

ASPECTS OF THE CHEMISTRY OF SOME FLUOROPHOSPHINE DERIVATIVES
OF GROUP VI ELEMENTS.

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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. The thesis is my own composition, and has not been submitted in any form for any other degree or professional qualification. Unless otherwise stated, the results have not been published prior to the submission of this thesis.

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ABSTRACT OF THESIS.

A range of topics relating to the chemistry of fluorophosphine derivatives of group VI elements have been investigated, with particular reference to fluorophosphine sulphides. A brief outline of the early developments in this field is presented, and greater attention is paid to more recent work concerning preparative methods, ^{19}F and ^{31}P nuclear magnetic resonance spectroscopy, structural properties, and π donor properties. The behaviour of the three classes of compounds are compared, phosphorus (III) difluorides, four-coordinate phosphorus (V) fluorides (phosphoryl compounds) and five-coordinate phosphorus (V) fluorides (fluorophosphoranes).

The use of bis-(difluorophosphino)sulphide as a preparative agent is examined, in particular for the preparation of silyl and germyl thiodifluorophosphine derivatives, and fluorothio-phosphoryl chlorides. These reactions led to the successful preparation of the novel compound, difluoro(germylthio)phosphine. The preparation, spectroscopic and chemical characterisation are described, together with some reactions of GeH_3SPF_2 with diborane and norbornadienetetracarbonylmolybdenum (0), four coordinate platinum (II) compounds, and chlorodiphenylphosphine. The gas phase molecular structure of the compound has been studied using electron diffraction, and the molecular parameters obtained are compared with ^{those of} other fluorophosphines. The conformation of the molecule has been discussed in terms of weak hydrogen-fluorine interactions stabilizing the structure with the Ge-S bond trans to the phosphorus lone pair.

The preparation and uses of group VI fluorophosphine anions

$(YPF_2)^-$ (Y = O, S, Se) as synthetic intermediates have been investigated. The possible oxidation state of the phosphorus atom in these ions is discussed, but not conclusively identified. The reactions of the ions with chlorophosphines are described and explained, but the reactions with trialkylsilylhalides are confusing, and no positive results were obtained. It is suggested that the formation of silicon fluorides leads to the formation of the complex anion $(SP(PF_2(S))_2)^-$ or a similar, neutral compound.

Included as an appendix is a copy of a paper "The preparation, properties and gas-phase molecular structure of difluoro(germylthio) phosphine.

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(E.A.V. Ebsworth, E.K. Macdonald and D.W.H. Rankin
Monatshefte für Chemie (1980), 111, 221.)

CHAPTER 11.1 Early history of fluorophosphine-sulphur chemistry.

The first preparation of the parent compound trifluorophosphine was reported by Moissan in 1884 (1), but relatively little work was carried out in the field until the 1950's. Chlorodifluorophosphine (2) and bromodifluorophosphine (3) were reported in 1939. Detailed study of these compounds made full use of vacuum line techniques, as they are poisonous gases or volatile liquids, with a tendency to hydrolyse or ignite in air, and having a very bad odour. However the field of study widened in the fifties and sixties, the main areas of interest being fluorophosphites, aryl-, halogeno- and pseudohalogeno-fluorophosphines, phosphoryl difluorides and fluorophosphoranes, and the extensive coordination chemistry of fluorophosphines.

Much of this work took place before 1970 and has been comprehensively reviewed. Schmutzler (4) in 1965 covered general phosphorus-fluorine compounds, and Kruck (5) reviewed the coordination chemistry of trifluorophosphine with transition metals. Nixon (6) specifically covered fluorophosphine chemistry up to 1970. More recently, Schmutzler and Fild (7) reviewed phosphorus halides in general, including a section on fluorophosphines.

Despite the interest shown, many main group derivatives remained unknown, particularly derivatives of the group V and group VI elements. Derivatives of nitrogen have now been extensively studied, since Rankin (8) and Cohn (8a) prepared aminodifluorophosphine in 1971. Many substituted amines F_2PNHR and F_2PNR_2 (6,9) had been known for a long time previously. The secondary

and tertiary aminofluorophosphines $(PF_2)_2NH$ (10) and $(PF_2)_3N$ (10a) have been prepared, and a wide range of silyl and germyl derivatives $(PF_2)_xNH_y(MH_3)_{3-x-y}$ (11, 11a), (M= Si, Ge; x= 1, 2; y= 0, 1), and $F_2PN(Me)(SiMe_3)$ (12). A wide range of biphosphines have also been prepared and studied, for example F_2PPF_2 (13), F_2PPH_2 (14), $P(PF_2)_3$ (15), $F_2PP(CF_3)_2$ (16) and more recently $F_2PP(GeH_3)_2$ and $F_2PP(SiH_3)_2$ (17).

In the field of group VI, most of the efforts have been directed towards oxygen, with fluorophosphites F_2POR (R= aryl, alkyl) well known. Group VI compounds are particularly interesting from the point of view of oxidation-reduction chemistry. Therefore as well as the range of difluorophosphites, there are equivalent phosphoryl fluorides for study $(O)PF_2R$. In the range of sulphur compounds, the possible use of $(PF_2)_2S$ (18) has been studied as a synthetic intermediate, reacting for example with alcohols ROH to form the tervalent species $ROPF_2$, and releasing $(S)PF_2H$. $(PF_2)_2S$ and $((CF_3)_2P)_2S$ combine to form $PF_2SP(CF_3)_2$ (19). Other compounds F_2PSR have recently been prepared (20-23).

The fluorophosphine hydride derivatives of group VI elements exist exclusively in the pentavalent oxidation state, $(Y)PF_2H$ (24, 25) as do the phosphoryl halides YPF_2X (Y= O, S, Se; X=halogen) (26-28). Other sulphur derivatives which have been reported are $(S)PF_2SH$ (29), $F_2PSP(S)F_2$ (30), $(S)PF_2SCH_3$, $(S)PF_2OCH_3$ (31), and $((S)PF_2)_2Y$ (32) (Y=O, S). The nuclear magnetic spectra of $Cl(CH_3)_2SnSP(S)F_2$ and $(CH_3)_3SiSP(S)F_2$ (33) have been described.

The thiophosphoryl compounds mentioned above are examples of four-coordinate phosphorus(V). Also reported are some five-coordinate thiophosphoranes, $RSPF_4$, $(RS)R'PF_3$ and $(RS)R'_2PF_2$ (34) (R, R'= Me, Et, Ph).

1.2. Preparative methods.

The normal starting point for the preparation of fluorophosphines is dimethylaminodifluorophosphine F_2PNMe_2 , which is readily converted to the halogenodifluorophosphine F_2PX by reaction with the relevant hydrogen halide (35). An alternative route to F_2PX is direct fluorination of the phosphorus trihalide PX_3 using antimony trifluoride, or sodium fluoride (52). This route is not a convenient synthesis however, as the monofluoro- and trifluoro-phosphines are also prepared as by products, and strict control of the reaction conditions must be maintained to maximise the yield of the difluorophosphine halide. The halides themselves offer convenient routes to a wide range of ter- and penta-valent fluorophosphines. Difluoroiodophosphine will react with sulphur to form $(S)PF_2H$ (37). When shaken on its own with mercury, F_2PI forms F_2PPF_2 (13).

Bromodifluorophosphine reacts with bis-(tri-n-butyltin) sulphide to form $(PF_2)_2S$, a more convenient route than the reaction of PF_2Br and $(SiH_3)_2S$ (38). $(PF_2)_2S$ itself has been found to be a useful synthetic intermediate, with cleavage of one phosphorus-sulphur bond being observed. Thus main group halides MH_3X react to form F_2PSMH_3 and F_2PX ($M = Ge, X = Cl; M = Si, X = I$). The analogous reaction with alcohols ROH (39) has already been mentioned, and some progress has been made studying the reaction of thiols RSH , to form $RSPF_2$ (23). An alternative route to alkyl fluorophosphine sulphides is the reaction of methyl(tri-n-butyltin) sulphide with F_2PBr , leading to F_2PSCH_3 in good yield (23).

In the preparation of thiophosphoryl fluorides, $(S)PF_2I$ and $(S)PF_2SH$ have played an important part. $(S)PF_2SH$ is formed by the

reaction of $(\text{SPF}_2)_2\text{H}$ and elemental sulphur, or alternatively the reaction of $(\text{SPF}_2)_2\text{I}$ and hydrogen sulphide (29). $(\text{SPF}_2)_2\text{I}$ eliminates iodine when shaken with mercury, and forms $(\text{S})\text{PF}_2\text{SPF}_2$ (30). It will also react with oxygen to form $((\text{S})\text{PF}_2)_2\text{O}$ (32). $(\text{S})\text{PF}_2\text{SH}$ reacts with F_2PNMe_2 to form $(\text{S})\text{PF}_2\text{SPF}_2$ (30), and reacts with group IV compounds; for example trimethylsilane reacts to form $\text{Me}_3\text{SiSP(S)F}_2$, and trimethyltin chloride reacts to form $\text{ClMe}_2\text{SnSP(S)F}_2$ (33).

Thiofluorophosphoranes have not been so widely studied. Their preparation involves the reaction of (trimethylsilyl) alkyl sulphides RSSiMe_3 with alkyl fluorophosphoranes, $\text{R}'_x\text{PF}_{5-x}$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}, \text{Ph}$; $x = 0, 1, 2$). Trialkylsilyl fluoride R_3SiF is eliminated, giving rise to $(\text{RS})\text{R}'_x\text{PF}_{4-x}$ (31, 34).

1.3 Nuclear magnetic resonance spectroscopy of fluorophosphine-sulphur compounds.

Nuclear magnetic resonance (n.m.r.) spectroscopy has been of particular importance in the study of fluorophosphines, as both elements have nuclear spin $I = \frac{1}{2}$ in 100% natural abundance. The spectra of simple fluorophosphine compounds are usually first order, but most bis- and tris-difluorophosphines have extremely complex spectra, of which the most common are the $(\text{AX}_2)_2$ spin systems (40). The spectra of $(\text{PF}_2)_2\text{S}$, $(\text{PF}_2)_2\text{Se}$ and $(\text{PF}_2)_2\text{NH}$ have been analysed using the equation of Harris. A great deal of interest has centred on the variations with temperature of the vicinal and long range fluorine - fluorine coupling constants, and the phosphorus - phosphorus coupling constants, and these fluctuations have been explained in relation to the structures of bis-difluorophosphine systems (41, 42).

The values of the ^{31}P and ^{19}F chemical shifts, and the value of the phosphorus - fluorine coupling constants ($^1J_{\text{PF}}$), give a good indication of the type of compound being studied, and this work has tried to apply these observations whenever possible in the identification of unknown or novel compounds. Trivalent phosphorus fluorides are generally observed to high frequency (positive chemical shift) of the conventional standard, 85% phosphoric acid. PF_3 is observed at the lowest chemical shift (~ 100 ppm) and the range of shifts extends to about 300 ppm, with $(\text{PF}_2)_2\text{Te}$ (43) one of the highest phosphorus chemical shifts reported. Within this range, types of compounds can be listed in order of decreasing chemical shift: $\text{RPF}_2 > \text{PF}_2\text{I} > \text{RSPF}_2 > \text{PF}_2\text{Br} > \text{PF}_2\text{Cl} > \text{PF}_2\text{NR}_2 > \text{PF}_2\text{OR} > \text{PF}_3$.

Pentavalent phosphoryl fluorides are observed at lower frequencies, generally in the range 0 to +100 ppm. Divisions between types of compounds are less distinct than shown by the trivalent phosphorus compounds and there are several anomalies. For example, when comparing the two series of fluorophosphine halides, PF_2X and $(\text{S})\text{PF}_2\text{X}$, it is observed that the trivalent halides are arranged in order of decreasing chemical shifts $\text{I} > \text{Br} > \text{Cl} > \text{F}$, but the pentavalent compounds are arranged $\text{I} > \text{Cl} > \text{F} > \text{Br}$.

A selection of n.m.r. data for a wide range of fluorophosphine compounds is presented in table 1.1. A more specific selection of data for fluorophosphine - sulphur compounds is summarised in table 1.2. These figures clearly show the division between trivalent and pentavalent phosphorus sulphides. Simple thiophosphines are generally observed above 200 ppm, an exception being $\text{Me}_2\text{NC}(\text{S})\text{SPF}_2$ ($\delta_{\text{P}} = 153$ ppm). This is probably a result of intramolecular exchange of the PF_2 group between the two sulphur atoms. In the

TABLE 1.1.

^{31}P and ^{19}F Nuclear Magnetic Resonance Parameters of a selection of
Fluorophosphine Compounds.

Compounds	δP (ppm)	δF (ppm)	$^1J_{(\text{PF})}$ (Hz)	Reference
PF_3	104	-34	1400	6
PF_2Cl	176	-37	1390	51, 52
PF_2Br	218	-40	1388	51
PF_2I	242	-46	1340	53
PF_2CH_3	250	-93	1157	54, 56
PF_2OCH_3	110	-53	1278	4
PF_2SCH_3	237	-62	1261	21
$\text{PF}_2\text{SeSiH}_3$	255	-59	1286	43
PF_2NH_2	147	-58	1200	8
PF_2NHCH_3	140	-71	1191	57
$\text{PF}_2\text{N}(\text{CH}_3)_2$	143	-65	1197	45
PF_2PH_2	293	-88	1203	14
$(\text{PF}_2)_2\text{O}$	111	-38	1358	43, 53
$(\text{PF}_2)_2\text{S}$	219	-64	1303	43
$(\text{PF}_2)_2\text{NH}$	144	-62	1253	43
$(\text{PF}_2)_3\text{N}$	150	-62	1224	43
$(\text{PF}_2)_3\text{P}$	245	-88	1225	15
$(\text{O})\text{PF}_3$	-35	-93	1055	26
$(\text{S})\text{PF}_3$	-32	-51	1182	26, 27
$(\text{O})\text{PF}_2\text{H}$	-5	-62	1121	24
$(\text{S})\text{PF}_2\text{H}$	68	-49	1153	24
$(\text{Se})\text{PF}_2\text{H}$	76	-37	1217	25
PF_5	-30	-72	930	52
PF_4Cl	-50	+23	1030	43
PF_3Cl_2	-26	+31	1048	52
PF_2Cl_3	-9	+115	1045	52
PFCl_4	-23	+143	996	52

TABLE 1.2.

^{31}P and ^{19}F Nuclear Magnetic Resonance Parameters of a selection of Fluorophosphine-sulphur Compounds.

Compounds	δP (ppm)	δF (ppm)	$^1\text{J}_{(\text{PF})}$ (Hz)	Reference
CH_3SPF_2	233 (237)	-62	1248 (1261)	20(21)
CF_3SPF_2	212 (215)	-69	1307 (1302)	20(22)
p- $\text{CH}_3\text{C}_6\text{H}_4\text{SPF}_2$	222	-66	1272	20
GeH_3SPF_2	232	-57	1285	43
SiH_3SPF_2	229	-57	1298	43
PF_2SPF_2	219	-64	1303	43
(S) PF_2SPF_2	148/264	-14/-66	1217/1322	58,30
(S) PF_3	-32	-51	1182	26,27
(S) PF_2Cl	50	-16	1219	26
(S) PF_2Br	28	-2	1250	26
(S) PF_2I	70	+11	1271	26,28
(S) PF_2H	68	-46	1153	24
(S) PF_2OCH_3	n.o.	-48	1126	28
(S) PF_2SCH_3	n.o.	-27	1207	28
(S) $\text{PF}_2\text{SSi}(\text{CH}_3)_3$	88	-12	1200	33
(S) $\text{PF}_2\text{SSnCl}(\text{CH}_3)_2$	98	-14	1210	33
((S) PF_2) $_2\text{O}$	25	-40	1171	32,59
((S) PF_2) $_2\text{S}$	60	-17	1254	32,59
((S) PF_2) $_2\text{NCH}_3$	55	-40	1133	32
(O) PF_2OPF_2 (S)	n.o.	-41	1177	32
CH_3SPF_4	-34	-45	1032	34
(CH_3S) PF_3	2	1.2 (a)	925	34
		-75 (e)	1062	
(CH_3S)(C_6H_5) $_2\text{PF}_2$	-39	-25	760	34

n.o. not observed

(a) axial

(e) equatorial

range of pentavalent compounds, $(S)PF_2SPF_2$ is observed to have a high phosphorus (V) chemical shift (148ppm) and also a high value for the phosphorus (III) shift (264ppm).

The largest directly bonded phosphorus - fluorine coupling constant is observed in trifluorophosphine ($^1J_{PF} = 1400\text{Hz}$), and the absolute value of $^1J_{PF}$ for a series of compounds PF_2Z increases along the series $Z = R- < R_2N- < CX_3- < RO- < F$, (R= alkyl, X= halogen), and similarly in order $I < Br < Cl < F$ (44). Generally, trivalent phosphorus fluorides have larger coupling constants than the equivalent pentavalent phosphines. The five-coordinate phosphoranes exhibit still smaller coupling constants.

Fluorine chemical shifts also appear to depend largely on the electronegativity of the substituents, and are spread over a narrower range than the phosphorus shifts. Within structurally similar series PF_2X , the value of $\delta(^{19}F)$ increases regularly with the electronegativity of X ($X = F, OR, NR_2$) (45), which is in the opposite direction to $\delta(^{31}P)$. Correlation between phosphorus and fluorine chemical shifts appears to be much better in the phosphoryl fluorides $XYP(O)F$, depending on the nature of X and Y, and it has been suggested that this may reflect smaller bond angle changes at phosphorus within the whole series (46).

N.m.r. parameters are being used to predict overall structural properties of fluorophosphines. The molecule CH_3SPF_4 (34) has been shown to have non-equivalent axial fluorine atoms at low temperature, and this has been attributed to the interaction between one axial fluorine and the protons of the methyl group. Similarly, the molecules $F_2PNH(GeH_3)$ and $(PF_2)_2N(GeH_3)$ (47) have been described as existing in conformations with the fluorine atoms close to the germyl protons, on the basis of $^2J_{PH}$ being maximised

(by interaction of the proton with the phosphorus lone pair) and $^3J_{PH}$ minimised with the lone pair of the phosphorus remote from the germyl group. The proposed conformations of GeH_3SPF_2 and SiH_3SPF_2 (43) were suggested on the basis of $^4J_{PF}$ being positive and this has been shown to be a valid assumption by the electron diffraction study described in this work. Some recent gas phase diffraction studies have shown that weak F---H interactions have a significant effect on the conformations of group V and group VI fluorophosphine compounds (48,49).

1.4. Some structural properties of fluorophosphine compounds.

The nature of fluorophosphine compounds, generally gases or volatile liquids, makes them ideal for structural investigation, using gas phase electron diffraction methods. Microwave spectroscopy has also been used in the study of some of the simpler fluorophosphines. In table 1.3, some structural parameters, relevant to trivalent and pentavalent fluorophosphine sulphur compounds, are recorded

The contrast between trivalent and pentavalent phosphorus sulphides is best shown by the three parameters $r(P-S)$, $r(P-F)$ and the angle FPS. As one might expect the P=S double bond length (186 - 187 pm) is significantly shorter than the P - S single bond (207 - 213 pm). The P - F bond length is also marginally shorter in compounds with the phosphorus atom in the higher oxidation state. In the trivalent compounds the effect of the lone pair is observed to tighten the bond angles at phosphorus, the FPF angle is slightly smaller in the trivalent phosphines, and the FPS angle is significantly smaller. Alternatively, the FPS angle in phosphorus (III) compounds can be compared with the FPX angle

TABLE 1.3.

Some Bond Lengths and Angles of some Trivalent and Pentavalent
Fluorophosphine-sulphur Compounds.

Compound	r(P-S)	r(P-F)	\angle FPF	\angle FPS	\angle FPX	Reference
(S)PF ₂ H	187.6	155.1	98.3	115.9	103.4	60
(S)PF ₂ Cl	186.4	153.7	100.6	115.7	102.0	61
(S)PF ₂ Br	188.1	154.3	98.3	118.2	100.1	62
CH ₃ SPF ₂	207.6	157.7	98.1	101.0	—	63
F ₂ PSPF ₂	212.7	157.3	97.5	98.9	—	64
GeH ₃ SPF ₂	211.5	159.0	97.0	99.9	—	This work

Distances in pm

Angles in degrees

in pentavalent phosphine sulphides; in this case imagining the sulphur atom to be in the lone pair position (see figure 1.1). The comparison of these angles shows that the bond angles at phosphorus are generally smaller in trivalent fluorophosphines.

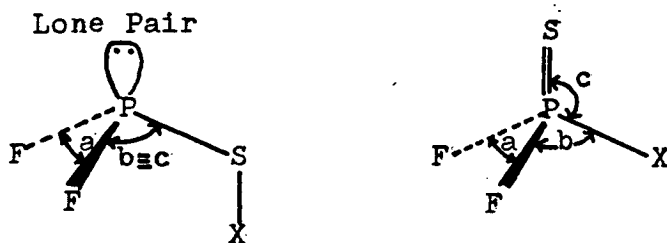


Figure 1.1.

Structural Arrangement of Tri- and Penta-valent Fluorophosphines.

Structural studies of fluorophosphine - group VI compounds are helpful in understanding the observed equilibria between phosphorus (III) and phosphorus (V) compounds. For example the compounds F_2PYMH_3 ($M = C, Si, Ge; Y = O, S, Se$) (11, 43) and $(CF_3)_2PSH$ (50) appear to exist exclusively with phosphorus in the +3 oxidation state, whereas $(Y)PF_2H$ (60) exist with pentavalent phosphorus. The compounds of trivalent phosphorus have the capacity to form five membered rings, with weak F----H interactions to stabilize the structures, whereas the pentavalent isomers are unable to do this. Similarly, F_2PYH can only form at best a four-membered ring, and the Y - H bond would be polarised to such an extent that intramolecular rearrangement would be quite impossible. Even at temperatures as low as 173K no evidence for the trivalent F_2PYH compounds is observed.

1.5. Fluorophosphine complexes with transition metals and borane.

Phosphines generally behave as soft bases and coordinate to compounds classified as class B acids by Chatt (65) or soft acids

by Pearson (66). The presence of fluorine atoms significantly lowers the ability of the phosphorus atom to donate its lone pair, with the result that trifluorophosphine is a very weak base. The basicity is considerably enhanced if one or more fluorine atom is replaced by an electropositive group, for example an alkylamino group.

The bonding in such complexes can be described as a combination of a σ -bond contribution and a $d_{\pi} - d_{\pi}$ interaction from a filled metal orbital to the empty 3d orbitals of the phosphorus (67). The importance of this π bonding has been questioned (68-71) and the soft character of the ligands has been attributed to the domination of the σ effects; but in fluorophosphine - transition metal complexes the π effect could be more important as the presence of fluorine atoms should enhance the back - donation of metal electrons by lowering the energy of the phosphorus 3d orbitals.

Early studies of fluorophosphine - transition metal complexes concentrated on the use of PF_3 as the ligand, and its properties as a ligand were compared closely with those of carbon monoxide (5). More recent interest has centred on the possible use of bis- and tris-difluorophosphino compounds as multidentate ligands. King (72-77) has used methylamino (bis-difluoro-)phosphine as a monodentate, bidentate and bridging ligand, isolating a wide range of compounds, examples of which are shown in figure 1.2.

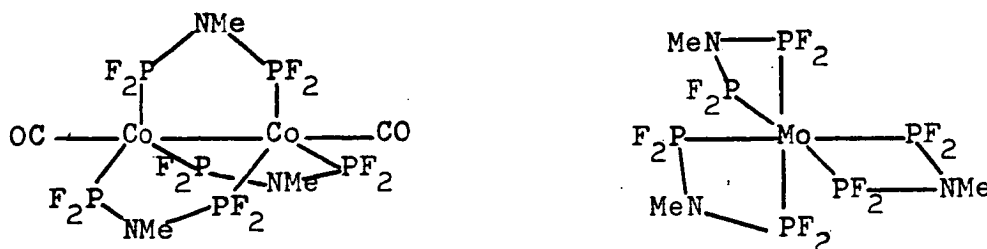


Figure 1.2. Examples of the coordination behaviour of $\text{MeN}(\text{PF}_2)_2$.

$(PF_2)_2S$ has been observed to act as a bidentate ligand towards the $Mo(CO)_4$ moiety, and there is also some evidence for monodentate behavior. Whitelock (81) has prepared a wide range of group VI fluorophosphine platinum complexes of the form $(PEt_3)_2XPtPF_2(Y)$ ($X = H, Cl, Br, I$; $Y = O, S, Se$), and Hunter (81) is currently investigating the use of $(O)P(OPF_2)_3$ as a tridentate ligand.

Another area of interest lies in the formation of complexes with borane. There have been several attempts to relate the n.m.r. parameters of phosphine - borane complexes to the base strength of phosphines, but the empirical relationship between $^1J(^{31}P - ^{11}B)$ and dative bond strength is useful only for restricted ranges of similar phosphines.

An interesting point concerning bis-difluorophosphine compounds is the apparent difficulty of binding two BH_3 groups. $(PF_2)_2O$ (78) and $(PF_2)_2S$ (38) only bind one BH_3 group, which has been explained as resulting from electron interchange between the PF_2 units via the π system of the group VI atom (78). This enhances the base strength of the coordinated fluorophosphine group and correspondingly reduces the base strength of the uncoordinated group. This is not possible in $(PF_2)_2CH_2$, which is observed to bind two BH_3 groups (79). Presumably two PF_2 groups widely separated in the same molecule would also be able to bind two borane groups. P_2F_4 is only observed to bind one borane group but n.m.r. studies suggest that there is rapid interchange of the BH_3 group between the two phosphorus atoms (80).

A convenient way of following the formation of complexes is to observe the change in n.m.r. parameters as the free ligand is bound to the Lewis acid. The phosphorus chemical shift of the

compound is normally observed to low frequency of the free ligand, and this is normally combined with a decrease in the value of $^1J_{\text{PF}}$. For example, the coordination shift $\text{Mo}(\text{CO})_4((\text{PF}_2)_2\text{S})$ is -78ppm , and for $\text{PF}_2\text{SPF}_2:\text{BH}_3$ -39ppm . There appears to be no simple relationship between the coordination shift and the type of compound formed.

The chemistry described above forms the background to work described in this thesis, and the basis for the consideration of the results obtained. Some results have defied explanation, and for every question answered, another problem remains unsolved. However, the correct route to these answers will hopefully be clearer as a result of the experiments that are detailed here, and also some of the experiments which have not been carried out.

CHAPTER 22.1 Introduction

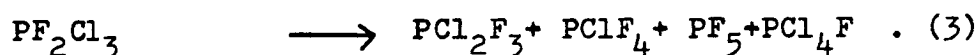
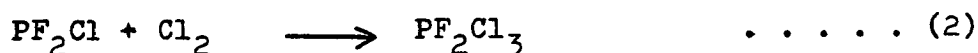
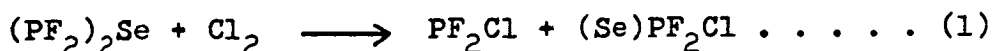
In the study of $(PF_2)_2Se$, Arnold (43) reported several reactions as possible synthetic routes to a wide range of fluorophosphine compounds. The reactions of $(PF_2)_2S$ with alcohols and thiols have now been widely investigated (18,23), but some of the other reactions have not been pursued to any great extent. It was proposed to carry out some of these reactions on a preparative scale and investigate their suitability for synthetic work. In particular, the compounds $(Se)PF_2Cl$ had not been previously reported and it was hoped that the compound could be isolated. The corresponding sulphur compounds $(S)PF_2X$ ($X=Cl, Br, I$) (28,52,82-84) have been studied in detail, and are useful synthetic intermediates in the formation of phosphorus (V) sulphides. The selenium compound would also be of interest structurally, for comparison with the sulphur series; and spectroscopically, for the magnetic study of ^{77}Se is still at an early stage (92). It seemed that the reaction of $(PF_2)_2Y$ with halogens would provide a convenient route to $(Y)PF_2X$ compared with published methods.

The reaction between chlorine and $(PF_2)_2S$ proceeds by cleavage of the P-S bond. In the same way, the reaction between $(PF_2)_2S$ and main group halides might react to form mixed silyl or germyl fluorophosphines, or mixed alkyl phosphine-fluorophosphine systems. Such compounds were first reported by Arnold (11) in the case of the group IV species, and by Hutchinson in the case of the group V compounds (17). The reported form of these compounds provides an interesting contrast: the group IV species $(H_3M)SPF_2$ are described as phosphorus (III) compounds, whereas the group V species are

described as mixed valence phosphines, with ^{the Ratio of} the PF₂ group being pentavalent (S)PF₂PR₂. The isolation of both types of compounds, with a view to comparing the structures, would be of great assistance in explaining the contrast. Unfortunately it was only possible to isolate one of the products (GeH₃SPF₂) observed in the preliminary experiments, and this is described fully in chapters 3 and 4.

2.2 Reaction of (PF₂)₂S with Cl₂

Arnold (43) reported that in addition to the cleavage of the phosphorus-selenium bond by chlorine, excess halogen caused further oxidation and disproportion of the initial products, leading to the full range of chlorofluorophosphoranes according to the reactions 1-3 set out below.



This occurred when an excess of chlorine was used. It was felt that under controlled conditions using only the minimum amount of chlorine necessary (an equimolar mixture of Cl₂ and (PF₂)₂S), the reaction would not proceed beyond the first stage.

The reaction between (PF₂)₂S and Cl₂ was carried out either by mixing the reagents as liquids in a single bulb, or by allowing the reactants to mix as gases at room temperature using a double bulb apparatus. The method made no difference to the products obtained, nor did the scale of the reaction, provided the reactants were present in equimolar quantities. If the chlorine was present in excess, the yield of PF₂Cl decreased, and some PF₂Cl₃ was recovered in the less volatile fraction along with the (S)PF₂Cl.

The difference in volatilities of the two major products was such that no problems were experienced with the separation of the very volatile PF_2Cl from the less volatile $(\text{S})\text{PF}_2\text{Cl}$. Both products were identified by infra-red and ^{31}P n.m.r. spectroscopy, and molecular weight measurements. The reactions proceeded almost quantitatively, with a very small amount of PF_3 formed as a by product.

The present methods of preparing $(\text{S})\text{PF}_2\text{X}$ (36) are generally time-consuming reactions. For example, the reaction of SPF_2NMe_2 with hydrogen halides yields $(\text{S})\text{PF}_2\text{X}$ (85), but the preparation of the amino compound requires a reaction time of 5 days for the completion of the reaction between sulphur and PF_2NMe_2 . Alternatively, the range of thiophosphoryl halo fluorides $(\text{S})\text{PF}_n\text{X}_{3-n}$ can be obtained by partial fluorination of thiophosphoryl trihalides (83,84). This however has the problem of separating the three products obtained. Given the correct starting materials, the reaction of $(\text{S})\text{PF}_2\text{NMe}_2$ with HX is probably the most convenient route to $(\text{S})\text{PF}_2\text{X}$, but in the absence of these reagents, the reaction of $(\text{PF}_2)_2\text{S}$ with chlorine provides a good alternative, giving rise to high yields of product, with little impurity.

The reaction between $(\text{PF}_2)_2\text{Se}$ and chlorine was not successful, either in the gas phase or the liquid phase. In each case the reaction proceeded with the deposition of large quantities of red solid (presumably selenium) on the walls of the reaction vessel and vacuum system. Analysis of the volatile products by n.m.r. and infra-red spectroscopy showed PF_2Cl as the only product collected. The results reported by Arnold (43) were obtained from a reaction carried out in a sealed n.m.r. tube with C_6D_6 and SiMe_4 as solvent. $(\text{Se})\text{PF}_3$ is reported to be light sensitive (87), decomposing to

selenium and PF_3 . A similar decomposition could be the cause of not observing $(\text{Se})\text{PF}_2\text{Cl}$ in this case. In a sealed tube, being studied by n.m.r. spectroscopy, the reaction mixture would not be affected by light. Also, the decomposition may be inhibited in some way by the presence of solvent.

2.3. The reactions of $(\text{PF}_2)_2\text{S}$ with silyl compounds

These reactions were carried out in sealed n.m.r. tubes, with a mixture of toluene and deuteriated toluene as solvent. The reactions were studied using ^{31}P n.m.r. spectroscopy. Several compounds were observed in more than one reaction: the n.m.r. parameters of these compounds are listed in table 2.1. The parameters of the relevant products are noted in the text and summarised in table 2.2.

2.3.1. $(\text{PF}_2)_2\text{S} + \text{Me}_3\text{SiCl}$

The reaction mixture was warmed to room temperature but no reaction between the $(\text{PF}_2)_2\text{S}$ and silyl species was observed. In addition to $(\text{PF}_2)_2\text{S}$, a large amount of $(\text{S})\text{PF}_2\text{H}$ and some PF_2Cl was observed, but no signal which could have been assigned to the expected product $\text{Me}_3\text{SiSPF}_2$.

2.3.2. $(\text{PF}_2)_2\text{S} + \text{Me}_3\text{SiBr}$

As the tube was warmed to room temperature, reaction occurred. PF_2Br was observed in the spectrum, along with some $(\text{S})\text{PF}_2\text{H}$, and unreacted $(\text{PF}_2)_2\text{S}$. A triplet was observed centred at $\delta\text{P} = 238.3\text{ppm}$, with a coupling constant $^1J_{\text{PF}} = 1269\text{ Hz}$. These figures are consistent with a trivalent phosphorus sulphide, and the resonance was assigned to $\text{Me}_3\text{SiSPF}_2$. After allowing the reaction mixture to remain at

TABLE 2.1.

^{31}P n.m.r. parameters of the minor products observed in the reactions of $(\text{PF}_2)_2\text{S}$ with silyl and germyl halides

Compound	$\delta\text{P(a)}$ ppm	$^1\text{J}_{\text{PF}}$ (Hz)
PF_3	102 - 104	1400
PF_2Cl	178 - 180	1390
PF_2Br	199 - 201	1364
PF_2I	240	1335
$(\text{PF}_2)_2\text{S}$	219 - 222	1303 (b)
$(\text{S})\text{PF}_2\text{H}$	62 - 65	1153

(a) Precise values depend on temperature and concentration.

(b) Splitting observed is $^1\text{J}_{\text{PF}} + ^3\text{J}_{\text{PF}}$.

TABLE 2.2.

^{31}P n.m.r. parameters of the major products observed in the reactions of $(\text{PF}_2)_2\text{S}$ with silyl and germyl halides.

