EXCHANGE REACTIONS OF GROUP IV PHOSPHINES

by

Douglas James Hutchison

A thesis presented for the degree of Doctor of Philosophy in the Faculty of Science of the University Of Edinburgh, 1980.

CONTENTS

This thesis is the original composition of the author's work, unless stated otherwise, and has not been submitted previously for any other degree.

SIGNED.

ACKNOWLEDGMENTS

I wish to express my thanks to those, whose help in many ways made this work possible.

To Dr. S. Cradock, I owe a debt for initiating me into the mysteries of photoelectron spectoscopy. I am indebted to Dr. A.S. Boyd for running some of the n.m.r. spectra and to Dr. D.W.H. Rankin for patiently explaining electron diffraction matters as well as how to log on and off a computer terminal. I should like to thank the University of Edinburgh for laboratory facilities and the University of Manchester Institute of Science and Technology for Electron Diffraction facilities. Without exception my colleagues in the research group gave practical assistance, for which I am most grateful.

Above all I should like to thank my supervisor, Professor E.A.V. Ebsworth, not only for his weekend operation of the n.m.r. spectrometer when he should have done the garden, but also for his help, good sense and guidance with all the problems associated with this work. I have to thank him for his patience and persuasion that this work is presented.

For financial support I am grateful to the Science Research Council.

Finally I am grateful to Mrs. Barba for typing the manuscript.

ABSTRACT

This thesis describes a variety of exchange reactions of phosphorus derivatives of the type Q_3P where Q can be silyl, germyl trimethylsilyl, tributyltin and trimethyltin. These phosphines are treated with silyl and germyl halides and the products of reaction are investigated by n.m.r. spectroscopy.

Farther exchange reactions were carried out on the phosphines (type Q_3P) with PF_2Br. A new diphosphine $(GeH_3)_2PPF_2$ was isolated and many other diphosphines were prepared in solution, though for a variety of reasons no other derivatives were found to be isolable. It was possible to obtain the n.m.r. parameters of a wide variety of compounds.

The formation of bis(PF_2) and tris (PF_2) was observed in the n.m.r. spectrum of a reaction involving the tin phosphine $(Bu^n_3Sn)_3P$ and an excess of PF_2Br. The doubly and triple substituted phosphines i.e. $(PF_2)_2PSnBu^n_3$ and $(PF_2)_3P$ could be identified in the various spectra that were recorded.

Borane adducts were prepared of several of the new diphosphines and were likewise characterised by n.m.r. analysis.

As $(GeH_3)_2PPF_2$ was isolable, it was characterised by vibrational spectroscopy. The photoelectron spectrum was recorded and preliminary structural ideas could be made. The gas phase electron diffraction study enabled the bond lengths and angles to be measured.

The diphosphine $(GeH_3)_2PPF_2$ was farther subjected to reaction with a variety of reagents to investigate cleavage of the P-P bond, co-ordination on to organometallic compounds and possible farther exchange.

Conclusions and suggestions for farther work are made.

TO

MY PARENTS.

'N uair a bhios an sgadan mu thuath,
bithidh Murchadh Ruadh mu dheas.

Gaelic Proverb.

INTRODUCTION

PREAMBLE

For some 120 years the chemistry of diphosphanes has been investigated. The first diphosphane to be prepared was P_2I_4 which was described by Ritter (1) in 1855 - it took until 1966 when P_2F_4 was first prepared by Rudolph (2) for the series P_2X_4 (where X = I, Br, Cl & F) to be completed.

The preparation of PH_3 from calcium phosphide yields a small amount of P_2H_4. A modification of this processby use of electric discharge improves the yield to 30% of P_2H_4. The mixed fluorophosphine compound PF_2PH_4 was prepared by Rudolph (4) and Baudler (5).

Varying substituents of the organic sort have been found in diphosphanes notably CF_3, CH_3, Ph and studies of the alkyl diphosphanes have been undertaken, using n.m.r. conformational analysis, by Harris (6). The conformations of di methyl di phosphane and methyl diphosphane have been similarly postulated. The preparation of the last two phosphines utilized electron discharge techniques. CF_3 derivatives of diphosphine were first noted in the form of $[(CF_3)_2P]_2$ by Haszeldine & Emeléus (8) in 1953 while Rudolph prepared the non symmetrical diphosphine $F_2PP(CF_3)_2$ in 1971 (9).

The first silyl derivative of diphosphine was reported by Baudler in 1973,(7) when $(Ph.Me_3SiP)_2$ was prepared by treatment of $(KPh\ P)_2$ with Me_3 Si Cl.

This study of diphosphines confines itself to the investigation of compounds with the general formula :

$PF_2 - PQ_2$, Q = CH_3, SiH_3, Me_3Si, GeH_3, Me_3Sn, Bu_3 Sn.

In postulating synthesis of these reactions one can therefore consider three basic reaction mechanisms.

i) Simple exchange $Q_3P + PF_2X \rightarrow Q_2PPF_2 + QX$
ii) Ionic mechanism $^{+}MP^{-}Q_2 + PF_2X \rightarrow Q_2PPF_2 + {}^{+}MX^{-}$
iii) Iodine abstraction $Q_2PI + F_2PI + Hg$ -- $(CF_3)_2PPF_2 + Hg_2I_2$

In order to investigate the reactions outlined in the preamble it is necessary to outline aspects of :

a) Silyl and Germyl Chemistry,
b) Organo - silyl, - germyl, - tin chemistry with phosphorus
c)(i) Fluorophosphine chemistry and ii) P-P bonds in general.
d) n.m.r. techniques concerning phosphorus chemistry.
& other physical methods.

a) Silyl & Germyl Chemistry

Drake and Riddle's review published in 1970 (11) describes in great detail the synthesis, structure and properties of silyl and germyl compounds of the type

MH_3X, $(MH_3)_2Y$, $(MH_3)_3Z$ where $X = I, Br, Cl, F$

$Y = S, Se, Te$. & $Z = N, P, As$. This review shows by various diagrams the reaction schemes involved by the chemistry of the above compounds. Since 1970 there has not been much new reported chemistry in volatile silyl and germyl chemistry with the exception that the mixed sulphide from the following reaction was reported:

$$(SiH_3)_2S + GeH_3X \rightarrow GeH_3SSiH_3 \quad (12)$$

Preparation of this compound also took place by an ionic mechanism in which

$NH_4^+(S^-SiH_3)$ was treated with GeH_3Br. Subsequently however disproportionation took place (13)

Ebsworth discusses reactions of the salts $Li^+(YSiH_3)^-$ (14)

The review by Drake and Riddle deals with M-P chemistry (M=Si, Ge) at great length and requires some bringing up to date for the purpose of this work in relation to Methyl and trifluorosilyl phosphines

$(SiF_3)_3P$ has been prepared by the photolysis of mixtures of Si_2H_6 and PF_3 (15). Hydrolysis of the $(SiF_3)_3P$ yielded $(SiF_3)_2PH$ & SiF_3PH_2 the latter having been prepared by exchanging the trimethyl tin group of Me_3SnPH_2 for SiF_3 with SiF_3Br, (16) and (17).

The properties of MH_3PH_2 + $(MH_3)_2PH$ have been further investigated by Fritz (18) who prepared metallation compounds of the type Li Al $(PH\,SiH_3)_4$ and by Dahl et al. (19) where the decomposition and redistribution of GeH_3PH_2 is described as follows :

$$GeH_3PH_2 \xrightarrow{\text{rapidly}} H_2Ge(PH_2)_2 + HGe(PH_2)_3 + GeH_4$$

$$H_2Ge(PH_2)_2 \xrightarrow{\text{slowly}} (GeH_3)_2PH + (GeH_3)_3P + PH_3$$

Photoelectron spectra of SiH_3PH_2 and GeH_3PH_2 are described as well as those of $(SiH_3)_3P$ & $(GeH_3)_3P$ by Ebsworth (20).

Recent electron diffraction studies of mixed silyl/methyl phosphines in the series :

$$SiH_3PH_2\ ;\ SiH_3PHMe,\ SiH_3PMe_2$$

show that in contrast to the nitrogen analogues no large geometrical effects occur on the substitution of H by SiH_3 (21)

b) <u>Organo silicon , - germanium , - tin chemistry</u>

Organo tin , germanium and lead phosphines were discussed in great detail by Schumann in 1969 (22), he describes the synthesis of phosphines and arsines . At this stage ^{31}P n.m.r. was rather a novelty and coupling constants between tin and phosphorus had not been measured although the chemical shifts (of ^{31}P) were recorded.

In 1959 the first reports of a tin phosphine appeared - namely Et_3Sn-P-Ph_2 (23). The first tertiary organotin phosphine $(Me_3Sn)_3P$ was reported in 1960 (24).

Early preparative methods involved heating Ph_4Sn with phosphorus in a sealed tube .

Improvements, however, appeared in specific syntheses when Glockling & Hooton in 1963 (25) prepared a variety of tin, lead & germanium phosphines by the following routes using triethylamine. to remove HX.

$$R_3MX + R'_2PH \longrightarrow R_3M - PR^1{}_2$$

R' = alkyl

$$2\,R_3MX + R'PH_2 \longrightarrow (R_3M)_2PR'$$

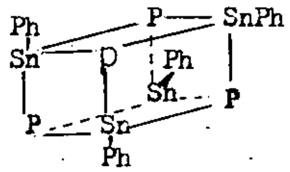
Secondary organometallic phosphines using R^1PH_2 were obtained in 1964 (26) with the tris organometallic phosphines $(R_3M)_3P$ resulting from treatment of a mixture of PH_3 and R_3MX with triethylamine.

thus,

$$3R_3MX + PH_3 + Et_3N \longrightarrow (R_3M)_3P + 3\,Et_3N^+HCl^-$$

Schumann discusses the preparation of $R_2M(PR'_2)_2$, where the dihalides, R_2MX_2 are used instead of R_3MX.

The trihalides eg RMX_3 (R = Bu, Me) react with phosphine to give only polymeric products while a tetrameric phenyl stannyl phosphine derivative was isolated from a mixture of $PhSnCl_3$, PH_3 and Et_3N.



The tetra chloride, $SnCl_4$ reacted to give $(Ph_2P)_4$ Sn on treatment with $Ph_2PH + Et_3N$.

Reactions of phenyl-tin (& germanium) phosphines are described by Schumann in 1969 (28)

Organosilicon phosphines have been investigated by Fritz in 1966 (27). The simple tris trimethyl silyl phosphine was first mentioned in 1959 (30) and its chemistry is thoroughly reviewed by Bürger (31).

