semi preparative scale. On the semi preparative scale 0.5 mmol P₂F₄ was reacted with 0.5 mmol BCl₃ in a 50 ml glass ampoule. The mixture was observed by infra red spectroscopy in a gas cell and the species present identified as PClF₂⁽⁷²⁾ and BCl_nF_(n-3)⁽⁸³⁾.

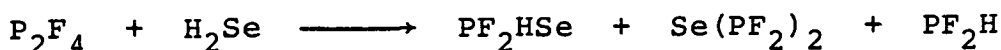
A.2.7 The reaction of P₂F₄ with PCl₂NMe₂

This reaction appeared rapid and complete at -80°C and produced PClF₂, PF₂NMe₂, PF₃ and an orange solid (perhaps (PCl)_n). The reaction may therefore be represented as follows.



A.2.8 The reaction of P₂F₄ with H₂Se

This reaction was found to be slow, requiring 2 - 10 hours at room temperature for complete reaction and resulted in the formation of PF₂HSe, Se(PF₂)₂ and PF₂H.



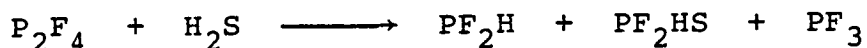
A.2.9 The reaction of P₂F₄ with PF₂HSe

This reaction was very slow at room temperature and was well advanced after a few days at room temperature. The reaction resulted in the formation of Se(PF₂)₂ and PF₂H. The reaction therefore appears to be as follows.



A.2.10 The reaction of P₂F₄ with H₂S and PF₂HS

Only slight reaction had occurred after one day but the reaction was well advanced after 9 days at room temperature. The reaction was observed to produce PF₂H, PF₂HS and PF₃ and can be summarised as follows.



PF₂HS was observed to be inert towards P₂F₄ over a period of 9 days at room temperature when these compounds were mixed in a sealed 5 mm n.m.r. tube.

A.2.11 The reaction of P₂F₄ with CDCl₃

No reaction occurred between these two reagents on standing at room temperature. On photolysing the mixture however PF₂Cl and PF₂CCl₂D were formed. PF₂CCl₂D was identified by its n.m.r. spectra and had the following parameters.

$$\delta(\text{P}) = 160 \text{ ppm}$$

$$\delta(\text{F}) = -94 \text{ ppm}$$

$${}^1J_{\text{PF}} = 1235 \text{ Hz}$$

Although this is a novel compound little doubt is left to its identity by comparing its n.m.r. parameters with those of the related compound PF₂CCl₂H.⁽¹⁾

A.2.12 The reaction of P₂F₄ with SiH₃Br

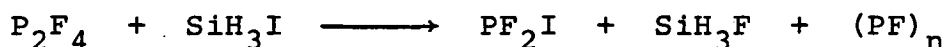
This reaction was carried out in both an n.m.r. tube and on a semi preparative scale. N.m.r. spectra showed that PF₂Br and SiH₃F were formed and an orange solid was observed in the n.m.r. tube. On a preparative scale P₂F₄ (1.0 mmol) was reacted with SiH₃Br (1.0 mmol) in a 50 ml ampoule. The products were separated by fractional condensation through -120°C. The PF₂Br (1.0 mmol) was retained at -120°C while SiH₃F (1.0 mmol) passed this trap and was held at -196°C, again an orange solid was formed. From the stoichiometry the orange solid must be (PF)_n polymer and the reaction appears to be:



The reaction appeared complete at -84°C when carried out in an n.m.r. tube.

A.2.13 The reaction of P₂F₄ with SiH₃I

This reaction appeared to be essentially similar to that of P₂F₄ with SiH₃Br and was only carried out in an n.m.r. tube. SiH₃F and PF₂I along with an orange solid were formed.



At low temperatures some multi-phosphorus species were observed as described in Section A.1. The reaction was rapid at -90°C.