Product	δP ppm	$^1\text{J}_{\text{PF}}$ (Hz)	$^3\text{J}_{\text{PH}}$ (Hz)
$\text{Me}_3\text{SiSPF}_2$	238.3	1269	-
H_3SiSPF_2	230.0 (229.5)	1287 (1298)	14.6 (13.3)
$\text{MeGeH}_2\text{SPF}_2$	236.8	1272	12.2
H_3GeSPF_2	235.4 (232.0)	1272 (1285)	13.4 (11.8)

Values quoted in brackets are from reference 103.

room temperature overnight, no further reaction was observed.

2.3.3. $(PF_2)_2S + MeSiH_2Cl$

Although the $(PF_2)_2S$ reacted as the tube was warmed to room temperature, with PF_2Cl and $(S)PF_2H$ being observed in the phosphorus n.m.r spectrum, no evidence for the expected product $MeSiH_2SPF_2$ was observed.

2.3.4. $(PF_2)_2S + SiH_3Cl$

As in the previous reaction, the $(PF_2)_2S$ was observed to form $(S)PF_2H$ and PF_2Cl , but no evidence for the expected product SiH_3SPF_2 was observed. This contrasts with reactions between $(SiH_3)_2S$ and PF_2Br , when the mixed silylfluorophosphine species was observed (11).

2.3.5. $(PF_2)_2S + SiH_3Br$

As the reaction mixture was warmed to 233K, the $(PF_2)_2S$ reacted to form PF_2Br and a small amount of $(S)PF_2H$. Also observed, to high frequency of the $(PF_2)_2S$ resonance was a triplet centred at $\delta P = 230.0$ ppm, with a coupling constant $^1J_{PF} = 1287$ Hz. When proton coupling was retained, each line of the triplet was further split into a quartet with splitting $^3J_{PH} = 14.6$ Hz. This resonance was assigned to H_3SiSPF_2 , and the measured n.m.r. parameters are in agreement with those reported by Arnold (11,43). The species was not stable as the solution was warmed to room temperature, and after a short time only PF_2Br and $(S)PF_2H$ were observed in the n.m.r. spectrum.

This reaction was also carried out on a preparative scale in the absence of solvent. The volatile products were examined by

n.m.r. spectroscopy, and although a small quantity of H_3SiSPF_2 was observed, this decomposed eventually, leaving PF_2Br and $(\text{S})\text{PF}_2\text{H}$ as the only species present.

2.3.6. $(\text{PF}_2)_2\text{S} + \text{SiH}_3\text{I}$

When this reaction mixture was warmed to 233K, almost equimolar quantities of $(\text{PF}_2)_2\text{S}$, PF_2I and H_3SiSPF_2 were observed. On warming to room temperature the amount of $(\text{PF}_2)_2\text{S}$ decreased, with a corresponding increase in the amount of PF_2I and H_3SiSPF_2 . Although a small quantity of $(\text{S})\text{PF}_2\text{H}$ was observed, the silyl species appeared to be more stable in this case than in the previous reaction. The ^{31}P n.m.r. spectrum of this reaction is shown in figure 2.1.

2.4. Reactions of $(\text{PF}_2)_2\text{S}$ with Germyl Halides.

As in the previous series of reactions, these were carried out in sealed tubes using toluene and deuteriated toluene mixed as a solvent. The n.m.r. parameters of the main products are listed in table 2.2.

2.4.1. $(\text{PF}_2)_2\text{S} + \text{MeGeH}_2\text{Cl}$

The reaction proceeded at 233K, and in addition to $(\text{PF}_2)_2\text{S}$, PF_2Cl and $(\text{S})\text{PF}_2\text{H}$ a triplet was observed at $\delta\text{P} = 236.8\text{ppm}$, with a coupling constant $^1\text{J}_{\text{PF}} = 1272\text{Hz}$. When proton coupling was retained, each line was further split into a triplet with a coupling constant $^3\text{J}_{\text{PH}} = 12.2\text{Hz}$. This resonance was assigned to the expected product $\text{MeGeH}_2\text{SPF}_2$. Spectra were obtained at room temperature and the product appeared to be quite stable at normal temperature.

2.4.2

- A - PF_2I
- B - PF_2SSiH_3
- C - $(\text{PF}_2)_2\text{S}$

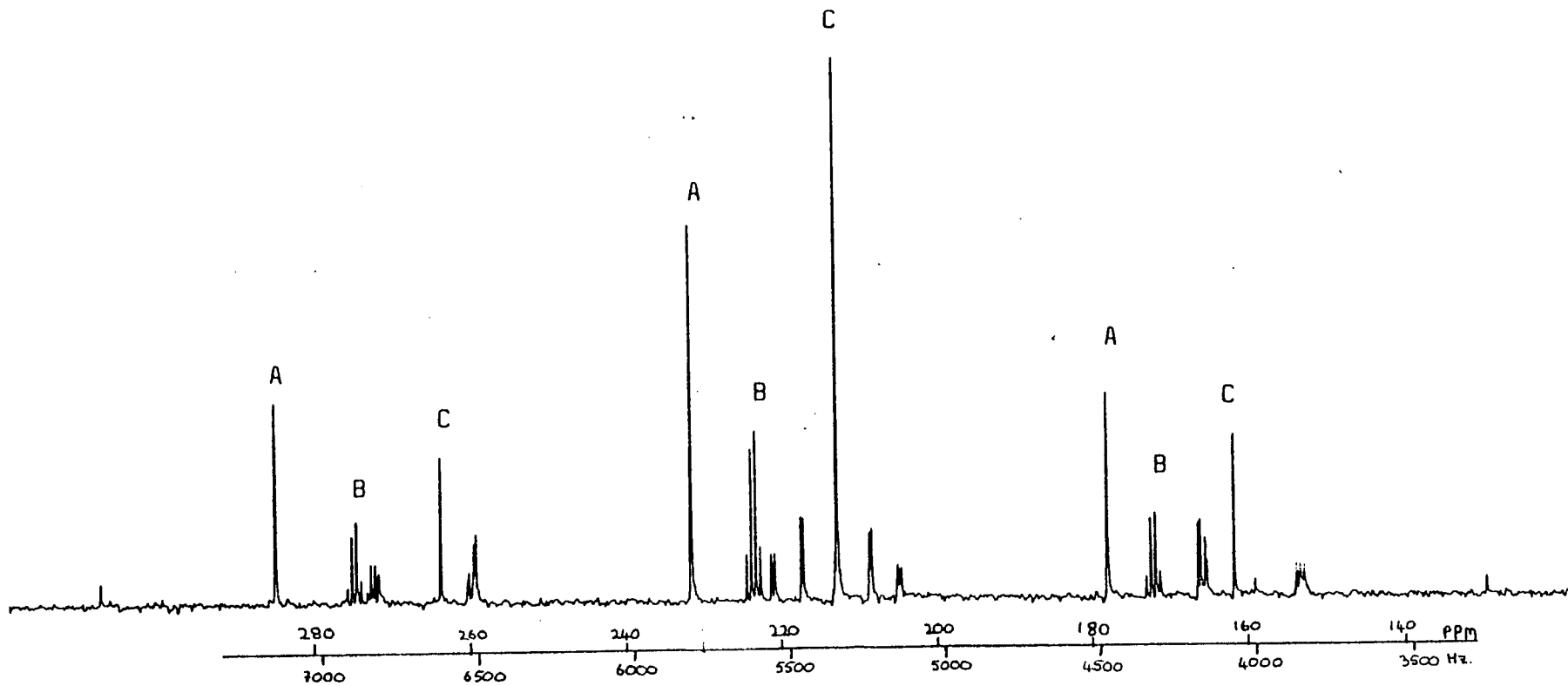


Figure 2.1. ^{31}P n.m.r. spectrum of the reaction between $(\text{PF}_2)_2\text{S}$ and SiH_3I .

2.4.2. $(\text{PF}_2)_2\text{S} + \text{GeH}_3\text{Cl}$

Reaction was observed initially at 223K, and a triplet was observed at $\delta\text{P} = 235.4\text{ppm}$, with a coupling constant $^1\text{J}_{\text{PF}} = 1272\text{Hz}$. With proton coupling retained, each line was split further into a quartet with coupling constant $^3\text{J}_{\text{PH}} = 13.4\text{Hz}$. This resonance was assigned to the expected product H_3GeSPF_2 . At room temperature this species was the major product, along with PF_2Cl , and small amounts of $(\text{PF}_2)_2\text{S}$ and $(\text{S})\text{PF}_2\text{H}$ were also observed. Subsequent attempts to carry out this reaction on a preparative scale, in the absence of solvent, were successful and are discussed fully in Chapter 4.

2.4.3. $(\text{PF}_2)_2\text{S} + \text{GeH}_3\text{I}$

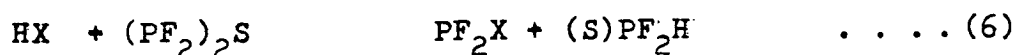
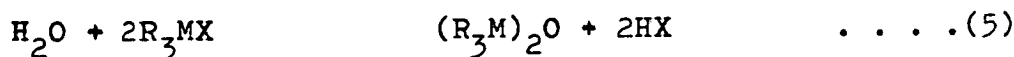
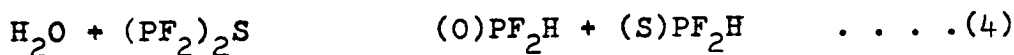
This reaction proceeded along similar lines to those described above and H_3GeSPF_2 was observed in the n.m.r. spectrum at $\delta\text{P} = 235.4\text{ppm}$ with coupling constants $^1\text{J}_{\text{PF}} = 1273\text{Hz}$ and $^3\text{J}_{\text{PH}} = 13.4\text{Hz}$. The extent of reaction appeared much lower than in the case of the reaction of GeH_3Cl and a significant amount of $(\text{PF}_2)_2\text{S}$ remained unreacted.

2.5. Discussion and Conclusions

The first series of experiments show that the reaction of $(\text{PF}_2)_2\text{S}$ with chlorine is a very convenient route to $(\text{S})\text{PF}_2\text{Cl}$, but the analogous compound $(\text{Se})\text{PF}_2\text{Cl}$ appears to be unstable. The logical extension of this reaction is to try and prepare $(\text{S})\text{PF}_2\text{Br}$ and $(\text{S})\text{PF}_2\text{I}$ by the same method. However in these cases, the disadvantages of the reaction are highlighted by the difficulty of handling bromine and iodine in a vacuum system, and a more convenient route to these compounds is the reaction between $(\text{S})\text{PF}_2\text{NMe}_2$ and

hydrogen bromide or hydrogen iodide (85,86), which are easier to handle than the halogens.

When studying the results obtained from the reactions of $(PF_2)_2S$ with the group IV halides (summarised in figure 2.2), the first point to note is the presence of $(S)PF_2H$ in so many of the reactions. This could arise in two ways. Firstly, trace amounts of water in the reaction mixtures could react either with $(PF_2)_2S$ directly to form $(S)PF_2H$ and $(O)PF_2H$, or with the silyl or germyl halide to form $(P_3M)_2O$ and HX , the hydrogen halide reacting in turn with $(PF_2)_2S$ to form PF_2X and $(S)PF_2H$. This is more likely in the case of the liquid trialkyl silyl or germyl halides. Secondly, in the case of H_3MX , traces of hydrogen halide could be present, reacting with $(PF_2)_2S$ as before. These routes are summarised in equations 4 - 6 below.



The relative rates of reaction and equilibrium positions of the reactions involving the silyl halides follows the series $I > Br > Cl$, while the reverse is true for the germyl halides. This is consistent with studies of the reactivity of silyl and germyl halides (88,89). Also, the products of the reactions involving the silyl halides appear to be less stable than the germyl species. The major decomposition product appears to be silyl fluoride, which is often a major factor affecting the attempted preparation of silyl-fluorophosphine compounds, as silyl fluoride is the most stable silyl halide (89). It was this that prompted the extension of these experiments to investigate the preparation and properties of H_3GeSPF_2 .

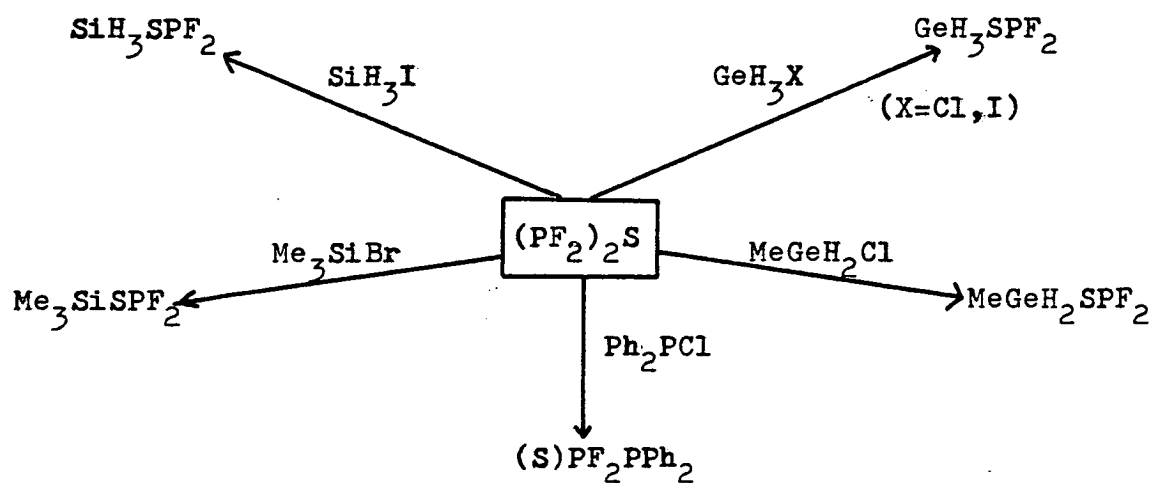


Figure 2.2.

Summary of the reactions of $(PF_2)_2S$ with main group halides.

The next point to note is the assignment of these compounds as trivalent phosphorus compounds. The basis for this assignment is the ^{31}P chemical shift and the phosphorus-fluorine coupling constants (90). There are two main factors which will determine the oxidation state of the phosphorus atom. Firstly, a trivalent phosphorus compound of this type will be stabilised by delocalisation of the lone pair electrons of the sulphur atom into the vacant d-orbitals of the silicon or germanium and phosphorus atoms (91). Also with the hydrogen and fluorine atoms four bonds apart, it is possible to visualize the molecule in a conformation such that the hydrogen and fluorine atoms are close enough to form hydrogen bonds and stabilize the trivalent phosphorus state (48,49). If one of these compounds could be prepared, it would be possible to confirm this through a gas phase electron diffraction study, and this was proposed as the next step after the characterisation of the compound. From the results obtained in this series of experiments, one compound stood out as offering the greatest chance of success. The following two chapters describe the preparation, properties and gas-phase structure of germyl(difluorophosphino-)sulphide.

CHAPTER 3

3.1 Introduction

There has been very little work on germyl-sulphur compounds. Early studies began with $(\text{GeH}_3)_2\text{S}$ (93-95), H_3GeSCH_3 (96-98) and GeH_3SH (93), concentrating on spectroscopy and structural properties. GeH_3SH (99) was also reported. More recently, Drake (100-102) has concentrated on alkyl germyl sulphides generally and has prepared a wide range of compounds of the type GeH_3YR and $(\text{R}_n\text{GeH}_{3-n})_2\text{Y}$. (R = alkyl, Y = O, S, Se, Te)

The first report of the compound GeH_3SPF_2 (43,103) was in the study of exchange reactions of bromodifluorophosphine with digermyl sulphide already mentioned. Arnold was unable to build up high concentrations of the compound during the course of the reaction. The results from the previous chapter suggested that it would be possible to obtain GeH_3Cl and $(\text{PF}_2)_2\text{S}$, if careful attention was paid to the concentrations of the reactants. Compared with the analogous silyl compound, GeH_3SPF_2 , was more stable to temperature in solution, and as both $(\text{PF}_2)_2\text{S}$ and $(\text{GeH}_3)_2\text{S}$ are gaseous and easy to manipulate in vacuum systems it was hoped that the mixed compounds would also be as easy to handle.

The main object of the preparation of this compound was to study the structure. Although the oxidation state of the phosphorus is determined by (p-d) π bonding between the sulphur and the phosphorus and germanium atoms, the geometry of the molecule is probably governed by the formation of hydrogen bonds, as the fluorine and hydrogen atoms are separated by four bonds. This is supported by the shift to high frequency in the proton n.m.r. spectrum compared to $(\text{GeH}_3)_2\text{S}$ (43), and the positive values of $^4J_{\text{FH}}$. This conformation has been confirmed by an electron diffraction study which is reported

in detail in Chapter 4.

One other point to investigate was the suitability of the compound as a synthetic intermediate. The possibility of cleavage of the germanium-sulphur or phosphorus-sulphur bonds could give rise to a range of new germyl-sulphur or fluorophosphine-sulphur compounds.

3.2. Preparation

Arnold (43) reported that the reaction between $(\text{GeH}_3)_2\text{S}$ and PF_2Br went completely to $(\text{PF}_2)_2\text{S}$, no matter what ratio of the concentration of the reactions was used. However, the reaction between PF_2Cl and $(\text{GeH}_3)_2\text{S}$ was very slow. It was therefore decided to approach the problem from the opposite direction, and study the reaction of $(\text{PF}_2)_2\text{S}$ and GeH_3Cl . Preliminary n.m.r. studies of the reaction gave favourable results, and on extension to a preparative scale, the reaction of the two compounds in the absence of solvent also proceeded favourably. Other possible reactions were considered and rejected. CH_3SPF_2 (21) had been prepared from CH_3SH , Me_3N and PF_2Br , or more conveniently from Bu_3SnSMe and PF_2Br (23), but the analogous reactions involving GeH_3SH were not feasible because of the instability of germane thiol (99). The reaction between $\text{Bu}_3\text{SnSPF}_2$ and GeH_3Cl was attempted, but $\text{Bu}_3\text{SnSPF}_2$ is prepared in the presence of Bu_3SnBr (18) and exchange of the halogens occurred with GeH_3Br recovered almost quantitatively.

The reaction between GeH_3Cl and $(\text{PF}_2)_2\text{S}$ proceeded cleanly, but care had to be taken with the quantities used. An excess of GeH_3Cl would lead to the formation of $(\text{GeH}_3)_2\text{S}$, significantly decreasing the yield. An excess of $(\text{PF}_2)_2\text{S}$ would lead to problems in the trap-to-trap distillation of the product. Both $(\text{PF}_2)_2\text{S}$ and

$(\text{GeH}_3)_2\text{S}$ would probably have similar volatilities to GeH_3SPF_2 , and the presence of either of these in the product mixture would make purification of the product more difficult.

$(\text{S})\text{PF}_2\text{H}$ was frequently observed in the reaction, and proved quite difficult to separate from the product. The likely source of this impurity was HCl in the GeH_3Cl starting material, or trace amounts of moisture on the walls of the reaction vessel or the vacuum line. It was not seen to interfere with the reactions of GeH_3SPF_2 .

3.3. Characterisation.

GeH_3SPF_2 was characterised by its physical and spectroscopic properties, and its reactions with chlorine, hydrogen chloride and hydrogen bromide.

3.3.1. Physical Properties

GeH_3SPF_2 is a colourless liquid at room temperature with a vile smell. It is water sensitive, and probably air sensitive also.

The molecular weight was measured as 180.6 and measurements were consistently higher than the calculated value of 178.6. An impurity such as $\text{HPF}_2(\text{S})$ would cause the value to decrease, and $(\text{PF}_2)_2\text{S}$ or $(\text{GeH}_3)_2\text{S}$ would have no significant effect as the molecular weights of these compounds are of the same order. The source of the error must therefore lie in the compound dissolving in the grease on the tap of the molecular weight bulb, giving a higher weight of gas than expected for the pressure used.

The vapour pressure at 273K was measured as 31.5mm Hg and is lower than one might expect when compared with $(\text{PF}_2)_2\text{S}$ and $(\text{GeH}_3)_2\text{S}$. This could well be attributed to intermolecular hydrogen

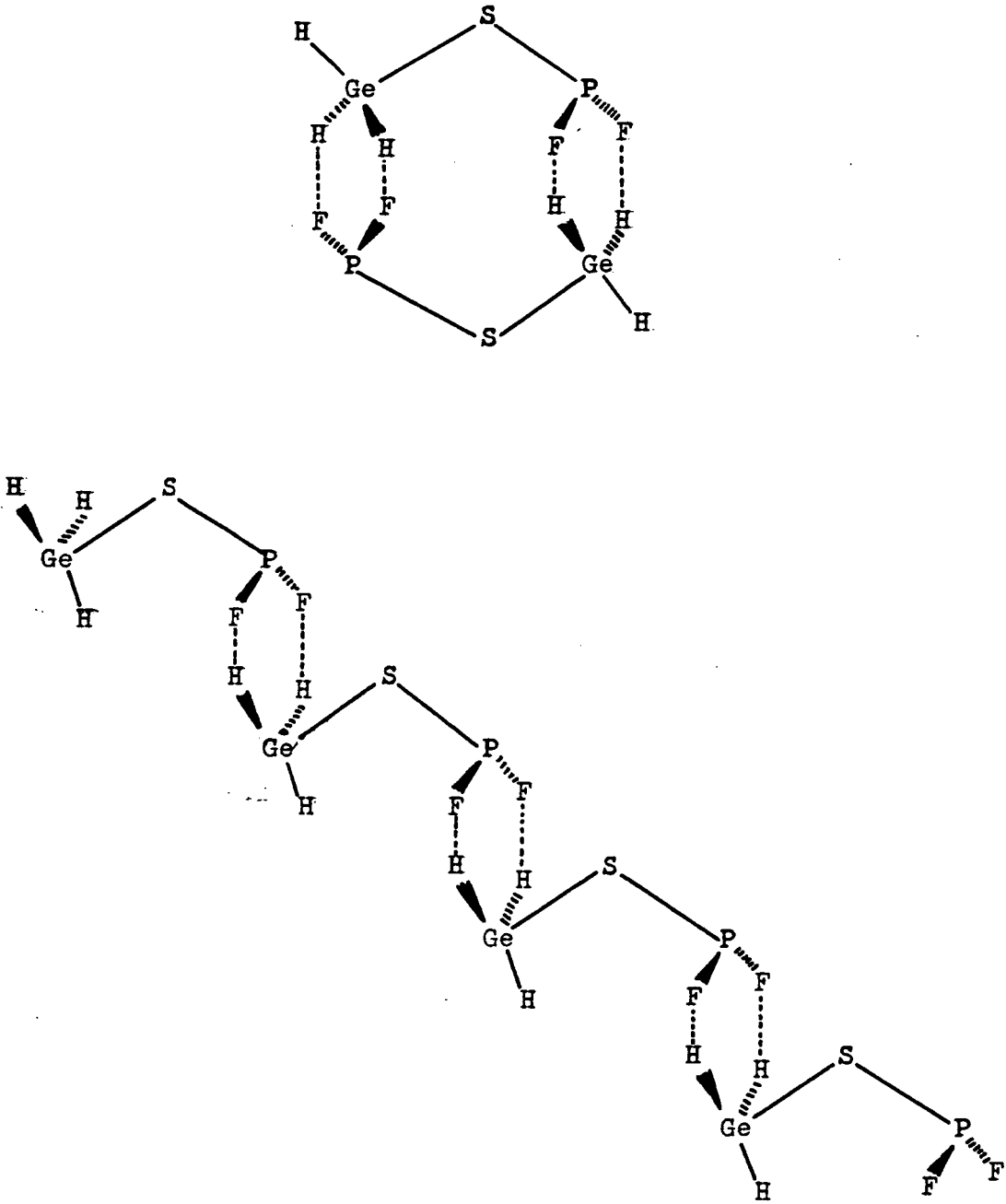


Figure 3.1.

Association of GeH_3SPF_2 in the liquid phase.

(Possible arrangements)

bonding in the liquid state, forming dimers or chains as shown in figure 3.1.

The melting point was measured in a plunger apparatus as 199 ± 1 K.

3.3.2 Nuclear Magnetic Resonance Spectra.

The compound was fully characterised by direct observation of all the magnetic nuclei. The ^{31}P spectrum consisted of a 1:2:1 triplet centred at δ 233.7ppm with a coupling constant $^1J_{\text{PF}} = 1280\text{Hz}$. When proton coupling was retained each line was further split into a 1:3:3:1 quartet with $^3J_{\text{PH}} = 12.6\text{Hz}$. This was complemented in the ^{19}F spectrum by a doublet of quartets, centred at $\delta\text{F} = -56.5\text{ppm}$ with coupling constants $^1J_{\text{PF}} = 1280\text{Hz}$. The proton spectrum consisted of a doublet of triplets centred at $\delta\text{H} = 4.8\text{ppm}$ and coupling constants as observed above. The data are summarised in table 3.1., and the spectra shown in figures 3.2. and 3.3.

As described earlier, the phosphorus chemical shift is entirely consistent with a trivalent phosphorus-sulphur compound. The chemical shift is slightly higher than the corresponding silyl compound and significantly higher than the reactant $(\text{PF}_2)_2\text{S}$ (43). The fluorine chemical shift varies little whether the MH_3 group is silyl or germyl, but the effect of substituting a methyl group is marked. The position of the proton resonance moves to higher frequency of $(\text{GeH}_3)_2\text{S}$. This has been interpreted as being caused by hydrogen bond formation in a five membered ring.

The observed coupling constants are entirely consistent with the compound as formulated, and all the observed parameters agree with those reported previously.

TABLE 3.1.

Nuclear Magnetic Resonance of GeH_3SPF_2 Compared With Some Other
Difluorophosphinosulphides.

Compound	δ_P ppm	δ_F ppm	δ_H ppm	$^1J_{PF}$ Hz	$^3J_{PH}$ Hz	$^4J_{FH}$ Hz	Reference
GeH_3SPF_2	233.7	-56.5	4.8	1280	12.6	3.4	
SiH_3SPF_2	229.5	-57.3	4.35	1298	13.3	2.7	103
CH_3SPF_2	n.o.	-72.2	2.0	1248	7.3	2.2	21
F_2PSPF_2	219.4	-64.3	-	1303	-	-	103

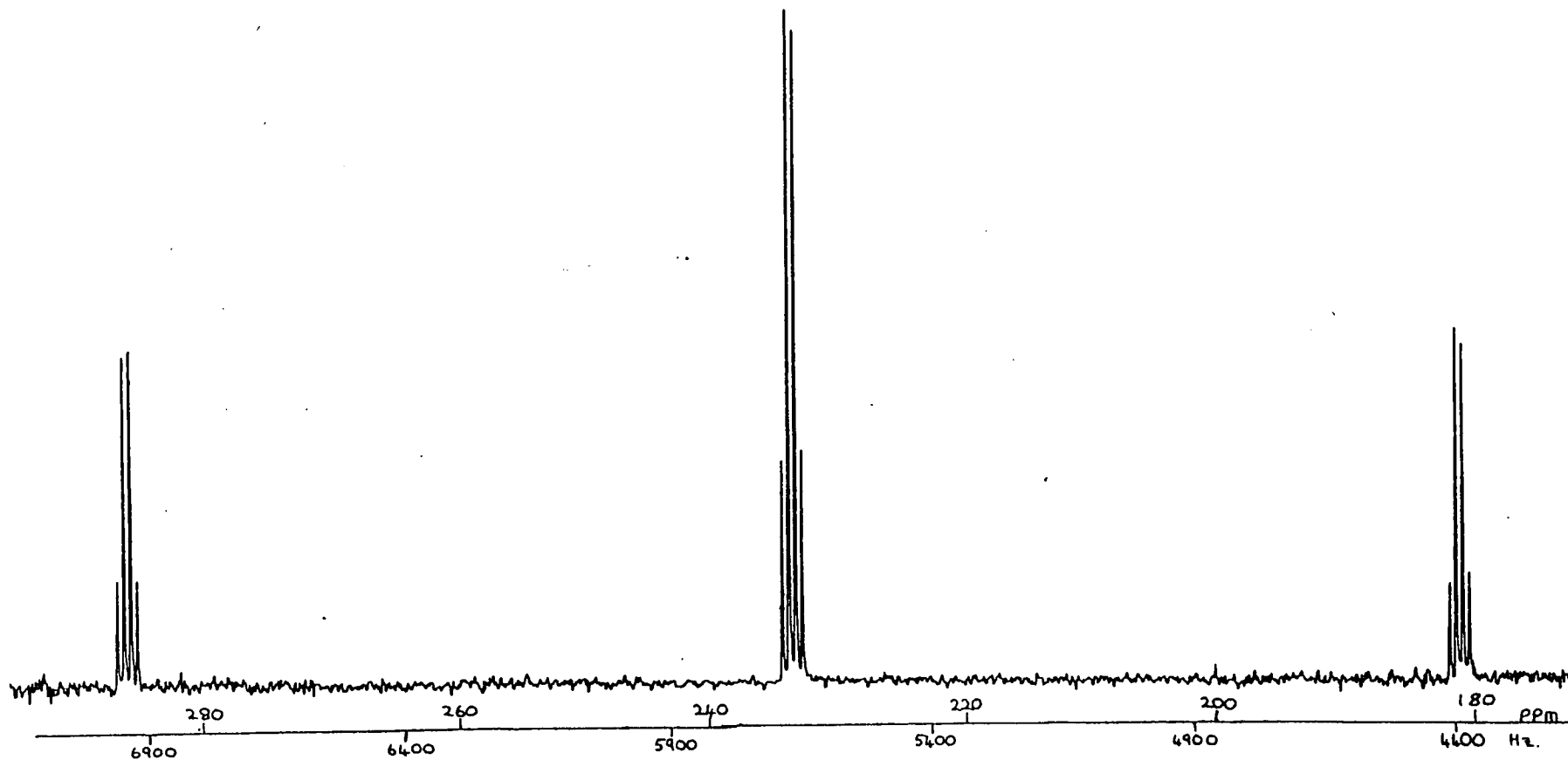


Figure 3.2. ^{31}P n.m.r. spectrum of GeH_3SPF_2 .

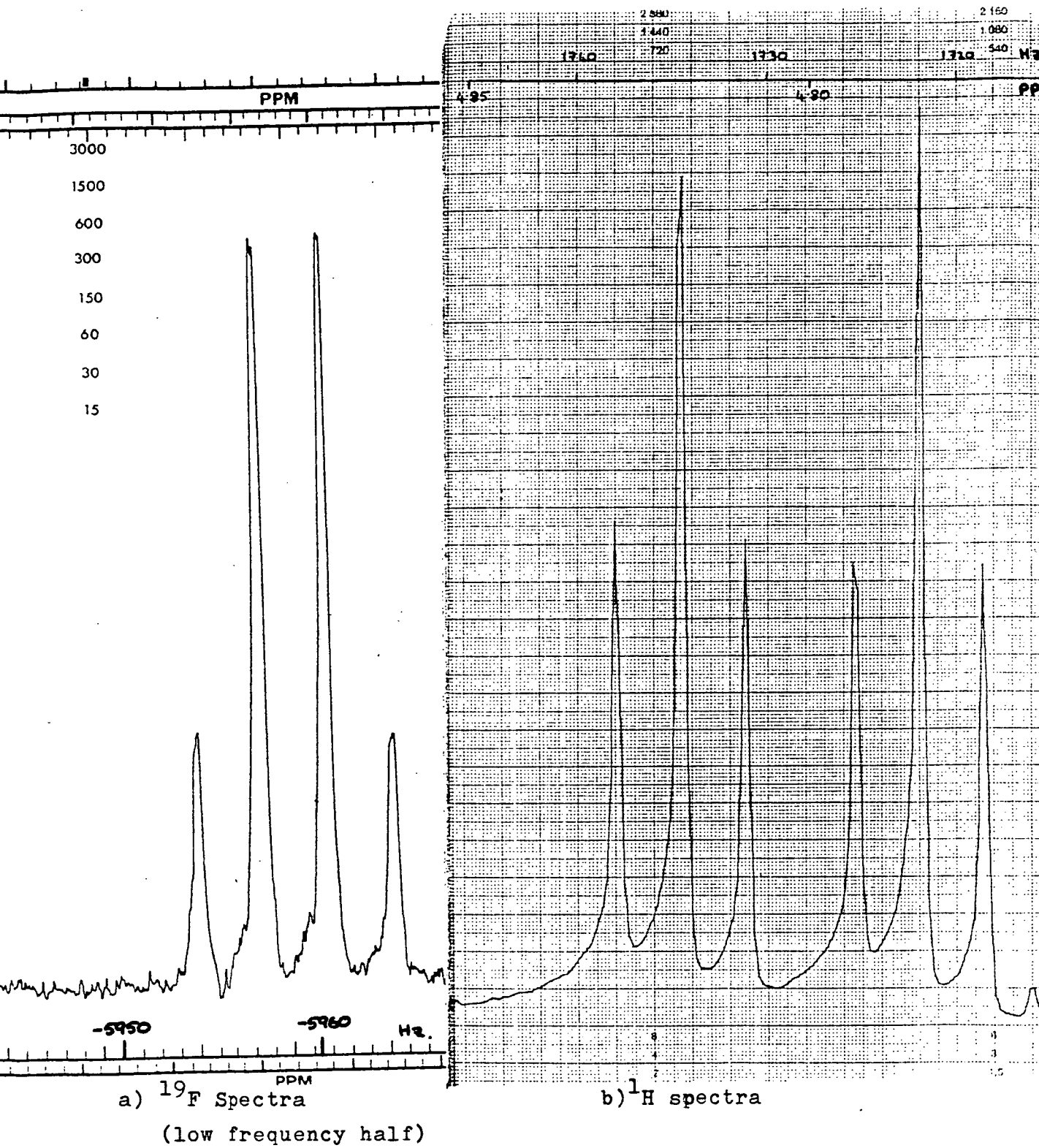


Figure 3.3. N.m.r. spectra of GeH_3SPF_2

3.3.3. Vibrational Spectra.

The position of the lines observed in the i.r. spectrum of GeH_3SPF_2 in the gas phase and in the Raman spectrum of the liquid phase are given in table 3.2. Reported values for $(\text{PF}_2)_2\text{S}$ and $(\text{GeH}_3)_2\text{S}$ are also given for comparison. The assignment of vibrational modes to particular frequencies is exceptionally difficult, as most of the bands are at fairly low frequencies. The electron diffraction study indicates that the molecule is not greatly distorted from C_s symmetry, and assignment of the vibrations have been made on that basis.

The vibrational modes may be classified as in table 3.3., although considerable mixing is to be expected. The two A' modes and one A'' mode of the GeH_3 stretching vibrations are easily assigned as a group as are the P-S stretch (514 cm^{-1}) and the S-Ge stretch (425 cm^{-1}). However it is impossible in the infra red spectrum to distinguish the PF_2 stretches from the GeH_3 deformations. These are assigned in the Raman spectrum, the more intense band at 868 cm^{-1} being attributed to one of the GeH_3 deformations, and the weaker band at 830 cm^{-1} to one of the PF_2 stretches. The GeH_3 rocking modes are identified under the broad band at 590 cm^{-1} .