A 24% yield of $(Me_3Si)_3P$ results from the reaction of Li_3P and Me_3SiCl.

Reaction of $(Me_3Si)_3$ P and H_2O resulted in two reaction schemes.

$$(Me_3Si)_3P + H_2O \longrightarrow Me_3Si\,PH_2 + (Me_3Si)_2O.$$

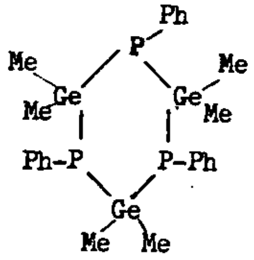
$$(Me_3Si)_3P + \tfrac{1}{2}H_2O \longrightarrow (Me_3Si)_2PH + \tfrac{1}{2}(Me_3Si)_2O$$

Fritz's work with lithium salts of the anions PR_2^- where R ranges from H, SiH_3 and Me_3Si, enabled him to assemble a range of phosphines which he characterised by n.m.r. and infra red spectroscopy. (32), (33)

Recent work on organosilicon , - germanium and tin phosphines has been dominated by Schumann. In 1971 cyclic organometallic phosphines were prepared (34).

Thus:

$$3\ Me_2GeCl_2 + 3PhPH_2 + 6\ Et_3N \longrightarrow$$



Choice could be made of the metal and starting phosphine and good yields were obtained - in the case above a yield of 58% was obtained.

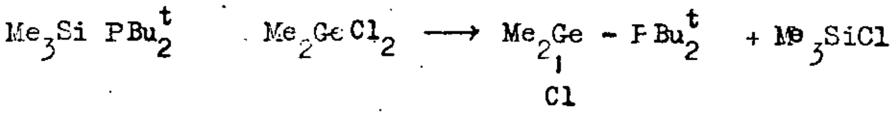
$(Me_3M)_2\ P\ Bu^t$ and $Me_3MP\ (Bu^t)_2$ were prepared, again by Schumann (35) using the organometal chloride and magnesium. eg.

$$2\ Me_3SiCl + Bu^tP\ Cl + 2Mg \xrightarrow{THF} Bu^t(SiMe_3)_2 + 2\ MgCl_2$$

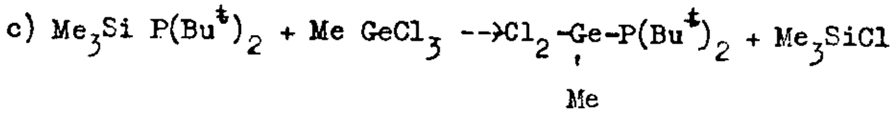
Similarly, use of Bu^tPCl & PCl_3 resulted in $Bu^t PSiMe_3$ & $(Me_3Si)_3P$ being formed. In the latter case a yield of 62% was obtained.

Having prepared these phosphines, reactions of these phosphines were studied and exchange reactions yielded yet more phosphines.

eg a) $Me_3Si\ P\ Ph_2 + Me_3GeCl \longrightarrow Me_3Ge\ P\ Ph_2 + Me_3SiCl$

b) 

$$Me_3Si\ PBu^t_2 \quad Me_2GeCl_2 \longrightarrow \underset{\mathrm{Cl}}{Me_2Ge} - PBu^t_2 + Me_3SiCl$$

c) 

$Me_3Si\ P(Bu^t)_2 + Me\ GeCl_3 \dashrightarrow Cl_2\text{-}\underset{Me}{Ge}\text{-}P(Bu^t)_2 + Me_3SiCl$

d) $\quad$ " $\quad + GeCl_4 \dashrightarrow Cl_3Ge\ P(Bu^t)_2 + Me_3SiCl$

e) $(Me_3Si)_3P + 3(Me_2Ge\ Cl_2) \dashrightarrow (Me_2GeCl)_3\ P + 3Me_3SiCl$

In the case of (e) above a yield of 97% was obtained from $(Me_3Si)_3$ P and considering the good yields made on the preparation of $(Me_3Si)_3P$ the reaction route of exchange of metal proved successful in the synthesis of other phosphines.

The one exception to the exchange series outlined above proved to be $SnCl_4$. On treatment of Bu^t_2 P $SiMe_3$ with $SnCl_4$ (37), Bu^t_2 PCl + $SnCl_2$+Me_3SiCl were formed which implies an oxidative cleavage of a Si-P bond during the exchange.

If, however, the reaction is carried out in benzene and there is an excess of Bu^t_2 P Si Me_3 then elimination of Bu^t_2 PCl will take place.

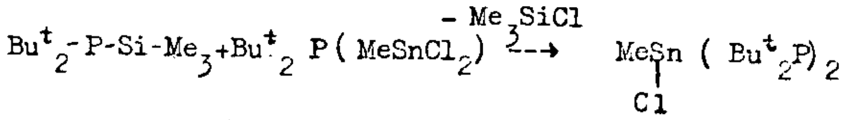
$$2\ Bu^t_2\ P\ Si\ Me_3 + E\ Cl_4 \dashrightarrow (Bu^t_2P)_2\ E\ Cl_2 + 2Me_3SiCl$$

E = Ge, Sn

$$\dashrightarrow Bu^t_2\ PE\ Cl + Bu^t_2\ PCl + 2\ Me_3SiCl$$

Reaction of Bu^t P Si Me_3 with other phosphines , to lose Me_3Si Cl has also been studied by Schumann. (38)

a) $Bu^t_2\ P\ Si\ Me_3 + Bu^t_2\ P\ (Me_2SnCl) \xrightarrow{-\ Me_3\ SiCl} Me_2Sn\ (\ Bu^t_2P)_2$

b) 

$$\mathrm{Bu^t_2\text{-}P\text{-}Si\text{-}Me_3 + Bu^t_2\,P(MeSnCl_2)} \xrightarrow{-\mathrm{Me_3SiCl}} \underset{\mathrm{Cl}}{\mathrm{MeSn}}\mathrm{(Bu^t_2P)_2}$$

c) (i) Fluorophosphine Chemistry

Fluorophosphine chemistry has come a long way since Moissan first prepared PF_3 in 1884 (42). Many reviews have been written on this aspect of chemistry and Nixon's is probably the best known and comprehensive. (39)
Schmutzler (40), (41) has also been active in this field.

As with silyl and germyl chemistry, vacuum and/or inert atmosphere techniques have to be used in the investigation of fluorophosphines as they are often poisonous, pyrophoric, easily hydrolysable as well as having unpleasant smells.

From 1970 onwards fluorophosphine derivatives of the groups V & Vl were reported as being isolated.

Sharp prepared compounds of the type PF_2-NHR
R = Me, Et, Bu^n, Bu^t (43) while Rankin (44) prepared PF_2NH_2 and $(PF_2)_2NH$; the compound $(PF_2)_3N$ was detected by mass spectrometry.

P_2F_4(45) + PF_2PH_2(46) & $(PF_2)_3P$ (47) are described in Nixon's review and as well as in the original journals.

David Arnold in his thesis describes the reactions of PF_2X (49) with $P(SiH_3)_nH_{3-n}$ while J. Wright in his, discusses the amine derivatives $PF_2X/N(MH_3)_nH_{3-n}$ where M = Ge,Si. (50)

Of the Group Vl fluorophosphine derivatives , those of oxygen are best known.

Nixon discusses PF_2OR compounds and $(PF_2)_2O$ has been known since 1966 (51).

$(PF_2)_2S$ was first prepared in good yields following the preparation of $(PF_2)_2O$ by Centofani in which $(Bu^n{}_3Sn)_2O$ was treated with PF_2Br.
$S(Bu^n{}_3Sn)_2$ was similarly treated with PF_2Br to give $(PF_2)_2S$ (53).

$(PF_2)_2Se$ has also been reported and reactions, structural implications and spectroscopic properties have been described, (54)& (55)
$(PF_2)_2Se$ was detected in an n.m.r. tube reaction in which $(SiH_3)_2Se$ had been treated with PF_2 Br (49).

It is generally standard practice to prepare a borane adduct of any new difluorophosphine compound. The BH_3 adducts of P_2F_4, PF_2PH_2 & PF_2 $P(CF_3)_2$ (9) & (56) are discussed by Rudolph. Other workers have made adducts using the higher boranes eg $(PF_2N\ Me_2):B_2H_4$, $PF_2H: B_3H_7$, $(PF_2H)_2:B_2H_4$,$(PF_2N\ Me_2)\ B_3H_7$, $(P_2F_4):B_2H_4$ (57) & (58).

Parry has prepared a wide variety of BH_3 adducts of the types :
$PF_2X.\ BH_3$, $F_n\ P(NMe_2)_{3-n}:\ BH_3$ (50) & (60).

The Chemistry of the P-P bond

i) Phosphorus, red, black or yellow can be found as P_4 and the element itself is reported to have been isolated in 1669 by Brand who prepared it from urine.

The study of the P-P bond since then has been mainly confined to polyphosphide chemistry and von Schnering has been most active in this field. In 1973 he reported the X-ray diffraction of the clathrates $Ge_{38}A_8X_8$ where A = P, As, Sb, X = Cl, Br, I (61).

In the example above the 38 Ge & 8A atoms build up a three dimensional framework of tetra hedrally bound atoms. In 1976 the magnesium polyphosphide was reported and P-P distances of between 2.184A° and 2.252 Å were noted. This compound was prepared by heating Magnesium filings with red phosphorus with trace additions of sulphur & Iodine (62).

The compound KP_{15}, reported in 1967 (63) is said to be triclinic with P-P distances of 2.18Å - 2.30Å,

(ii) Routes to the P-P bond.

Diphosphine itself is prepared on the hydrolysis of Ca_3P_2. This reaction also yields much PH_3 and the pyrophoric nature of PH_3 itself is said to be due to small amounts of P_2H_4 present. P_2H_4 first reported in 1936 (64) is unstable and decomposes to give PH_3 and polymeric phosphorus hydrides of variable composition (65).

The Tetrahalo-diphosphines.

P_2F_4 is prepared by the coupling of two PF_2 groups,

$$2PF_2I + 2Hg \longrightarrow P_2F_4 + Hg_2I_2 \quad (2)$$

P_2F_4 is easily hydrolysed to give $(PF_2)_2O + PF_2H$.

P_2Cl_4 is prepared by the electron discharge of a mixture of $PCl_3 + H_2$ under reduced pressure (66).