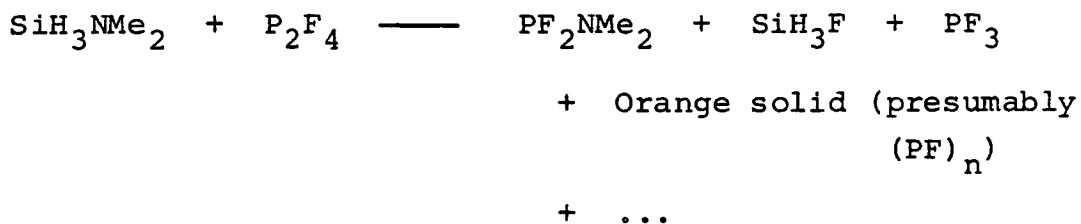
A.2.14 The reaction of P₂F₄ with SiH₃F

No reaction was observed between SiH₃F and P₂F₄ at room temperature.



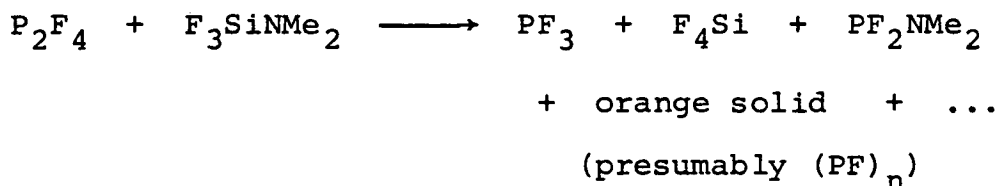
A.2.15 The reaction of P₂F₄ with SiH₃NMe₂

This reaction produced PF₂NMe₂, PF₃ and SiH₃F and an orange solid. The reaction was very rapid at -90°C and again some multi-phosphorus species were observed as described in Section A.1. The major reaction therefore appears as follows:



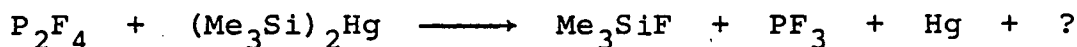
A.2.16 The reaction of P_2F_4 with F_3SiNMe_2

This reaction appears to be similar to that above, proceeding with cleavage of the P-N bond and formation of an Si-F bond. N.m.r. spectroscopy showed that PF_2NMe_2 , PF_3 and SiF_4 had been formed along with multi-phosphorous species described in Section A.1. Thus reaction was rapid at room temperature and appears to be as shown below.



A.2.17 The reaction of P_2F_4 with $Hg(SiMe_3)_2$

The reaction appeared slow at room temperature, producing Me_3SiF and PF_3 along with some multi phosphorus species described in Section A.1. Difficulty was experienced in obtaining good n.m.r. spectra due to the presence of elemental mercury in the reaction mixture. The reaction can therefore be represented as follows:



The stoichiometry of this reaction is uncertain and the reaction is clearly complex.

A.2.18 The reaction of P_2F_4 with Si_2H_6 , Si_2Me_6 and $N(SiH_3)_3$

P_2F_4 did not react with Si_2H_6 , Si_2Me_6 or $N(SiH_3)_3$ even after many hours at room temperature.

A.2.19 The reaction of P_2F_4 with $S(SiH_3)_2$

This reaction appeared slow at room temperature, requiring several days for reaction to be evident. The reaction produced SiH_3F , PF_2H , $S(PF_2)_2$ and SiH_3SPF_2 along with multi-phosphorus species described in Section A.1. The major reaction may therefore be summarised as shown below.



A.2.20 The reaction of P_2F_4 with GeH_3Cl

This reaction appeared slow at room temperature, being complete after 5 days. The reaction produced $(GeH_3)_2PPF_2$, GeH_4 , $P(GeH_3)_3$, PF_2H , PF_3 and PF_2Cl . A brown solid was also produced which may have been $(GeH_2)_n$ as this is often formed in germyl chemistry.