The lowest polarised mode in the Raman spectrum must be assigned to the PSGe bending vibration, 116 cm^{-1} . This agrees well with the value reported for $(\text{GeH}_3)_2\text{S}$ (110 cm^{-1}) (94) but not with that reported for $(\text{PF}_2)_2\text{S}$ (237 cm^{-1}) (38). The depolarised band at 125 cm^{-1} in the Raman spectrum of $(\text{PF}_2)_2\text{S}$ is unlikely to be assigned incorrectly as the bending mode would give rise to a polarised band, and torsional vibrations would appear as depolarised. The other frequencies are difficult to assign as they are observed

TABLE 3.2.

Vibrational Spectra of GeH_3SPF_2 , compared with the related digermyl- and bis(difluorophosphino)-sulphides.

<u>GeH_3SPF_2</u>		<u>$(\text{GeH}_3)_2\text{S}$ (94)</u>		<u>$(\text{PF}_2)_2\text{S}$ (38)</u>		<u>Assignment</u>
I.R.	Raman	I.R.	Raman	I.R.	Raman	
2114s	2110 s,p	2110	2071			$\nu(\text{GeH}_3)$
		2097				
830	868 m,dp	872	865	840	855 w,p	$\nu(\text{PF}_2)$, $\delta(\text{GeH}_3)$
810 ^{s,br}	830 m,dp	849	842		835 w,p	
		823	800		820 w,pd	
		816				
590 m	600 m,dp	577	608			$\rho(\text{GeH}_3)$
		556	585	498	515 m,p	$\delta(\text{PF}_2)$
					490 vw,dp	
514 s	508 s,p	412	408	579	580 s,p	$\nu(\text{PS})$
425 s	422 s,p	382	370	447	444 m,dp	$\nu(\text{GeS})$
	380 s,p			407	408 s,p	$\delta, \omega(\text{PF}_2)$
				401		
	305 w,dp			319	318 vw,dp	$\rho(\text{PF}_2)$
	116 s,p		110		237 s,p	$\delta(\text{GeSP})$
					125 s,dp	$\tau(\text{PF}_2)$

TABLE 3.3.Vibrational Modes of GeH_3SPF_2 (Point Group C_s).

	A'	A''
GeH_3 Stretch	2	1
PF_2 Stretch	1	1
GeH_3 Deformation	2	1
PF_2 Deformation	1	1
GeS Stretch	1	
PS Stretch	1	
PSGe Deformation	1	
GeH_3 Rock	1	1
PF_2 Rock	1	
GeS Torsion		1
PS Torsion		1

solely in the Raman spectrum. The torsional modes are probably too low to be observed. The remaining frequencies to be assigned are from deformations of the PF_2 group. The wag and rock can be assigned with reference to $(\text{PF}_2)_2\text{S}$ at 380 cm^{-1} and 305 cm^{-1} respectively, but there are no bands observed in the $520 - 480\text{ cm}^{-1}$ region comparable to those in the spectrum of $(\text{PF}_2)_2\text{S}$. The only possibility is that they are weak, or coincident with the absorption due to the P-S stretch at 514 cm^{-1} .

3.3.4. Mass Spectrum

The main peaks in the mass spectrum are listed in table 3.4. Because of the number of isotopes of germanium (Mass nos 70, 72, 73, 74, 76) each germyl fragment was shown as a multiplet, and it was difficult to determine the number of protons present in each fragment. It appears that the groups of peaks centred at 178 and 109 mass units arose from ions with three hydrogen atoms, while the group at 158 mass units arose from ions with two hydrogens. Breakdown of the parent ion can take place by three distinct routes. Firstly, the elimination of HF would give rise to the fragment of 158 mass units. Secondly, cleavage of the P-S bond gives rise to the fragment at 109 mass units, or thirdly, cleavage of the Ge-S bond gives rise to the fragment at 101 mass units. The sequential loss of hydrogen does not appear to be a significant decomposition process.

The strength of the $(\text{HPF}_2\text{S})^+$ peak at 102 mass units is not entirely unexpected, with GeH_2 elimination a well known process (106). An alternative source of this fragment could be hydrolysis, or recombination of some fragments.

3.3.5/

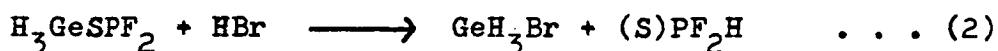
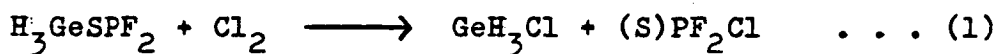
TABLE 3.4.

Mass Spectrum of PF₂(SGeH₃).

m/e	Relative Abundance	Assignment
178	20	(PF ₂ (SGeH ₃)) ⁺
158	20	(PF(SGeH ₂)) ⁺
109	20	(GeH ₃) ⁺
102	100	(PF ₂ HS) ⁺
101	12	(PF ₂ S) ⁺
88	5	(PF ₃) ⁺
82	25	(PFS) ⁺
69	50	(PF ₂) ⁺
63	25	(PS) ⁺
50	5	(PF) ⁺
34	3	(SH ₂) ⁺
32	2	(S) ⁺
31	2	(P) ⁺
20	1	(FH) ⁺
metastable		
39.5	weak	(PF ₂ S) ⁺ → F ₂ + (PS) ⁺

3.3.5. Chemical Characterisation

Characterisation of the compound was completed by its reaction with chlorine, hydrogen chloride and hydrogen bromide. The reactions with Cl_2 and HBr were carried out in n.m.r. tubes and in each case the only products observed were the expected products according to equations (1) and (2).



The products were identified by ^{31}P and ^1H n.m.r. spectroscopy.

The reaction of GeH_3SPF_2 with HCl was carried out on an analytical scale. The products were separated by fractional trap to trap distillation and, after the quantities were measured, identified by infra-red and n.m.r. spectroscopy. The sole products obtained were GeH_3Cl and $(\text{S})\text{PF}_2\text{H}$ as expected.

3.4. Donor Reactions of Phosphorus.

A great deal of interest in phosphorus (III) chemistry lies in the behavior of these compounds as Lewis Bases. Many of the studies concerning fluorophosphines have attempted to link the dative bond strength for the BH_3 adducts to the magnitude of $^1J_{\text{PB}}$. Rudolph and Schultz (104) reported that for a series of phosphines such as $\text{Me}_{3-n}\text{PF}_n:\text{BH}_3$, $\text{H}_{3-n}\text{PF}_n:\text{BH}_3$, PF_2X ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) there was an empirical relationship between J_{PB} and the dative bond strength, but in cases where the phosphines were of different types, the correlation was not carried over. Cowley and Damasco (105) studied a series of 15 different phosphines and also concluded that such a correlation existed, and it was explained as a combination of σ effects, dative π bonding from substituents on the phosphine,

and borane hyperconjugation, arising from interaction between the B-H σ bonding electrons and the phosphorus 3d orbitals. Foester and Cohn (21) paid particular attention to the effects of (p-d) π bonding in the series Me.PF_2 , Me_2NPF_2 , MeOPF_2 , MeSPF_2 , $(\text{MeS})_2\text{PF}$. The value of J_{PB} mirrored the base strength except for CH_3PF_2 , which is the strongest base but has an intermediate coupling constant, and the series also reflected the smaller extent of (p-d) π bonding expected.

The borane adduct of GeH_3SPF_2 was prepared in solution in a sealed n.m.r. tube and the parameters are shown in table 3.5. The adduct was characterised by direct observation of all the magnetic nuclei. All spectra showed first order splitting patterns. The ^{31}P spectrum appeared as a triplet ($^1J_{\text{PF}} = 1255\text{Hz}$) of 1:1:1:1 quartets ($^1J_{\text{PB}} = 47\text{Hz}$), centred at $\delta\text{P} = 193.9\text{ppm}$. The ^{19}F spectrum consisted of a doublet ($^1J_{\text{PF}} = 1255\text{Hz}$) of 1:3:3:1 quartets ($^3J_{\text{F}(\text{BH}_3)} = 18.2\text{Hz}$). No coupling was observed to the boron atom.

The ^{11}B spectrum consisted of a 1:3:3:1 quartet ($^1J_{\text{BH}} = 102.8\text{Hz}$) of 1:1 doublets ($^1J_{\text{PB}} = 47\text{Hz}$) centred at $\delta\text{B} = -60.6\text{ppm}$. The ^1H spectrum showed a doublet ($^3J_{\text{P}(\text{GeH}_3)} = 8.7\text{Hz}$) of triplets ($^4J_{\text{F}(\text{GeH}_3)} = 2.0\text{Hz}$) at $\delta\text{H} = 5.17\text{ppm}$, and a very broad 1:1:1:1 quartet centred at $\delta\text{H} = 0.98\text{ppm}$. Each broad line had the appearance of a 1:3:3:1 quartet, but this in fact arises from the coincidence of the values of $^2J_{\text{P}(\text{BH}_3)}$ and $^3J_{\text{F}(\text{BH}_3)}$ and is an overlapping doublet ($^2J_{\text{P}(\text{BH}_3)} = 16\text{Hz}$) of triplets ($^3J_{\text{F}(\text{BH}_3)} = 18.2\text{Hz}$). These spectra are shown in figures 3.4 and 3.5.

The value of $^1J_{\text{PB}}$ is consistent with the idea of (p-d) π bonding increasing the base strength of the phosphine (21). Although this effect is smaller when second row elements are

TABLE 3.5.

N.m.r. parameters of some fluorophospine-borane and molybdenum-tetracarbonyl adducts.

a) Chemical shifts (ppm)

	A	B	C	D	E	F
SH	5.2	2.4	3.6	-	4.9	-
SH'	1.0	n.o.	n.o.	1.3	-	-
SB	-60.6	-58.1	-65.0	-56.8	-	-
SF	-54.1	-68.1	-65.6	-56.6	-15.7	-27.6
SF'	-	-	-	-57.8	-	-
SP	193.9	164.9	93.7	182.1	226.6	156.3
SP'	-	-	-	200.8	-	-

b) Coupling Constants Hz

$^1J_{PF}$	1255	1235	1280	1267	1201	1299
$^1J_{PF'}$	-	-	-	1336	-	-
$^1J_{PB}$	47	41.4	69.3	n.o.	-	-
$^2J_{BH'}$	102.8	101.3	98.4	107	-	-
$^2J_{PH'}$	1.6	n.o.	n.o.	12	-	-
$^2J_{PP}$	-	-	-	68	45	82
$^3J_{PH}$	8.7	12.4	11.2	-	-	-
$^3J_{PF}$	-	-	-	-	3	47
$^3J_{FH'}$	18.2	15.1	15.1	19	-	-
$^4J_{FH}$	2.0	2.4	n.o.	-	-	-
$^4J_{FF'}$	-	-	-	-	n.o.	7.5
$^4J_{FF''}$	-	-	-	-	n.o.	0.0

TABLE 3.5. (Cont).

Reference A	$\text{GeH}_3\text{SPF}_2(\text{BH}'_3)$	
B	$\text{CH}_3\text{SPF}_2(\text{BH}'_3)$	(21)
C	$\text{CH}_3\text{OPF}_2(\text{BH}'_3)$	(21)
D	$\text{F}'_2\text{P}'\text{SPF}_2(\text{BH}'_3)$	(38)
E	<i>cis</i> $(\text{GeH}_3\text{SPF}_2)_2\text{Mo}(\text{CO})_4$	
F	$\text{S}(\text{PF}_2)_2\text{Mo}(\text{CO})_4$	(38)

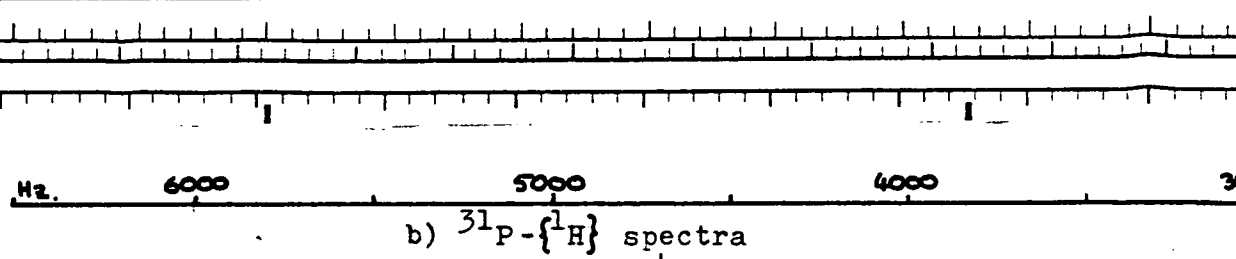
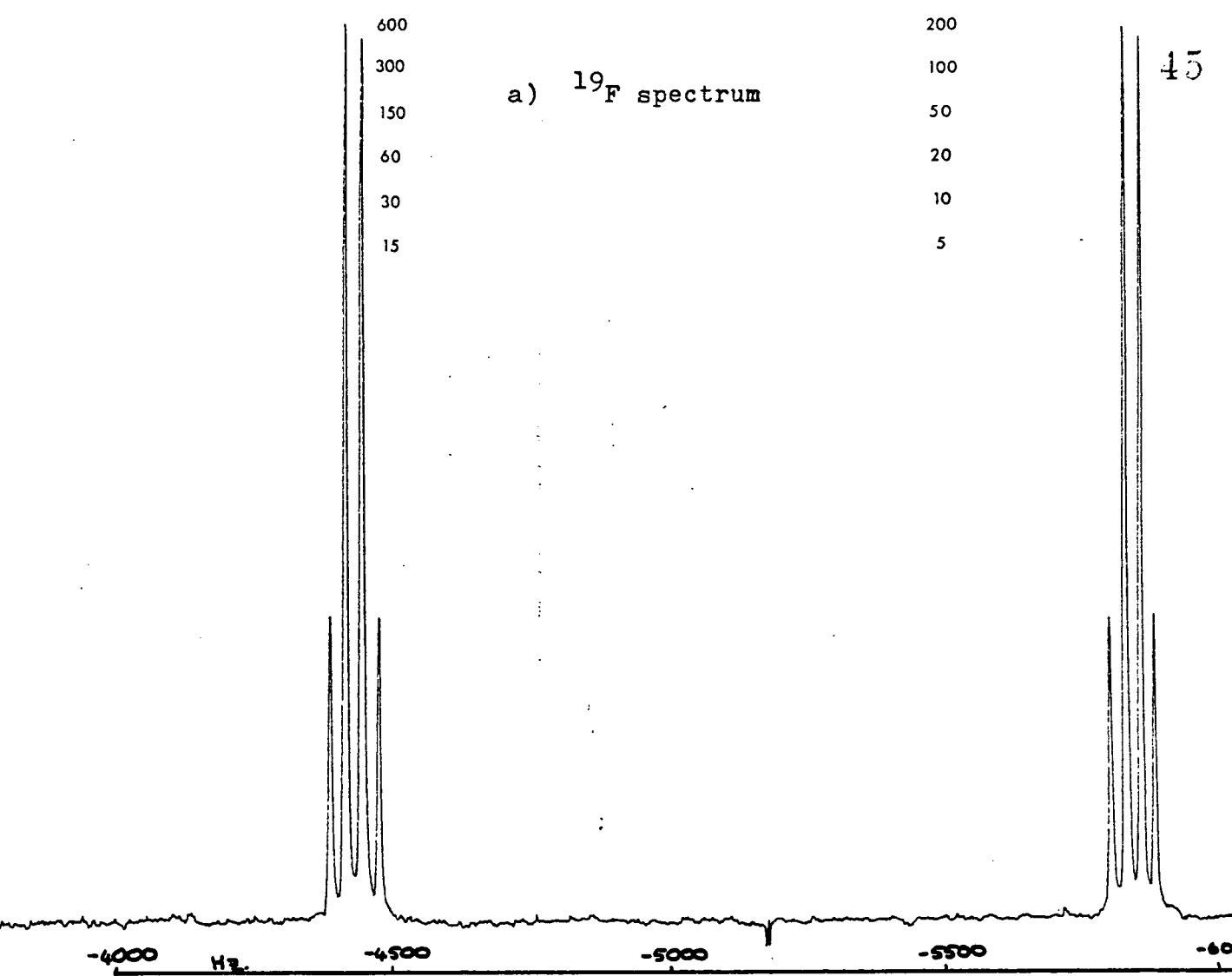
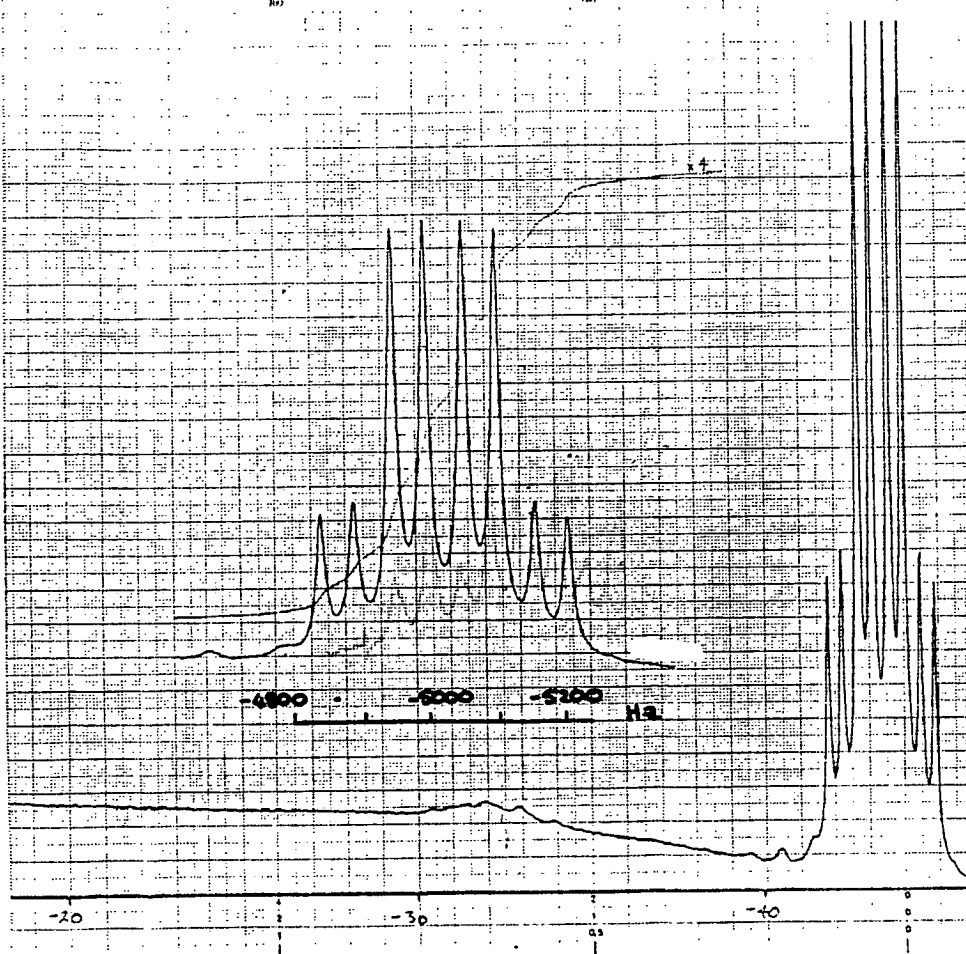


Figure 3.4. N.m.r. spectra of $\text{GeH}_3\text{SPF}_2\text{BH}_3$

a) ^{11}B spectrum

1
Hz 4 320
Hz 2 160
Hz 1 080

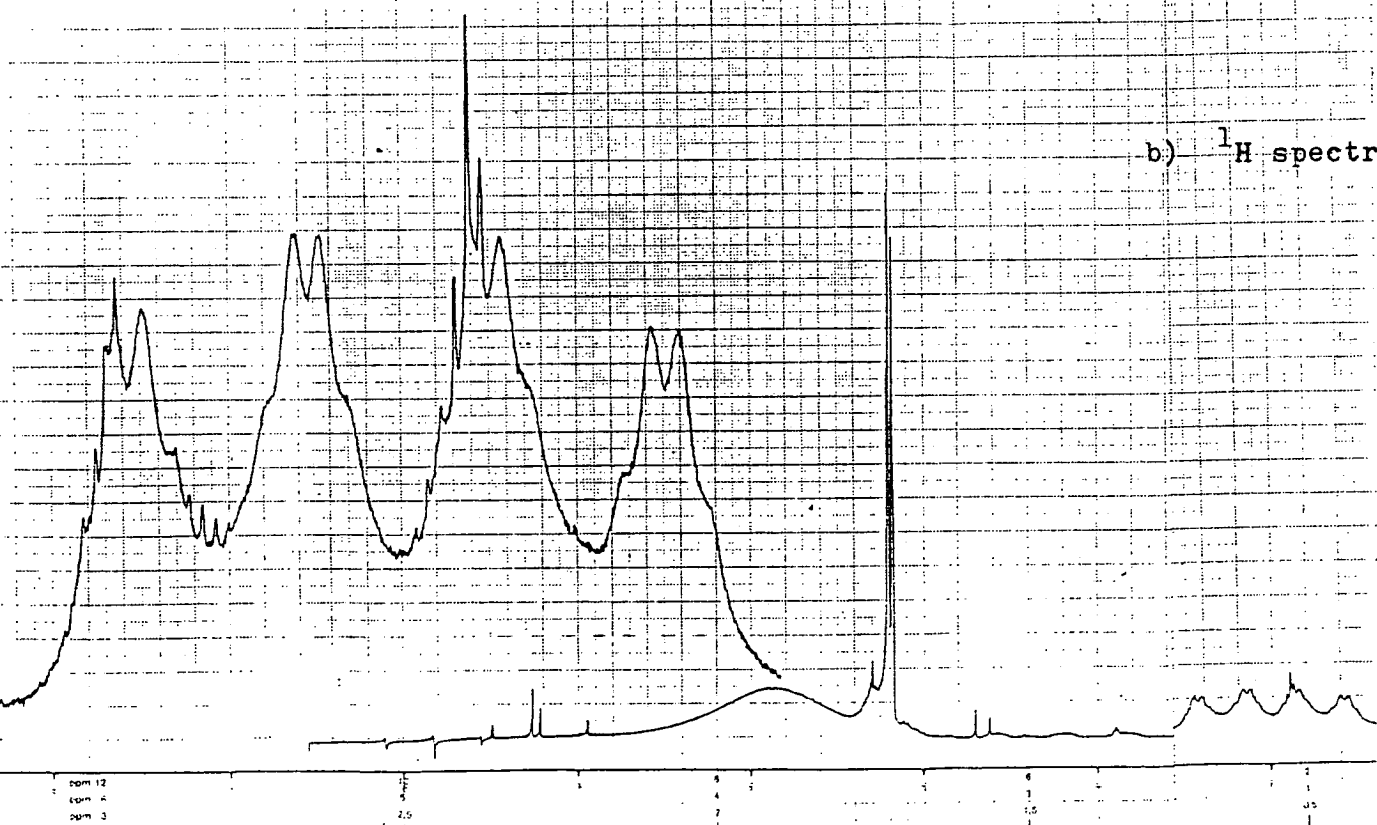
1
3 600
3 600
3 600

1
2 800
1 440
720

1
2 100
1 050
540

1
720
360
180

550 500 470 400 350 300 280 200 150 Hz

b) ^1H spectrum

ppm 12
ppm 11
ppm 10
ppm 9
ppm 8
ppm 7
ppm 6
ppm 5
ppm 4
ppm 3
ppm 2
ppm 1
ppm 0.5
ppm 0

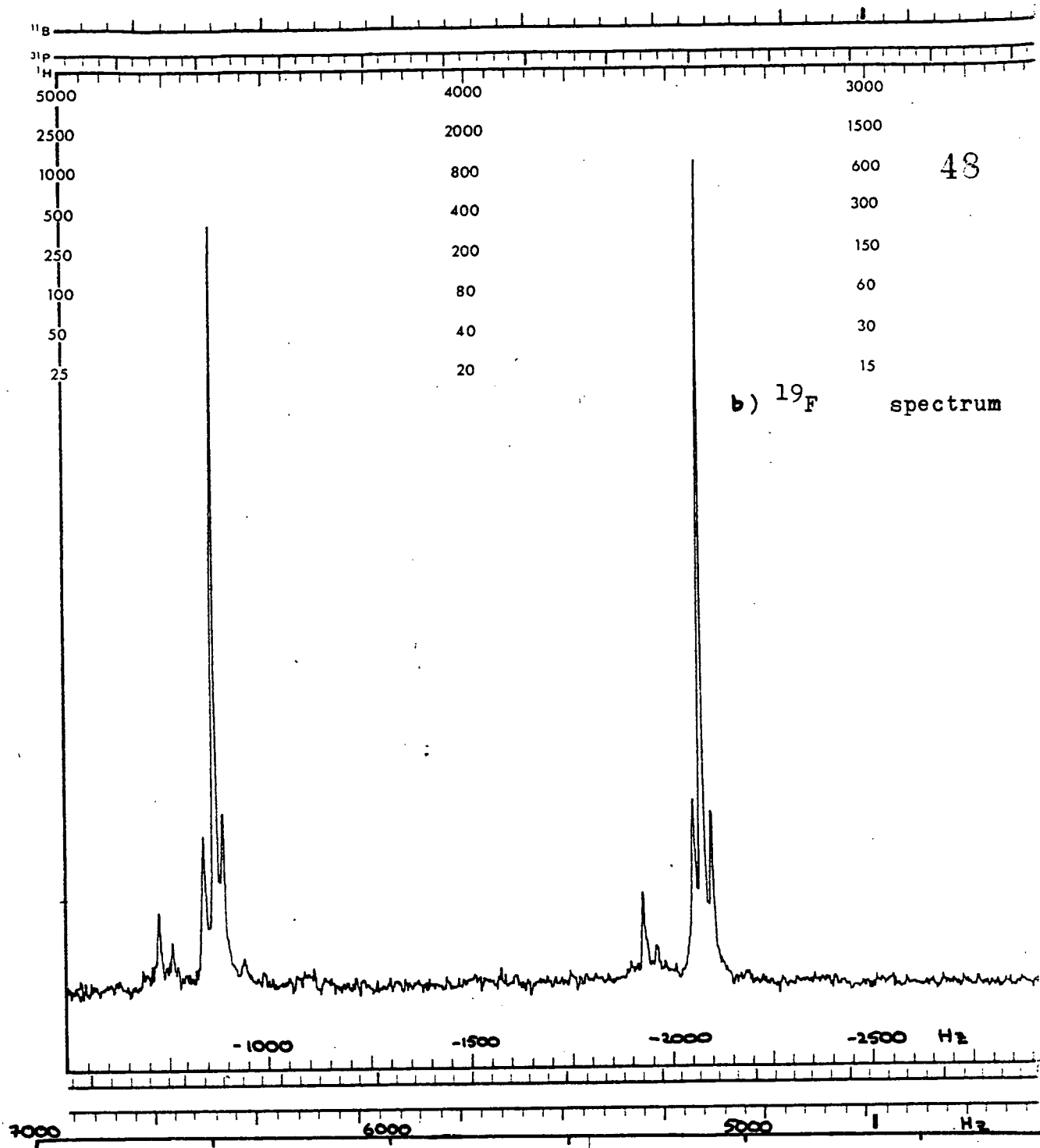
Figure 3.5. N.m.r. spectra of $\text{GeH}_3\text{SPF}_2\text{BH}_3$

involved (hence $^1J_{PB}$ for $CH_3SPF_2: BH_3$ (41.4Hz) is less than for $CH_3OPF_2: BH_3$ (69.3Hz)), the π system will be extended throughout the molecule in GeH_3SPF_2 , involving the vacant germanium d-orbitals also, hence the greater value for $^1J_{PB}$ in $GeH_3SPF_2: BH_3$.

GeH_3SPF_2 undergoes a displacement reaction with tetracarbonyl (norbornadiene) molybdenum (0) to form the bis-substituted $(GeH_3SPF_2)_2Mo(CO)_4$. The spectra were second order but not as complex as the $(A(X)_2)_2$ systems observed in the case of the corresponding $(PF_2)_2S$ and $(PF_2)_2Se$ adducts. This is probably because the long-range F...F and P...F interactions are much smaller as a result of the lack of constraint when two ligands are involved rather than a bidentate ligand. The complex is observed in the ^{31}P spectrum as a basic triplet, with the central peak flanked by two small doublets, and the outer peaks flanked by two peaks, as shown in figure 3.6(a). The chemical shift is 226.6ppm, with the triplet splitting 1197Hz, which is a measure of $^1J_{PF} + ^3J_{PF}$ (40). The ^{19}F spectrum shows only slight second order effects, and is basically a doublet (splitting 1197Hz) centred at $\delta F = -15.7ppm$ with two smaller peaks associated with each of the main peaks. When proton coupling is retained, no effect is seen in the fluorine spectrum, as can be seen in the figure 3.6(b).

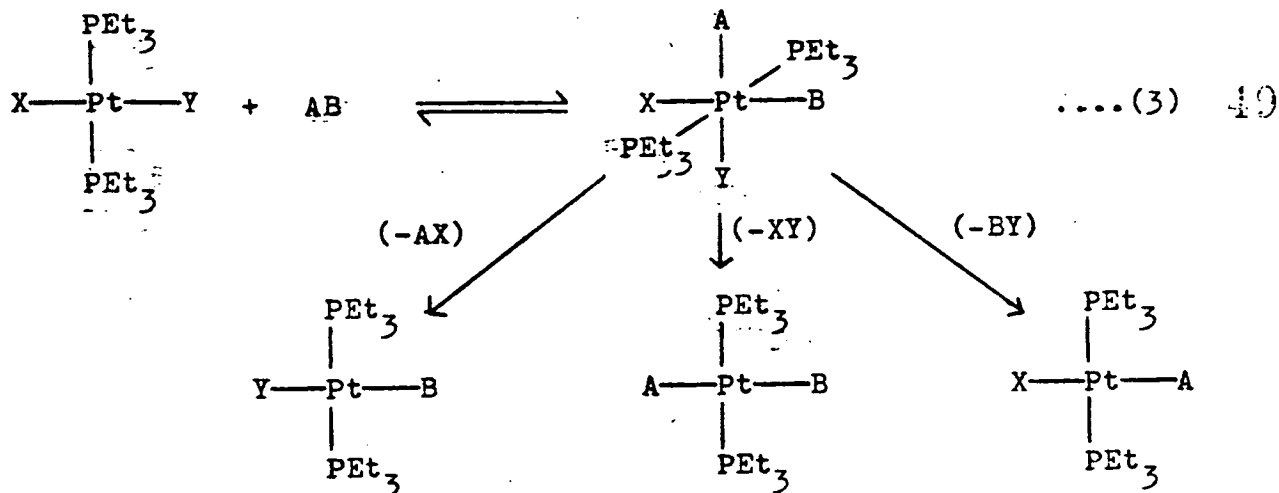
3.5. Reactions with Four-Coordinate Pt(II) Systems.

Platinum (II) systems are reactive to a wide range of substrates. The important reaction to consider here is the oxidation addition process. In most systems this involves the formation of an octahedral Pt(IV) intermediate which then decomposes, usually with the loss of HX , H_2 or X_2 to the new Pt (II) compound, shown schematically in (3) below.

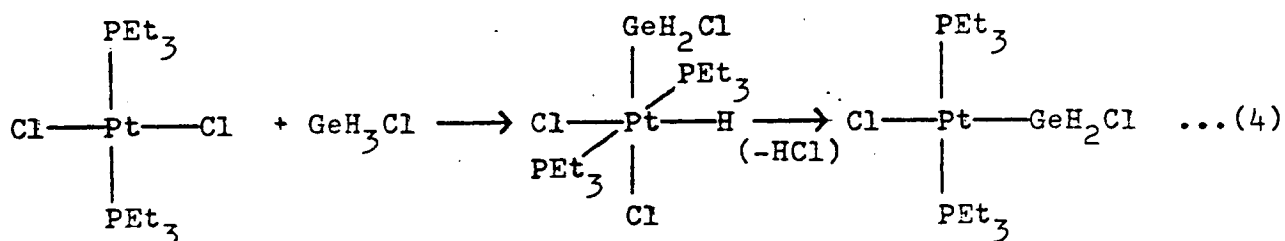


a) $^{31}\text{P} - \{^1\text{H}\}$ spectrum

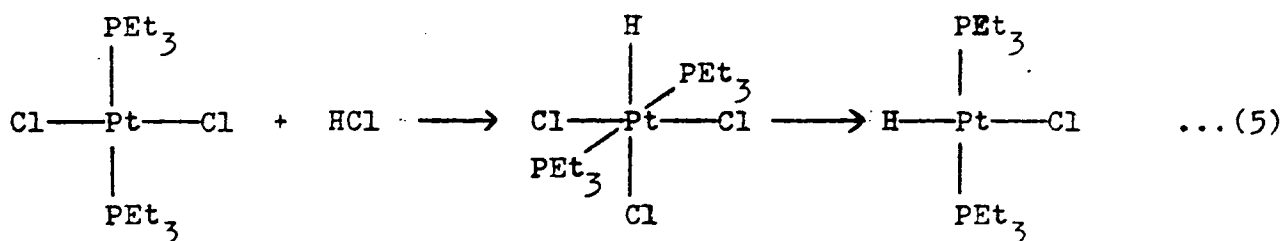
Figure 3.6. N.m.r. spectra of $(\text{CO})_4\text{Mo}(\text{PF}_2\text{SGeH}_3)_2$



It is seen that many different products can be formed by the decomposition of the octahedral intermediate, depending on the relative stabilities of the products, and the relative rates of elimination. A great deal of work has concentrated on the formation of platinum hydrides of main group elements, by the oxidative addition of the M-H bond (107, 108) for example equation (4) shows the reaction of GeH_3Cl with trans- $\text{Cl}_2\text{Pt}(\text{PEt}_3)_2$.

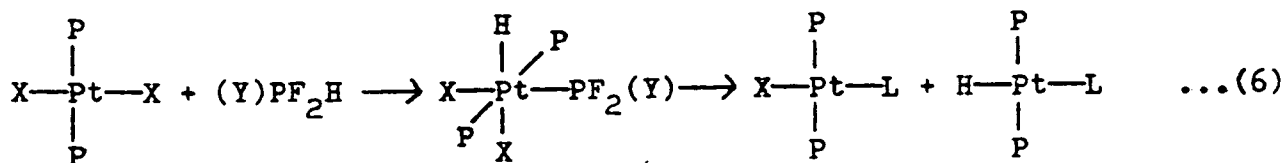


In this case, free HCl can react with the starting material to set up an equilibrium mixture of the trans- $\text{Cl}_2\text{Pt}(\text{PEt}_3)_2$ and trans- $\text{HPtCl}(\text{PEt}_3)_2$ as in equation (5).