P_2I_4 was first prepared by Ritter (1), when he dropped a solution of iodine in glacial acetic acid into phosphorus trichloride. P_2I_4 can also be prepared by the simple solution of P_4 & I_2 in CS_2. The reactions of P_2I_4 are summarised in Schmutzler's review (41).

Emsley and Hall in their book 'The Chemistry of Phosphorus' (67) list the main ways of making diphosphines under the following headings.

i) Dehydrohalogenation.

$$R_2PH + R'_2PX \dashrightarrow R_2P\text{-}PR'_2 + HX$$

The HX can be removed by heat or by the use of base eg. Et_3N.

This method is especially useful for the preparation of asymmetric di-phosphines or even for chain lengthening.

$$\text{eg } 2Ph_2PH + Br_2PPh \xrightarrow[Et_3N]{} Ph_2P\text{-}P(Ph)\text{-}PPh_2 + 2Et_3\overset{+}{N}H\overset{-}{Br}.$$

ii) Coupling Reactions

Treatment by alkali metals, Hg, Mg & Bu^n_3P on phosphorus halides,

$$\text{ie. } 2R_2PCl + 2Na \xrightarrow{\text{dioxan}} R_2P\text{-}PR_2 + 2NaCl.$$

and , $2\ Ph_2PCl + Bu^n_3P \longrightarrow Ph_2PPPh_2 + Bu^n_3PCl_2$

iii) '<u>Anomalous</u>' <u>Grignard Reactions</u>

In this case diphosphine disulphides are produced using alkyl grignard reagent. Aryl grignards give the expected $P(S)Ar_3$ on treatment with $PSCl_3$.

eg $2\ PSCl_3 + 6R\ MgX \dashrightarrow R_2P(S) - P(S)R_2$

$+ 6MgXCl + R\text{-}R$

The resultant disulphides can be desulphurised by Bu^n_3P or Fe or, Cu,

iv) <u>Reactions involving diphosphines</u>

Chemical attack on the diphosphines usually results in the cleavage of the P-P bond.

This can be brought about using the following reagents Alkali metals (68), Halogens (69), water, alkenes (71), Lithium alkyls (71) & disulphides or diselenides.

Lewis acid behaviour depends upon the groups attached to the phosphorus . As reported before, the standard reaction of any fluorphosphine compound is the borane adduct formation and the diphosphine is also treated in this way; as $P\text{-}SiH_3$ is remarkably non-basic, the adduct would be expected at the PF_2- section of the molecule with a silyl and fluorophosphine 'end'.

D) <u>Physical Methods in Characterising phosphine derivatives</u>

<u>FOURIER TRANSFORM N.M.R.</u>

Great use of F.T. n.m.r. was made to characterise the phosphines prepared and here it must be noted that the convention used in this work regarding sign of chemical shift is that positive shifts are those which occur to higher frequency than resonances of the standard employed.

These shifts are naturally of the opposite sign when the field convention was in use.

^{31}P n.m.r. was of most use in characterisation and a clear account of the technique is given in Emsley and Hall (67) and in 'Topics of Phosphorus Chemistry' (72). Harris, in a quarterly review (73), discusses the n.m.r. possibilities as far as other nuclei are concerned, excluding ^{1}H, ^{31}P, ^{19}F and ^{13}C. Of interest to this work are the n.m.r. spectra of tin. ^{119}Sn is readily observed and although the gyromagnetic ratio is negative, thus resulting in a negative Nuclear Overhauser Enhancement on proton decoupling good spectra may nevertheless be obtained, if gated decoupling techniques are used. This is explained in detail by Kaptein and others (74). Involved, is a pulse delay of some 30 seconds, allowing the relaxation time (T_2) to be completed before the decoupler is switched on again.

^{31}P n.m.r.:

Engelhardt (75) in 1972 correlated a large range of ^{31}P chemical shifts for phosphines of the type.

$(R_3M)_nPX_{3-n}$ where M=Si,Ge,Sn. R=H, CH_3, C_6H_5 , C_4H_9. X=H,CH_3,C_6H_5

Use of van Wazers theory (72) and chemical shift increments for the type and number of R_3M groups, imply that $(p\rightarrow d)\pi$ bonding is important in Ge-P and Sn-P bonds, which is not the case in Si-P bonds.

Engelhardt related the chemical shift of the range of phosphines to the electronegativities of the substituent groups and the occupancy of the $P(3d)\pi$ orbital, n_{π}.

thus $\delta = 11828.5 - 7719\,\xi\,,\ -408\,n_\pi$

where ξ is a measure of the electro negativity

The difference between experimental and calculated values was a measure of the relative non importance of $(p \rightarrow d)\pi$ bonding.

Other empirical methods have been used in the study of ^{31}P chemical shifts notably by Fritz (32,33,75,76), A range of silyl phosphines of the type $(R)PH_2$, $(R)PH.CH_3$, $(R)P(CH_3)_2$, $(R)_2PH$, $(R)_2PCH_3$ and $(R)_3P$ was prepared where $(R) = (CH_3)_nSiH_{3-n}$. Data resulting from the ^{31}P spectrum was studied and a formula for evaluating the resultant shifts was proposed.

$$\delta^{31}P = 120a + 80b + 20.5c + 2d - 12e - 5.5ab - 10bc - 11ae.$$

where a= number of P-Si bonds, b= no. of P-H bonds.

c = no. $P-CH_3$ bonds, d = no of Si H bonds
e = no. of Si = CH_3 bonds.

Fritz stated that use of this formula gave resultant theoretical shifts which were 2.5 ppm. within the experimental figure.
For his silyl phosphines Fritz also correlated the coupling constant, $J\,^{29}Si\ ^{31}P$,
In 1974 Schumann detected (77) all the possible compounds (ie 10) when $(Me_3Si)_3P$ was treated with Me_3GeCl & Me_3SnCl. The resultant shifts of the new compounds were assigned on the basis of the empirical methods outlined.
There has been recently much discussion concerning the ^{31}Pn.m.r. spectra of P-P compounds.
Conformational analysis by n.m.r. alone took over a page in the

Chemical Society Annual reports of 1975. This discussion is also recorded in communications relating to diphosphines, notably by Harris (79) (80) & McFarlane (81), where the tetra alkyl diphosphines have been studied.

Consideration of n.m.r. parameters, mainly J (PP) obtained from ^{31}P n.m.r. spectroscopy, backed up with ^{13}C + ^{1}H n.m.r. spectroscopy led to the promotion of a structure involving the gauche configuration.

J(PP) was found to vary considerably with the substituent on the phosphorus atoms. This variation is noted below.

Di phosphine.	$^1J(PP)$	Reference.
H_2PPH_2	-108	86
$(CH_3)_2$ PP $(CH_3)_2$	-180	85
F_2 P PH_2	-211	4
F_2 P PF_2	-230	84
$(CF_3)_2$ PP F_2	-234	83
$(CF_3)_2$ PP $(CH_3)_2$	-256	83
Et_2 PP $(C_6H_{12})_2$	-282	82
$CH_3.Bu^t$ PP $Bu^t.CH_3$	-290	81
$(CH_3)_2PP(Bu^t)_2$	-318	81
$(CH_3)_2$ PP $(Bu^t)_2$	-318	81
Bu^t_2 P P $Bu^t{}_2$	-451	81

The dramatic effect of addition of the t- butyl groups is shown in the variation in J (PP)

This difference arose for two reasons.

i) Orientation of the lone pairs on phosphorus

ii) Hybridization changes in phosphorus itself arising from the bulk of the t-butyl groups.

Reference shows that only 5% at most of $Bu^t_2PPBu^t_2$ is in the trans configuration at - 60°C and that the gauche case is predicted as being the predominating rotamer.

Structural Methods

As a large number of phosphine & fluorophosphine compounds are volatile they are ideally suited to gas phase electron diffraction. In 1934 Brockway and Wall (87) determined the gas phase structure of PF_3.

Since then many fluorophosphine derivatives have been examined. Other volatile phosphines have been studied in the same manner, eg. the gas phase structures of the silyl phosphines SiH_3PH_2, $SiH_3PH.CH_3$ & $SiH_3P(CH_3)_2$ (89) showed that they had more in common with $(CH_3)_3P$ and the methyl phosphines than $(SiH_3)_3N$ which is planar.

$(GeH_3)_3N$ is planar (92) whereas $(SiH_3)_3P$ and $(GeH_3)_3P$ (95) are not - they have bond angles $M\hat{P}M$ of 96.5° & 95.4° respectively. The structures of F_2PNCO, F_2PNCS & $F_2PNH{\cdot}SiH_3$ (90) (91) have recently been determined - the latter structure has to be interpreted in terms of a mixture of two conformers, this idea is also suggested by the infra red spectrum of the vapour. Short H..... F non bonded distances exist and the conformation about N is assumed to be planar.

Di phosphine structures have been determined for P_2F_4 & $P_2(CF_3)_4$ (88). A brief description follows:

P_2F_4 showed a trans conformation with the gauche conformer being present at less than 10%. P_2H_4 and $P_2(CH_3)_4$ were also discussed (93) (94). The structure of PF_2 PH_2 was determined by microwave spectroscopy by Rudolph (96).

A table of J(PP) and r(P-P) is shown below.

Compound	J(PP)	r(P-P)
F_2PPF_2	-227.4	2.281
H_2PPH_2	-108.2	2.219
F_2PPH_2	-211	2.218
$(CH_3)_2\,PP(CH_3)_2$	-179.7	2.192
$(CF_3)_2\,PP(CF_3)_2$	not known	2.182

The data available show that all gaseous phosphines have the trans conformation with the exception of P_2H_4. The trans conformation can be understood to be the most stable by invoking steric repulsion and/or lone pair interactions. The two effects are least felt by P_2H_4.

With the exception of microwave, gas phase structures can only show an average picture of the molecule in terms of trans and gauche conformations.

In a study of $P_2(CH_3)_4$ by RAMAN and Infra Red spectroscopy, the trans conformer was found to be dominant in the solid state, however the liquid structure was found to be gauche.

Durig et al (97) discuss rules for the determination and prediction of conformational stabilities.

The P-P bond length, with the exception of r(P-P) in P_2F_4 is shown to be insensitive to substituents as the table of bond lengths illustrates. From these observations it seems that conformations and bond lengths do not suggest or support the theory of $p_{\pi} \rightarrow d_{\pi}$ bonding where the 3p electrons of the one phosphorus atom are capable of overlap with the nominally unoccupied 3d orbitals of the other phosphorus. The P-P bond is basically a σ bond with each phosphorus having two substituent groups and an electron pair.