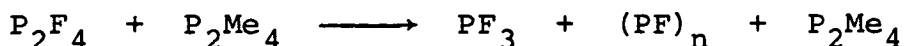
A.2.21 The reaction of P_2F_4 with GeH_3I

This reaction appeared to occur at a similar rate to that of the GeH_3Cl/P_2F_4 reaction but produced only PF_2I , PF_2H , PF_3 and a brown solid (again presumably $(GeH_2)_n$).

A.2.22 The reaction of P_2F_4 with P_2Me_4

This reaction was carried out on a semi-preparative scale on a vacuum line. P_2F_4 (1.2 mmol) was condensed into a 40 ml ampoule containing P_2Me_4 (1.2 mmol) and the mixture warmed to room temperature. A rapid reaction occurred

producing an orange solid. The volatile components were then fractionated through a trap held at -78°C . The fraction passing the -78°C trap was held at -196°C and identified by infra-red spectroscopy as PF_3 (1.2 mmol). The material held at -78°C was similarly identified as P_2Me_4 (1.2 mmol). From the stoichiometry the orange solid must therefore be $(\text{PF})_n$ and the overall reaction can be summarised by the following equation.



This suggests that P_2Me_4 catalyses the decomposition of P_2F_4 and this is consistent with the observation that extensive decomposition of P_2F_4 occurred if it was passed through sections of vacuum line in which P_2Me_4 had been manipulated. The reaction was also carried out in an n.m.r. tube and found to occur at -90°C . In addition to PF_3 and P_2Me_4 very small amounts of some rather interesting species were observed. PF_6^- was observed but no species could be clearly identified as the corresponding cation which must have been present. A small amount of a species which produced a doublet of doublets of doublets of doublets in the ^{19}F n.m.r. spectrum.

$$\delta(\text{F}) = -43 \text{ ppm}$$

$$J = 6 \text{ Hz}$$

$$J' = 56 \text{ Hz}$$

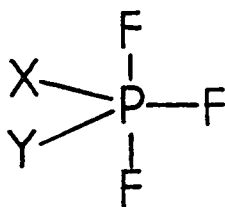
$$J'' = 175 \text{ Hz}$$

$$J''' = 925 \text{ Hz}$$

This multiplet was clearly associated with a doublet of triplets in the same spectrum.

$$\begin{aligned}\delta(\text{F}) &= -79 \text{ ppm} \\ J' &= 56 \text{ Hz (producing a triplet)} \\ J'''' &= 789 \text{ Hz (producing a doublet)}\end{aligned}$$

It is likely that the species producing these multiplets is of the form shown below.



J^1 has been assigned to ${}^2J_{\text{FF}}$ and J'''' and J''''' to ${}^1J_{\text{PF}}$. The other couplings observed must be due to the presence of other spin $\frac{1}{2}$ nuclei (probably other phosphorus and fluorine atoms) in the groups X and Y although signals due to these units were not observed.

Another species which produced a complex multiplet in the ${}^{31}\text{P}$ and ${}^{19}\text{F}$ n.m.r. spectra was also observed. This produced the following multiplets.

(a) A triplet of doublets of doublets of doublets, slightly broadened when proton coupling was retained.

$$\begin{aligned}\delta(\text{P}) &= 336 \text{ ppm} \\ J &= 1125 \text{ Hz (producing a triplet)} \\ J' &= 439 \text{ Hz (producing a doublet)} \\ J'' &= 119 \text{ Hz (producing a doublet)} \\ J''' &= 13 \text{ Hz (producing a doublet)}\end{aligned}$$

(b) A doublet of doublets of doublets in the ^{19}F n.m.r. spectrum.

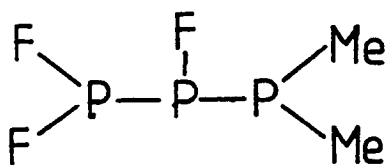
$$\delta(\text{F}) = -79 \text{ ppm}$$

$$J = 1125 \text{ Hz}$$

$$J' = 89 \text{ Hz}$$

$$J'' = 41 \text{ Hz}$$

From consideration of these couplings it seem likely that this species may be of the form shown below.