Recent attention has been shown to the reaction of PF_2 compounds with platinum (II) systems (109). The reaction of $(\text{Y})\text{PF}_2\text{H}$ with such compounds appears to be straightforward oxidative

addition of the P-H bond to form a mixture of the compounds trans-XPt(PF₂(Y))(PEt₃)₂ and trans-HPt(PF₂(Y))(PEt₃)₂ as in equation (6).



(P = PEt₃; L = PF₂(Y).)

PF₂Cl also appears to react in this way, forming the unstable ClPt(PF₂H)(PEt₃)₂, which reacts further to form the binuclear cationic species (Cl(PEt₃)₂Pt-PF₂-Pt(PEt₃)₂Cl)⁺. This would involve a third type of reaction, displacement of a halide ion by a neutral phosphine, forming the singly charged Pt (II) cation.

GeH₃SPF₂ therefore provides an interesting substrate for study. There are three possible routes of reaction shown in figure 3.7. The fluorophosphine may displace another ligand: there may be oxidative addition with a P-S, a Ge-S or more likely a Ge-H bond adding across the platinum, perhaps followed by elimination: or there may be an exchange reaction with an SPF₂ or an SGeH₃ group displacing another ligand.

The reactions were carried out in sealed n.m.r. tubes and followed by ³¹P n.m.r. spectroscopy. The products observed are summarised in table 3.6. No six coordinate intermediates were observed, and the reactions appeared to proceed by the straightforward substitution of the halide by the PF₂S group, and evolution of GeH₃X.

3.5.1. Reaction with trans-Cl₂Pt(PEt₃)₂

The reaction was carried out in a sealed n.m.r. tube with

CDCl_2 as the solvent, and the reaction proceeded rapidly as the mixture was warmed to room temperature. No evidence for any six-coordinate intermediates was observed (identifiable by the small value of $^1J_{\text{PtP}}$ (1600 - 1800Hz). In the proton decoupled ^{31}P n.m.r. spectrum, a 1:2:1 triplet ($^1J_{\text{PF}} = 1162\text{Hz}$) of 1:1:1 triplets ($^2J_{\text{PP}} = 24.4\text{Hz}$) was observed at $\delta\text{P} = 131.7$ ppm, in the pentavalent fluorophosphine region of the spectrum. Platinum satellites were identified as being associated with these peaks, with a coupling constant $^1J_{\text{PtP}} = 5317\text{Hz}$. In the ethylphosphine region of the spectrum, a doublet ($^2J_{\text{PP}} = 24.4\text{Hz}$) of triplets ($^3J_{\text{PF}} = 9\text{Hz}$) was observed at $\delta\text{P} = 18.9$ ppm, with associated satellites observed with a coupling constant $^1J_{\text{PtP}} = 2351\text{Hz}$. This was identified as trans- $\text{PtCl}(\text{PEt}_3)_2(\text{PF}_2\text{S})$ (109). Also observed were two single peaks in the ethylphosphine region, at $\delta\text{P} = 16.0$ ppm, $^1J_{\text{PtP}} = 2192\text{Hz}$ and $\delta\text{P} = 14.7$ ppm, $^1J_{\text{PtP}} = 2270\text{Hz}$, which were not identified. Germyl chloride was observed in the proton spectrum.

3.5.2. Reaction with trans- $\text{PtHCl}(\text{PEt}_3)_2$.

The reaction mixture was warmed to room temperature, and initially a 1:2:1 triplet of broad peaks ($^1J_{\text{PF}} = 1201\text{Hz}$) with associated platinum satellites ($^1J_{\text{PtP}} = 3062\text{Hz}$), was observed at $\delta\text{P} = 218.4$ ppm. In the ethylphosphine region, a broad peak was observed at $\delta\text{P} = 18.6$ ppm. On cooling the reaction mixture to 223K, the fine structure of the peaks was resolved, and a further triplet splitting ($^2J_{\text{PP}} = 29.3\text{Hz}$) was observed in the fluorophosphine region. The ethylphosphine signal was resolved into a doublet ($^2J_{\text{PP}} = 29.3\text{Hz}$) of triplets ($^3J_{\text{PF}} = 6.1\text{Hz}$), and platinum satellites were observed with $^1J_{\text{PtP}} = 2490\text{Hz}$. At room temperature, with



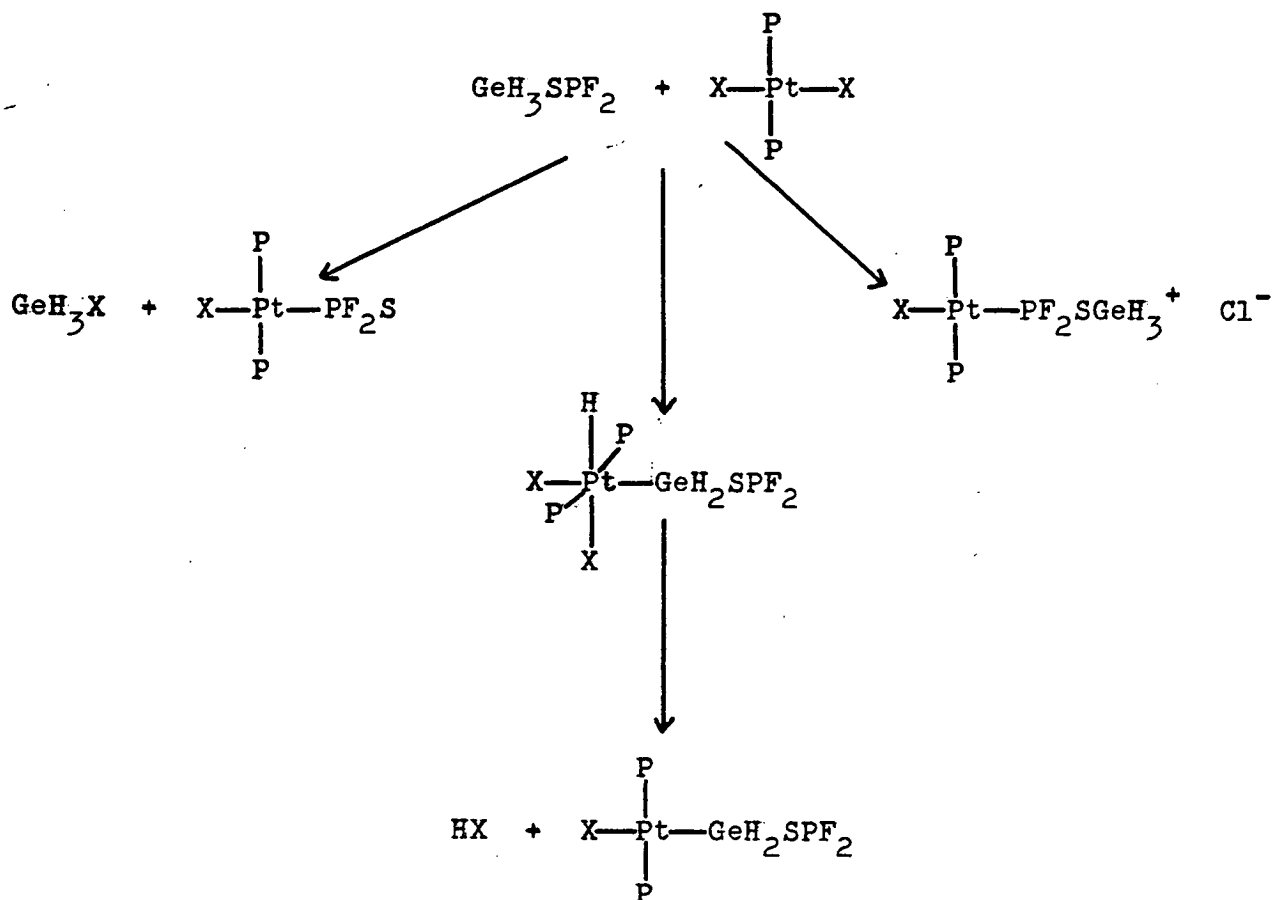


Figure 3.7.

Three possible reactions of GeH_3SPF_2 with trans- X_2PtP_2 .

TABLE 3.6.

Summary of reactions of GeH_3SPF_2 with 4-coordinate Pt(II) systems.

Product	<u>$\text{XPtP}_2\text{PF}_2\text{S}$</u>	<u>$\text{HPtP}_2\text{PF}_2\text{S}$</u>	<u>GeH_3X</u>	<u>Other</u>
Substrate				
$\underline{\text{t}}\text{-Cl}_2\text{Pt}(\text{PEt}_3)_2$	✓(X=Cl)	×	GeH_3Cl	
$\text{t-HPtCl}(\text{PEt}_3)_2$	✓(X=Cl)	✓	GeH_3Cl	
$\text{t-I}_2\text{Pt}(\text{PEt}_3)_2$	✓(X=I)	×	GeH_3I	GeH_3Cl
$\text{HPt}(\text{PEt}_3)_3(\text{BPh}_4)$	×	✓	GeH_3Cl	PEt_3

proton coupling retained, a trans-proton coupling to the fluoro-phosphine group was observed (${}^2J_{\text{PH}} = 266\text{Hz}$). This species was identified as trans-PtH(PEt₃)₂(PF₂S). This product decomposed slowly at room temperature, to give trans-PtCl(PEt₃)₂(PF₂S) as the only product. GeH₃Cl was observed in the proton spectrum, but no GeH₄ as would be expected from the decomposition. This suggests that the solvent, chloroform, must be involved in the reaction.

3.5.3. Reaction with trans-I₂Pt(PEt₃)₂.

This reaction proceeded rapidly even at low temperature. At 193K, a triplet (${}^1J_{\text{PF}} = 1177\text{Hz}$) of triplets (${}^2J_{\text{PP}} = 20.7\text{Hz}$) with platinum satellites (${}^1J_{\text{PtP}} = 5268\text{Hz}$) was observed at $\delta\text{P} = 138.4$ ppm. Associated with this signal was a doublet (${}^2J_{\text{PP}} = 19.5\text{Hz}$) of triplets (${}^3J_{\text{PF}} = 9.7\text{Hz}$) at $\delta\text{P} = 11.8$ ppm, with platinum satellites observed with a coupling constant ${}^1J_{\text{PtP}} = 2378\text{Hz}$. This species was identified as trans-PtI(PEt₃)₂(PF₂S) by comparison of the n.m.r. parameters with recorded data (109). In the proton spectrum, a small amount of GeH₃I was observed, but about four times as much GeH₃Cl was identified.

3.5.4. Reaction with PtH(PEt₃)₃(BPh₄).

The reaction proceeded cleanly and rapidly at room temperature to give a species with similar ${}^{31}\text{P}$ n.m.r. parameters to those observed in the case of trans-PtH(PEt₃)₂(PF₂S), i.e. $\delta\text{PF}_2 = 219.7$ ppm, ${}^1J_{\text{PF}} = 1201\text{Hz}$, ${}^1J_{\text{PtP}} = 3054\text{Hz}$, ${}^2J_{\text{PH}} = 268\text{Hz}$, $\delta\text{PEt}_3 = 15.0$ ppm. Free triethyl phosphine was observed when the sample was cooled to 190K, at $\delta\text{P} = 18.2$ ppm. The fine structure of the peaks was resolved, showing ${}^2J_{\text{PP}} = 29.3\text{Hz}$, ${}^1J_{\text{PtPEt}_3} = 2468\text{Hz}$,

$\delta\text{PEt}_3 = 18.1$ ppm. In this case, decomposition to the chloride does not occur, but GeH_3Cl is observed in the proton spectrum. This is unexpected, and the solvent, dichloromethane, must be involved in some way. One possible mechanism has been proposed which involves an unstable triethyl(germyl)phosphonium intermediate, which could react with dichloromethane to give chlorogermane.

3.6. The Reaction of GeH_3SPF_2 with Chlorodiphenylphosphine.

This reaction was performed to investigate the possible use of GeH_3SPF_2 as a synthetic intermediate to prepare mixed alkylphosphine - fluorophosphine systems (17). The reaction proceeded at room temperature and several products were observed. The major signal observed in the phosphorus n.m.r. spectrum was a triplet ($^1J_{\text{PF}} = 1274\text{Hz}$) of doublets ($^1J_{\text{PP}} = 366\text{Hz}$) centred at $\delta\text{P} = 114.0$ ppm, associated with a doublet ($^1J_{\text{PP}} = 366\text{Hz}$) of triplets ($^2J_{\text{PF}} = 18.3\text{Hz}$) centred at $\delta\text{P} = -1.9$ ppm. This was assigned to the mixed alkylphosphine - fluorophosphine species $(\text{S})\text{PF}_2\text{PPh}_2$ by comparison with the parameters observed for $(\text{S})\text{PF}_2\text{PMe}_2$ (18). No evidence for the completely reduced species F_2PSPPH_2 was observed. One other fluorophosphine species was observed, a triplet ($^1J_{\text{PF}} = 1157\text{Hz}$) at $\delta\text{P} = 68.7$ ppm, assigned as $(\text{S})\text{PF}_2\text{H}$.

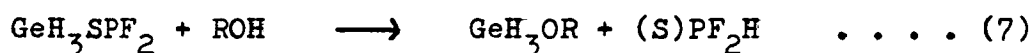
Two single lines were observed, and assigned to PPh_2Cl ($\delta\text{P} = 81.8$ ppm) and PPh_3 ($\delta\text{P} = 22.9$ ppm). Also observed was an AB pattern, the two lines to high frequency centred at $\delta\text{P} = 45.1\text{ppm}$ and showing a splitting $^1J_{\text{PP}} = 253.9\text{Hz}$. The two low frequency lines were separated by the same amount, and centred at $\delta\text{P} = -13.3\text{ppm}$. This was identified as $(\text{S})\text{PPh}_2\text{PPh}_2$ with reference to the parameters reported by Harris for $(\text{S})\text{PMe}_2\text{PMe}_2$ (110). The presence of this

compound would seem to indicate that some cleavage of the P-S bond also occurs, giving $\text{PPh}_2(\text{SGeH}_3)$ as an intermediate, which must react with free chlorodiphenylphosphine to give $(\text{SPh})_2\text{PPh}_2$.

3.7. Conclusions.

The reactions of difluoro(germylthio)phosphine described in the preceding sections are quite representative of the chemical properties of the compound. The reactivity of the compound appears to be governed by the strength of the Ge-S bond, and the cleavage of this bond is the key to the use of GeH_3SPF_2 as a synthetic intermediate. In this way it could be used in the same way as $(\text{PF}_2)_2\text{S}$, to introduce thiodifluorophosphine- or germyl groups into a wide range of compounds.

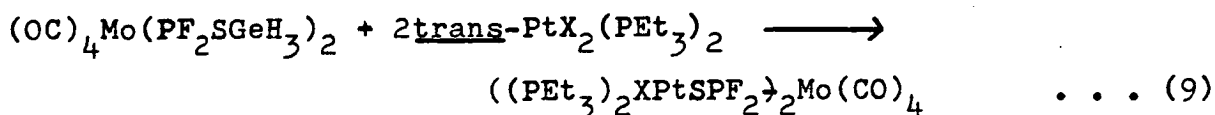
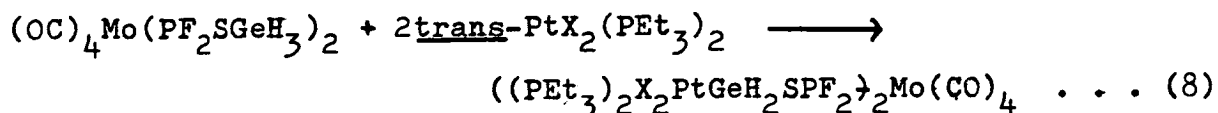
The reaction of $(\text{PF}_2)_2\text{S}$ with alcohols and thiols have already been discussed (18). The equivalent reactions involving GeH_3SPF_2 would result in the formation of germyl ethers and esters, as shown in equation (7).



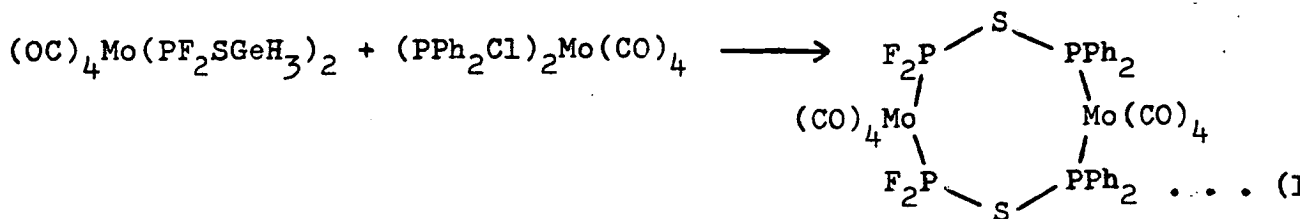
Recent extensions of the reaction of $(\text{PF}_2)_2\text{S}$ with ROH species has led to the formation of $(\text{O})\text{P}(\text{OPF}_2)_3$ (23). The corresponding germyl compound $(\text{O})\text{P}(\text{POGeH}_3)_3$ could be prepared from difluoro(germylthio)phosphine. Other reactions involving the cleavage of the Ge-S bond leading to novel compounds are those with the heavier main group element halides, for example trialkyl tin halides and dialkyl arsines and stibines.

The other major use of GeH_3SPF_2 is in the field of mixed metal compounds. The donor properties of the phosphorus atom towards Lewis acids have been demonstrated. If the lone pair

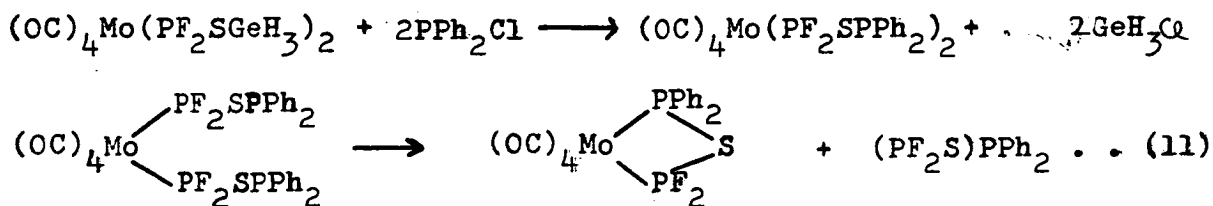
position could be blocked with the $\text{Mo}(\text{CO})_4$ group, the reactivity of the GeH_3 group towards platinum (II) or iridium (I) complexes might be enhanced, with the possibility that a mixed molybdenum-platinum complex could be formed, linked by a P-S-Ge bridge. Alternatively, a mixed molybdenum-platinum complex linked by a P-S bridge would be formed if a germyl halide was preferentially eliminated (equation (8) and (9)).



The same principle could be used to form mixed metal compounds linked by a fluorophosphine-sulphur-alkylphosphine bridge. This could arise from the reaction between coordinated GeH_3SPF_2 and coordinated PR_2X , eliminating GeH_3X . This might result in an eight-membered ring compound as shown in equation (10).



Alternatively, reaction of the coordinated GeH_3SPF_2 with free PR_2X might lead initially to the formation of unidentate F_2PSPR_2 , which could go bidentate with the displacement of unreacted GeH_3SPF_2 (equation (11)).



There are therefore a wealth of reactions which could be investigated, leading to a wide range of products. The reaction involving mixed metal formation would be especially interesting in line with the current investigations in this field.

CHAPTER 44.1. Introduction

Structural Studies of $(PF_2)_2Y$ (18,43,111,112) and $(MH_3)_2Y$ (113-118) have concentrated on the size of the angle at Y, and the bond lengths associated with the central atom. The wide angles and short bond lengths when Y is oxygen (113, 116) led to suggestions that significant (p-d) π bonding occurred from the lone pairs of the oxygen to the vacant d-orbitals of the phosphorus, silicon or germanium atoms. When Y is sulphur or selenium (114-117), the bond lengths and angles are found to be much closer to predicted values, and the conclusion is that (p-d) π interactions are not so important in these cases.

An alternative explanation of bond lengths and angles has been developed from Bartell's concept of "hard sphere" radii (119). While bond lengths are determined by valence forces, bond angles are governed mainly by non-bonded forces between nearest neighbour atoms. From these non-bonded contact distances, hard sphere radii were obtained for atoms bonded to a common central atom, and the sum of two such radii is a good estimate of the distance of minimum approach for the two atoms concerned. The initial studies related to carbon as the central atom, but later work has extended this to silyl derivatives of nitrogen and some fluorophosphine compounds, the latter study investigating specifically the non-bonded F...F distance in F_2P moieties. Clearly these interactions will be important in determining the conformation of a molecule such as GeH_3SPF_2 , where the P...Ge non-bonded distance will have a bearing on any interactions between the fluorine and hydrogen atoms.

As well as these bonds and angles being important, the other

parameters to be considered are the twists of the PF_2 and GeH_3 groups about the P-S and Ge-S bonds respectively. The symmetric molecules $(\text{PF}_2)_2\text{Y}$ and $(\text{MH}_3)_2\text{Y}$ show no twist about these bonds, only a large amplitude of vibration about the mean position. As has been described earlier, the PF_2 group in GeH_3SPF_2 might be expected to be fixed in a position almost 180° from the defined zero (see figure 4.1.), bringing the lone pair of the phosphorus trans to the Ge-S bond and the fluorine atoms within possible hydrogen bonded distance of the GeH_3 group. Although a great deal of spectroscopic evidence has been presented for H...F interactions in this and similar compounds (43,103) very little direct structural evidence is available. Schmutzler (34) has interpreted the nuclear magnetic resonance spectra of some alkylthiofluorophosphoranes showing non-equivalent axial fluorines in terms of the interaction between one fluorine and the alkyl protons. Ebsworth (11, 47) has used similar arguments to describe the possible structures of some germylaminodifluorophosphines having the lone pairs of the phosphorus atom trans to the N-Ge bond, thus maximising $^2J_{\text{PH}}$ and minimising $^3J_{\text{PH}}$. There is structural evidence for H...F interactions in $\text{HPF}_2(\text{NH}_2)_2$ (120) and, PF_2NH_2 has been shown to exist in two conformations in the gas phase, the major conformation with C_{2v} symmetry being stabilised by four such interactions, and the minor conformation showing only two interactions. More recently, PF_2NHMe has also been shown to behave in such a way. It is not unreasonable therefore to expect a study of the structure of GeH_3SPF_2 to confirm that the orientation of the PF_2 group will be such that at least one H...F contact is of the order of 260pm.

4.2./

4.2. Molecular Model

The starting point for the definition of the molecular model was to assume that the GeH_3S group possessed local C_{3v} symmetry, and the PF_2S group local C_s symmetry. The molecule was defined in terms of the P-F, P-S, S-Ge and Ge-H bond distances, the angles $\widehat{\text{P}}\widehat{\text{S}}\widehat{\text{Ge}}$, $\widehat{\text{S}}\widehat{\text{Ge}}\widehat{\text{H}}$, $\widehat{\text{F}}\widehat{\text{P}}\widehat{\text{F}}$ and $\widehat{\text{F}}\widehat{\text{P}}\widehat{\text{S}}$, and the two twist angles describing the rotation of the GeH_3 and PF_2 units about the Ge-S and P-S bonds respectively.

The initial orientation of the molecule, with both twist angles zero, consisted of one hydrogen atom in the same plane as the PSGe skeleton and trans to the P-S bond. The bisector of the $\widehat{\text{F}}\widehat{\text{P}}\widehat{\text{F}}$ angle was also in this plane and trans to the Ge-S bond. With the sulphur atom placed at the origin, this conformation is shown in figure 4.1.

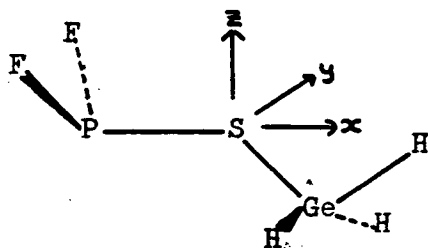


Figure 4.1.

A positive twist angle was defined as a clockwise rotation about the bond in question, when viewed from the phosphorus atom or germanium atom towards the sulphur atom. The combination of two general subroutines defining respectively the coordinates of an XMH_3 group and an XPF_2 group enabled the model to be easily compiled.

There was no evidence to suggest that there would be any problems arising from a mixture of conformers as was the case in the recent study of $(\text{PF}_2)_2\text{NH}$ by Huntly (49). The radial distribution

curve did not appear to show any impurities as was the case in the studies of $(\text{PF}_2)_2\text{S}$ and $(\text{PF}_2)_2\text{Se}$, which necessitated the inclusion of a correction factor for the presence of $(\text{S})\text{PF}_2\text{H}$ or $(\text{Se})\text{PF}_2\text{H}$.

4.3. Refinement.

With the bonded distances and bond angles set at typical values, a series of refinements was carried out to determine which of the parameters would refine satisfactorily. These proved to be the P-S, Ge-S, Ge-H and P-F bond distances, and the PSGe and FPS bond angles. The amplitudes of the P-F bonded distance and F...S and P...Ge non bonded distances refined satisfactorily and also, when tied together the P-S and Ge-S amplitudes. When other parameters were allowed to refine with this combination the value of R_g was unstable and invariably increased.

With the above parameters refining freely, several R_g factor loops were carried out to fix the other parameters at their optimum values. This entailed plotting the value of R_g over a wide range of values of the parameters in question. In this way the $\widehat{\text{SGeH}}$ and $\widehat{\text{FPF}}$ bond angles were determined, and the two twist angles about the P-S and Ge-S bonds. These parameters were then included in the combination of refining parameters, but this was not entirely satisfactory. The $\widehat{\text{FPF}}$ angle did not move significantly from the value obtained from the R_g plot. When the P-S twist angle was allowed to refine the e.s.d. observed was very large compared to the errors observed for the other refining angles, so this parameter was fixed. On refining the $\widehat{\text{SGeH}}$ or $\widehat{\text{GeS}}$ twist angles the value of R_g increased rapidly, and the effect was seen in the

correlation matrix, so these values were also fixed. The R_g loops are shown in graph form in figures 4.5. to 4.8., plotting R_g against angle.

Most of the significant amplitudes refined satisfactorily, the exception being that related to the F...Ge distances. When this was allowed to refine the value rose dramatically, and the e.s.d. was much greater than the other e.s.d's listed. The independent parameter having the greatest effect on this amplitude is obviously the PS twist angle, so a series of R-factor loops were carried out on this angle, with the amplitude fixed at different values from 15 to 35 pm. These plots are shown in figure 4.9. and suggest that a value of about 25 pm is the optimum setting, The final value of R_g was 0.08.

4.4. Results and Discussion.

The parameters obtained in the refinement are given in table 4.3. while elements of the correlation matrix and the weighting function correlation parameters and scale factor information are presented in tables 4.2. and 4.1. The intensity data and radial distribution curves are shown in figures 4.2. to 4.4.

The bond lengths are all slightly longer than might be expected when compared with the Shoemaker-Stevenson calculated values (121). With these values being higher than expected, the possibility of an overall scaling error must be considered. The calibration procedure used for wavelength determination should eliminate this possibility. The procedure involves recording the diffraction patterns of benzene and of GeH_3SPF_2 in the same experiment, and analysing the benzene structure as if it were an unknown compound. The wavelength is then adjusted to bring the

TABLE 4.1.Weighting functions, correlation parameters and scale factors.

Camera height mm	s nm ⁻¹	s _{min} nm ⁻¹	sw1 nm ⁻¹	sw2 nm ⁻¹	s _{max} nm ⁻¹	p/h	Scale factor
128.35	4	60	80	280	300	0.20	0.866(19)
285.56	2	30	38	120	138	0.25	0.854(17)

TABLE 4.2.

Least squares correlation matrix multiplied by 100 (only elements greater than 50 are included).

r1	r2	r3	r4	∠1	∠2	∠3	u1	u3	u6	u7	k1	k2	
100		54					61						r1
	100				51		-51						r2
		100		81	-79		61						r3
			100										r4
				100	-84		59						1
					100		-63						2
						100							3
							100						u1
								100		58			u3
									100				u6
										100			u7
											100	63	k1
												100	k2

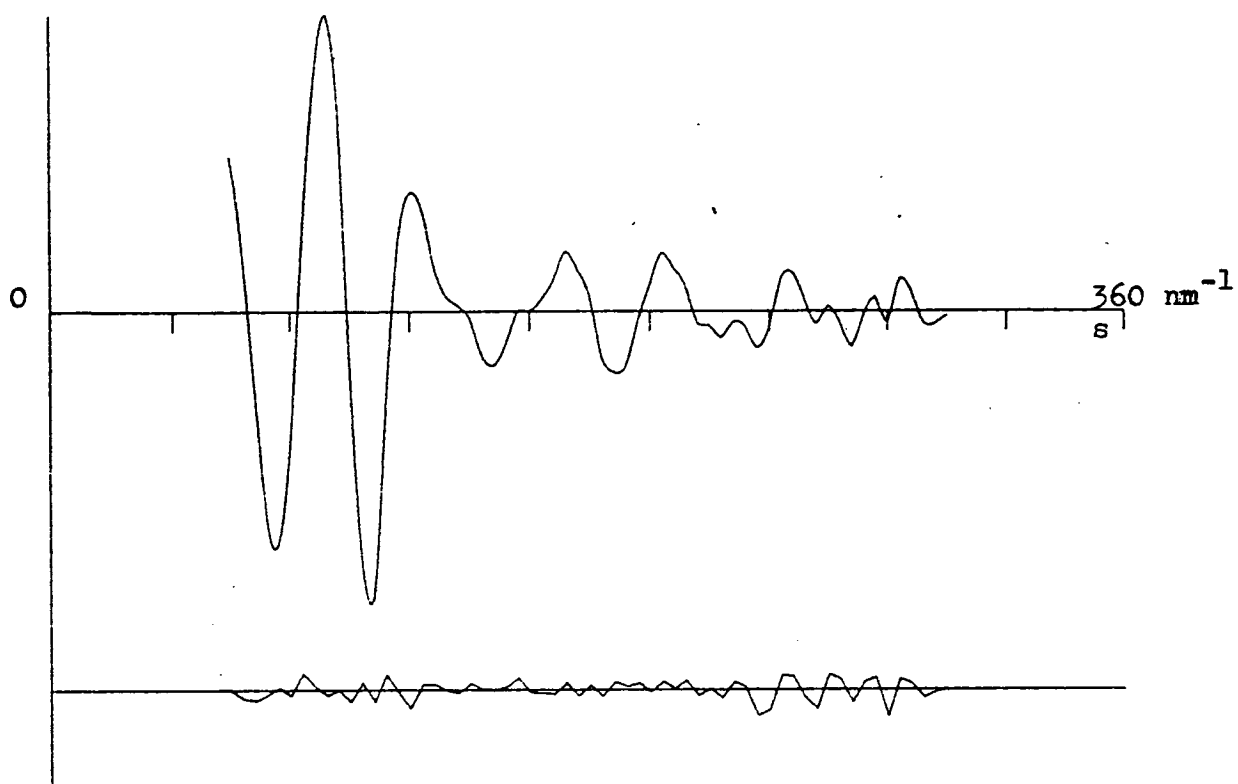
TABLE 4.3.

Molecular parameters for GeH₃SPF₂ (a)

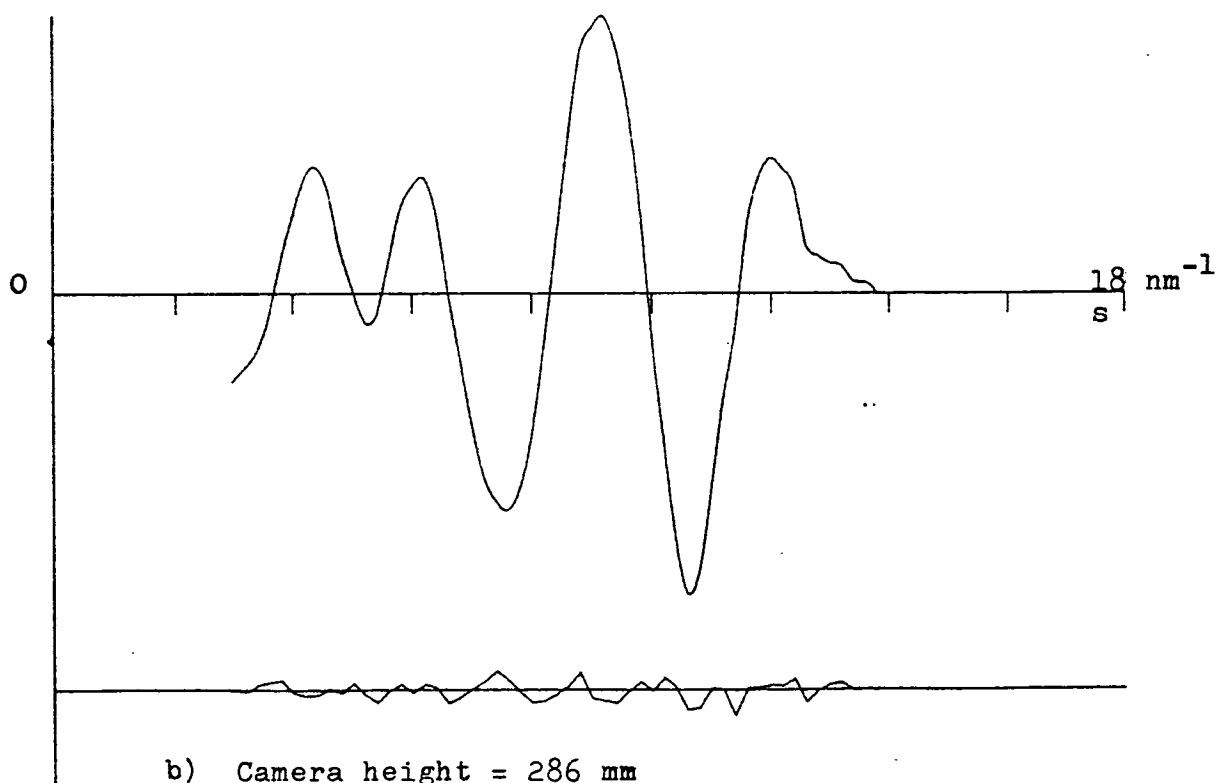
<u>Independent Distances</u>	<u>Distance/pm</u>	<u>Amplitude/pm</u>
r 1 P-S	211.5(8)	5.6(8)
r 2 Ge-S	225.6(4)	
r 3 P-F	159.0(9)	5.7(5)
r 4 Ge-H	153.8(15)	7.1(fixed)
<u>Dependent Distances</u>		
d 5 F...F	238.3(14)	6.7(fixed)
d 6 S...F	285.7(13)	8.5(6)
d 7 Ge...P	332.6(17)	12.5(9)
d 8 Ge...F	299.5(18)	22.3(fixed)
d 9 Ge...F	350.6(16)	
Shortest F...H	271.3(17)	
<u>Independent Angles /°</u>		
∠ 1 Ge-S-P	99.0(6)	
∠ 2 F-P-F	97.0(10)	
∠ 3 S-P-F	99.9(4)	
∠ 4 S-Ge-H	110 (3) (b)	
∠ 5 PF ₂ twist	161.8(17) (b)	
∠ 6 GeH ₃ twist	29 (14) (b)	

(a) All distances are r_a . Quoted errors are estimated standard deviations obtained in the least squares analysis, increased to allow for systematic errors.