Chapter 1

Exchanges of Group IV derivatives on Group IV phosphines

INTRODUCTION

In 1970 the method reviewed for the preparation of trigermyl phosphine was via an exchange process, thus:

$$(SiH_3)_3P + GeH_3Br \dashrightarrow (GeH_3)_3P + 3SiH_3Br$$

The preparation of trigermyl phosphine is therefore relatively straightforward once trisilyl phosphine is available.

Trisilyl phosphine was reported to have been made by the reaction of SiH_3I, with white phosphorus as well as by the method of Amberger & Boetters. (116)

$$3\ SiH_3Br + 2KPH_2 \dashrightarrow (SiH_3)_3P + 2PH_3 + 3KBr$$

The latter method was found to be the most satisfactory of the two but yields obtained were never high enough to warrant experiments using more than 1 m mole of phosphine at a time. It was therefore thought that an easier way to prepare the trisilyl and tri germyl phosphines was required.

Ideally an exchange type reaction would be the best - if a triphosphine involving three good leaving groups could be prepared in quantity and the leaving groups exchanged for silyl or germyl groups then the preparation of the trisilyl and trigermyl phosphines could be simplified.

Conditions, that is temperature and reaction times would be studied by ^{31}P n.m.r. spectroscopy.

Where exchange of silyl and germyl groups on sulphur involve only one intermediate i.e. $H_3SiSGeH_3$, two intermediates are involved in exchanges on phosphorus. Isolation of these would be difficult due to the range of intermediates.

$$M_3P \longrightarrow M_2PQ \longrightarrow MPQ_2 \longrightarrow PQ_3$$

where M and Q are both hydride or alkyl derivatives of silicon, germanium or tin.

This investigation was therefore prompted by a wish to prepare $(GeH_3)_3P$ readily, and in large amounts.

Results and discussion.

The systems investigated were as follows :

Rn 1.1. $(SiH_3)_3P + GeH_3X$ X = Cl, Br
Rn 1.2. $(GeH_3)P + SiH_3I$
Rn 1.3. $(Me_3Si)_3P + GeH_3X$ X = Cl, Br
Rn 1.4. $(Me_3Si)_2PH + GeH_3X$ X = Cl, Br
Rn 1.5. $(Me_3Si)_3P + SiH_3Br$
Rn 1.6. $(Bu^n{}_3Sn)_3P + GeH_3Cl$
Rn 1.7. $(Bu^n{}_3Sn)_3P + GeH_3Br$
Rn 1.8. $(Bu^n{}_3Sn)_3P + Me_3SiCl$
Rn 1.9. $(Me_3Sn)_3P + GeH_3Cl$
Rn 1.10 $(Me_3Sn)_3P + SiH_3Br$

R.1.1. $(SiH_3)_3P$ + GeH_3X:

The reaction had always been used previously in the preparation of $(GeH_3)_3P$ but no intermediate compounds ie.$(SiH_3)_2 P GeH_3$ + $(GeH_3)_2 P SiH_3$ had been detected. Low temperature n.m.r. work was employed and a ratio of 3 germyl bromide to 2 phosphine was used.

In the ^{31}P spectrum, lines were assigned to $(SiH_3)_3P$ + $(GeH_3)_3P$ at - 378 ppm and - 337 ppm respectively. Two lines lying between were therefore assigned to $(SiH_3)_2 P GeH_3$ and $SiH_3 P (GeH_3)_2$ with line positions - 366 and -352 respectively. In the above, proton coupling was removed by decoupling experiments. Selective decoupling of the silyl and germyl protons was not possible. However examination of spectra obtained by proton n.m.r. corroborated the intermediate theory. It was possible to measure $^4J_{HH}$ for $SiH_3P(GeH_3)_2$ by observing the ^1H spectrum employing phosphorus decoupling at the frequency obtained from the ^{31}P spectrum.

The GeH_3 - lines were shown to be of quartet splitting, the silyl shown to be septet splitting $^{4}J_{HH} = 0.8Hz$.

When the n.m.r. tube was warmed to room temperature the trisilyl phosphine was gradually used up and lines due to $(GeH_3)_3P$ increased in the ^{31}P spectrum.

This system was also observed with GeH_3Cl with the same results.

Rn.1.2. $(GeH_3)_3P$ + SiH_3I.

This is the 'back' reaction of the above. SiH_3I is very reactive and the exchange of the Iodine to germanium is well known.

Rn 1.3. $(Me_3Si)_3P$ + GeH_3X:

Treatment of $(Me_3Si)_3P$ on an n.m.r. tube scale with GeH_3Cl resulted in only $(GeH_3)_3P$ being observed when the ^{31}P n.m.r. spectrum was recorded. The reaction had gone to completion after 100 seconds at - 50°C. The next step taken was to make $(GeH_3)_3P$ on a preparative scale. This involved the condensation of GeH_3Cl on to $(Me_3Si)_3P$. When the mixture was allowed to warm to room temperature the products could be fractionated on the vacuum line and the reaction was found to be quantitative in Me_3SiCl.

$$(Me_3Si)_3P + 3\ GeH_3Cl \longrightarrow (GeH_3)_3P + 3\ Me_3SiCl$$

The chloride was used as Me_3SiCl is readily separable from $(GeH_3)_3P$ on fractional distillation.

R.n. 1.4. $(Me_3Si)_2\ PH\ +\ GeH_3X$

$(Me_3Si)_2PH$ which was prepared by treatment of $(Me_3Si)_3P$ with H_2O was farther treated with a 1:1 ratio of GeH_3Br on an n.m.r. tube scale. The products which were detected and assigned by examination of their n.m.r. spectra were as follows .(Chemical shifts are shown)

$(Me_3Si)_3P$ - 253 ppm

$(Me_3Si)_2PH$:- 237.6 , $(GeH_3)_2PH$: - 300.5, Me_3Si-P-$(GeH_3)_2$-309
(Me_3Si)-PH_2: - 236.1 , GeH_3PH_2 : - 268 , $(Me_3Si)_2P\ GeH_3$ -280
(Me_3Si) PH GeH_3 : - 269.2 ,$(GeH_3)_3P$ - 337

In assigning peaks in the n.m.r. spectrum use was made of the proton decoupled & non decoupled spectrum to differentiate $-PH_2$, $>PH$ & $\diagdown\underset{|}{P}\diagup$ type phosphorus as the large $^1J(PH)$ shows how many hydrogens are directly bonded to phosphorus. The finer proton - phosphorus couplings could be selectively decoupled thus enabling the distinction between Me_3Si + GeH_3 groups to be made. The difference in chemical shifts between $(Me_3Si)_3P$ + $(GeH_3)_3P$ is large enough to work out the intermediate compounds expected chemical shift value. (See correlation charts)

The presence of $(GeH_3)_3P$ must be explained. $(Me_3Si)_3$ P is involatile and as the products of the reaction between $(Me_3Si)_3$ P + H_2O were fractionated, and the $(Me_3Si)_2PH$ was distilled into the n.m.r. tube, it must be concluded that no $(Me_3Si)_3$ P was present at the start of the n.m.r. tube experiment. Some disproportionation of the type $2(R)_2PH \dashrightarrow RPH_2 + R_3P$ must have taken place where R = GeH_3 or Me_3Si. $(Me_3Si)_2$ PH itself showed no tendency to disproportionate although farther experiments with derivatives of $(GeH_3)_3$ P showed in fact some tendency to disproportionation.

Rn 1.5 $(MeSi)_3P$ + SiH_3Br

The reaction between SiH_3Br and $(MeSi)_3P$ in a 2:1 ratio was followed using the variation temperature facility of the n.m.r. spectrometer. After warming to - 50°C for a few minutes the products were assigned by a chemical shift study as follows:

$(Me_3Si)_2P\ SiH_3$ - 279 ppm

$Me_3SI\ P\ (SiH_3)_2$ - 337 ppm

$P\ (SiH_3)_3$ - 375 ppm

The results were obtained using the proton decoupling facility of the spectrometer. When the decoupling ceased no directly bonded PH coupling was observed proving no hydrolysis of the phosphines.

This method of preparation of $(SiH_3)_3P$ is not practical on a large scale as it is difficult to separate Me_3SiX from $(SiH_3)_3$ P. It was possible in the n.m.r. experiments to selectively decouple the SiH_3 & Me_3Si protons. The values of ^2JPH for the SiH_3 protons was 16Hz and for the $^3J_{PH}$ value for the methyl protons, 5Hz were measured.

Rns 1.6. $(Bu^n{}_3Sn)_3$ P + GeH_3Cl

In this reaction and the next two (with SiH_3Br, Me_3SiCl) problems were encountered as the ^{31}P spectrum of $(Bu_3Sn)_3P$ was found to be temperature dependent in both δ + $^1J(SnP)$. When the exchange reactions were carried out , spectral lines were often broad and separation between the two sets of tin satellites was not always resolved.

$(Bu_3Sn)_3P$ was treated with GeH_3Cl in a 1:2 ratio. At - 50°C the spectrum recorded, showed only $(GeH_3)_3P$. The experiment was repeated with another solvent (CD_2Cl_2 instead of $CDCl_3$) and again only $(GeH_3)_3$ P could be detected. However towards lower frequency two broad resonances were observed. These were not assigned.

Rns 1.7 $(Bu^n{}_3Sn)_3P$ + SiH_3 Br

Use of the above method, with a 1:2 ratio of phosphine to bromide, enabled the route to $(SiH_3)_3P$ to be studied. The intermediate products $(Bu_3Sn)_2PSiH_3$ + (Bu_3Sn) P SiH_3 were identified. The chemical shifts range from - 358 for $(Bu_3Sn)_3P$

at - 60°C to $(SiH_3)_3$ P at - 375. The number of Sn groups bonded to phosphorus could be determined by the relative heights of the tin satellites. Both ^{117}Sn and ^{119}Sn satellites were observed. $(Bu_3Sn)_2P\ SiH_3$ was therefore identified at chemical shift position at -364 ppm, the tin couplings were 784, 732.5Hz. $Bu_3Sn\ P(SiH_3)_2$ had position - 375 ppm and tin couplings 667.0 + 635.0Hz. (Sn has isotopes ^{117}Sn + ^{119}Sn).