Clearly the multiplets observed can be assigned to the $-\text{PF}_2$ groups in the above molecule however the lack of observation of signals due to the other spin $\frac{1}{2}$ nuclei leaves some doubt as to the identity of this species.

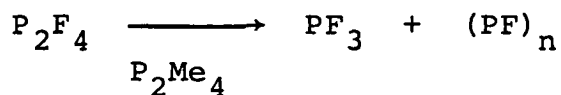
A small amount of PF_2PMe_2 was observed in the ^{31}P n.m.r. spectrum although only signals due to the PF_2 group were observed.

$$\delta(\text{P}) = 291 \text{ ppm}$$

$${}^1J_{\text{PF}} = 1200 \text{ Hz}$$

$${}^1J_{\text{PP}} = 250 \text{ Hz}$$

It is therefore clear that the reaction mechanism is not simple and that reaction produces some complex species. These species may well be intermediates in the overall reaction as shown below.



A.2.23 The reaction of P_2F_4 with Sulphamic Acid

The reaction was slow, after two days at room temperature large amounts of PF_3 and an orange solid had been formed. A small amount of the species assigned $P(PF_2)_2I$ was also formed (see Section A.1.1).

APPENDIX 2

PUBLISHED MATERIAL

"General Method for Preparation of Multidentate
Fluorophosphane Ligands", by Ernest R. Cromie,
George Hunter, and David W.H. Rankin.
Angew.Chem.Int.Ed.Engl., (1980), 19, 316.

Similar reactions also occur with primary and secondary amines and, more slowly, with thiols. Thus, by choosing a suitable substrate, a product may be made with almost any desired spatial arrangement of fluorophosphino groups. Two typical syntheses are described, that of bis[2-(difluorophosphino)ethyl]sulfide (5) and that of phosphoryltrioxytris(difluorophosphane) (6).



Experimental

Preparation of (5): Compound (1)^[5] (4 mmol) is condensed into a glass ampoule (at -196°C) containing $\text{S}(\text{CH}_2\text{CH}_2\text{OH})_2$ (1.7 mmol) and the reagents are warmed to room temperature for 45 min. After the volatile products have been distilled out at -78°C , (5) (1.4 mmol, 80% yield) is obtained in a pure form by distillation *in vacuo* at room temperature. Subsequent manipulation of (5) is by syringe in an inert atmosphere^[6].

Preparation of (6): Compound (1) (16.5 mmol) is condensed into a glass ampoule (at -196°C) containing 100% H_3PO_4 (4.5 mmol). On warming to room temperature, effervescence occurs and the solid material disappears. After 30 min, the volatile products are removed, and (6) (4.3 mmol, 95% yield) is obtained as a clear liquid, involatile at -45°C , by fractional condensation *in vacuo*^[7].

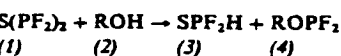
Received: September 3, 1979 [Z 440 IE]
German version: *Angew. Chem.* 92, 323 (1980)

General Method for Preparation of Multidentate Fluorophosphane Ligands^[*1]

By Ernest R. Cromie, George Hunter, and David W. H. Rankin^[*1]

Although fluorophosphanes are well known as monodentate ligands^[1], very little work has been done with multidentate fluorophosphanes^[2], and few suitable ligands are readily available. They are of interest because they can bond in a number of different ways: for example, $\text{CH}_3\text{N}(\text{PF}_2)_2$ may form two bonds to a single metal atom^[3] or a bridge between two metal atoms^[4]. We report here a reaction which may be used to prepare a wide variety of fluorophosphanes which may prove to be useful multidentate ligands.