(b) See text.



a) Camera height = 128 mm



b) Camera height = 286 mm

Figure 4.2. Intensity data.

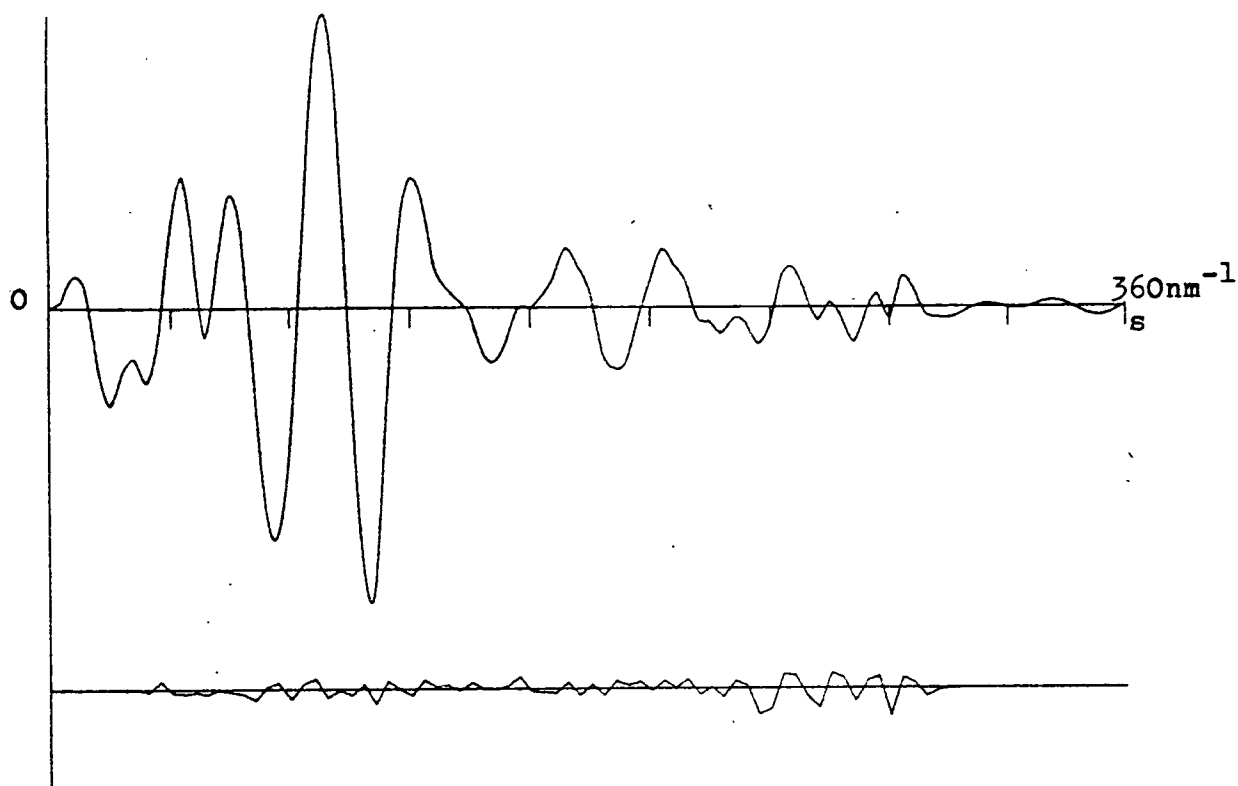


Figure 4.3. Combined intensity data.

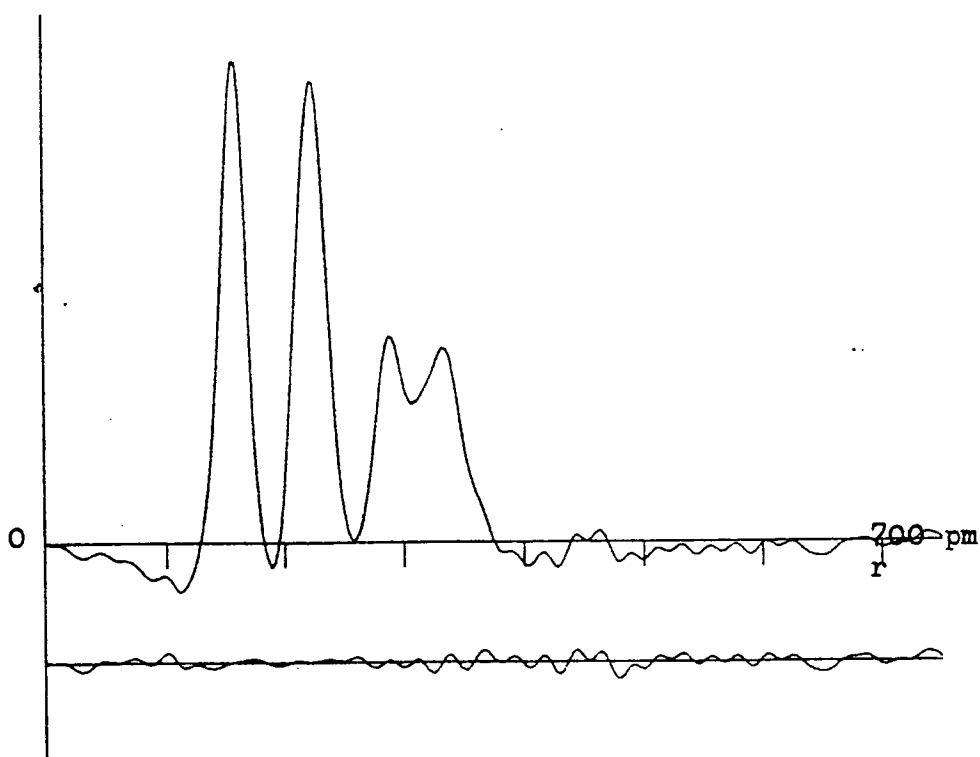


Figure 4.4. Radial distribution curve.

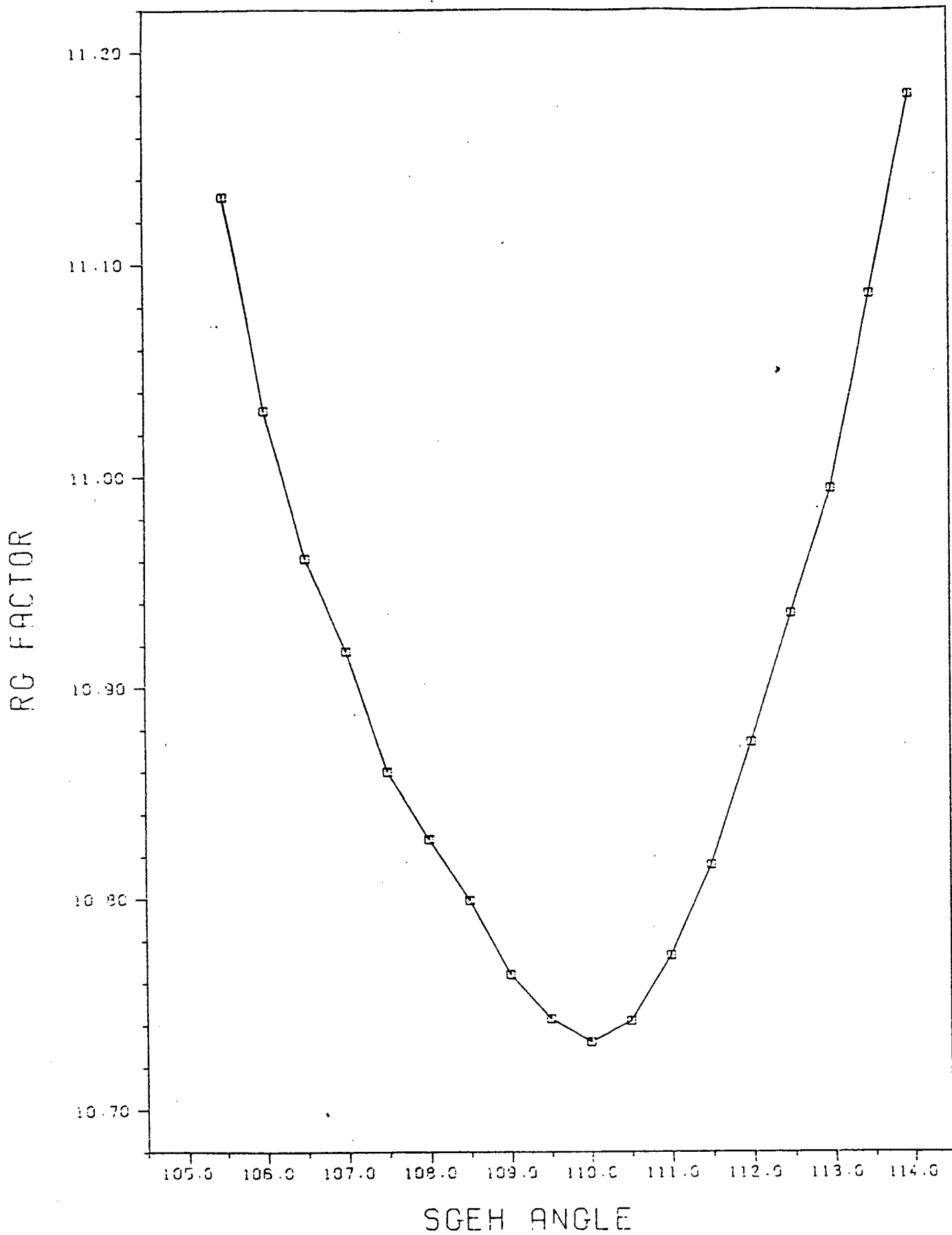


Figure 4.5. R Factor loop for SGeH angle

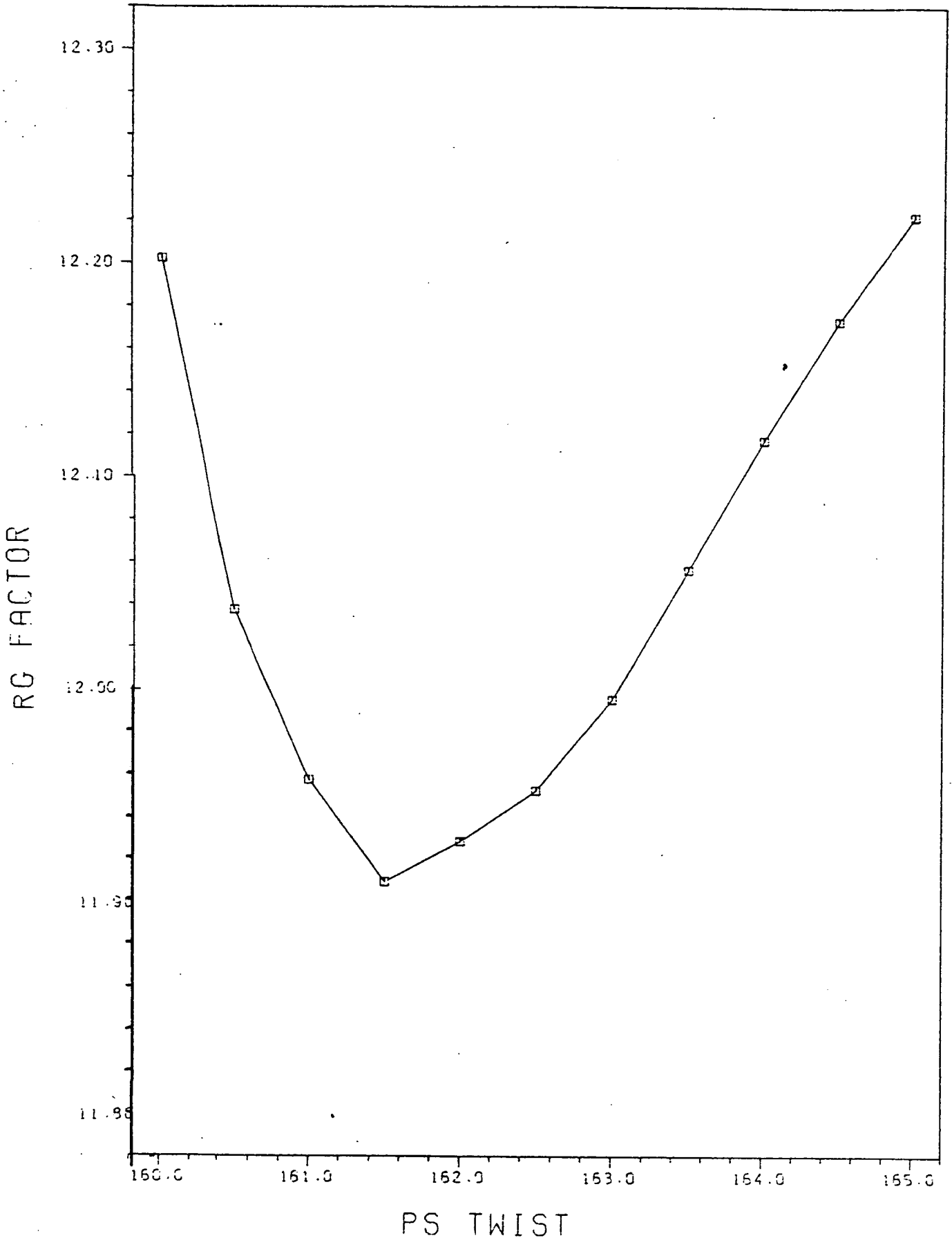


Figure 4.6. R Factor loop for PS twist

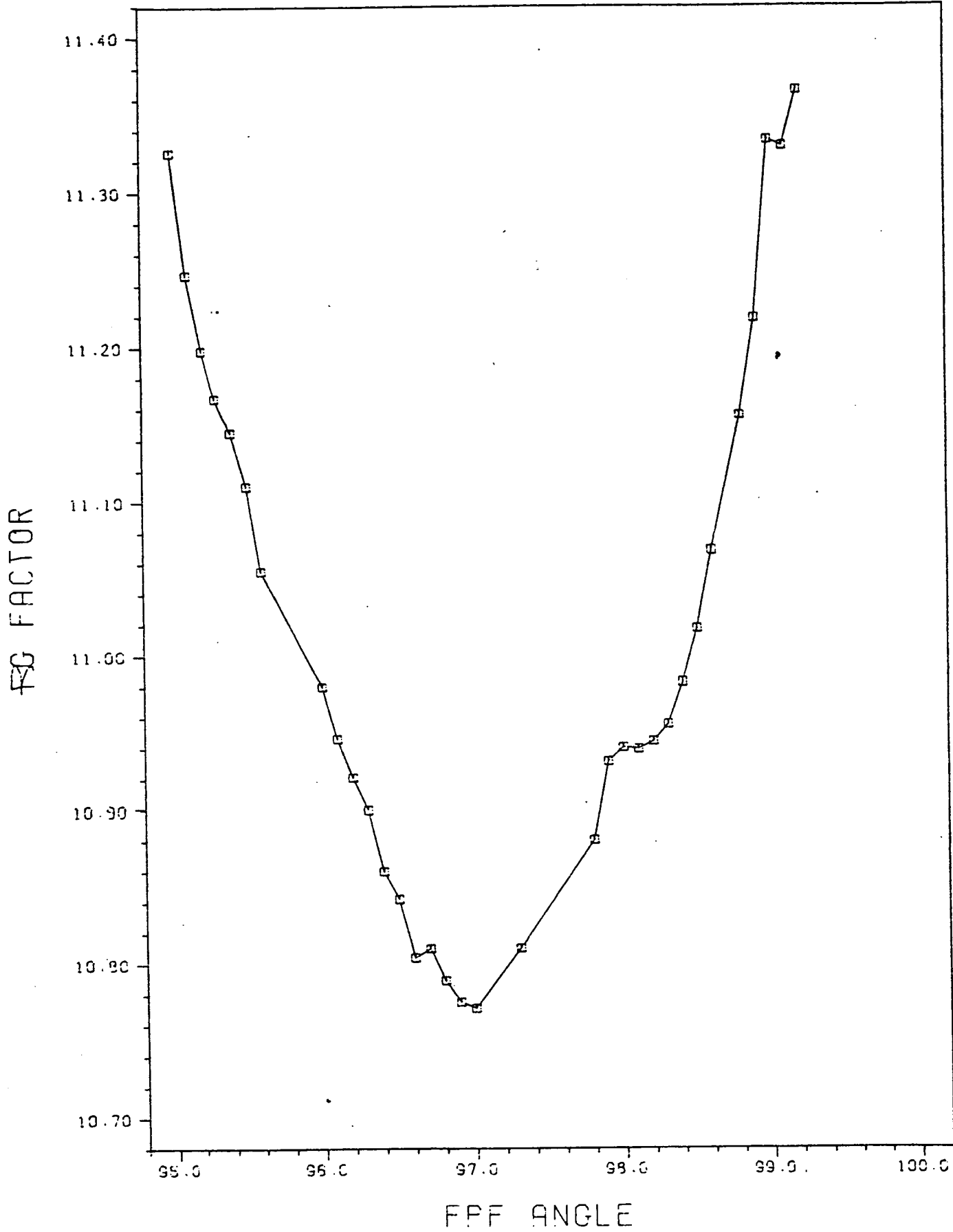


Figure 4.7. R Factor loop for FPF angle

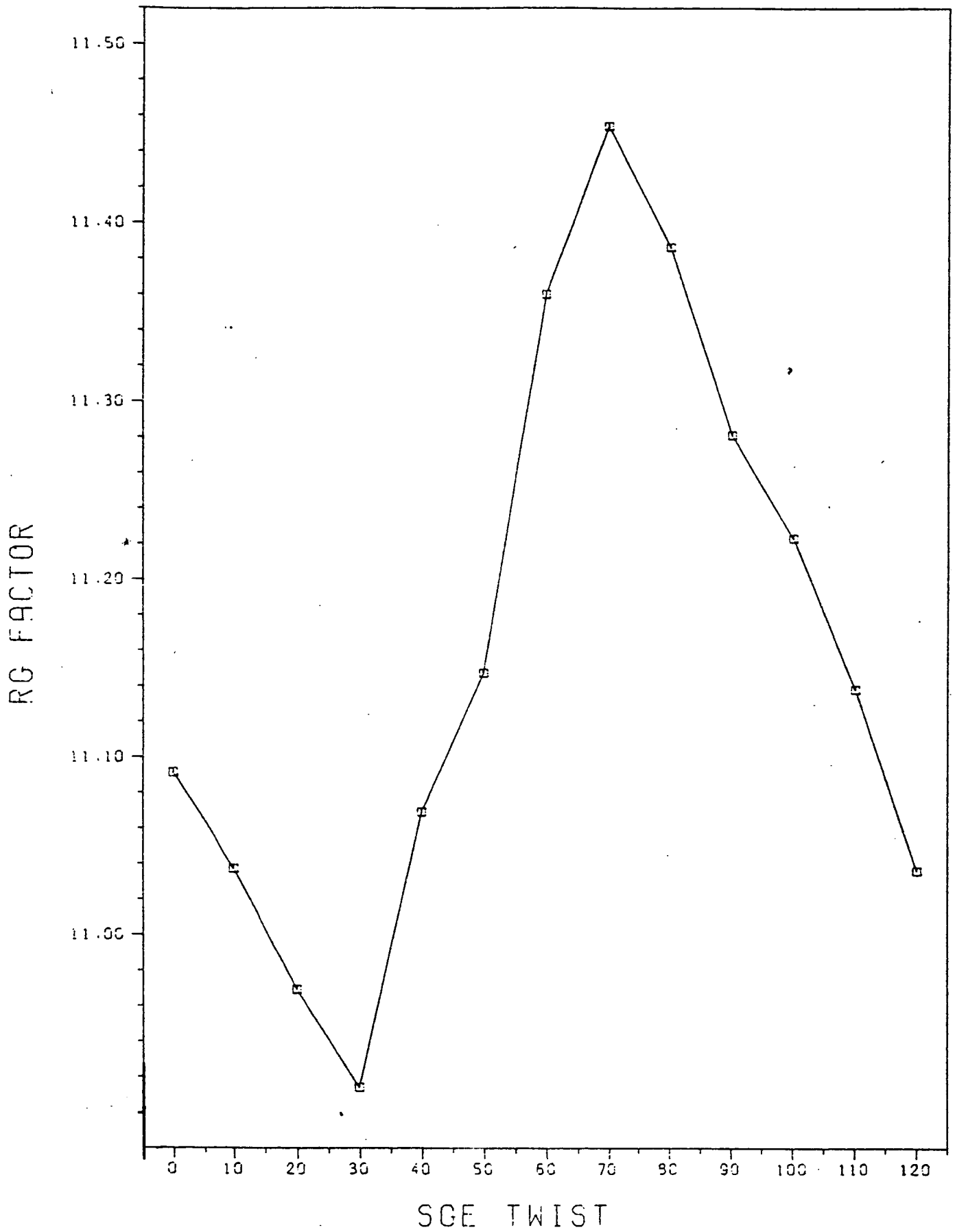


Figure 4.8. R Factor loop for SGe twist

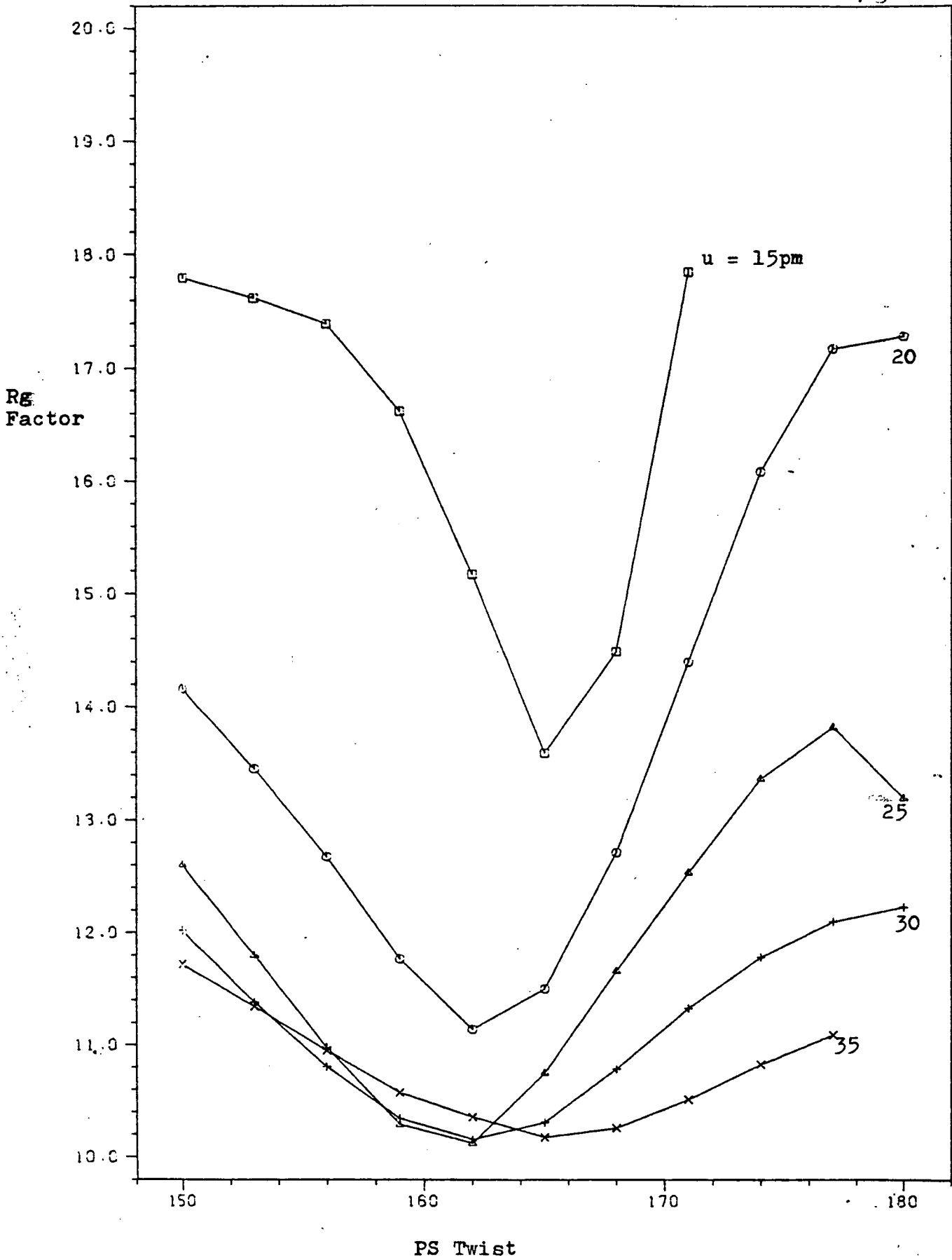


Figure 4.9. R Factor loops for PS twist, with fixed values for u_{FGe}

C-C distance of benzene to 139.70 pm, thereby eliminating the possibility of a systematic scaling error.

The P-S bond length (211.5 pm) is slightly shorter than that observed in $(\text{PF}_2)_2\text{S}$ (212.7 pm) (18) and longer than the equivalent bond in PF_2SCH_3 (207.6 pm) (63). The Ge-S bond on the other hand is significantly longer than the bond length observed in $(\text{GeH}_3)_2\text{S}$ (220.9 pm) (114). As the expected Ge-S bond length, based on covalent radii derived from structures of ethane (119), dimethylsulphide (122) and methylgermane (123) is 221.3 pm, the observed bond length of 225.6 pm must be regarded as being exceptionally long.

The P-F (159.0 pm) and Ge-H (153.8 pm) bond lengths are longer than observed in $(\text{PF}_2)_2\text{S}$ (157.3 pm) and $(\text{GeH}_3)_2\text{S}$ (151.2 pm), and while the two P-F bonds have been defined as being of equal length, and likewise the three Ge-H bonds, there is probably a difference in size between the bonds to the fluorine and hydrogen atoms which are interacting, and the bonds to the remaining fluorine and hydrogen atoms. The $\widehat{\text{FPF}}$ angle (97.0°) is slightly narrower than is found in $(\text{PF}_2)_2\text{S}$ (97.5°), although the values are within experimental error, and the non-bonded F...F distance of 238.3 pm compares well with the sum of the hard sphere radii for fluorines bonded to phosphorus (238 pm) while the distance in $(\text{PF}_2)_2\text{S}$ (236 pm) is smaller than this figure.

The twist of the PF_2 group about the P-S bond and the GeH_3 group about the Ge-S bond clearly shows that some interaction between the fluorine and hydrogen atoms is present. (In the diagram of the molecule shown in figure 4.10. the P-F₍₁₎ bond and the Ge-H₍₁₎ bond are almost coplanar). This twist contrasts with the symmetric sulphides where $(\text{PF}_2)_2\text{S}$ is described as having a large torsional vibration about the zero position with each

GEH3SPF2

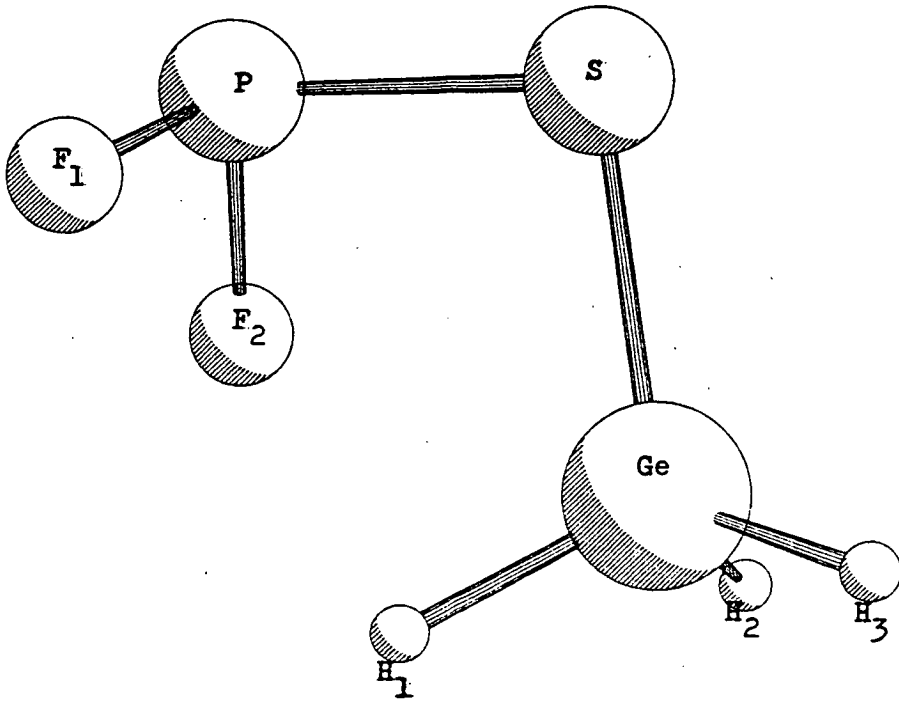


Figure 4.10.

Configuration of GeH_3SPF_2 .

phosphorus lone pair eclipsing the further S-P bond, and $(\text{GeH}_3)_2\text{S}$ is described as having opposite twists of about 15° about each Ge-S bond, to preserve the overall symmetry of the molecule. CH_3SPF_2 exhibits a smaller twist angle (110°) but this does bring the fluorine and hydrogen atoms closer together than in GeH_3SPF_2 , the closest F...H distance in CH_3SPF_2 being about 265 pm, compared to 271.3 pm in GeH_3SPF_2 . This smaller twist is no doubt as a result of the CH_3 group being closer to the PF_2 group because of the shorter C-S bond length. These F...H distances compare with a value of 255 pm for the sum of the van der Waal's radii of fluorine and hydrogen. Some notably short F...H distances which complete a five-membered ring are observed in $\text{PF}_2\text{N}(\text{CH}_3)_2$ (253 pm) (8), $\text{PF}_2\text{NHSiH}_3$ (267 pm) (11) and $\text{PF}_2\text{C}_6\text{H}_5$ (228.3 pm) (124). The major conformer of $\text{PF}_2\text{NHSiH}_3$ is also stabilised by a short N(H)...F interaction of 252 pm (11), with the minor conformer showing two N(H)...F interactions with the separation slightly wider.

These distances would appear to indicate that other factors should also be taken into consideration. The value of $r(\text{P...Ge})$, 333.5 pm is significantly larger than the sum of the hard sphere radii of phosphorus and germanium bonded to sulphur, so there is no real problem sterically. If the FPSGeH ring were completely coplanar the F...H distance would be of the order of 210 pm. This is obviously too close, but there is still no real steric hindrance even if the atoms were separated by the sum of their Van der Waal's radii. The conclusion must be that the conformation is not strained.

The bond angle at sulphur is the same as that in $(\text{GeH}_3)_2\text{S}$, but wider than $(\text{PF}_2)_2\text{S}$ and slightly narrower than CH_3SPF_2 . In $(\text{PF}_2)_2\text{S}$, the lone pairs of the phosphorus atoms are pointing

towards each other, but the steric interaction of the two groups is minimal, hence the narrower angle at sulphur. In CH_3SPF_2 the methyl group is closer to the PF_2 group generally, hence the wider PSC angle and smaller twist angle than GeH_3SPF_2 . The relevant parameters for these molecules and some other fluorophosphine compounds are compared in table 4.4.

The early predictions of Arnold (43, 103) concerning the structure of GeH_3SPF_2 have been confirmed. The structure also supports the conclusions of Ebsworth (11(a), 47) and Schützler (34) about the possible structures of other group IV fluorophosphine and fluorophosphorane compounds. Structural studies of these compounds would be very useful for comparative purposes, as would low temperature x-ray crystal studies. This would show any association in the solid phase, and any change of conformation caused by such association.

TABLE 4.4.

Comparison of some structural parameters of GeH_3SPF_2 with related compounds, X-Y-PF_2 .

X	Y	r(P-X)	r(X-Y)	r(P-F)	(XYP)	(FPF)	Shortest r((M)H...F)
GeH_3	S	211.5	225.6	159.0	99.0	97.0	271.3
CH_3	S	207.6		157.7	103.2	98.1	267
PF_2	S	212.7	-	157.3	95.6	97.5	-
$(\text{GeH}_3)_2$	S	-	2.209	-	98.9	-	-
CH_3	NCH_3	168.0	147.9	158.3	122.0	95.3	253
CH_3	NH	164.8	144.8	159.3	125.3	94.1	250
H	NH	166.1		158.1		95.3	-
SiH_3	NH	165.4		157.4	127.9	100.8	267

CHAPTER 5

5.1. Introduction

Nucleophilic substitution of halides has always been a particularly useful synthetic route, which is not confined to organic chemistry. There have been some attempts recently to introduce small inorganic groups into molecules with a certain amount of success. Jessep (125) was able to generate the $(YSiH_3)^-$ ions ($Y=S, Se$) and reacted them with several different systems with a view to forming new compounds containing silicon-sulphur linkages. The analogous fluorophosphine anions $(YPF_2)^-$, ($Y=O, S, Se$) have been reported (24, 78, 126), but no attempts have been made to characterize them. Charlton (24) observed in the reaction between trimethylamine and $(S)PF_2H$ a white solid in acetonitrile at 238K. The proton magnetic resonance spectrum showed the presence of the trimethylammonium ion and the ^{19}F spectrum showed a simple doublet at $\delta F = -34ppm$, with a coupling constant $^1J_{PF} = 1180Hz$. This signal was assigned to the ion $(SPF_2)^-$ but it was stated that "... because of the extreme instability of the species in solution further characterization was not possible". Centofani (78) has identified the oxygen analogue, and Campbell (126) observed some evidence for $(SePF_2)^-$.

The intention was to carry out a preliminary study on these systems, and expand on those experiments offering a chance of success. Although some evidence for new compounds was observed, the study showed severe limitations in the use of these anions as synthetic intermediates, and no preparative experiments were attempted.