$(SiH_3)_3P$ could not be detected but as it also has a chemical shift of -375 ppm it is likely to have been obscured.

This scheme wouldhave potential in the preparation of $(SiH_3)_3P$ as $(Bu_3Sn)_3$ P is readily prepared, stored and can be conveniently used in reaction with SiH_3Br. The co- product Bu_3SnBr is separable from $(SiH_3)_3P$.

Rn 1.8 $(Bu^n{}_3Sn)_3$ P + Me_3SiCl

The above method was used with a 3:5 ratio of phosphine to Me_3SiCl. This time however there was no reaction apparent by ^{31}P n.m.r. detection methods at - 60°C. Warming to room temperature produced no new phosphines, the only change which had occurred was a chemical shift change for $(Bu_3Sn)_3P$. After 8 hours it was no longer possible to resolve the tin couplings although the average value did not change.

There was no trace of $(Me_3Si)_3$ P in the spectrum or of any other phosphine of the type:

$$(Me_3Si)_nP\ (SnBu_3)_{3-n}$$

Rn 1.9 $(Me_3Sn)_3P$ + GeH_3Cl

$(Me_3Sn)_3P$ was treated with a 2:1 ratio of GeH_3Cl at - 60°C $(GeH_3)_3P$ could be identified by its ^{31}P chemical shift and the spectrum of the non-proton-decoupled spectrum. Another peak at - 339 showed a septet with proton decoupling removed, suggesting the formation of $(GeH_3)_3$ $PSnBu^n_3$. The spectrum of the tube contents when brought to room temperature was complex as broad lines appeared. The transfer of $(Me_3Sn)_3P$ into an n.m.r. tube involves some glove bag procedure in which it is difficult to ensure the total absence of water. In this experiment some $(GeH_3)_2$ PH was observed.

Rn 1.10. $(Me_3Sn)_3$ P+ SiH_3Br

As in the case of the germyl reaction (1.9), a 2:1 addition of SiH_3Br was made to $(Me_3Sn)_3P$. Products identified at - 60°C were $(SiH_3)_3P$ at -374 ppm and a disilyl phosphine postulated as $(SiH_3)_2$ P $SnMe_3$.

APPENDIX

Reaction of $(Bu_3Sn)_3P$ and HCl:

An n.m.r. tube scale reaction was followed by ^{119}Sn and ^{31}P n.m.r. spectroscopy involving direct observation of the nuclei. $(Bu_3Sn)_3$ P was treated with an equivalent amount of HCl gas.

A range of phosphine products was produced: $(Bu_3Sn)_3P$, $(Bu_3Sn)_2PH$ Bu_3Sn PH_2 + PH_3.

These were identified by the proton coupling of the proton directly coupled to phosphorus. The ^{119}Sn tin spectrum was also directly observed, using gated decoupling techniques. The n.m.r. data of these tin phosphines is tabled below

Phosphine	$(Bu_3Sn)_3P$	$(Bu_3Sn)_2PH$	$(Bu_3Sn)PH_2$	PH_3
ppm δP	-347	-326	-289	-242
Hz $^1J(PSn)$ (119,117)	914.2,873	727,700	$\approx$500	-
$^1J(PH)$	-	157.3	170.0	186.0
$\delta^{119}Sn$	+36	+30	+17	-

The value of J (Sn-Sn) was 283 Hz in the case of $(Bu^n_3Sn)_3P$.

Conclusion:

The results already discussed show the way in which phosphorus n.m.r. spectroscopy can be used to monitor a reaction. In the case of the preparation of $(GeH_3)_3P$, once the conditions were established for exchange on an n.m.r. tube scale then preparative scale syntheses could be employed.

The study enabled the inter mediate phosphines to be detected and the chemical shift comparisons obtained have proved useful in assigning the much more complicated reactions involving fluorophosphine derivatives. Such correlations are shown in the following chapters.

The prospect of preparations of a variety of silyl derivatives from the phosphines provides a simpler and more secure way to study these species.

CHAPTER 2

The Prepartion and identification of diphosphines of the type PF_2-PQQ' with some reactions.

Introduction:

This chapter describes the chemistry of several phosphines in their reactions on treatment with PF_2X (where X = normally Br sometimes Cl & I).

Many reactions were carried out in a 5 mm n.m.r. tubes, consequently reaction pathway and products are discussed in the light of experimental spectra obtained for each reaction.

SUMMARY

The formation of $(PF_2)_2S$ and its selenium analogue from treatment of disilyl sulphides and selenides with PF_2Br suggested that a similar reaction might occur between PF_2Br and the group IV phosphines, indeed the compound $(SiH_3)_2$ PPF_2 had already been obtained on an n.m.r. tube scale by the addition of PF_2Br to $(SiH_3)_3P$. When this experiment was repeated on a preparative scale it was found that the diphosphine could not be isolated.

Treatment of $(GeH_3)_3P$ with PF_2Br resulted in a stable & isolable diphosphine $(GeH_3)_2PPF_2$ being formed. This reaction was considerably faster, at the same temperature, than that involving trisilylphosphine.

A comprehensive study of the reaction of phosphines and PF_2Br was carried out using n.m.r. spectroscopy. The various reactions are summarised below.

1) $Q_3P + PF_2Br \longrightarrow Q_2\ PPF_2 + Q\ Br$

where $Q = SiH_3, Me_3Si, Me_3Sn, Bu_3Sn, GeH_3$.

2) $R_2PQ + PF_2Br \longrightarrow R_2\ PPF_2 + Q\ Br$

$R = CH_3,\ Q = Me_3Si$

3) a) $Q_2PPF_2 + HCl \longrightarrow QPH.\ PF_2 + Q\ Cl$

b) $Q_2PPF_2 + MBr \longrightarrow Q.M.PPF_2 + QCl$

$Q = SiH_3,\ M = GeH_3$

4) $RPQ_2 + 2PF_2Br \xrightarrow{H_2O\ \&\ HBr} RPH.\ PF_2 + 2QBr + (PF_2)_2O$

^{31}P & ^{19}F n.m.r. spectra are readily observed and could be analysed in first order terms without difficulty.

Reaction Scheme 1 :

Routes to PF_2PQ_2 are summarised in the table appended (number 2.1). Reactions were investigated and in all examples ^{19}F & ^{31}P n.m.r. spectra were observed and it is pertinent to describe here the operation. Stick diagrams are inserted into the text for clarity.

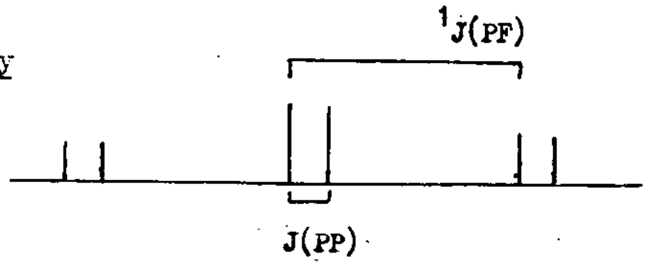
The ^{31}P spectrum of PF_2PQ_2

This spectrum comprises two sets of resonances, one set of which is due to the fluorophosphine phosphorus at high frequency and the other to the group IV phosphorus to low frequency, the separation is of the order of 500 ppm.

The proton decoupled spectra are illustrated below in stick diagrams, for each phosphorus.

^{31}P resonance to

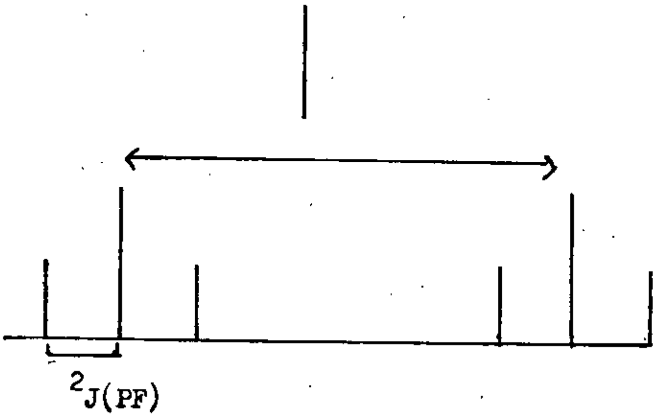
high frequency



^{31}P resonance to

low frequency

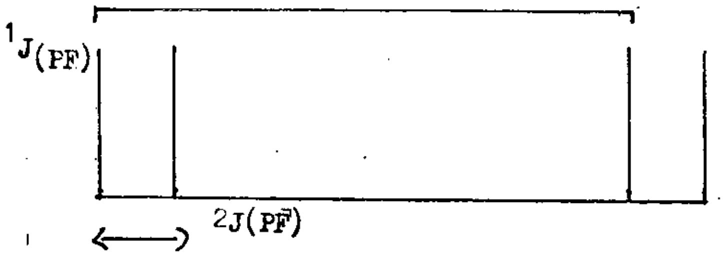
(expanded)



Without proton decoupling a more complex spectrum arises, In $(GeH_3)_2PPF_2$ each line is further split into seven.

The ^{19}F spectrum of PF_2PCl_2

In this case there is only one resonance, which when observed with proton decoupling is simply a doublet of doublets thus :



The determination of products obtained and formed in these reactions was carried out by observation of the fluorine and phosphorus n.m.r. spectra, as observed for the two phosphorus sets of resonances and for the fluorine set of resonances.

The resultant parameters are therefore :

$\delta P_{(F)}$ $\delta P_{(H)}$ δF , J(PP), $^{1}J(PF)$, $^{2}J(PF)$

with the proton couplings $^{2}J(PH)$, $^{3}J(PH)$, $^{4}J(FH)$

Isolation of one of the compounds with subsequent structure determination renders the assignment of the n.m.r. spectra unambiguous.

Table 2.2. shows the range of diphosphines produced and the n.m.r. data gathered from the reactions outlined below.

Rn2.1 $(SiH_3)_3P + PF_2Br$

A three to one excess of PF_2Br to phosphine was used and after 9 days $(SiH_3)_2PPF_2$ was detected, however attempts to isolate this diphosphine were thwarted by the concurrent formation of SiH_3F at the room temperature of reaction. In this case the ^{1}H spectrum can also be observed and this reaction is described elsewhere (49).

Rn2.2 $(GeH_3)_3P + PF_2Br$

A 3.1 ratio was again used and the ^{1}Hspectrum was observed which was similar to that described above. In both cases a doublet of doublets of triplets is obtained. This reaction proved to be rather faster and unlike the silyl reaction,no GeH_3F could be detected.