We have observed that bis(difluorophosphino)sulfide (1)^[5] reacts with organic and inorganic mono- and polyhydroxy compounds (2) to give difluorophosphane sulfides (3) and the desired difluorophosphinoxy compounds (4).



The product (4) is normally much less volatile than (3), and may therefore easily be obtained in a pure form. Use of an excess of hydroxy compound (2) should be avoided, as a slow substitution reaction of (3) occurs, yielding less volatile products (SPFHR , SPHR_2).

The group R may be almost any organic group, such as primary, secondary, or tertiary alkyl, aryl or acyl, and inorganic "hydroxides" such as phosphoric acid may also be used. With 1,2-diols PF_3 is eliminated from the initial products to give 2-fluorodioxaphospholanes, which may also be of interest as ligands.

^[*1] Dr. D. W. H. Rankin, E. R. Cromie, G. Hunter
Department of Chemistry, University of Edinburgh
West Mains Road, Edinburgh EH9 3JJ (Scotland)

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- [1] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.* 13, 363 (1970), and references cited therein.
[2] C. A. McAuliffe, W. Leason: *Phosphine, Arsine and Stibine Complexes of the Transition Elements*. Elsevier, Amsterdam, 1979, 9, 310, and references cited therein.
[3] R. B. King, J. Gimeno, *J. Chem. Soc. Chem. Commun.* 1977, 142.
[4] M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, J. Gimeno, *J. Chem. Soc. Chem. Commun.* 1977, 531.
[5] Preparation, see D. E. J. Arnold, E. R. Cromie, D. W. H. Rankin, *J. Chem. Soc. Dalton Trans.* 1977, 1999.
[6] ¹H-NMR (CDCl_3): $\delta = 2.81$ (4 H, t, $J = 7$ Hz), 4.19 (4 H, q, $J_{\text{PH}} = J_{\text{HH}} = 7$ Hz); ¹³C-NMR: $\delta = 32.4$ (d, $J_{\text{PC}} = 3$ Hz), 62.1 (t x d, $J_{\text{PC}} = 9$ Hz, $J_{\text{PC}} = 3$ Hz); ¹⁹F-NMR: $\delta = -48$ (d, $J_{\text{FP}} = 1294$ Hz); ³¹P-NMR: $\delta = 112$ (t x t, $J_{\text{FP}} = 1294$ Hz, $J_{\text{PH}} = 7$ Hz); IR (film): 2970, 2910, 1465, 1425, 1405, 1295, 1200, 1050, 1005, 965, 805, 760, 560 cm^{-1} .
[7] ³¹P-NMR (CDCl_3): $\delta = 108$ (3 P, t x d, $J_{\text{PP}} = 1385$ Hz, $J_{\text{FP}} = 28$ Hz), -41 (1 P, m); ¹⁹F-NMR: $\delta = -38$ (d x d, $J_{\text{FP}} = 1384$ Hz, $J_{\text{FP}} = 10$ Hz); IR (gas): 1345, 1042, 988, 867, 728, 529, 469, 399 cm^{-1} ; m. p. -19°C , vapor pressure at 0°C , 1 torr.