5.2/

5.2. The reactions of (Y)PF₂H with strong base.

The reactions of the fluorophosphoryl compounds with trimethylamine were carried out in sealed n.m.r. tubes at 220K, using deuteriated chloroform as solvent. Products were identified by phosphorus n.m.r. spectroscopy. In each case, when the reaction mixture was warmed to room temperature a yellow solid was deposited and the only product observed in the spectrum was PF₃.

5.2.1. (O)PF₂H + Me₃N

When the reaction mixture was warmed to 220K, a triplet was observed in the phosphorus spectrum, (proton decoupled), centred at $\delta P = 125.6\text{ppm}$, with a coupling constant $^1J_{PF} = 1209\text{Hz}$. This signal was attributed to the anion $(OPF_2)^-$. Other products observed in small but significant quantities were a quartet ($^1J_{PF} = 1400\text{Hz}$) centred at $\delta P = 104\text{ppm}$, identified as PF₃, and a doublet ($^1J_{PF} = 975\text{Hz}$) centred at $\delta P = 1.3\text{ppm}$, which on further examination showed a proton coupling, $^1J_{PH} = 681\text{Hz}$. Also observed, at very low frequency, was a doublet ($J = 957\text{Hz}$) of quintets ($J = 823.6\text{Hz}$) of doublets ($J = 732.1\text{Hz}$). These peaks were not initially assigned, and the fluorine spectrum was recorded also at 220K. In this spectrum, a doublet ($^1J_{PF} = 1209\text{Hz}$) was observed at $\delta F = -17.9\text{ppm}$ and was assigned to $(OPF_2)^-$. Three other signals were observed: a doublet ($^1J_{PF} = 976\text{Hz}$) at $\delta F = -36.4\text{ppm}$ which also showed a doublet proton coupling ($^2J_{HF} = 125\text{Hz}$) was identified as the pentavalent phosphorus anion $(O_2PFH)^-$ (127): the coupling constants observed in the other signals suggested that they were associated with the same species. At $\delta F = -57.1\text{ppm}$, a doublet ($^1J_{PF} = 825\text{Hz}$) of doublets

(${}^2J_{\text{HF}} = 125\text{Hz}$) of doublets (${}^2J_{\text{FF}} = 45\text{Hz}$) was observed, with a doublet (${}^1J_{\text{PF}} = 732\text{Hz}$) of quintets (${}^2J_{\text{FF}} = 45\text{Hz}$) at $\delta\text{F} = -66.5\text{ppm}$. The ratio of the intensities of these two signals was approximately 4:1, and the identity of the product was proposed as the octahedral anion $(\text{HPF}_5)^-$. This was confirmed by comparison with recorded spectroscopic data (128, 129).

5.2.3. $(\text{S})\text{PF}_2\text{H} + \text{Me}_3\text{N}$

At 220K, the phosphorus spectrum consisted of a triplet (${}^1J_{\text{PF}} = 1181\text{Hz}$) centred at $\delta\text{P} = 276.6\text{ppm}$. Also observed were a quartet (${}^1J_{\text{PF}} = 1400\text{Hz}$) at $\delta\text{P} = 104\text{ppm}$ assigned to PF_3 and a smaller amount of unreacted $(\text{S})\text{PF}_2\text{H}$, observed as a triplet (${}^1J_{\text{PF}} = 1157\text{Hz}$) at $\delta\text{P} = 68.5\text{ppm}$. In the fluorine spectrum, complementary patterns were observed as three doublets at $\delta\text{F} = -37.1\text{ppm}$ (${}^1J_{\text{PF}} = 1191\text{Hz}$) $\delta\text{F} = -34\text{ppm}$ (${}^1J_{\text{PF}} = 1400\text{Hz}$) and $\delta\text{F} = -48.7\text{ppm}$ (${}^1J_{\text{PF}} = 1157\text{Hz}$). The first mentioned signal was assigned to the anion $(\text{SPF}_2)^-$.

The same reaction was carried out in deuteriated methylene chloride. The results obtained were substantially the same as those observed in CDCl_3 , with a slight change of the phosphorus chemical shift and coupling constant of the $(\text{SPF}_2)^-$ ion ($\delta\text{P} = 278.0\text{ppm}$, ${}^1J_{\text{PF}} = 1183\text{Hz}$). Also observed were a quartet assigned to PF_3 , and two doublets, at $\delta\text{P} = 103.0\text{ppm}$, ${}^1J_{\text{PF}} = 1023\text{Hz}$ and $\delta\text{P} = 61.5\text{ppm}$, ${}^1J_{\text{PF}} = 1018\text{Hz}$. The intensity of the signal from the second species decreased as the reaction mixture was warmed to room temperature and the species was not identified. The first doublet was tentatively assigned to the anion $(\text{S}_2\text{PFH})^-$, although no spectroscopic evidence for the presence of hydrogen was obtained.

5.2.3. (Se)PF₂H + Me₃N

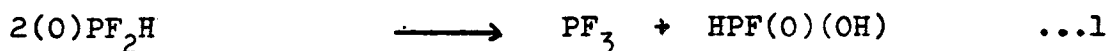
This system was studied in detail by Campbell (126). The results were inconclusive, and not very promising for future work. Several attempts were made to prepare the ion (SePF₂)⁻ from this reaction, varying the solvent, and only one attempt gave a result that could have been positive. In deuteriated acetone at 200K, a triplet (¹J_{PF} = 1170Hz) was observed in the phosphorus spectrum at δP = 315.1ppm. This is in broad agreement with the parameters reported by Campbell, but the phosphorus-selenium, (77 Se) coupling constant was not observed. There were two other signals present in the spectrum; a quartet (¹J_{PF} = 1369Hz) at δP = 89.7ppm, and a triplet (¹J_{PF} = 1335Hz) at δP = 113.5ppm. The chemical shift and coupling constant of the first species is consistent with a coordinated PF₃ species, but it is difficult to see what the acceptor could be. The second species is probably (PF₂)₂O, with the difference between the observed and reported n.m.r. parameters attributed to the reaction conditions.

5.2.4. Discussion

The first point to note concerning the preceding results is that they were not consistent. The experiments were repeated on several occasions, and although the anions were usually observed in the spectra, the identity of the minor products varied considerably, which complicated the interpretation of the results.

The generation of the anion (O₂PFH)⁻ was not entirely unexpected. Centofani has reported the decomposition of (O)PF₂H according to equation 1, and suggested that the reaction with

base can be represented by equation 2 (127).



This has been rationalised by the suggestion that in the liquid phase, $(\text{O})\text{PF}_2\text{H}$ is associated through extensive (p-d) π donation between the oxygen and phosphorus atoms forming chains of molecules as in figure 5.1.(a), hence facilitating disproportionation. Association through hydrogen bond interactions is also possible, but the decomposition would be a different route (figure 5.1.(b)).

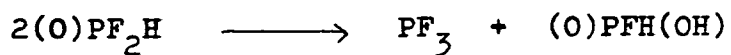
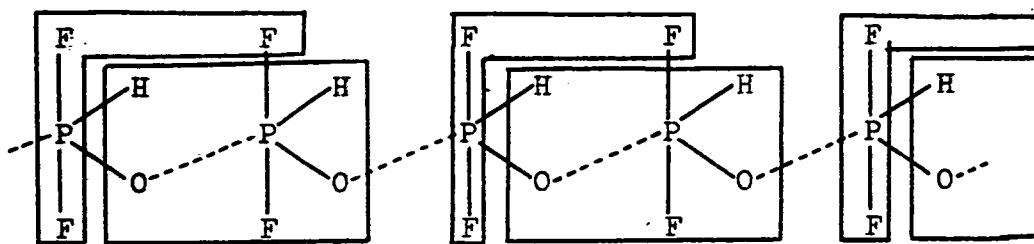
The origin of the $(\text{HPF}_5)^-$ ion is unclear, but might well involve the generation of fluoride ions in a similar manner to that proposed by Cowley for the reaction between base and HPF_4 (figure 5.2.). The first step involves the formation of an amine-phosphine adduct, which ionises, forming $(\text{PF}_4)^-$. This decomposes to PF_3 and a fluoride ion, which attacks a second HPF_4 molecule to give the octahedral $(\text{HPF}_5)^-$ ion. Alternatively, traces of HF caused by hydrolysis could promote the reaction.

The spectra of the major ionic products were relatively easy to assign, by comparison with reported data. Rationalisation of the observed parameters was not so straightforward. The results are summarised in table 5.1. with the n.m.r. parameters of the parent phosphoryl compounds and related difluorohalophosphines included for comparison. The high chemical shifts observed are consistent with the anions being described as trivalent phosphorus compounds, but the coupling constants are comparable with the pentavalent phosphines. The high chemical shifts are the more important factors when considering the charge distribution,

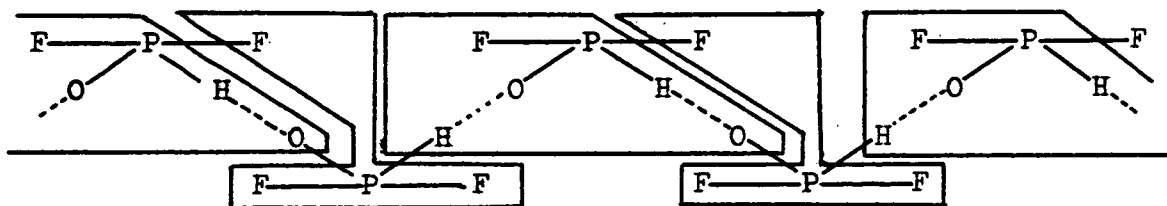
TABLE 5.1.

Observed n.m.r. parameters for $(\text{Me}_3\text{NH})^+(\text{Y}\text{PF}_2)^-$ compared with $(\text{Y})\text{PF}_2\text{H}$
and PF_2X .

	$\delta^{31}\text{P}$ ppm	$\delta^{19}\text{F}$ ppm	$^1J_{\text{PF}}$ Hz	Reference
OPF_2^-	125.6	-17.9	1209	
$(\text{O})\text{PF}_2\text{H}$	-4.7	-62.0	1121	24
PF_3	104.0	-34.0	1400	1
SPF_2^-	276.6	-36.8	1189	
$(\text{S})\text{PF}_2\text{H}$	62.3	-48.7	1153	24
PF_2Cl	180.5	-36.6	1390	51, 52
SePF_2^-	305.6	n.o.	1186	126
$(\text{Se})\text{PF}_2\text{H}$	74.2	-37.0	1192	25
PF_2Br	201.1	-39.7	1364	51

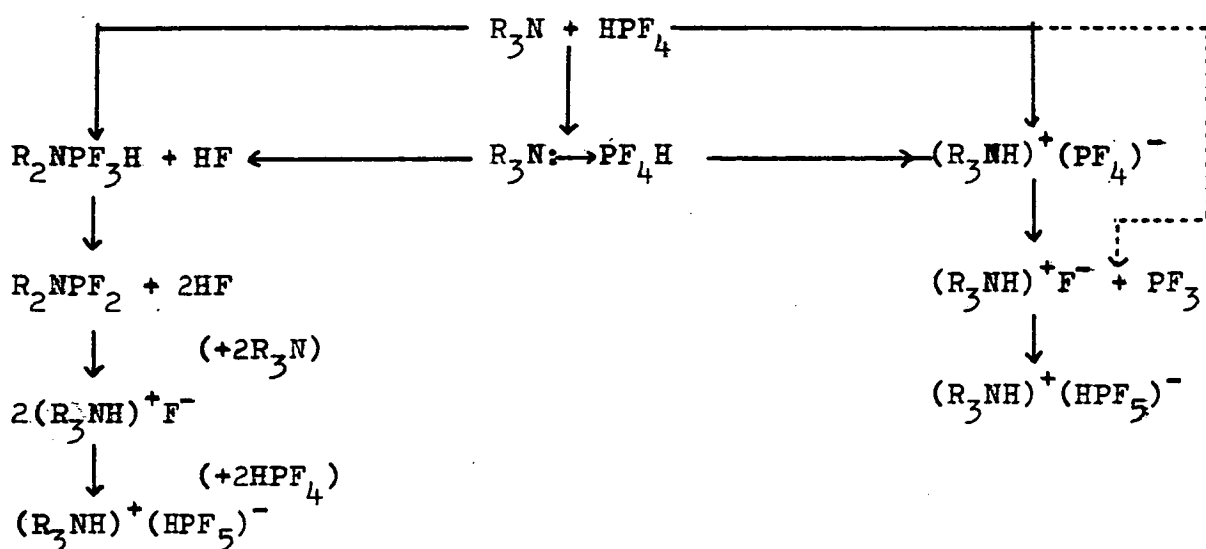


(a) Association of $(\text{O})\text{PF}_2\text{H}$ through $(\text{p-d})\pi$ bonding.



(b) Association of $(\text{O})\text{PF}_2\text{H}$ through hydrogen bonding.

Figure 5.1.



Stoichiometries:

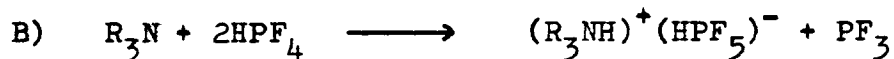


Figure 5.2.

Suggested mechanism for the reaction between HPF_4 and amines. For tertiary amines, (B) must be the pathway as amine substitution is impossible.

and suggest that the negative charge is concentrated on the oxygen, sulphur or selenium atom, with the phosphorus atom essentially in the trivalent state. This would lead to a large deshielding effect being experienced by the phosphorus atom. The small value of $^1J_{PF}$ probably reflects the effects of the negative charge on the bonding in the molecule.

Because of the thermal instability of the salts, no attempts were made to purify and isolate them on a preparative scale for analysis or further characterisation. An attempt was made to study the infra-red spectrum of the sulphide by preparation in situ in a low temperature infra-red cell, but apart from showing the presence of a trimethylammonium salt, no further information was obtained. Further characterisation would be obtained from the proposed reactions. To this end, the various minor products observed in the reactions described above were not expected to interfere with the course of the proposed experiments.

One or two preliminary reactions were carried out using the oxide, but most were performed with the sulphide. In all cases the reactants (amine, phosphine and substrate) were mixed in deuteriated solvents in a sealed n.m.r. tube at 195K, and the spectra recorded at about 210K. It is convenient to discuss the reactions with reference to the type of substrates used, and the next section can be divided into the reaction with group IV compounds and those with group V compounds.

5.3. Reactions of the ions $(YPF_2)^-$ with group IV halides.

5.3.1. $(OPF_2)^- + Me_3SiCl$

This reaction was carried out in deuteriochloroform at 210K.

In the phosphorus spectrum a triplet ($^1J_{\text{PF}} = 1299\text{Hz}$) was observed at $\delta\text{P} = 111.6\text{ppm}$. In the fluorine spectrum a doublet ($^1J_{\text{PF}} = 1299\text{Hz}$) was observed at $\delta\text{F} = -33.2\text{ppm}$. These signals were assigned to the trivalent compound $\text{F}_2\text{POSiMe}_3$ on the basis of the observed chemical shifts and coupling constant. Also observed in both spectra were significant amounts of PF_3 , but no other product.

5.3.2. $(\text{SPF}_2)^- + \text{Bu}_3\text{SnCl}$

This reaction was studied at 210K, with CDCl_3 as the solvent. In the phosphorus spectrum a triplet ($^1J_{\text{PF}} = 1243\text{Hz}$) was observed at $\delta\text{P} = 253.0\text{ppm}$. These parameters are similar to those reported for the trivalent phosphine $\text{F}_2\text{PSSnBu}_3$ (39). Also observed was a triplet ($^1J_{\text{PF}} = 1243\text{Hz}$) centred at $\delta\text{P} = 120.7\text{ppm}$. This could be attributed to a pentavalent phosphine sulphide $(\text{S})\text{PF}_2\text{SnBu}_3$, or alternatively the trivalent compound $\text{F}_2\text{POSnBu}_3$, whose parameters have been reported (39). A triplet ($^1J_{\text{PF}} = 1101\text{Hz}$) centred at $\delta\text{P} = 46.1\text{ppm}$ was not identified, but could be attributed to the pentavalent $(\text{O})\text{PF}_2\text{SnBu}_3$. In the fluorine spectrum, doublets were observed to correspond with the above species at $\delta\text{F} = -49.3\text{ppm}$ ($^1J_{\text{PF}} = 1243\text{Hz}$), $\delta\text{F} = -21.6\text{ppm}$ ($^1J_{\text{PF}} = 1243\text{Hz}$), and $\delta\text{F} = -35.7\text{ppm}$ ($^1J_{\text{PF}} = 1101\text{Hz}$) respectively. Also observed in both spectra was a significant amount of PF_3 . An interesting point is that couplings to the magnetic tin nuclei, ^{117}Sn and ^{119}Sn are not observed. This suggests intermolecular exchange of the (SPF_2) groups, by cleavage of either the Sn-S or S-P bond. This would be an unusual process in such a system, involving fast exchange of relatively bulky groups at low temperatures. On warming, a yellow deposit was observed to form in the tube and the only species observed in the spectra was PF_3 . A similar effect was observed

in all other reactions of this type.

5.3.3. $(\text{SPF}_2)^- + \text{Me}_3\text{SiX}$

This reaction was the first in a series of reactions with alkyl silyl halides which produces so many inconsistencies that the work was finally abandoned in a confused and unsatisfactory state. Initially the reactions were relatively straightforward and the results looked promising, but once the complications arose the results were almost impossible to rationalize.

The initial reaction performed was between $(\text{SPF}_2)^-$ and trimethylsilyl chloride in CDCl_2 . In the phosphorus spectrum at 210K a triplet ($^1J_{\text{PF}} = 1188\text{Hz}$) was observed at $\delta\text{P} = 275.5\text{ppm}$ and assigned as the unreacted anion. Another triplet ($^1J_{\text{PF}} = 1268\text{Hz}$) was observed at $\delta\text{P} = 239.9\text{ppm}$. These parameters are consistent with the expected trivalent phosphine product $\text{F}_2\text{PSSiMe}_3$ (and are comparable with the parameters recorded for F_2PSSiH_3). A third signal was observed at $\delta\text{P} = 116.4\text{ppm}$ with a triplet splitting ($^1J_{\text{PF}} = 1167\text{Hz}$), the parameters being characteristic of a pentavalent difluorothiophosphoryl compound. PF_3 and $(\text{S})\text{PF}_2\text{H}$ were also identified.

The fluorine spectrum at 210K complemented the phosphorus spectrum and the products were identified as follows: $\text{F}_2\text{PSSiMe}_3$ showed a doublet ($^1J_{\text{PF}} = 1269\text{Hz}$) at $\delta\text{F} = -60.7\text{ppm}$; $(\text{SPF}_2)^-$ appeared as a doublet ($^1J_{\text{PF}} = 1180\text{Hz}$) at $\delta\text{F} = 37\text{ppm}$; PF_3 and $(\text{S})\text{PF}_2\text{H}$ were identified; and the unknown thiophosphoryl compound was observed as a doublet ($^1J_{\text{PF}} = 1168\text{Hz}$) at $\delta\text{F} = -6.1\text{ppm}$.

Further reaction must have occurred while the fluorine spectrum was being recorded, because new signals were observed at $\delta\text{F} = -40\text{ppm}$, a doublet ($^1J_{\text{PF}} = 1030\text{Hz}$) of doublets ($J_{\text{HF}} = 89\text{Hz}$), and at

$\delta F = -16\text{ppm}$, a doublet ($^1J_{\text{PF}} = 1260\text{Hz}$) of doublets ($^2J_{\text{PF}} = 63\text{Hz}$), which seemed to exhibit some second order effects. The spectrum is shown in figure 5.3.

The phosphorus spectrum was recorded again, and a complex pattern of lines was observed centred at $\delta P = 139\text{ppm}$. The pattern under low resolution appeared as a triplet ($^1J_{\text{PF}} = 1257\text{Hz}$) of doublets ($J = 628\text{Hz}$) of doublets ($J = 33\text{Hz}$). Under higher resolution the peaks were split further, and the spectrum is shown in figure 5.4. At this stage the product was not identified, and the reaction was repeated.

The results from this second reaction were not consistent with the earlier observations. No evidence was observed for the product $\text{F}_2\text{PSSiMe}_3$ or for the unreacted anion, but at a higher frequency a doublet ($^1J_{\text{PF}} = 1177\text{Hz}$) was observed, at $\delta P = 304\text{ppm}$. After some consideration this was assigned to the ion $(\text{SPFCl})^-$ formed presumably by straightforward halogen exchange at silicon in conjunction with the formation of Me_3SiF , a frequent reaction in $\text{R}_3\text{SiX}/\text{F}_2\text{PX}$ systems (34, 130). The unidentified second order pattern was observed, at $\delta P = 139\text{ppm}$, along with several other products. To try and elucidate the processes involved, a series of reactions were performed in scaled tubes and the results are listed in table 5.2.

The majority of the species have not been identified with any degree of certainty. Some, of course, such as PF_3 (product C), $(\text{PF}_2)_2\text{O}$ (product D) and $(\text{S})\text{PF}_2\text{H}$ (product F) have been observed throughout the work. The species with coupling constants greater than about 1200Hz , and phosphorus chemical shifts greater than 100ppm are likely to be trivalent $\text{F}_2\text{PO-}$ compounds. Those with

TABLE 5.2.

Products observed during the reactions of $(\text{SPF}_2)^-$ with methylsilyl halides.

a)n.m.r. parameters

	SP ppm	SF ppm	$^1J_{\text{PF}}$ Hz	Other J Hz	Assignment
A	139	- 16	1259	$^1J_{\text{PP}}628$ $^2J_{\text{PF}}64$	$(\text{SP}(\text{PF}_2(\text{S}))_2)^-$
B	303.2	- 69.0	1179		$(\text{SPFCl})^-$
C	102	- 32.5	1401		PF_3
D	n.o.	- 37.7	1376		$(\text{PF}_2)_2\text{O}$
E	37.8	- 46.0	1195		$(\text{S})\text{PF}_3$
F	70.3	n.o.	1157		$(\text{S})\text{PF}_2\text{H}$
G	108.2	- 33.4	1314		
H	111.8	-102.4	1299		
J	n.o.	- 38.6	1133		
K	118.2	- 29.2	1271		
L	n.o.	- 36.6	1100		
M	116.8	n.o.	1164		
N	109.2	n.o.	1250		
P	55.1	n.o.	1300		

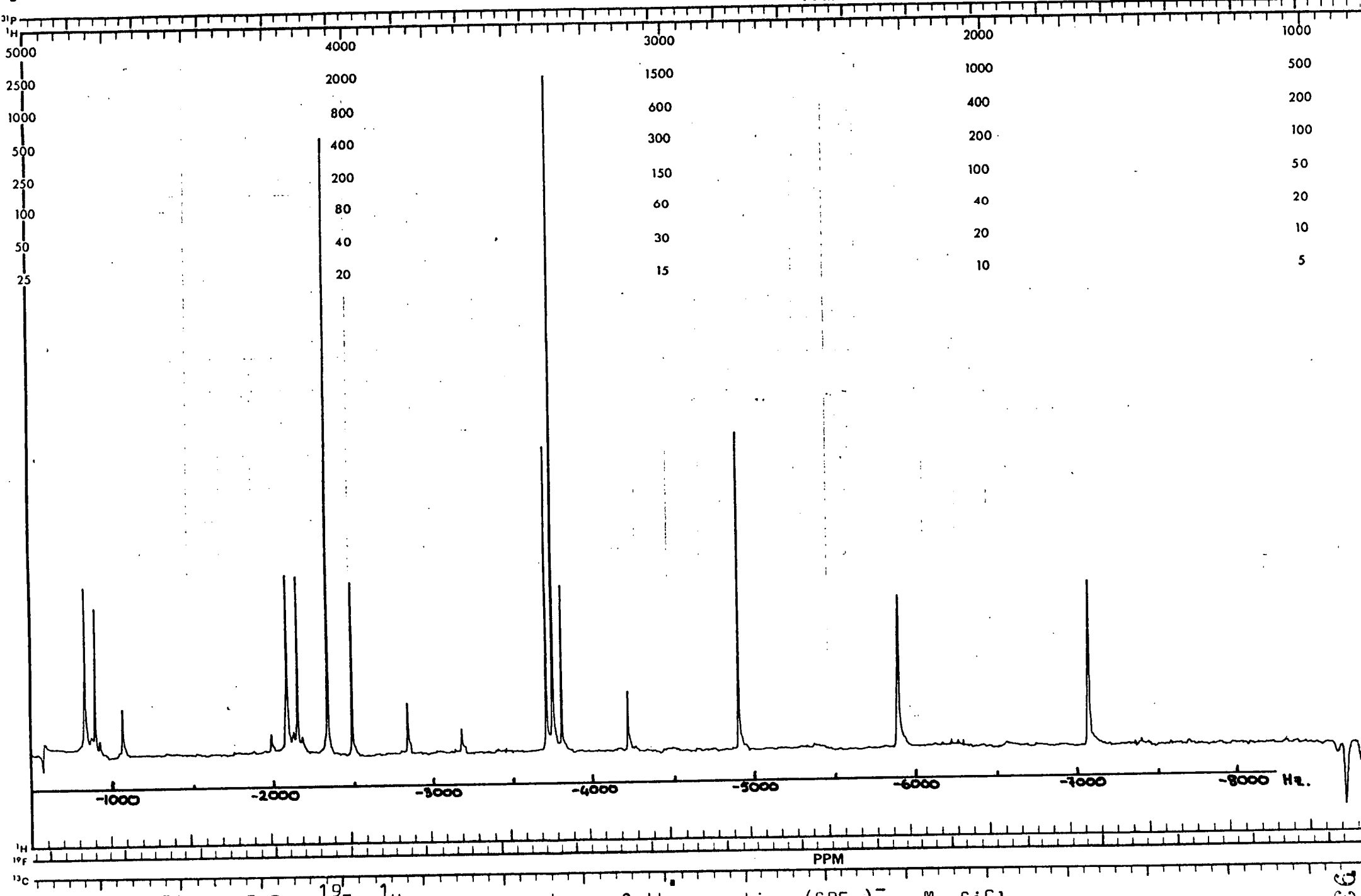
TABLE 5.2.

b) Substrates used in the reactions of $(\text{SPF}_2)^-$ and methylsilyl halides.

	Me_3SiCl	Me_2SiCl_2	$\frac{1}{2}\text{Me}_2\text{SiCl}_2$	Ph_2SiCl_2	$\frac{1}{2}\text{Ph}_2\text{SiCl}_2$	Me_3GeCl
A	P F	P F	P F	F	F	F
B	P F	P F	P F	P F	P F	P F
C	P F	P F	P F	P F	F	P F
D	F	F				
E	F	P F	P F	F	F	F
F	P F	F	F	F	F	
G	F	F	F			
H	P-	P	P			
J					F	
K		P	P			F
L						F
M		P	P			
N	P					
P						P

P- Product observed in ^{31}P n.m.r. spectrum

F- Product observed in ^{19}F n.m.r. spectrum



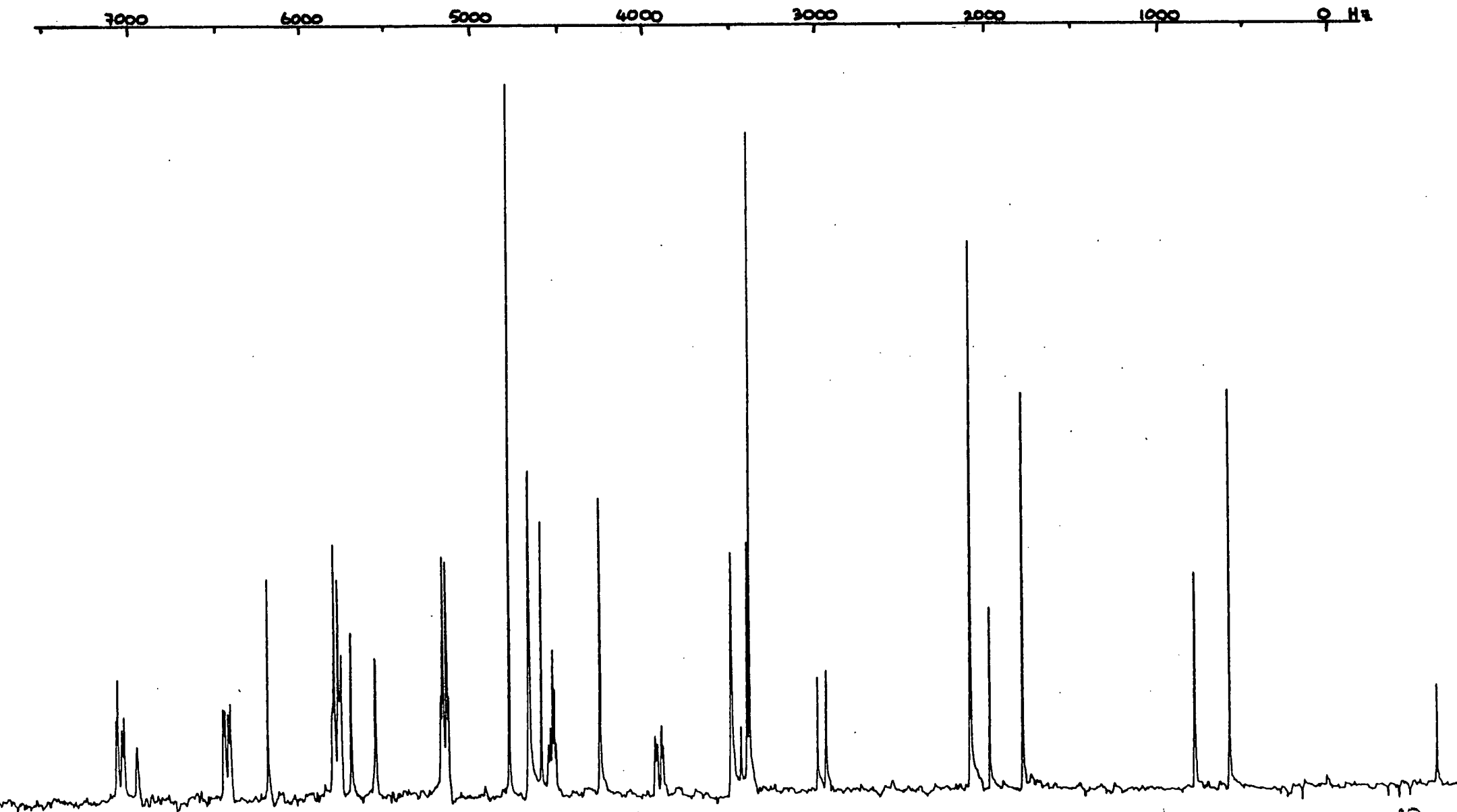
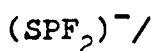


Figure 5.4. N.m.r. spectrum of the reaction $(\text{SPF}_2)^- + \text{Me}_3\text{SiCl}$.

smaller coupling constants (1100 - 1200Hz) could be pentavalent (S)PF₂- compounds. However, the major products in the reactions appeared to be the (SPFX)⁻ ion observed as a doublet (¹J_{PF} ~ 1180Hz) at δP ~ 305ppm, and the as yet unidentified second order spectrum at δP ~ 139ppm. It seemed that the spectrum as seen was incomplete. It was suggested that the large doublet coupling (J = 628Hz) was a directly bonded phosphorus-phosphorus coupling. The phosphorus spectrum was recorded on a very wide spectral width, and a second order pattern was observed at δP = -109ppm, shown in figure 5.5. This was a pair of quintets of doublets flanking a complex pattern of lines. The separation between the sets of quintets was 620Hz, the quintet splitting 65Hz and the small doublet splitting about 15Hz. The patterns observed are similar to those described (17) by Hutchinson for RP(PF₂)₂ species, and the species has been tentatively identified as the anion ((S)P(PF₂(S)₂)⁻. The value of ¹J_{PP} = 628Hz is one of the largest reported, and from the chemical shift of the difluorophosphino groups they are presumed to be in the pentavalent oxidation state. No other groups can be identified as being bound to the central phosphorus atom, but the presence of groups such as Me₃Si- or Me₃SiS- cannot be eliminated. The only route that has been suggested for the formation involves the sequential reaction of (SPF₂)⁻ with the silyl compound, forming (SPFCl)⁻, then attack by (SPF₂)⁻, and repeating the process.

The reaction scheme is summarised in equations (3) to (6).