Both reactions appear to be complete after the 1st. fluorophosphine has replaced an MH_3 group as no evidence of $(PF_2)_2PSiH_3$ or $(PF_2)_2PGeH_3$ or even $(PF_2)_3P$ was found under the conditions used.

Rn 2.3 $(Me_3Si)_3P + PF_2Br$ / PF_2Cl :

In this experiment, use was made of the same ratios as above and the diphosphine - $PF_2P(SiMe_3)_2$ was observed after studying the n.m.r. spectra obtained. The compound Me_3SiF was also detected in the ^1H and ^{19}F spectra.

Reaction 2.4. $(Bu^n_3Sn)_3P + PF_2Br$:

If the conditions used above are applied in this reaction then an abundance of unidentifiable,red, polymeric and insoluble material results. In order to detect a diphosphine at all then a 1:1 ratio of reactants was used and the n.m.r. spectra were recorded at -60°C. The tin satellites from $^{117,119}Sn$ were observed on the characteristic spectra outlined above in the stick diagrams. It was later found that a 3:1 ratio of PF_2Br resulted in the formation of $(PF_2)_3P$, which is unstable at room temperature, although was reasonably stable at -60°C.Details of the bis and tris difluorophosphino - phosphines are described in the following chapter (Chapter 3).

Reaction 2.5. $(Me_3Sn)_3P + PF_2Br$:

This reaction proved to be much more vigorous than the one described immediately above. The product $PF_2P(SnMe_3)_2$, which was observed from the reaction, was so unstable that only one ^{31}P spectrum could be obtained from one n.m.r. tube reaction at a time. The fluorine spectrum of this species was not found. The reaction was found to have taken place at -95°C. Excess PF_2Br results in the formation of $(PF_2)_3P$.

(2) Reaction Scheme 2:

Reaction 2.6: $R_2PQ + PF_2Br \longrightarrow R_2PF_2 + QBr$.

$R = CH_3$, $Q = Me_3Si$.

The phosphine $Me_3Si\text{-}P\text{-}Me_2$ was made and treated with a 1:1 ratio equivalent of PF_2Br. At room temperature a vigorous reaction was noted and a red, insoluble and polymeric material formed, from which no spectrum could be obtained.

Repetition of the experiment at -60°C proved to be more successful in that the ^{31}P spectrum showed the characteristic patterns. A fresh n.m.r. tube had to be made up for each part of the ^{31}P spectrum as well as for the ^{19}F spectrum. An attempt was made to record the proton spectrum but with no success. The ^{31}P and ^{19}F spectra show that $(CH_3)_2PPF_2$ has been formedbut that is is very unstable. Attempts to prepare $PF_2P(CH_3)_2$ from reactants $KPMe_2 + PF_2Cl$ proved unsuccessful as PF_3 was the only product observed; details shown as experiment 2.6(a).

Reaction Scheme 3

$$Q_2PPF_2 + MX \longrightarrow Q.M.\ PPF_2 + Q-Cl$$

i) M = H Q = GeH_3 , X = Cl

ii) M = SiH_3, Q = GeH_3, X = I

iii) M = GeH_3, Q = SiH_3, X = Br

Rn. 2.7

$$PF_2P(GeH_3)_2 + HCl \longrightarrow (GeH_3)PH.\ PF_2 + GeH_3Cl$$

$(GeH_3)_2PPF_2$ had already been isolated and it is discussed in detail in Chapter 4.

The ^{31}P spectrum obtained with proton decoupling, showed peaks which were assigned to starting material & to $PF_2PH.GeH_3$ on the basis of the low frequency resonances.

A doublet of doublet of doublets was also detected and this was assigned to $PF_2PH\ GeH_3$ on the basis of the presence of non equivalent fluorines on the phosphorus to high frequency. This assignment was borne out by the ^{19}F spectrum when resonances due to the two fluorines could be observed. The ^{19}F spectrum could be described in '1st order terms' and a geminal F-F coupling could be measured.

The non equivalence of the fluorines must be due to the chirality of the second phosphorus.

The AB pattern expected is doubled by each phosphorus making a total of 16 lines altogether. This compound was examined at both room temperature & -60°C and the compound had a lifetime long enough to fully observe the spectrum of both phosphorus's & fluorines although a gradual disproportionation to $(GeH_3)_2\ PH$ & $(GeH_3)_3\ P$ was detected accompanied by the precipitation of a yellow solid from the solution. The solid was not identified.

Rn 2.8

$$(SiH_3)_2\ PPF_2 + GeH_3\ Br \dashrightarrow SiH_3\ GeH_3\ PPF_2 + SiH_3\ Br$$

An n.m.r. tube containing $(SiH_3)_3P + PF_2Br$ was left at room temperature for 10 days and knowing that $(SiH_3)_2\ PPF_2$ was present, the products were distilled into another tube and germyl bromide was added in a 2:3 ratio -(of $(SiH_3)_3$ P to (GeH_3Br).)
Both sections of the observed ^{31}P spectra obtained showed three sets of patterns, already typical of di-phosphines

a) $(SiH_3)_2PPF_2$ - known to be here

b) $(GeH_3)_2\ PPF_2$ - known from above

c) $(SiH_3)\ (GeH_3)\ PPF_2$ - postulated as it has a phosphorus chemical shift to low frequency intermediate to that of the $(SiH_3)_2\ PPF_2$

& $(GeH_3)_2PPF_2$. The ^{19}F spectrum and low frequency ^{31}P spectrum illustrated non - equivalence of F in the case of the 'mixed' diphosphine, $SiH_3(GeH_3)PPF_2$.

Rn 2.9 Preparation of other QPH PF_2 phosphine derivatives:

$$(Me_3Si)_2PH + PF_2Cl \quad \text{--X-} \quad PF_2PH\text{-}SiMe_3$$

It is known from David Arnolds thsis that tratment of $(SiH_3)_2PH$ with PF_2Br produced, albeit short lived, $SiH_3.PH.PF_2$. When the reaction with $(MeSi)_2PH$ was similarly undertaken only $(Me_3Si)_2PPF_2$ could be detected in the spectrum ie there was no $PF_2-PH-SiMe_3$.

As $(Me_3Si)_3P$ is involatile under vacuum at room temperature only $(Me_3Si)_2PH + Me_3SiPH_2$ (trace) could have been present in the tube, originally, before addition, by distillation, of PF_2Cl. The range of phosphines PH_3, Me_3SiPH_2, $(Me_3Si)_2PH$ & $(Me_3Si)_3P$ was also detected which implies that disproportionation by catalysts had occurred. Such disproportionations had also been observed earlier. The $(Me_3Si)_3P$ had been added to the n.m.r. tube in a glove bag witha syringe, prior to treatment with water.

Rn 2.10 $(Bu_3Sn)_2PH + PF_2Br \; \text{-X}\rightarrow \; (Bu_3Sn)PHPF_2$

$\text{-X}\rightarrow$ or $(PF_2)_2PH$

From results obtained in earlier experiments it was known that $(Bu_3Sn)_3P$ when heated with HCl gas reacted to give $(Bu_3Sn)_2PH$. An n.m.r. tube was made up with $(Bu_3Sn)_3P$ & treated with HCl. Addition of PF_2Br, with the idea of forming both the mono-PF_2 compound and the bis PF_2 compound, followed but as in the example above only $PF_2P(SnBu_3)_2$ could be detected from a range of temperatures from - 60°C to 10°C. At this high temperature the solution solidified to a red mass with the consequent disappearance of the ^{31}P resonances. Treatment of $(Bu_3Sn)_3P$ with HCl would also yield Bu_3SnPH_2 which on further treatment with PF_2Br would be expected to yield PF_2PH_2, however none was detected.

Reaction Scheme 4:

$$RPQ_2 + 2PF_2Br \xrightarrow{H_2O/HBr} R.PH.PF_2 + 2\,Q\,Br + (PF_2)_2O$$

$R = CH_3$ $\quad$ $Q = SnBu_3$

Rn 2.11 $CH_3P(SnBu^n)_2 + PF_2Br \xrightarrow{X} CH_3P(SnBu_3)\,PF_2$
(Postulation)

$$\xrightarrow{X} CH_3P(PF_2)_2$$

In all attempts at the above reaction only $PF_2PH\,CH_3$ could be detected. All precautions were taken against moisture entering the systemthrough reagents and all fluorophosphine was purified to remove HBr. The presence of $CH_3PH.PF_2$ however persisted and its assignment was made as it had previously been prepared by the treatment of $(PF_2)_2S$ with $MePH_2$.

$$\longrightarrow PF_2\,PH.CH_3 + HPF_2{=}S$$

$PF_2PH.CH_3$ was found to be longer lasting than $PF_2P(CH_3)_2$ as far as the observation of n.m.r. spectra was concerned. Where $PF_2P(CH_3)_2$ lasted an hour at - 60°C, $PF_2PH\,CH_3$ was found to be stable for several hours at -40°C enabling a full set of spectra to be obtained.

Rn 2.12 $(Bu_3Sn)_2PMe + 2\ GeH_3Cl \dashrightarrow (GeH_3)_2PMe$
$+ 2\ Bu_3SnCl$

$(GeH_3)_2PMe + PF_2Br \xrightarrow{X} PF_2P(CH_3)GeH_3$

In the example illustrated above, only $PF_2PH.CH_3$ could be detected, under similar conditions applied.
From results described in Chapter 1, $(GeH_3)_2PMe$ was prepared via an exchange route on $(Bu_3Sn)_2PMe$ with germyl chloride.

It should be noted that in all the reactions involving tin phosphines large amounts of PF_3 were formed on warming the tube. The actual amounts of diphosphines were small and the difficulties in recording the multiplet resonances were not aided by 'fold back' from PF_3 and starting materials.

Discussion of the properties of PF_2PQ_2 + $PF_2PQ'Q$

This section must be dealt with in terms of ^{31}P n.m.r. & ^{19}F n.m.r. as data from these spectra are the only physical data available as most of the compounds were not isolable. Reactions of $(GeH_3)_2PPF_2$ are dealt with separately.
Studies of the chemistry have been described and the reactions with B_2H_6 follow.
Comment has already been made on thermal stabilities of the various diphosphines prepared.
The n.m.r. data for the disphosphines produced is shown in table 2.2.
The parameters which were readily observed are $\delta P_{(F)}$ $\delta P_{(M)}$, $^1J(PF)$ $^2J(PF)$ and $^1J(PP)$
It can be seen from the table that the chemical shifts of the high frequency phosphorus nuclei are all around + 300 ppm (n.b. positive

shifts are those defined as to higher frequency than H_3PO_4).