REFERENCES

1. J.F. Nixon, Adv.Inorg.Chem.Radiochem., (1970), 13, 363.
2. L.F. Centofanti and R.W. Parry, Inorg.Chem., (1968), 7, 1005.
3. D.F. Shiver, The Manipulation of Air Sensitive Compounds, McGraw Hill, (1969).
4. H.W. Schiller and R.W. Rudolph, Inorg.Chem., (1971), 10, 2500.
5. G.G. Flaskerud, K.E. Pullen and J.M. Shreeve, Inorg.Chem., (1969), 8, 728.
6. E.R. Cromie, Private Communication.
7. L.F. Centofanti and R.W. Rudolph, Inorg.Synth., (1970), 12 281.
8. W. Bett, Private Communication.
9. C.M. Huntley, Private Communication.
10. N. McManus, Private Communication.
11. G.N. Bockerman and R.W. Parry, J.Fluorine.Chem., (1976), 7, 1.
12. K.W. Morse and R.W. Parry, J.Amer.Chem.Soc., (1967), 89, 172.
13. A. Stewart, Honours Research Project, Edinburgh University (1980).
14. J.Campbell, Honours Research Project, Edinburgh University (1980).
15. E.R. Cromie, G. Hunter and D.W.H. Rankin, Angew.Chem.Int. Ed.Engl., (1980), 19, 316.
16. D.J. Arnold, Ph.D. Thesis, Edinburgh University (1976).
17. R. Foester and K. Cohn, Inorg.Chem., (1972), 11, 2590.
18. J. Grosse and R. Schmutzler, J.Chem.Soc., Dalton Trans., (1976), 405.
19. M. Lustig, J.K. Ruff and C.B. Colburn, J.Amer.Chem.Soc., (1966), 88, 3875.

20. J.F. Nixon, J.Chem.Soc.(A), (1968), 2689.
21. J.G. Reiss, J.Amer.Chem.Soc., (1966), 88, 2339.
22. R.W. Rudolph, R.C. Taylor and R.W. Parry, J.Amer.Chem.Soc., (1966), 88, 3729.
23. T.L. Charlton and R.G. Cavell, Inorg.Chem., (1969), 8, 2436.
24. D.D. Des Marteau, J.Amer.Chem.Soc., (1969), 91, 6211.
25. R.R. Holmes and W.P. Gallagher, Inorg.Chem., (1963), 2, 433.
26. M. Lustig and W.E. Hill, Inorg.Chem., (1967), 6, 1448.
27. M. Lustig, Inorg.Chem., (1968), 7, 2054.
28. M.Zh. Ivanova, Zh.Obshch,Khim., (1964), 34, 858.
29. E.K. MacDonald, Ph.D. Thesis, Edinburgh University (1980).
30. D.J. Hutchison, Private Communication.
31. G.I. Drozd and S.Z. Ivin, Zh.Obshch,Khim., (1968), 38, 1907.
32. R.K. Harris, Can.J.Chem., (1964), 42, 2275.
33. R.W. Rudolph and R.W. Parry, J.Amer.Chem.Soc., (1967), 89, 1261.
34. R.K. Harris, J.R. Woplin, P.E. Dunmur, M. Murray and R. Schmutzler, Ber.Bunsenges.Phys.Chem., (1972), 76, 44.
35. D.E.J. Arnold, E.R. Cromie and D.W.H. Rankin, J.Chem.Soc. Dalton Trans., (1977), 1977.
36. G.N. Bockerman and R.W. Parry, Amer.Chem.Soc. Meeting, Chicago, 1967.
37. E.A.V. Ebsworth, D.J. Hutchison and D.W.H. Rankin, to be published.
38. (a) R.T. Paine and R.W. Parry, Inorg.Chem., (1972), 11, 210.
(b) R.W. Rudolph and H.L. Hodges, Inorg.Chem., (1972), 11, 2845.
39. R. Mathieu and R. Poilblanc, Inorg.Chem., (1972), 11, 1858.