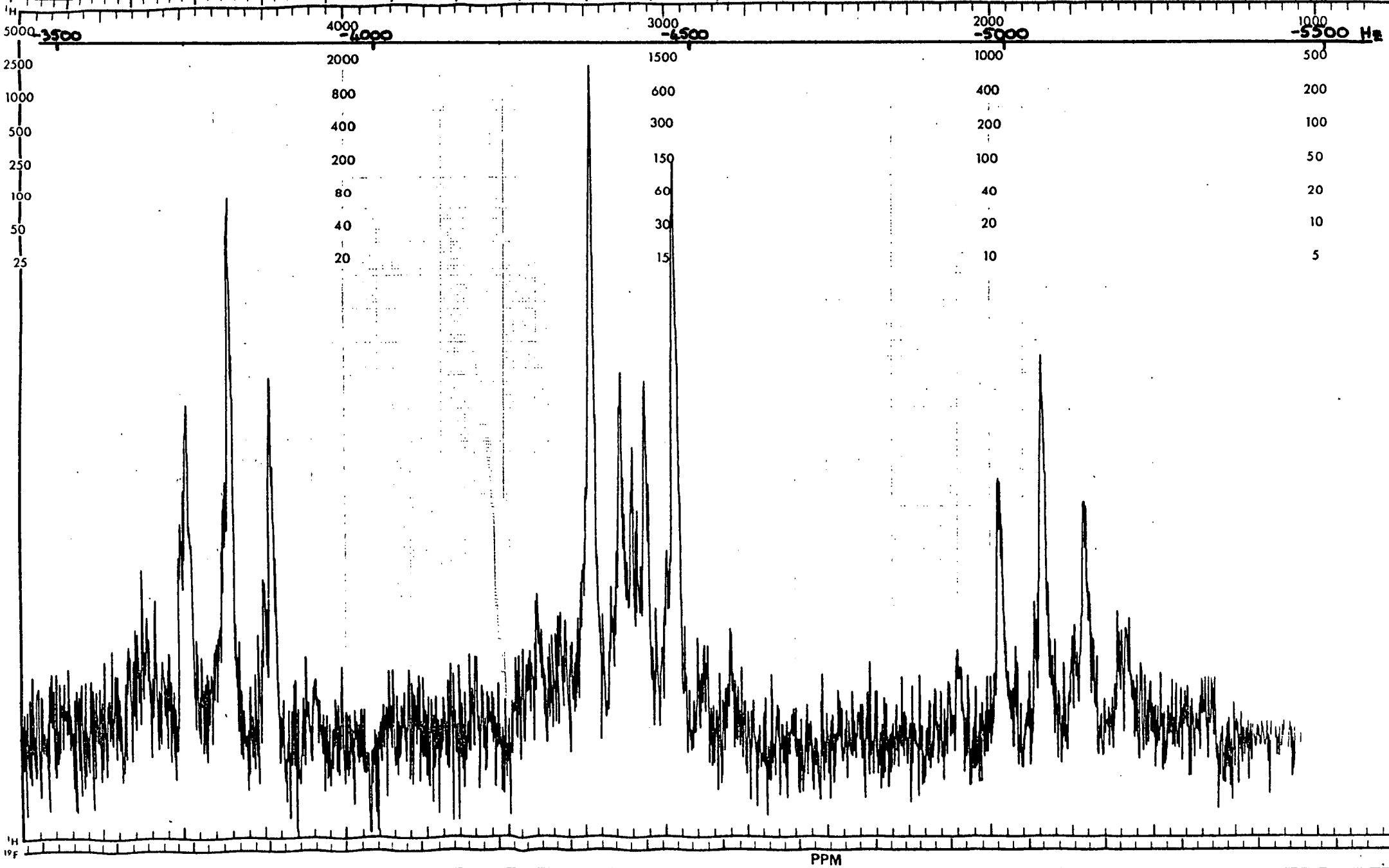
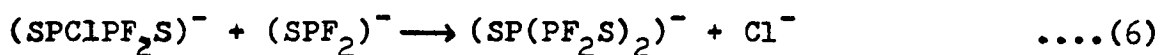
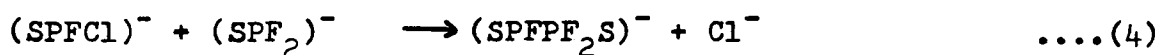
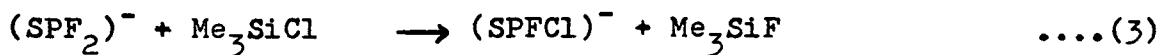
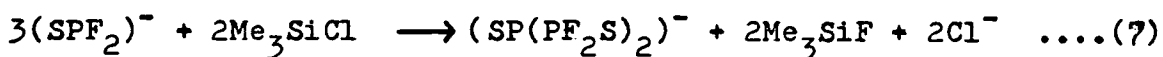


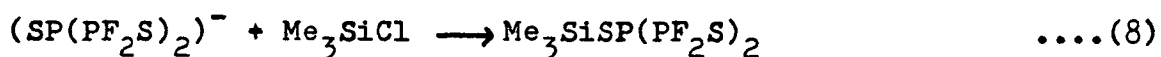
Figure 5.5. Very low frequency end of ^{31}P n.m.r. spectrum of $(\text{SP}(\text{PF}_2(\text{S}))_2)_2$



Overall:



The ion could then react with a third molecule of substrate to form the silyl species $\text{Me}_3\text{SiSP}(\text{PF}_2\text{S})_2$ as in equation (8).



With so many different processes occurring in these systems, it is not possible to ensure that the reaction will follow the intended pathway. Therefore these reactions of the thiofluorophosphine anion with the group IV alkyl halides were not pursued further, as the prospect of developing the reaction to a valid preparative method seemed very remote indeed.

5.4. Reactions of SPF_2^- with chlorophosphines.

The two reactions studies used dimethylchlorophosphine and diphenylchlorophosphine. The point of interest with these reactions was the oxidation state of the phosphorus atoms in the final products, and the location of the sulphur. The three types of products which could be formed would all be easily distinguished in the phosphorus n.m.r. spectrum. The species R_2PSPF_2 would show a high δP for the fluorophosphine group ($>200\text{ppm}$) and a low δP for the PR_2 group ($<0\text{ppm}$). A product of the form $(\text{S})\text{PF}_2\text{PR}_2$ would show a low PF_2 shift ($\sim 100\text{ppm}$) and a low PR_2 shift, and also a higher phosphorus-phosphorus

coupling constant ($^1J_{PP} = 200 - 400\text{Hz}$). The third possibility (S) PR_2PF_2 would show a large PF_2 shift and a higher PR_2 shift ($\delta P \sim 0\text{ppm}$). The n.m.r. data from these reactions are summarised in table 5.3.

5.4.1. $(SPF_2)^- + Me_2PCl$.

At 210K, the phosphorus spectrum showed a triplet ($^1J_{PF} = 1260\text{Hz}$) of doublets ($^1J_{PP} = 347\text{Hz}$) centred at $\delta P = 133.6\text{ppm}$. At a chemical shift $\delta P = -39.5\text{ppm}$ a doublet ($^1J_{PP} = 347\text{Hz}$) of triplets ($^2J_{PF} = 17\text{Hz}$) was observed. These parameters identified the product as $(S)PF_2PMe_2$. On allowing the reaction mixture to warm to room temperature, the intensity of the signals decreased, and new signals appeared. A pair of doublets formed an AB type pattern, the high frequency doublet at $\delta P = 37.6\text{ppm}$, separated by 221Hz, and the low frequency doublet at $\delta P = -56.2\text{ppm}$, with the same separation. A singlet was observed at $\delta P = 5.0\text{ppm}$. With proton coupling retained the peaks of the doublets broadened and could not be resolved. The single peak split into a doublet ($^1J_{PH} = 450\text{Hz}$) of septets ($^2J_{PH} = 14.1\text{Hz}$), and these parameters are consistent with the pentavalent thiophosphine $(S)PMe_2H$. The AB pattern is consistent with the biphosphine $(S)PMe_2PMe_2$, and the recorded parameters for both species are in agreement with reported data (131, 132).

The mechanism for the formation of these products is not clear, but it is possible that they arise from the decomposition of the mixed fluorophosphine-alkyl phosphine. The migration of sulphur and selenium from the fluorophosphine group to the more basic alkylphosphine group is a well known process, and it could be fast under these conditions. In the fluorine n.m.r. spectrum

TABLE 5.3.

N.m.r. parameters of products observed in the reactions between

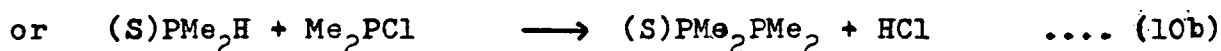
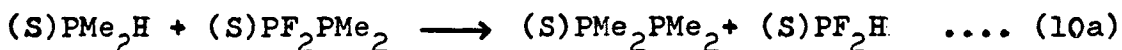
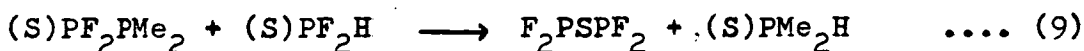
SPF_2^- and $\text{P}'\text{R}_2\text{Cl}$.

	($\text{SPF}_2\text{P}'\text{Me}_2$)	($\text{SPF}_2\text{P}'\text{Ph}_2$)	($\text{SP}'\text{Me}_2\text{H}$)	($\text{SP}'\text{Ph}_2\text{H}$)	($\text{SPMe}_2\text{P}'\text{Me}_2$)	($\text{SPPh}_2\text{P}'\text{Ph}_2$)
SP	133.6	115.5	-	-	- 56.2	- 13.8
SP'	- 39.5	- 4.6	5.0	22.0	37.6	45.5
SF	- 37.8	- 36.2	-	-	-	-
$^1\text{J}_{\text{PF}}$	1260	1277	-	-	-	-
$^1\text{J}_{\text{PP}'}$	347	369	-	-	221	254
$^1\text{J}_{\text{P}'\text{H}}$	-	-	450	474	n.r.	n.r.
$^2\text{J}_{\text{P}'\text{F}}$	17	19.5	-	-	-	-
$^2\text{J}_{\text{P}'\text{H}}$	n.o.	-	14	-	n.r.	-

n.o. not observed

n.r. not resolved

at 210K the product is observed as a doublet ($^1J_{PF} = 1260\text{Hz}$) of doublets ($^2J_{PF} = 17\text{Hz}$) centred at $\delta F = -37.8\text{ppm}$. A small amount of PF_3 was observed, and some unreacted $(S)\text{PF}_2\text{H}$. A possible mechanism would involve the rearrangement of the biphosphine $(S)\text{PF}_2\text{PR}_2$, with sulphur migration, to form $(S)\text{PR}_2\text{PR}_2$ and PF_2SPF_2 as in equations (9) and (10) but there is no direct evidence to favour any particular mechanism.



5.4.2. $(\text{SPF}_2)^- + \text{Ph}_2\text{PCl}$.

In deuteriochloroform at 210K, a similar reaction was observed between $(\text{SPF}_2)^-$ and chlorodiphenylphosphine. The phosphorus spectrum consisted of a triplet ($^1J_{PF} = 1277\text{Hz}$) of doublets ($^1J_{PP} = 369\text{Hz}$) centred at $\delta P = 115.5\text{ppm}$, with a doublet ($^1J_{PP} = 369\text{Hz}$) of triplets ($^2J_{PF} = 19.5\text{Hz}$) centred at $\delta P = -4.6\text{ppm}$. These peaks were assigned to $(S)\text{PF}_2\text{PPh}_2$. The fluorine spectrum consisted of a doublet ($^1J_{PF} = 1277\text{Hz}$) of doublets ($^1J_{PF} = 195\text{Hz}$) centred at $\delta F = -36.2\text{ppm}$. As the tube was warmed to room temperature, an AB pattern was observed, the high frequency doublet ($^1J_{PP} = 254\text{Hz}$) at $\delta P = 45.5\text{ppm}$ and the low frequency doublet at $\delta P = -13.8\text{ppm}$ with the same separation. This was assigned to $(S)\text{PPh}_2\text{PPh}_2$. A single peak at $\delta P = 22.0\text{ppm}$ which split into a doublet ($^1J_{PH} = 474\text{Hz}$) of unresolved multiplets when proton coupling was retained was assigned to $(S)\text{PPh}_2\text{H}$. Despite careful variable temperature experiments, no intermediates in the decomposition of the original biphosphine product could be identified.

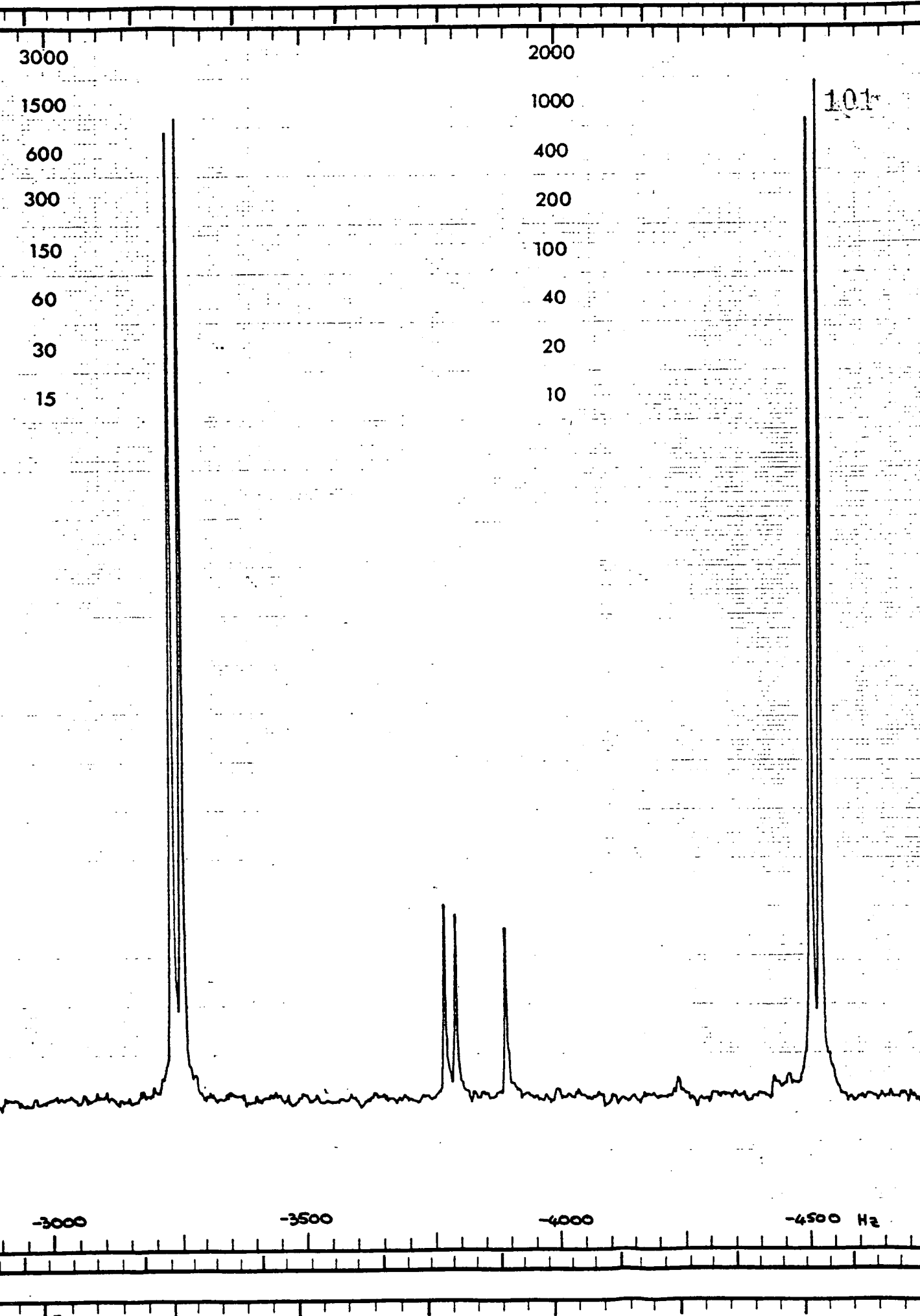


Figure 5.6. ^{19}F - $\{^1\text{H}\}$ n.m.r. spectrum of $(\text{SF}_2)\text{PMe}_2$

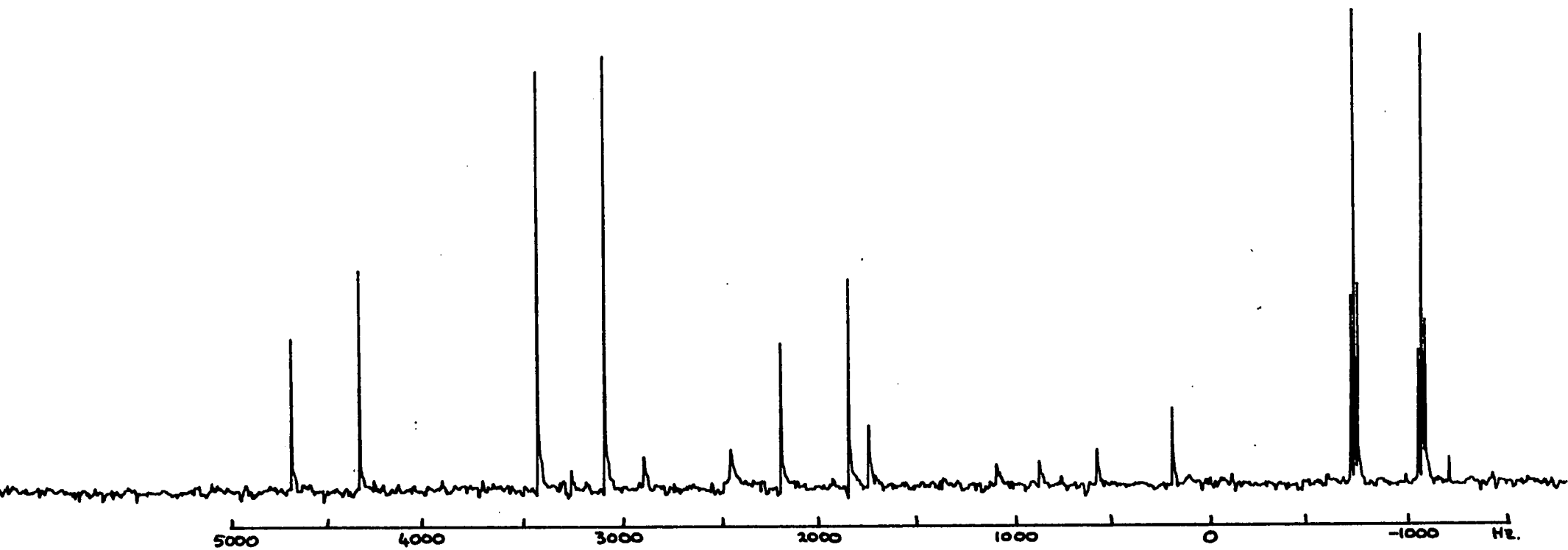


Figure 5.7. $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of $(S)\text{PF}_2\text{PMe}_2$.

In the reaction mixture at room temperature, the relative intensities of the alkyl phosphine peaks and fluorophosphine peaks in the phosphorus spectrum suggested that the major part of the phosphorus was as alkyl phosphine, with only a small quantity of PF_3 and $(\text{S})\text{PF}_2\text{H}$ present. In fact this can be explained by the different sensitivities of the different types of phosphorus nuclei, arising from different relaxation times. Therefore, although the apparent proportion of fluorophosphine as observed in the phosphorus spectrum is very small, the true PF_2 concentration is of the same order as the alkyl phosphine concentration, in the form of $(\text{S})\text{PF}_2\text{H}$ and PF_3 .

5.4.3. $(\text{SPF}_2)^- + \text{PF}_2\text{X}$ (X = Cl, Br)

The reactions were carried out in deuteriochloroform at 210K, and the phosphorus spectrum showed no evidence for the expected products $(\text{PF}_2)_2\text{S}$. The unreacted halodifluorophosphines were observed at the relevant phosphorus chemical shifts, and the ionic species was also observed. On warming to room temperature the peaks attributed to the anion decayed, to be replaced by peaks assigned to PF_3 , but PF_2X species did not react.

5.5. Conclusions.

The foregoing series of experiments highlighted the difficulty of handling highly reactive species with conventional techniques. The results suggest that the ionic conditions in the solutions were too severe for the reactants and products. Consequently many side reactions were observed, leading to unexpected products, and aiding the decomposition of the expected products. Despite this, the experiments proved a useful exercise and brought up

one or two interesting points.

The first interesting point is the description of the oxidation state of the phosphorus atom in the anions, which has already been discussed. The second point to consider is the extent of halogen exchange which is observed in the silyl systems. While this process is well known in simple silyl systems (89, 133) it was not expected under these conditions. Halogen exchange must therefore be an important factor when discussing attempts to prepare silyl-fluorophosphine derivatives. It may well be that the trifluorosilyl-fluorophosphine compounds are more stable than their simple silyl counterparts.

The third, and probably most important point to consider, is the oxidation states of the products formed during the course of these reactions. The group IV fluorophosphines were observed to have an M-S-P backbone, with a trivalent phosphorus atom, whereas the alkyl phosphine-fluorophosphines formed a P-P bond, with the fluorophosphine group being pentavalent. This contrasts with evidence that it is the tendency of the more basic alkyl phosphines to become pentavalent, with transfer of the sulphur (or selenium) atom (60, 134). It may be that such a process is occurring on an inter- or intra-molecular basis, causing coalescence of the phosphorus n.m.r. spectrum as the reaction mixture approached room temperature, and at high temperatures a similar effect might be observed in the spectrum of the $(S)PR_2PR_2$ species observed at room temperature, as observed by Brown (134). However, the spectra show no sign of line broadening, so this does appear unlikely.

An alternative explanation may lie in the structure of the different compounds. The structures of compounds of the form

MH_3SPF_2 have already been discussed, in terms of H...F interactions stabilizing the molecule in five membered ring conformation.

By the same reasoning, alkyl phosphine compounds, if trivalent, would form a six-membered ring and this would also be expected to stabilize the structure. But there might be steric and strain effects caused by the presence of two lone pairs, and the steric interference of the methyl groups. This would be less marked if the molecule had one pentavalent phosphorus atom, yet the orientation would still allow for H...F interactions to complete a five-membered ring. The mixed oxidation state structure would also allow interaction of the trivalent phosphorus lone pair with empty 3d orbitals of the pentavalent phosphorus atom, and allow for the phosphorus-sulphur π system to be extended to the trivalent phosphorus atom.

The reactions described in this chapter were eventually of more interest because of the anomalies that were observed in the results rather than the results themselves. It has been shown in earlier chapters that the type of compounds that were expected to be prepared are accessible by less severe reactions, and the use of anions as synthetic intermediates was not a viable proposition. It would however be a worthwhile exercise to study the systems and try and explain their anomalous behaviour.

In particular the triphosphine species is a suitable product for further investigation. This would complement recent work by Hutchison (17) and Hunter (23) concerning multifunctional fluorophosphine compounds such as $\text{GeH}_3\text{P}(\text{PF}_2)_2$ and $\text{OP}(\text{OPF}_2)_3$. A similar mechanism was observed by Bett (135) in the reaction of trisilylborate $(\text{SiH}_3\text{O})_3\text{B}$ and bromodifluorophosphine,

leading to the formation of $(F_2PO)_2PF$. These compounds will be of particular interest in the continuing research into multi-dentate ligands for transition metals.

CHAPTER 66.1. General

All volatile compounds were handled on a glass vacuum line fitted with Sovirel greaseless taps and ground glass joints. A rotary oil pump in series with a mercury diffusion pump pulled a vacuum of 10^{-3} torr, monitored by a Pirani gauge. Pressures in the line were measured with a spiral gauge balanced against a mercury monometer. Quantities of materials were measured in a calibrated section of the vacuum line.

Volatile compounds were purified by trap-to-trap distillation using acetone/solid CO_2 (195K) or solvent/liquid nitrogen slush baths (chlorobenzene 227K, chloroform 209K, toluene 177K, diethylether 153K). An initial assessment of the purity of a compound was made on the basis of its infra-red spectrum. Having obtained a satisfactory infra-red analysis, with any major impurities reduced to a low concentration in the spectrum, the molecular weight was determined, and the product was acceptable if this was within 2-3% of the calculated value. In most cases, the compound would also be checked for nuclear magnetic resonance spectroscopic purity, an important factor when the product was intended for use in small scale reactions to be studied by n.m.r. spectroscopy. When a high degree of purity was required, such as the sample required for electron diffraction, the vapour pressure was also determined and the sample treated until the measurements were consistent to within 0.5 torr.

Solvents for n.m.r. spectroscopy were obtained commercially, degassed and stored over molecular sieves in ampoules fitted with

with Sovirel greaseless taps. Other products were stored in sealed ampoules at 77K when not in use.

6.2. Instrumentation.

Infra-red spectra were recorded in the range $4000-200\text{cm}^{-1}$ using a Perkin Elmer 577 grating spectrometer, using a 10cm gas cell with caesium iodide end plates. Raman spectra were obtained using a Cary 83 spectrometer, with 488nm argon-ion excitation. For mass spectra, an AEl MS902 was used with an ionization potential of 70eV. For nuclear magnetic resonance spectra, a number of different instruments were used: JEOL FX 60 (^1H , ^{31}P), Varian XL100 (^{31}P , ^{19}F), and Bruker WH360 (^1H , ^{11}B) spectrometers were all used depending on the resolution required. Apart from normal proton noise decoupling, double resonance experiments were not found to be necessary because of the availability of direct observation facilities on the instrumentation. Double resonance experiments would have been of most value if it was required to determine the signs of coupling constants. However, sign determination was not felt to be within the scope of this work, as many of the compounds considered here had already been studied for this purpose.

Most of the quoted n.m.r. parameters were measured from ^{31}P and ^{19}F spectra recorded over a 5000Hz range. The resolution at this spectral width is 1.2Hz, so coupling constants are accurate to about 2.5Hz, and chemical shifts are accurate to about 0.2ppm. ^1H spectra were recorded over a range of 1000Hz, with a resolution at this spectral width of 0.2Hz, and data quoted from these spectra should be accurate to 0.5Hz or 0.2ppm.

Electron Diffraction scattering intensities were recorded using the Cornell University diffraction apparatus now installed at Edinburgh University (49, 136). The apparatus was operated in the conventional convergent beam mode, using a sector designed to give uniform intensity from the centre. The sample and nozzle were maintained at room temperature (293K) during experiments. Photographs were recorded on Kodak Electron Image Plates, at two camera distances, 128mm and 286mm (3 plates at each distance), giving a range of scattering variable s , of $30\text{-}300\text{nm}^{-1}$. The electron wavelength, $5.779\pm 0.003\text{pm}$, was determined from the diffraction pattern of gaseous benzene.

Intensities were converted into digital form using a Jarrell-Ash double beam microphotometer (137) with spinning plates. Calculations were performed on an ICL 2970 using established data reduction (49) and least-squares refinement (138) programmes. In all calculations the complex scattering factors of Schäfer Yates and Bonham (139) were used.

6.3. Reagents.

Reagents were either prepared according to published methods or obtained commercially. Preparative methods have been considered generally in chapter 1, and the specific reactions used throughout this work are listed in table 6.1.

In one or two cases, published methods were found to be unsuitable, giving lower than expected yields of product. Alternative reactions were therefore used for the preparation of (O)PF₂H and (S)PF₂H.

6.3.1./

6.3.1. Preparation of (O)PF₂H.

(O)PF₂H was frequently observed as an impurity in the preparation of PF₂Br, and was attributed to traces of water vapour in the reactants. This tendency to hydrolyse was therefore put to use in the preparation of (O)PF₂H.

In a typical experiment, water (0.5ml) was frozen into a 500ml bulb and the apparatus evacuated. PF₂Br (15mmol) was frozen into the bulb, and the mixture was allowed to warm to room temperature and stand for about one hour. The products were removed from the bulb and separated by trap-to-trap distillation. Excess water was held at 195K, and (O)PF₂H (14.5mmol) was held at 153K. A small amount of PF₃ passed through the 153K trap and was held at 77K, along with HBr (13mmol). Presumably some HBr remained dissolved in the water.

6.3.2. Preparation of (S)PF₂H.

In a method analogous to the above reaction, PF₂Br and H₂S were co-condensed in a bulb, and allowed to react at room temperature. After one hour, the volatile products were removed and separated, and showed only 20% conversion to (S)PF₂H. A more rapid reaction was observed between (PF₂)₂S and H₂S. This also has the advantage of converting all the reactants into only one product, thereby simplifying the purification procedure. Typically, (PF₂)₂S (10mmol) was condensed in a 250ml bulb with an excess of H₂S (15mmol) and the mixture left at room temperature for about half an hour. The products were passed into a trap held at 177K, through which the excess H₂S passed. (S)PF₂H (19mmol) was recovered from the 177K trap.

6.4. Reactions of $(PF_2)_2S$ with halogens and main group halides.

6.4.1. $(PF_2)_2Y + Cl_2$ (Y = S, Se)

These reactions were performed in both vapour and liquid phases. In the vapour phase, $(PF_2)_2S$ (5mmol) and Cl_2 (5mmol) were frozen into the separate compartments of a double-bulb apparatus of capacities 250ml and 50ml respectively. The reactants were warmed to room temperature before the connecting tap was opened to allow mixing of the the vapours. The yellow colour of the chlorine disappeared within 2-3 minutes of mixing, when the volatile compounds were removed and separated by trap-to-trap distillation. $(S)PF_2Cl$ (5mmol) was held in a trap at 153K, and PF_2Cl (5mmol) passed through this trap and was collected at 77K.

Alternatively, $(PF_2)_2S$ (2.5mmol) and Cl_2 (3.0mmol) were condensed into a 250ml bulb and the mixture allowed to warm to room temperature. After 2-3 minutes the volatile products were removed and fractionated. $(S)PF_2Cl$ (3.0mmol) was recovered at 153K, and PF_2Cl (2.0mmol) recovered at 77K. On examination of the ^{31}P n.m.r. spectrum of the less volatile product, a weak triplet ($^1J_{PF} = 1048Hz$) was observed at $SP = -9.8ppm$, in addition to the signal from $(S)PF_2Cl$ (triplet $^1J_{PF} = 1220Hz$, $SP = 50.5ppm$). The intensities of the two signals were in the ratio of about 1:5, and this indicates that some 20% of the PF_2Cl has been oxidised to PF_2Cl_3 by the excess chlorine present in the reaction mixture.

The reactions were performed using $(PF_2)_2Se$, on approximately the same scale and using the same technique. On mixing the vapurs, a red solid was deposited on the walls of the

bulb, and PF_2Cl was recovered as the only volatile product, with some PF_3 impurity also observed.

6.4.2. $(\text{PF}_2)_2\text{S} + \text{R}_3\text{SiX}$

Six reactions were performed in sealed n.m.r. tubes using as substrates trimethyl-chloro- and bromo-silane, monomethyl-chlorosilane, and silyl chloride, bromide and iodide. Typically, equimolar quantities (0.2mmol) of $(\text{PF}_2)_2\text{S}$ and R_3SiX were condensed in a 5mm n.m.r. tube along with spectroscopic grade toluene and deuterotoluene as solvent. The tube was sealed under vacuum and kept at 77K until it was possible to record the n.m.r. spectra of the reaction mixtures.

The reaction between $(\text{PF}_2)_2\text{S}$ and SiH_3Br was also performed on a preparative scale. $(\text{PF}_2)_2\text{S}$ (1mmol) and SiH_3Br (1mmol) were condensed into a 250ml bulb and the mixture allowed to warm to room temperature. The volatile products were removed after 2-3 minutes and a sample (0.2mmol) sealed into an n.m.r. tube with toluene and deuterotoluene as solvent. The ^{31}P n.m.r. spectrum showed only a trace of SiH_3SPF_2 which decomposed, so the products were discarded.

6.4.3. $(\text{PF}_2)_2\text{S} + \text{R}_3\text{GeX}$

The substrates used were monomethylchlorogermane, germyl chloride and germyl iodide. $(\text{PF}_2)_2\text{S}$ (0.2mmol) and R_3GeX (0.2mmol) were condensed in an n.m.r. tube with toluene and deuterotoluene as solvent. The reactions were monitored by ^{31}P n.m.r. spectroscopy.

6.5./

6.5. Preparation and Reactions of GeH_3SPF_2 .

6.5.1. Preparation of GeH_3SPF_2 .

Chlorogermane (5.0mmol) was condensed with $(\text{PF}_2)_2\text{S}$ (5.5mmol) in a dry glass bulb (250ml), and the reagents were then warmed to 209K for 2 hours. The volatile products were examined by n.m.r. spectroscopy to ascertain the extent of reaction and the exact amount of GeH_3Cl required to convert the remaining $(\text{PF}_2)_2\text{S}$ was added. In this way allowance could be made for imbalance of quantities of the reagents, caused by slight impurities, reaction with surface moisture etc. Products were separated by fractional condensation, and difluoro(germylthio)-phosphine (4.8mmol, 87% yield) was collected at 209K. (M.wt 180.6 (Calc 178.7); v.p. (273K) 31.5mm; m.pt 199K). The other major product was PF_2Cl (5.0mmol), with traces of $(\text{S})\text{PF}_2\text{H}$, GeH_4 and GeH_3Cl .

6.5.2. Reaction with HCl.

GeH_3SPF_2 (2.5mmol) and HCl (2.5mmol) were condensed into a glass bulb (250ml) and warmed to room temperature for 5 minutes. The products were separated by fractional condensation yielding GeH_3Cl (2.5mmol) and $(\text{S})\text{PF}_2\text{H}$ (2.5mmol), identified by i.r. and n.m.r. spectroscopy.

6.5.3. Reactions with HBr, Cl_2 and PPh_2Cl .

In each case 0.2mmol of each reagent was taken and they were allowed to mix in CDCl_3 (0.5ml) at room temperature. The reactions were monitored by ^1H , ^{19}F and ^{31}P n.m.r. spectroscopy.

6.5.4. Reactions with B_2H_6 .

GeH_3SPF_2 (0.4mmol) and B_2H_6 (0.2mmol) were condensed in an n.m.r. tube with $CDCl_3$ (0.5ml) as solvent. N.m.r. spectra were recorded at 273K. In a second reaction GeH_3SPF_2 (0.8mmol) was condensed in a glass ampoule with B_2H_6 (1.1mmol), without a solvent. After warming to 195K for 5 minutes excess B_2H_6 (0.7mmol) containing a trace of GeH_4 , was removed. The combining ratio $GeH_3SPF_2 : B_2H_6 = 2:1$ was thus established.

6.5.5. Reaction with $Mo(CO)_4(C_7H_8)$.

GeH_3SPF_2 (0.4mmol) was added to an n.m.r. tube containing $Mo(CO)_4(C_7H_8)$ (0.060g, 0.2mmol) in $CDCl_3$, and the solution was warmed to room temperature before ^{31}P , ^{19}F and 1H n.m.r. spectra were recorded.

6.5.6. Reactions with platinum complexes.

The platinum complexes used as substrates were : trans- $PtCl_2(PEt_3)_2$, trans- $PtHCl(PEt_3)_2$, trans- $PtI_2(PEt_3)_2$, and $PtH(PEt_3)_3BPh_4$. In each case the platinum complex (0.2mmol) was weighed and dissolved in $CDCl_3$ or CD_2Cl_2 in an n.m.r. tube, and GeH_3SPF_2 (0.2mmol) was added. The progress of reactions was monitored by ^{31}P n.m.r. spectroscopy. When reactions were complete ^{19}F spectra were also recorded.

6.6. Preparation and reactions of $(YPF_2)^-$ ions (Y = O, S, Se).

6.6.1. Reaction of $(Y)PF_2H$ with trimethylamine

The reactions were performed in sealed n.m.r. tubes using $CDCl_3$ or CD_2Cl_2 as a solvent. $(Y)PF_2H$ (0.2mmol) and Me_3N (0.2mmol)

were condensed into the tube with solvent and kept at 77K, until spectra were recorded at 220K.

6.6.2. Reactions of $(YPF_2)^-$ with group IV and group V halides.

The reactions were carried out in sealed n.m.r. tubes at 195K. The substrates have been listed in table 5.2. In a typical experiment, $(Y)PF_2H$ (0.2mmol) and Me_3N (0.2mmol) were condensed in an n.m.r. tube along with $CDCl_3$ as the solvent. The mixture was then allowed to stand at 195K for about 10 minutes to ensure the formation of the anion. The silyl substrate was then condensed into the mixture and the tube sealed. Spectra were recorded at 210K.

TABLE 6.1.

Methods of preparation of some common starting material.