The chemical shift of the other phosphorus in the molecule ie. the shift to low freequency, shows much more variation. This variation is shown, with the aid of correlation diagrams, to be dependent on the 'metal' substituent on the phosphorus. Correlation diagrams, similar to those constructed in chapter 1 show parallel changes in δP with the substituent. Each diagram is later described in detail.

The values for δF , ^1JPF & ^2JPF do not show considerable variation - again it is worth pointing out the non-equivalence of the fluorines with $PF_2PH\,GeH_3$, the resultant set of δF & ^2JPF show some considerable internal variation.

The parameter which shows the most striking variation is J_{PP} which varies from 381 HZ in the case of $(Me_3Si)_3PPF_2$ to 235 HZ in $CH_3PH\,PF_2$. The coupling constant ^1JPP in $(GeH_3)_2PPF_2$ was found to be -ve in sign, as in the case of P_2F_4, hence the values assigned to the diphosphines for ^1JPP are assumed to be negative.

Table 2.3 illustrates the variation in JPP for a variety of diphosphines. No temperature dependence was found in the value of ^1JPP from room temperature to - 100°C and in the case of P_2F_4 none was found down to - 140°C.

For the simple hydride di-phosphines with silicon and germanium i.e. $(SiH_3)_2\,PPF_2$ & $(GeH_3)_2\,PPF_2$, JPP is 80 HZ smaller than for the alkylated metal diphosphines . eg. $(SiH_3)_2\,PPF_2$ J_{PP} = 301Hz.

$(Bu_3Sn)_2\,PPF_2$ J_{PP} = 382Hz.

$(Me_3Si)_2\,PPF_2$ J_{PP} = 381Hz.

As no detection of $Bu_3Sn\ PH.PF_2$ was made a general discussion of trends in $^1J_{PP}$ for compounds of the type QHP PF_2 is impossible although both SiH_3-PH-PF_2 & GeH_3-PH-PF_2 show reductions in ^1JPP of 45 HZ from the corresponding values for $(SiH_3)_2$ & $(GeH_3)_2$ PPF_2 respectively.

Commentary of the Correlation Diagrams D 3.1 --- D3.6

The diagrams illustrate the linear realtionships between the chemical shift and the no. of groups bonded, to the central phosphorus, of a particular type. The horizontal axis shows the chemical shift of the central phosphorus w.r.t. H_3PO_4 standard. The vertical axis shows the type & no. of groups.

D.3.1. shows the relationship between the groupings PF_2, H, SiH_3, bound to Phosphorus.

D.3.2. Groups PF_2, H, $SiMe_3$

This correlation, it must be noted, is by no means as successful. This is undoubtedly due to the variation in δP for the series $(Me_3Si)_3$ P --→ PH_3.

D.3.3. Groups PF_2, H, GeH_3.

This, like the diagram D 3.1 shows a clear linear relationship within the system. The central value of -164 lies on the precise experimental value for $PF_2PH\ GeH_3$ as measured, for δP(Ge). The 'not yet prepared' compounds $(PF_2)_2$ PH & $(PF_2)_2$ P GeH_3 have their δP $_{(M)}$ predicted from the diagram.

D.3.4:Groups PF_2, Me_3Si, GeH_3

The central position here would predict the value for SP(M)of $(SiMe_3)(GeH_3)PPF_2$. This compound was not prepared.

D.3.5 Groups PF_2, SiH_3, GeH_3

The central position is that for $PF_2P(SiH_3)GeH_3$ which has been observed in the n.m.r. spectrum of ^{31}P. The predicted value lies well within the experimental value.

D.3.6: Groups PF_2, H, $SnBu_3$.

Attempts to prepare $(PF_2)_2$ PH & $PF_2PH\ SnBu_3$ have been described. The predicted values for δP are indicated .

To sum up, the most successful correlations were found to be those which involved the groups PF_2, H, SiH_3 & GeH_3 (- any three of four) The groups Bu_3Sn & Me_3Si could be included only if H were to be excluded to illustrate the relationship.

The correlation diagrams illustrate another way of representing the relationship and interdependence of the groups on the central phosphorus to the chemical shift. As discussed in the introduction Engelhardt's relationship was found to be

$$\delta = 11828.5 - 7719\xi - 408\ n\pi$$

Where ξ was the electronegativity , $n\pi$ the πorbital P(3d) occupancy.

Fritz described a relationship concerned only with the type of substituent groups on Phosphorus.

$$\delta\,(^{31}P) = 120a + 80b + 20.5c + 2d - 12e$$
$$-5.5\,ab - 10\,bc - 11\,ac$$

The deviations in non linearity must be accounted for by slight structural charges due to crowding by the methyl & butyl groups on silicon and tin respectively.

Isolation and Stability of diphosphines

Of all the diphosphines prepared and observed spectroscopically in an n.m.r. tube only $(GeH_3)_2\,PPF_2$ was isolable. The compound is described in a later chapter more fully but it is worthwhile stating that it is stable in the gas phase at a pressure of 5 mm Hg, stable in the liquid phase at room temperature for a few minutes (it polymerises slowly) & stable in solution (benzene) for several weeks at room temperature.

$(SiH_3)_2PPF_2$, never isolated despite many varied attempts, could be distilled with some decomposition to SiH_3F; kept in solution (benzene) for several days, again with decomposition to PF_3 & SiH_3F.

Attempts to prepare the diphosphine by exchange of GeH_3 - for SiH_3- in $(GeH_3)_2\,PPF_2$ failed although GeH_3I was detected in the I.R. spectrum using SiH_3I as the exchanging group.

The tin phosphines were quite unstable in solution unless cooled. $(Bu_3Sn)_2\,PPF_2$ was eventually prepared readily in solution, once the correct temperatures & solvent had been assessed. The compound $(Me_3Sn)_2\,PPF_2$ proved to be the most elusive of all as only the ^{31}P spectrum could be determined despite several attempts to record /

observe the ^{19}F spectrum, with fresh n.m.r. tubes. Isolation of these diphosphines would prove to be impossible as separation from R_3SnBr (produced by the reaction) would have to be carried out .

As $(CH_3)_2PPF_2$ was not expected to be particularly unstable (in a vacuum) an attempt to prepare the diphosphines by condensation of PF_2Br & $(SiMe_3)P(CH_3)_2$, followed by warming to room temperature was made. This resulted in a vigorous evolution of heat with a red, polymeric insoluble material left, with only PF_3 & Me_3SiBr as the volatile components. The reaction could however be controlled, but even, at the temperature of reaction (about - 60°C) in solvent, the compound lasted only about an hour. The instability of this species is baffling and as yet no reasoning can be proposed for it.

Some reactions of diphosphines

In the earlier section various exchange reactions and additions of HX have been described,.

A chapter is devoted to $(GeH_3)_2PPF_2$ and its reactions.

The borane adducts of some of the diphosphines were prepared in n.m.r. tubes and these are discussed here with the borane adduct of $(GeH_3)_2PPF_2$ to complete the series.

R.n 2.13 $(GeH_3)_2PPF_2 + B_2H_6 \longrightarrow BH_3:PF_2P(GeH_3)_2$

When a 1:1 mixture of diphosphine & borane was allowed to warm in an n.m.r. tube, the proton spectrum showed that another species was present.

The observation of the ^{1}H spectrum showed two regions when Boron decoupling was employed. These were interpreted as being due to GeH_3 & BH_3 protons and from the consideration of coupling constants that the BH_3 group was associated with the PF_2 group and from the consideration of peak heights and area that only one BH_3 had co-ordinated.

Spectra were difficult to record due to broadening by ^{11}B. This was resolved successfully in the case of the high frequency phosphorus n.m.r. spectrum and the quartet splitting due to ^{11}B (I = 3/2) was clearly visible at J (PB) = 40Hz.

Attempts to resolve the low frequency phosphorus spectrum resulted in the splitting beginning to appear but not enough to enable a measurement of a coupling constant to be carried out.

The ^{19}F spectrum of the adduct proved to be interesting when the decoupler was switched off from decoupling protons. The decoupled spectrum shows a doublet of doublets with $^{1}J(PF)$ = 1210 Hz & $^{2}J(PF)$=31 Hz. When the proton coupling was retained $J(H_BF)$, was seen to be 23.5 Hz and the $J(H_{Ge}F)$, value is 2Hz When the boron proton splitting is considered a pseudo quintet results - consideration of the germyl proton splitting illustrates the 2Hz splitting into multiplets. (See spectra).

The proton couplings to fluorine and both phosphorus atoms were corroborated by the proton spectrum. The n.m.r. data are presented in table 2.4. The ^{11}B chemical shift was established from an experiment in which ^{11}B was 'tickled' from the protons in the observation of the proton spectrum. Without this decoupling no detection of the resonance due to hydrides of boron protons was possible. The J_{BF} was not detected, it must be very close to zero as can be seen on the spectrum.

Rn 2.14. $(Bu_3Sn)_2 PPF_2 + B_2H_6 \dashrightarrow BH_3 : PF_2 P(SnBu^n{}_3)_2$

$(Bu_3Sn)_2 PPF_2$ was first prepared in an n.m.r. tube and B_2H_6 added to the n.m.r. tube contents. The borane adduct was observed in both the ^{31}P spectra and the ^{19}F spectrum. The adduct proved to be as unstable as the di-tin-diphosphine itself and on warming to room temperature the contents of the n.m.r. tube solidified.

Rn 2.15. $PF_2P(CH_3)_2 + B_2H_6 \dashrightarrow BH_3 : PF_2P(CH_3)_2$

The diphosphine was prepared from treatment of $(Me_3Si)P Me_2$ with PF_2Br at - 78°C, then B_2H_6 was added in a 1:2 ratio. The high frequency phosphorus spectrum was the only one obtainable and a pattern of a triplet of doublets was obtained suggesting the adduct of $PF_2P(CH_3)_2$ was present. However it must be noted that the value for $^1J_{PP}$ decreased from 250 HZ in the diphosphine to 194HZ for the adduct. Normally the borane adduct causes an increase in $^1J_{PP}$. The adduct proved no more stable than the diphosphine and quickly decomposed.
In all the diborane/diphosphine experiment the adduct of PF_2H was detected.
In the case of $(SbBu_3)_2 PPF_2$ decomposition to PF_2H can only arise from water present or reaction with the boron hydride.