40. E.R. Falardeau, K.W. Morse and J.G. Morse, Inorg.Chem., (1974), 13, 2333.
41. E.A.V. Ebsworth, D.J. Hutchison, E.K. MacDonald and D.W.H. Rankin, to be published.
42. D. Solan and P.L. Timms, J.Chem.Soc.Chem.Comm., (1968), 23, 1540.
43. D.E.J. Arnold and D.W.H. Rankin, J.Chem.Soc., Dalton Trans., (1975), 889.
44. (a) J.F. Nixon, J.Chem.Soc.(A), (1968), 2689.
(b) J.F. Nixon, ibid, (1969), 1087.
45. R.B. King and J. Gimeno, Inorg.Chem., (1978), 17, 2390.
46. R.B. King and J. Gimeno, J.Chem.Soc., Chem.Comm., (1977), 142.
47. T.R. Johnson and J.F. Nixon, J.Chem.Soc.(A), (1969), 2518.
48. R.B. King, M.G. Newton, M. Chang and J. Gimeno, J.Amer.Chem.Soc., (1977), 99, 2802.
49. R.B. King, J. Gimeno and T.J. Lotz, Inorg.Chem., (1978), 17, 2401.
50. M.G. Newton, R.B. King, M. Chang, N.S. Pantaleo and J. Gimeno, J.Chem.Soc.Chem.Comm., (1977), 531.
51. R.B. King and J. Gimeno, Inorg.Chem., (1978), 17, 2396.
52. E.O. Fisher and G. Besl, J.Organomet.Chem., (1978), 157, C33.
53. N.R. Zack, K.W. Morse and J.G. Morse, Inorg.Chem., (1975), 14, 3131.
54. D.L. Gallup and J.G. Morse, Inorg.Chem., (1978), 17, 1340.
55. D.L. Gallup and J.G. Morse, Inorg.Chem., (1978), 17, 3438.
56. D.L. Gallup and J.G. Morse, J.Organomet.Chem., (1978), 159, 477.
57. J.G. Morse and K.W. Morse, Inorg.Chem., (1975), 14, 565.

58. This work.
59. H.G. Horn and A. Muller, Z.Anorg.Allg.Chem., (1966), 346, 266.
60. R. Schmutzler, Adv.Fluorine Chem., (1965), 5, 31.
61. W.K. Glanville, K.W. Morse and J.G. Morse, J.Fluorine Chem., (1976), 7, 153.
62. R.W. Rudolph and R.A. Newmark, J.Amer.Chem.Soc., (1970), 92, 1195.
63. D.E.J. Arnold, J.S. Dryburgh, E.A.V. Ebsworth and D.W.H. Rankin, J.Chem.Soc.Dalton Trans., (1972), 2518.
64. M. Barrow, Private Communication.
65. A.F. Wells, Structural Inorganic Chemistry, 4th Edn., (1965).
66. M.M. Crutchfield, C.H. Dungan and J.R. Van Wazer, Topics in Phosphorus Chemistry, Vol.5.
67. Handbook of Chemistry and Physics, 57th Edn., C.R.C. Press.
68. S.D. Ross, Inorganic Infrared and Raman Spectra, McGraw Hill (1972).
69. E.G. Finer and R.K. Harris, Prog.Nucl.Magn.Reson.Spectrosc., (1970), 6, 61.
70. J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance Spectroscopy, McGraw Hill (1959).
71. A. Engelbrecht and F. Sladky, Monatsh.Chem., (1965), 96, 161.
72. J.G. Morse, K. Cohn, R.W. Rudolph and R.W. Parry, Inorg.Synth., (1967), 10, 147.
73. R. Demuth and J. Grobe, J.Fluorine Chem., (1973), 2, 299.
74. A.D. Norman and W.L. Jolly, Inorg.Synth., (1968), 11, 15.
75. S.A. Butter and J. Chatt, Inorg.Synth., (1974), 15, 185.

76. G.R. Wilson and A.G. Smith, J.Org.Chem., (1961), 26, 557.
77. Chem.Abs., (1958), 52, 17805.
78. M.M. Rachut and H.A. Currier, J.Org.Chem., (1961), 26, 4626.
79. L. Pratt and G. Wilkinson, J.Chem.Soc., (1961), 2037.
80. W.J. Hickinbottom, Reactions of Organic Compounds, 3rd Edn, (1959), Longmans.
81. D.S. Payne, Quart.Rev., (London), (1961), 15, 189.
82. J.H. Current, J.K. Burdet, L. Hodges and V. Dunning, J.Phys.Chem., (1970), 74, 4053.
83. L.P. Lindemann and M.K. Wilson, J.Chem.Phys., (1956), 24, 242.

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