Reagent	Method	Reference
PCl_2NMe_2	$\text{PCl}_3 + 2\text{HNMe}_2$	35
PF_2NMe_2	$\text{PCl}_2\text{NMe}_2 + \text{NaF}$	35
PF_2X (X = Cl, Br, I)	$\text{PF}_2\text{NMe}_2 + 2\text{HX}$	35
$(\text{Bu}_3\text{Sn})_2\text{S}$	$2\text{Bu}_3\text{SnCl} + \text{Na}_2\text{S}$	38
$(\text{Bu}_3\text{Sn})_2\text{Se}$	$2\text{Bu}_3\text{SnCl} + \text{NMe}_3 + \text{H}_2\text{Se}$	38
$(\text{PF}_2)_2\text{Y}$ (Y = S, Se)	$(\text{Bu}_3\text{Sn})_2\text{Y} + 2\text{PF}_2\text{Br}$	38
$(\text{O})\text{PF}_2\text{H}$	$\text{PF}_2\text{Br} + \text{H}_2\text{O}$	This work
$(\text{S})\text{PF}_2\text{H}$	$(\text{PF}_2)_2\text{S} + \text{H}_2\text{S}$	This work
GeH_3Cl	$\text{GeH}_4 + \text{SnCl}_4$	140
$\text{C}_7\text{H}_8\text{Mo}(\text{CO})_4$	$\text{Mo}(\text{CO})_6 + \text{C}_7\text{H}_8$ in THF	141
B_2H_6	$\text{KBH}_4 + \text{H}_3\text{PO}_4$	142

TABLE 6.2.

Standard Reference Compounds for n.m.r. spectroscopy.

Nucleus	Compounds	Resonance Frequency (MHz)
^1H	$(\text{CH}_3)_4\text{Si}$	59.7 (FX60)
		100.1 (XL100)
		360.0 (WH360)
^{11}B	$(\text{CH}_3\text{O})_3\text{B}$	115.5 (WH360)
^{19}F	Cl_3CF	94.1 (XL100)
^{31}P	H_3PO_4 (85%)	24.2 (FX60)
		40.5 (XL100)

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

The work described in this thesis has provided considerable cause for thought. The bulk of the chemistry has involved the biphosphine bis(difluorophosphino)sulphide, whose reactions eventually led to the preparation and characterisation of the new compound difluoro(monogermylthio)phosphine. The suitability of these compounds for the preparation of related fluorophosphines has been shown. On the other hand, the reactions of the difluorothiophosphoryl anion were shown to be poor routes to new compounds.

The behavior of $(PF_2)_2S$ was not unexpected, and a significant amount of work has been done (18, 23) with a view to the preparation of multidentate fluorophosphine derivatives of polyfunctional alcohols. This could be extended to include fluorophosphine derivatives of organic acids which would possibly be fluxional molecules, with the fluorophosphine group undergoing intramolecular transfer from one oxygen to the other. An interesting molecule for study would be $RCOS(PF_2)$, to determine whether the fluorophosphine group would bind preferentially to the oxygen or sulphur atom, or similarly $RCONH(PF_2)$. Such systems would make interesting subjects for study using n.m.r. spectroscopy.

The characterisation of GeH_3SPF_2 is almost complete, but there are one or two areas that would benefit from further investigation. Particularly, the crystal structure of the compound would give an indication of any intermolecular interactions present at lower temperatures. Low temperature vibrational spectroscopy would complete the picture.

The uses of GeH_3SPF_2 are twofold. Firstly, it provides a convenient route to germyl ethers and esters, which complements recent work on silyl esters (135). Secondly it offers a potential route to some novel metal compounds, using the donor properties of the phosphorus atom, and the oxidative addition properties of Ge-H bonds towards platinum and indium compounds (143). These possibilities have been discussed in chapter 3.

The ionic nature of the (YPF_2) species proved to be unsuited for the simple preparation of fluorophosphine compounds. However, the experiments were not entirely fruitless as they did throw some light on the behavior of such species, and showed that there is scope for further investigation of the systems, for example, the route to the formation of the $((\text{S})\text{PF}_2)_2\text{PS}^-$ ion, and the identity of some of the other compounds. Perhaps the answer lies in using different substrates, as most of the problem seemed to be the ease of formation of silicon - fluorine compounds with the resulting breakdown of the fluorophosphine compounds.

Most of the proposals for future work have been outlined in the text, and they are generally under investigation at present. Three areas which are likely to be of most interest are the preparation of mixed alkylphosphine - fluorophosphine compounds for use as multidentate ligands, the use of GeH_3SPF_2 to prepare mixed metal complexes, and the continuing spectroscopic and structural analyses of fluorophosphine compounds. In particular, the reaction between GeH_3SPF_2 and silyl iodide could result in exchange of the silyl and germyl groups, and this would be the most promising way of isolating SiH_3SPF_2 . The reaction between $(\text{PF}_2)_2\text{S}$ or GeH_3SPF_2 with dichlorophosphines would appear to be a suitable method of preparing alkyl phosphine-bis(difluorophosphine)

compounds. Such experiments will undoubtedly be performed in the near future.

The main successes of this work have been the confirmation of the usefulness of $(PF_2)_2S$ as a synthetic intermediate, and the isolation and characterisation of GeH_3SPF_2 . The predictions of Arnold concerning the structure of GeH_3SPF_2 have been confirmed, and it has been shown that n.m.r. spectroscopy is a valuable and accurate investigative technique. However, the limitation of n.m.r. spectroscopy is clear when more than three or four compounds are present in the system, and peaks become difficult to assign. The lack of positive results from the reactions involving the fluorophosphine anions was a disappointment, and perhaps a different approach will be required to unravel these confused systems. There are, however, many other aspects of the subject to be investigated, and with instrumentation and techniques continually being improved, some of the results that have eluded this work will be easier to obtain in the future.

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The Preparation, Properties and Gas-Phase Molecular Structure of Difluoro(germylthio)phosphine

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Difluoro(germylthio)phosphine, $\text{PF}_2(\text{SGeH}_3)$, has been prepared by the reaction of $\text{S}(\text{PF}_2)_2$ with GeH_3Cl , and has been characterised by i.r., Raman, n.m.r. and mass spectroscopy. Cleavage reactions with Cl_2 and HBr , donor reactions of the phosphorus atom and exchange reactions with platinum complexes have been studied. The molecular structure of $\text{PF}_2(\text{SGeH}_3)$ in the gas phase has been determined by electron diffraction. Principal parameters (r_a) are: $r(\text{Ge—S})$ 225.6 (4) pm; $r(\text{P—S})$ 211.5 (8) pm; $r(\text{P—F})$ 159.0 (9) pm; $\angle(\text{GeSP})$ 99.0 (6)°; $\angle(\text{SPF})$ 99.9 (4)°; $\angle(\text{FPF})$ 97.0 (10)°. The conformation adopted is such that there are short non-bonded $\text{F}\cdots\text{H}$ contacts, with the PF_2 group twisted 18° from the position in which the FPF angle bisector eclipses the Ge—S bond.

[Keywords: B-11 NMR; Difluoro(germylthio)phosphine; Electron diffraction, $\text{PF}_2(\text{SGeH}_3)$; F-19 NMR; Germylthiophosphine, difluoro-; Molecular structure, $\text{PF}_2(\text{SGeH}_3)$; Phosphine, difluoro(germylthio)-; P-31 NMR]

Difluor(germylthio)phosphin. Darstellung, Eigenschaften und Molekülstruktur in der Gasphase

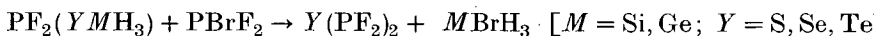
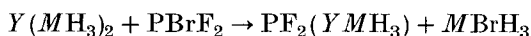
$\text{PF}_2(\text{SGeH}_3)$ wurde über die Reaktion von $\text{S}(\text{PF}_2)_2$ mit GeH_3Cl dargestellt und mittels IR, Raman, NMR und MS charakterisiert. Es wurden Spaltungsreaktionen mit Cl_2 und HBr , Donor-Reaktionen des Phosphor und Austauschreaktionen mit Platinkomplexen untersucht. Die Molekülstruktur von $\text{PF}_2(\text{SGeH}_3)$ in der Gasphase wurde mittels Elektronendiffraktion bestimmt. Die Hauptparameter (r_a) sind: $r(\text{Ge—S})$ 225,6 (4) pm; $r(\text{P—S})$ 211,5 (8) pm; $r(\text{P—F})$ 159,0 (9) pm; $\angle(\text{GeSP})$ 99,0 (6)°; $\angle(\text{SPF})$ 99,9 (4)°; $\angle(\text{FPF})$ 97,0 (10)°.

Introduction

Although compounds with two or more silyl¹, germyl² or difluorophosphino³ groups bound to a single atom have been known for many years, it is only relatively recently that the first compounds containing

a difluorophosphino group and a silyl or germyl group bound to a common atom have been reported⁴. Such species are of particular interest for three reasons. In the first place, if delocalisation of lone pairs of electrons on the central atom into vacant d orbitals on neighbouring atoms takes place, there may be expected to be competition between phosphorus and the group IV atoms for the available electrons, which will be reflected in the spectroscopic and structural properties of the compounds. Secondly, the conformations adopted by the molecules are important, and it seems that the most favourable arrangements are stabilised by weak H...F contacts⁴. Finally, they have potential as reagents for bridging between metal atoms in complexes, as substituted fluorophosphines are well known as electron pair donors⁵, behaving generally in a similar way to carbon monoxide, whereas silyl and germyl compounds readily undergo oxidative addition reactions to coordinatively unsaturated systems such as square-planar four-coordinate platinum(II)⁶ or iridium(I)⁷.

So far, the only reports of mixed difluorophosphino—silyl or germyl compounds being isolated have concerned amines^{4,8,9}. No similar mixed-substituent oxides have been reported, although the parent symmetrical oxides are well known¹⁻³. The only stable mixed derivative of second row elements to have been isolated is 1,1-difluoro-2,2-digermyl-biphosphine¹⁰. A study of the exchange reactions of disilyl and digermyl derivatives of sulphur, selenium and tellurium with bromodifluorophosphine¹¹ showed that both silyl or germyl groups could be replaced.



The two substitutions took place simultaneously, and it seemed that it would be impossible to obtain the mixed intermediates without disproportionation occurring. However, we have now studied the reverse exchanges, using $Y(PF_2)_2$ and MH_3Cl , and find that in one case it is possible to obtain the intermediate, free from either of the symmetrical species, and that disproportionation is very slow. We report here the results of our studies of $PF_2(SGeH_3)$.

Results and Discussion

Preparation of $PF_2(SGeH_3)$

When equimolar amounts of $S(PF_2)_2$ and GeH_3Cl were allowed to react together in the liquid phase at room temperature, an exchange reaction took place, yielding $PF_2(SGeH_3)$. Great care was needed to

ensure that the relative quantities of reagents were correct, as the product could not be separated from either $S(PF_2)_2$ or $S(GeH_3)_2$ by trap-to-trap distillation. Similarly, traces of moisture in the vacuum system or of HCl in the GeH_3Cl gave rise to $PF_2H(S)$, which also was inseparable from the desired product.

The observation that the first exchange of GeH_3 for PF_2 went to completion before the second one started was unexpected in view of the results for the reverse process reported earlier¹¹. It would appear that $PF_2(SGeH_3)$ is stable with respect to disproportionation, at least for short periods, but that the two stages of the exchange reaction of $S(GeH_3)_2$ with $PBrF_2$ take place at comparable rates.

Vibrational Spectra

Details of the gas-phase i.r. and liquid-phase *Raman* spectra are given in Table 1. These spectra provide strong evidence for the identity of the compound as there are peaks which may be assigned to stretching, deformation and rocking modes of the GeH_3 group, and others in the regions associated with vibrations of the PF_2 group. In addition there are three strong, polarised bands in the *Raman* spectrum, which we assign to the vibrations of the $PSGe$ skeleton. The highest frequency band of this group is at 508 cm^{-1} , compared with 580 and 444 cm^{-1} for the skeletal stretches of $S(PF_2)_2$ ¹², and 512 cm^{-1} for the P—S stretch in $PF_2(SCH_3)$ ¹³, and so is assigned as the P—S stretch in this case also. The second band, at 425 cm^{-1} , is assigned to be the

Table 1. *Vibrational spectra of $PF_2(SGeH_3)$*

I.r. (gas)	<i>Raman</i> (liquid)	Assignment
2114 s	2110 s, p	$\nu(GeH_3)$
830 } 810 } s, br	868 m, dp } 830 m, dp }	$\nu(PF_2), \delta(GeH_3)$
590 m	600 m, dp	$\rho(GeH_3)$
514 s	508 s, p	$\nu(P-S)$
425 s	422 s, p	$\nu(Ge-S)$
	380 s, p	$\delta, \omega(PF_2)$
	305 w, dp	$\rho(PF_2)$
	116 s, p	$\delta(GeSP)$

s = strong, m = medium, w = weak, br = broad, p = polarised,
dp = depolarised.

Ge—S stretch; equivalent stretches in $S(\text{GeH}_3)_2$ are at 408 and 370 cm^{-1} . The third band, at 116 cm^{-1} , must be the skeletal deformation, which comes at 110 cm^{-1} in $S(\text{GeH}_3)_2$, but the analogous mode in $S(\text{PF}_2)_2$ is at 237 cm^{-1} . There is a band at 125 cm^{-1} in the *Raman* spectrum of the latter compound but it is not polarised, and has been assigned as a torsion of the PF_2 groups.

Table 2. *N.m.r. parameters of $\text{PF}_2(\text{SGeH}_3)$ and some derivatives*

Compound	$\text{PF}_2(\text{SGeH}_3)$	$L \cdot \text{BH}_3'$	$\text{Mo}(\text{CO})_4L_2$
$\delta(^1\text{H})/\text{ppm}$	4.8	5.8	4.9
$\delta(^1\text{H}')/\text{ppm}$		1.0	
$\delta(^{11}\text{B})/\text{ppm}^a$		—60.6	
$\delta(^{19}\text{F})/\text{ppm}^b$	—56.5	—54.1	—15.7
$\delta(^{31}\text{P})/\text{ppm}^c$	233.7	193.9	226.6
$^1J(^{31}\text{P}^{19}\text{F})/\text{Hz}$	1280	1255	1201
$^1J(^{11}\text{B}^1\text{H}')/\text{Hz}$		102.8	
$^1J(^{31}\text{P}^{11}\text{B})/\text{Hz}$		47	
$^2J(^{31}\text{P}^1\text{H}')/\text{Hz}$		16	
$^2J(^{31}\text{P}^{31}\text{P})/\text{Hz}$			45
$^3J(^{31}\text{P}^1\text{H})/\text{Hz}$	12.6	8.7	2.5
$^3J(^{19}\text{F}^1\text{H}')/\text{Hz}$		18.2	
$^3J(^{31}\text{P}^{19}\text{F})/\text{Hz}$			3
$^4J(^{19}\text{F}^1\text{H})/\text{Hz}$	3.4	2.0	<2

^a Relative to $\text{B}(\text{OMe})_3$; ^b relative to CCl_3F ; ^c relative to 85% H_3PO_4 .

N.m.r. Spectra

The ^1H , ^{19}F and ^{31}P spectra of $\text{PF}_2(\text{SGeH}_3)$ provide unequivocal evidence of its identity and purity. In particular, the high ^{31}P chemical shift confirms that it is a phosphorus(III) species and not a phosphorus(V) derivative, $\text{S} = \text{PF}_2(\text{GeH}_3)$. The n.m.r. parameters are listed in Table 2.

Mass Spectrum

Details of the mass spectrum of $\text{PF}_2(\text{SGeH}_3)$ are given in Table 3. The multiplicity of germanium isotopes can make analysis of the spectra of GeH_3 derivatives difficult, but in the present case it appears that the groups of peaks centred at 178 and 109 mass units arose predominantly from ions with three hydrogen atoms, while the group at 158 mass units arose from ions with two hydrogens. Thus sequential loss of hydrogen atoms does not occur to any great extent. Breakdown

of the parent ion can take place by three distinct routes, involving as the initial step elimination of HF, or cleavage of either P—S or Ge—S bonds. The strength of the peak due to PF_2HS^+ suggests that elimination of GeH_2 is also an important process.

Table 3. *Mass spectrum of* $\text{PF}_2(\text{SGeH}_3)$

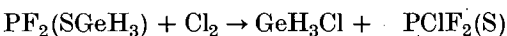
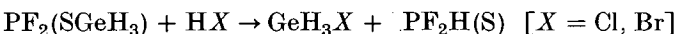
<i>m/e</i>	Relative Abundance	Assignment
178 ^a	20	$[\text{PF}_2(\text{SGeH}_3)]^+$
158 ^a	20	$[\text{PF}(\text{SGeH}_2)]^+$
109 ^a	20	$[\text{GeH}_3\text{S}]^+$
102	100	$[\text{PF}_2\text{HS}]^+$
101	12	$[\text{PF}_2\text{S}]^+$
88	5	$[\text{PF}_3]^+$
82	25	$[\text{PFS}]^+$
69	50	$[\text{PF}_2]^+$
63	25	$[\text{PS}]^+$
50	5	$[\text{PF}]^+$
34	3	$[\text{SH}_2]^+$
32	2	$[\text{S}]^+$
31	2	$[\text{P}]^+$
20	1	$[\text{FH}]^+$

metastable

39.5 weak $[\text{PF}_2\text{S}]^+ \rightarrow \text{F}_2 + [\text{PS}]^+$

Cleavage Reactions of the Ge—S Bond

When HCl, HBr and Cl_2 were allowed to react with $\text{PF}_2(\text{SGeH}_3)$, in each case cleavage of the Ge—S, rather than the P—S, bond took place, with a germanium—halogen bond being formed.



It seemed probable that similar reactions could be used to synthesize compounds containing SPF_2 groups and one such reaction was studied. At room temperature chlorodiphenylphosphine gave $\text{S} = \text{PF}_2\text{PPh}_2$ as the major product, identified by its n.m.r. parameters [δP 114.0, -1.9 ppm, $^1J_{\text{PF}}$ 1,274 Hz, $^2J_{\text{PF}}$ 18.3 Hz, $^1J_{\text{PP}}$ 366 Hz]. A small amount of $\text{S} = \text{PPh}_2\text{PPh}_2$, was also formed [δP 45.1, -13.3 ppm, $^1J_{\text{PP}}$ 254 Hz]: this would seem to indicate that some cleavage of the P—S bond also occurs, giving $\text{PPh}_2(\text{SGeH}_3)$ as an intermediate.

Donor Reactions of PF₂(SGeH₃)

On reaction with diborane, PF₂(SGeH₃) behaved as other fluorophosphines, giving a complex in which the phosphorus atom was the donor. There have been several attempts to relate n.m.r. parameters of borane-phosphine complexes to the base strengths of the phosphines¹³⁻¹⁵, but the empirical relationships between ¹J (³¹P ¹¹B) and dative bond strength are useful only for restricted ranges of similar phosphines¹⁴. The n.m.r. parameters for GeH₃SPF₂·BH₃ (Table 2) show the usual coordination shifts and coupling constants similar to those in related molecules. The ³¹P ¹¹B coupling is clearly resolved, although it is unresolved in F₂PSPF₂·BH₃, with a coupling constant of 47 Hz, compared with 41 Hz in PF₂(SCH₃)¹⁴. This is consistent with the suggestion¹³ that base strength is increased by π-bonding, which is extended in the present case through sulphur to germanium.

A displacement reaction occurred with tetracarbonyl(norbornadiene)molybdenum to form Mo(CO)₄(PF₂SGeH₃)₂, identified by its n.m.r. spectra. These were second order, and proton-decoupled spectra were analysed as arising from an [AX₂]₂ spin system, with very small long-range XX couplings: the n.m.r. parameters are listed in Table 2. The most noticeable feature is the small ³¹P coordination shift (7 ppm) compared with that found for Mo(CO)₄[S(PF₂)₂] (78 ppm)¹².

Reactions with Platinum Complexes

In reactions of PF₂(SGeH₃) with four-coordinate Pt(II) complexes, there are three possibilities. The fluorophosphine may displace another ligand: there may be oxidative addition, with a P—S, a Ge—S, or most likely a Ge—H bond adding across the platinum, perhaps followed by elimination: or there may be an exchange reaction, with an SPF₂ or an SGeH₃ group displacing another ligand.

In the reaction with *trans*-PtCl₂(PEt₃)₂, exchange occurred, giving GeClH₃ and *trans*-PtCl(PEt₃)₂(PF₂S), identified by its n.m.r. parameters¹⁶, with small amounts of two other unidentified platinum complexes. Similarly, *trans*-PtClH(PEt₃)₂ gave GeClH₃ and *trans*-PtH(PEt₃)₂(PF₂S)¹⁶, but on standing at room temperature the platinum product slowly gave PtCl(PEt₃)₂(PF₂S). As GeH₄ was not formed at the same time, it would appear that the solvent, chloroform, must be involved in the reaction. A third PF₂S complex, *trans*-PtI(PEt₃)₂(PF₂S), was also formed by an exchange reaction, with *trans*-PtI₂(PEt₃)₂. With ~~[PtH₂(PEt₃)₃]·[BPh₄]⁻~~, ~~*trans*-PtH(PEt₃)₂(PF₂S)~~ was again formed, together with PEt₃ and GeClH₃. The last product is unexpected, and its formation must involve the solvent, dichloromethane. One possible

mechanism would involve an unstable triethyl(germyl)phosphonium intermediate, which could react with dichloromethane to give chloro-germane.

Molecular Structure

In the refinements of the structure of $\text{PF}_2(\text{SGeH}_3)$ it was assumed that the SGeH_3 group had local C_3 symmetry, and that the SPF_2 group had local C_s symmetry. With these constraints the molecular geometry

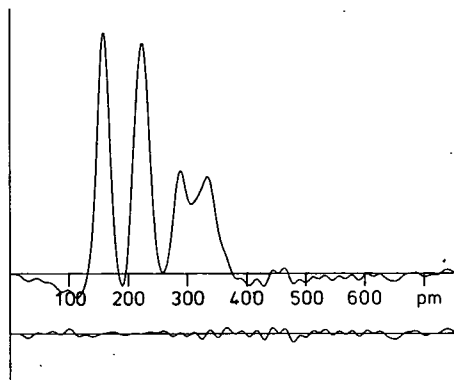


Fig. 1. Radial distribution curve, $P(r)/r$, for $\text{PF}_2(\text{SGeH}_3)$. Before Fourier inversion the data were multiplied by $s \cdot \exp [(-0.00002 s^2)/(Z_P - f_P)(Z_{\text{Ge}} - f_{\text{Ge}})]$

was defined by 10 parameters, chosen to be the P—F, P—S, Ge—S and Ge—H bond lengths, the P—S—Ge, S—Ge—H, F—P—F and F—P—S bond angles, and twist angles, which defined the conformation about the Ge—S and P—S bonds. The Ge—S twist angle was zero when one Ge—H bond was *trans* to the P—S bond, and the P—S twist angle was taken to be zero when the FPF bisector was *trans* to the Ge—S bond. Both twist angles were defined to be positive for a clockwise rotation of the GeH_3 or PF_2 group when viewed from Ge or P towards S.

The radial distribution curve (Fig. 1) shows four strong peaks. The first one includes contributions from two bonded distances, P—F and Ge—H, and although both distances could be refined, only one amplitude could be included. Similarly, the second peak had P—S, Ge—S and F···F components, and again the geometrical parameters dependent on these (the two bonded distances and the FPF angle) could be refined, but with only one amplitude of vibration. The third peak was attributed to just the S···F atom pairs, and the associated

Table 4. *Least squares correlation matrix multiplied by 100*
(only elements greater than 50 are included)

r_1	r_2	r_3	r_4	<1	<2	<3	u_1	u_3	u_6	u_7	k_1	k_2
100												
	100											
		54					61					
			100	81	51		-51					
					-79		61					
			100									
				100	-84		59					
					100		-63					
						100						
							100					
								100				
									100			
										100		
											100	
												63
												100

amplitude of vibration and the SPF angle both therefore refined easily. The final peak had a major contribution from the Ge...P distance, thus defining the GeSP angle, and substantial shoulders arising from the two Ge...F distances. The positions of these two determine the conformation of the PF₂ group, but it was found that there was considerable uncertainty about the amplitudes of vibration which would refine satisfactorily neither separately nor as a single parameter. The optimum values of both amplitudes of vibration and of the PF₂ twist angle were therefore found by comparing *R* factors with these parameters fixed at various values, and they were not subsequently refined.

The least squares correlation matrix (Table 4) shows several substantial correlations between parameters defining the heavy-atom skeleton, as would be expected, given the many overlapping peaks in the radial distribution curve. However, some of the parameters involving hydrogen did not appear to be strongly correlated with other parameters, but were not well determined. Studies of variations of *R* factors with values of some of these parameters showed that the SGeH angle was $110 \pm 3^\circ$, and that the GeH₃ twist angle was $29 \pm 14^\circ$.

The results of the final refinement, for which *R*_G was 0.08, are given in Table 5 and the intensity data and final difference curves are shown in Fig. 2. The bond lengths and angles of the PF₂S group are similar to the corresponding parameters for S(PF₂)₂¹⁷ and PF₂(SCH₃)¹⁸, but the Ge—S distance [225.6 (4) pm] is significantly longer than the equivalent distance in S(GeH₃)₂ [220.9 (4) pm].¹⁹ As the expected Ge—S bond length, based on covalent radii derived from structures of ethane²⁰, dimethylsulphide²¹ and methylgermane²² is 221.3 pm, the present

Table 5. *Molecular parameters for PF₂(SGeH₃)^a*

	Distance/pm	Amplitude/pm
Independent distances		
<i>r</i> 1 P—S	211.5 (8) } 225.6 (4) }	5.6 (8)
<i>r</i> 2 Ge—S		
<i>r</i> 3 P—F	159.0 (9)	5.7 (5)
<i>r</i> 4 Ge—H	153.8 (15)	7.1 (fixed)
Dependent distances		
<i>d</i> 5 F...F	238.3 (14)	6.7 (fixed)
<i>d</i> 6 S...F	285.7 (13)	8.5 (6)
<i>d</i> 7 Ge...P	332.6 (17)	12.5 (9)
<i>d</i> 8 Ge...F	299.5 (18) } 350.6 (16) }	22.3 (fixed)
<i>d</i> 9 Ge...F		
Shortest F...H	271.3 (17)	
Independent angles/°		
<1 Ge—S—P	99.0 (6)	
<2 F—P—F	97.0 (10)	
<3 S—P—F	99.9 (4)	
<4 S—Ge—H	110 (3) ^b	
<5 PF ₂ twist	161.8 (17) ^b	
<6 GeH ₃ twist	29 (14) ^b	

^a All distances are r_a . Quoted errors are estimated standard deviations obtained in the least squares analysis, increased to allow for systematic errors.

^b See text.

distance must be regarded as being exceptionally long. As the other bond lengths are towards the high end of their normal ranges, the possibility of an overall scaling error must be considered. The calibration procedure used for wavelength determination involved recording of the diffraction patterns of benzene and of PF₂(SGeH₃) in the same experiment, and analysing the benzene structure using the full procedure normally used for unknown structure determination. The wavelength was then adjusted to bring the C—C distance of benzene to 139.70 pm, thereby eliminating any possible systematic scale error.

The conformation adopted contrasts strikingly with those adopted by other PF₂SR compounds. In S(PF₂)₂ the overall symmetry is C_{2v}, with each phosphorus lone pair of electrons eclipsing the further S—P bond¹⁷. In PF₂(SCH₃) the PF₂ group is twisted 110°, at which point the

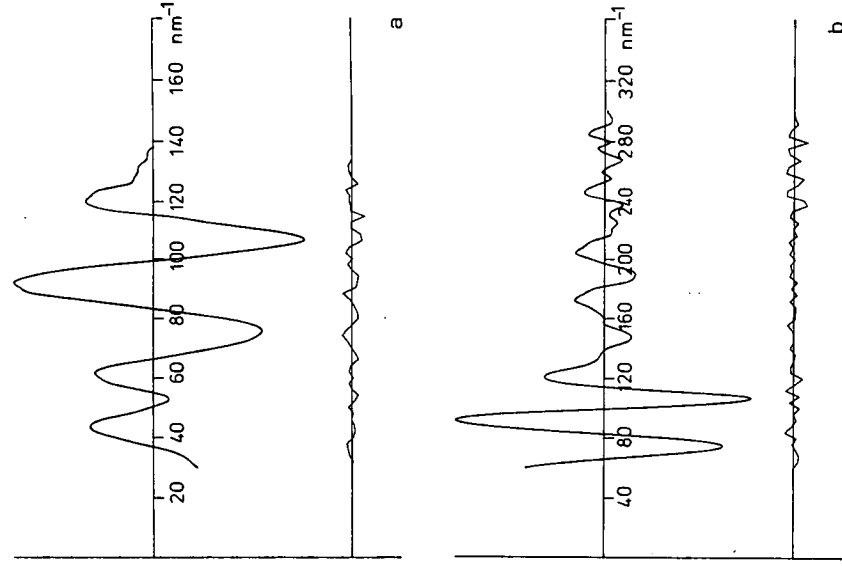


Fig. 2. Observed and final weighted difference molecular intensities for nozzle-to-plate distances of *a* 12.8 and *b* 286 nm

shortest H...F distance is ca. 265 pm¹⁸, close to the sum of the *van der Waals*' radii of hydrogen and fluorine. In the present case the twist angle is 162° and it is possible that the average value is actually 180°, with the observed distortion being caused by a large amplitude torsional vibration. The shortest H...F distance is 271 pm, and thus it seems that in these compounds with no steric crowding, the preferred conformation is one in which a weak fluorine-hydrogen contact is possible. Although the presence of small amounts of a second conformer cannot be ruled out, there is no evidence either from our refinements or from an inspection of the radial distribution curve for the existence of a second form.

Experimental

All volatile compounds were handled on a glass vacuum line fitted with Kovirel greaseless taps. Bis(difluorophosphino)sulphide was prepared from bis(tributylstannyl)sulphide and bromodifluorophosphine¹², and chlorogermane from monogermane and stannic chloride²³. Other reagents were prepared by published methods or obtained commercially.

Infra-red spectra were recorded in the range 4,000–200 cm^{-1} using a Perkin Elmer 557 spectrometer and Raman spectra were obtained using a Cary 83 spectrometer, with 488 nm argon-ion laser excitation. For mass spectra, an AEI MS902 spectrometer was used, and n.m.r. spectra were recorded on Varian XL100 (³¹P, ¹⁹F), HA 100 (¹H), JEOL FX 60 (³¹P) and Bruker WH360 (¹¹B) spectrometers.

Electron diffraction intensities were recorded photographically on Kodak Electron Image plates using the Cornell/Edinburgh diffraction apparatus^{24, 25}. Sample and nozzle were maintained at room temperature (293 K) during experiments. Data were collected using two camera distances, 128 mm (3 plates) and 286 mm (3 plates), giving data over a range of 30–300 nm^{-1} in the scattering variable, s . Intensities were obtained in digital form using a Jarrell-Ash double-beam microphotometer²⁶ with spinning plates. The electron wavelength, 5.779 ± 0.003 pm, was determined from the diffraction pattern of gaseous benzene.

Calculations were performed on an ICL 2970 computer using established data reduction²⁵ and least-squares refinement²⁷ programmes. Weighting points used in setting up the off-diagonal weight matrix are given in Table 6, together with scale factors and correlation parameters. In all calculations the complex scattering factors of Schäfer, Yates and Bonham²⁸ were used.

Table 6. *Weighting functions, correlation parameters and scale factors*

Camera height mm	Δs nm^{-1}	s_{\min} nm^{-1}	$sw1$ nm^{-1}	$sw2$ nm^{-1}	s_{\max} nm^{-1}	p/h	Scale factor
128.35	4	60	80	280	300	0.20	0.866 (19)
285.56	2	30	38	120	138	0.25	0.854 (17)

Preparation of $\text{PF}_2(\text{SGeH}_3)$

Chlorogermane (5.0 mmol) was condensed with $\text{S}(\text{PF}_2)_2$ (5.5 mmol) in a dry glass bulb (ca. 250 ml), and the reagents were then warmed to 209 K for 2 hours. The volatile products were examined by n.m.r. spectroscopy to ascertain the extent of reaction and the exact amount of GeClH_3 required to convert the remaining $\text{S}(\text{PF}_2)_2$ was added. In this way allowance could be made for imbalance of quantities of the reagents, caused by slight impurities, reaction with surface moisture etc. Products were separated by fractional condensation, and difluoro(germylthio)phosphine (4.8 mmol, 87% yield) was collected at 209 K. [M.wt. 180.6 (Calc. 178.7); v.p. (273 K) 31.5 mm; m.pt. 199 K]. The other major product was PClF_2 (5.0 mmol), with traces of $\text{PF}_2\text{H}(\text{S})$, GeH_4 and GeClH_3 .

Reaction with HCl

PF₂(SGeH₃) (2.5 mmol) and HCl (2.5 mmol) were condensed into a glass bulb (250 ml) and warmed to room temperature for 5 min. The products were separated by fractional condensation yielding GeClH₃ (2.5 mmol) and PF₂H(S) (2.5 mmol), identified by i.r. and n.m.r. spectroscopy.

Reactions with HBr, Cl₂ and PClPh₂

In each case 0.2 mmol of each reagent was taken and they were allowed to mix in CCl₃D (0.5 ml) at room temperature. The reactions were monitored by ¹H, ¹⁹F and ³¹P n.m.r. spectroscopy.

Reactions with B₂H₆

PF₂(SGeH₃) (0.4 mmol) and B₂H₆ (0.2 mmol) were condensed in an n.m.r. tube with CCl₃D (0.5 ml) as solvent. N.m.r. spectra were recorded at 273 K. In a second reaction, PF₂(SGeH₃) (0.8 mmol) was condensed in a glass ampoule with B₂H₆ (1.1 mmol), without a solvent. After warming to 195 K for 5 min excess B₂H₆ (0.7 mmol containing a trace of GeH₄) was removed. The combining ratio PF₂(SGeH₃): B₂H₆ = 2:1 was thus established.

Reaction with Mo(CO)₄(C₇H₈)

PF₂(SGeH₃) (0.4 mmol) was added to an n.m.r. tube containing Mo(CO)₄(C₇H₈) (0.060 g, 0.2 mmol) in CCl₃D, and the solution was warmed to room temperature before ³¹P, ¹⁹F and ¹H n.m.r. spectra were recorded.

Reactions with platinum complexes

In each case the platinum complex (0.2 mmol) was weighed and dissolved in CCl₃D or CCl₂D₂ in an n.m.r. tube, and PF₂(SGeH₃) (0.2 mmol) was added. The progress of reactions was monitored by ³¹P n.m.r. spectroscopy. When reactions were complete ¹⁹F spectra were also recorded.

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