To check this $(GeH_3)_2PPF_2$ was tested with B_2D_6 and the phosphorus spectrum was recorded. No trace of PF_2DBD_3 was observed when the tube was left at room temperature for several days allowing the contents to decompose.

It must be stated that other decomposition products included PF_3, $(PF_2)_2O$ over this time and as a precipitate had clouded over the tube good spectra were impossible to obtain, due to this and to fold back ofother peaks.

Some comments on the n.m.r. data:

The data in tables 2.2, 2.3 & 2.4. have been assembled mainly from this work. The actual tracings of spectra are presented here and a commentary on recording conditions is attached to each one.

Using the facility to switch decoupler and observe modes of the spectrometer, some ^{119}Sn spectra are recorded. Recognizable spectra were obtained after only 154 pulses, but as each pulse required a delay of 50 s. to eliminate the overhauser depletion, spectra took a long time to record.

Table 1.2 shows the values of $^1J_{PSn}$, $^2J_{PSn}$. and $^3J_{FSn}$ (^{119}Sn) and when a theoretical spectrum is evaluated the tracing can be superimposed on the rather noisy spectrum to verify the peak positions. This spectrum is appended.

In chapter 1, ^{119}Sn spectra are discussed with respect to the phosphines $(Bu_3Sn)_3P$ and $(Me_3Sn)_3P$ and their derivatives.

Appendix to Chapter .

A brief incursion was made into Arsenic chemistry. On an n.m.r. tube scale $(SiH_3)_3$ As was treated with PF_2Br, however after many months at room temperature no reaction could be observed.

It would be worth experimenting with $(Bu_3Sn)_3$ As or $(GeH_3)_3$ As to see if PF_2-As compounds could be prepared, in a similar route to the compound $P(PF_2)_3$.

Chapter 3

Introduction:

The preparation and identification of tri & tetra phosphines :

The tetra phosphine $(PF_2)_3P$ was first proposed by Solan & Timms in 1968 (47) by the thermal decomposition of P_2F_4. The product was identified on the basis of its n.m.r. & mass spectra.

$$P_2F_4 \xrightarrow[\text{5 mm quartz tube}]{\text{3 torr/900}^\circ\text{C}} \overset{\text{low temp fractionation.}}{(PF_2)_3\,P.}$$

The mass spectrum showed $P_4F_6{}^+$ at 238 m/e.

The product was observed to melt at -68°C, decompose rapidly in the vapour phase & in the liquid phase above 10°C.

A more conventional chemical process was sought to prepare this compound.

Chapter 2 describes how no farther substitution was observed in the case of the reactions involving treatment of $(GeH_3)_3P$ and $(SiH_3)_3P$ with PF_2X to form PF_2PQ_2.

The tin phosphines provided a ready route to $(PF_2)_3P$ by similar exchange and in fact alteration of the stoichiometry resulted in the preparation of $(PF_2)_2$ P Sn $Bu^n{}_3$ as well This part is concerned with the preparation and identification of the tri and tetra phosphines.

Attempts to prepare $(PF_2)_2$ PH & $(PF_2)_2$ PMe are described as are attempts to isolate the tetraphosphine itself.

The products of reaction were identified by ^{31}P n.m.r.

If the spectrum of the central, 'tin' phosphines is considered on a first order basis for each phosphine -- then,ignoring fluorine splittings. the basic pattern can be expected as follows.

Compound	Basic Pattern expected for P'.	
$F_2PP'(ShBu^n_3)_2$	P' split by one PF_2- group	doublet.
$(F_2P)_2P'(SnBu^n_3)$	P' split by two PF_2- groups	triplet.
$(PF_2)_3P'$	P' split by three PF_2- groups	quartet.

Continuing on a first order basis the fluorine splittings can be superimposed on the patterns predicted above.

Reaction 3.1 :

The reaction of $(Bu_3Sn)_3P + PF_2Br$:

A 3:1 ratio of fluorophosphine to tin phosphine mixture was made, and reaction, at room temperature, was allowed to proceed. On warming a rapid reaction took place which yielded PF_3 as the only volatile component together with a mass of red polymeric material. PF_3 was detected by I.R. spectroscopy. The reaction was repeated in an n.m.r. tube using the same ratio of reactants + solvent ($d_6$benzene)). When the n.m.r. tube was warmed to room temperature only PF_3 could be observed in the ^{31}P spectrum. The contents of the n.m.r. tube had by this time solidified to a red mass, which was not identified.

Low temperature n.m.r. work was then used to detect the various products expected from the reaction of $(Bu_3Sn)_3P$ with PF_2Br in ratios of 1:1, 2:1, 5:2 & 4:1 (PF_2Br; $P(SnBu_3)_3$). The solvent used initially was $CDCl_3$ which melts at -64°C.
When the ratio was 1:1 $(Bu_3Sn)_2PPF_2$ was detected among the products of reaction; for a ratio of 2:1, $(PF_2)_2PSnBu_3$ was identified, for a ratio of 5:2 both $(PF_2)_2PSnBu_3$ & $(PF_2)_3P$ were formed; while a ratio of 4:1, the only PF_2 product was $(PF_2)_3P$. Simple analysis by $\delta P(Sn)$ + coupling constants identified the components. Detailed analysis follows in the text.

These experiments were repeated in different solvents - CD_2Cl_2 & d^8 toluene. The temperature of the reaction was that of the probe of the n.m.r. machine. The 5:2 ratio tube was allowed to warm to -78°C in a slush of acetone & CO_2 before it was placed in the probe. At that temperature a slight yellow colour

could be seen in an otherwise clear solution. Only PF_2Br and $(Bu_3Sn)_3P$ with a little PF_3 could be detected. At -70°C no reaction took place. At -60°C however a reaction so vigorous occurred that it caused the lock, on deuterium, to be lost. On a quick examination of the tube, the contents were slightly yellower but nevertheless clear, and bubbling was noted. A recording of the spectrum resulted in the observation of resonances due to $(PF_2)_2P\ SnBu_3$, $(PF_2)_3P$ with some PF_2Br, $(Bu_3Sn)_3P$ & a little PF_3,
$(Bu_3Sn)_2\ P\ PF_2$ was the main compound found and the presence of it and the other fluorophosphines was corroborated by the ^{19}F spectrum.

The tin phosphine proved to be stable in solution at temperatures below -30°C. Decomposition took place rapidly above that temperature to PF_3 & red insoluble polymeric material.

RN 3.2 $(Me_3Sn)_3P + PF_2\ Br$:

Reaction mixtures of 1:1, 2:1 & 3:1 ratios of PF_2Br:Phosphine were allowed to react at -96°C in d^8toluene solvent in an n.m.r. tube. The compound $PF_2P(SnMe_3)_2$ was detected at that temperature and was stable for a few minutes so that only the high frequency spectrum of ^{31}P was observed. The chemical shift of + 326 ppm is the highest recorded. Repetition of the experiment failed to show $PF_2P(SnMe_3)_2$.
The 2:1 ratio failed similarly, showing only that PF_3 was present. However the 3:1 ratio resulted in the expected formation of $(PF_2)_3P$ which was stable in solution as before -($PF_2P(SnMe_3)_2$ is also discussed in Reaction 2.5.)

Isolation of $(PF_2)_3P$:

Rn 3.3.

It is not possible to isolate $PF_2P(SnBu_3)_2$ & $(PF_2)_2$ $PSnBu_3$ from solution as they would have to be separated from Bu_3SnBr at low temperature. Isolation of $(PF_2)_3$ P however at first sight appears to be possible in principle.

A 3:1 ratio mixture of PF_2Br and $(Bu_3Sn)_3P$ on an experimental preparative scale was allowed to warm in a glass ampoule to - 23°C and all the volatiles at this temperature were distilled into a clean pyrex trap. When the fraction was warmed to separate the components decomposition was noted on the glass walls of the trap. PF_3 & PF_2Br were the only products identified from the reaction. A yellow green deposit was left on the apparatus. This suggests that $(PF_2)_3$ P had in fact been formed, and as was stated by Solan & Timms (47) decomposition on warming after condensation occurred. The experimental section describes the quantities used.

Another route to $(PF_2)_3$ was attempted.

Rn.3.4., $3PF_2Cl + PH_3 + 3Et_3N \dashrightarrow (PF_2)_3P + 3Et_3NH^+Cl^-$

Accordingly, an n.m.r. tube was made up with equal proportions of PF_2Cl & Et_3N to a third of PH_3. The phosphorus spectrum showed only PF_3 present at -60°C, farther warming precipitated a brown solid in the n.m.r. tube. It is interesting to speculate on what is happening in this reaction, but the fact that PF_3 is so readily formed at so low a temperature suggests that $(PF_2)_3P$ has been produced and has decomposed, probably due to the presence of Et_3N.

Schemes to prepare other tri phosphines :

A reaction scheme to prepare the unknown compound $(PF_2)_2$ PH was devised.

Reaction 3.5: $(Bu_3Sn)_2PH + PF_2Br \longrightarrow (PF_2)_2PH + 2Bu_3SnBr$

Since $(SiH_3)_2$ PH, treated with PF_2Br (49) yielded $PF_2PH\,SiH_3$ then by analogy treatment of $(Bu_3Sn)_2$ PH with PF_2Br would yield both $PF_2PH\,SnBu_3$ & $(PF_2)_2$ PH if substitution occurred in a similar way as in the case of the tertiary phosphine $(Bu^n_3Sn)_3P$.

It is known from chapter 1 that treatment of $(Bu_3Sn)_3$ P with HCl in a 1:1 ratio produces $(Bu_3Sn)_2$ PH. An n.m.r. tube containing $(Bu_3Sn)_3$ P + HCl was treated with a 3:2 molar proportion of PF_2Br.

On warming to -60°C only $PF_2P(SnBu_3)_2$ could be detected and farther warmingto -20 produced no change until the usual decomposition took place. No sign of $(PF_2)_2$ PH or $PF_2PH\,SnBu_3$ could be detected in the ^{31}P spectrum. To be decisive this experiment would have to be repeated using pure $(Bu_3Sn)_2$ PH as the presence of Bu_3SnX (X=Cl,Br) in the reaction would prevent farther substitution due to an equilibrium being set up. The reaction described involved warming a mixture of $(Bu_3Sn)_3P$ and HCl before treatment with PF_2Br.

In chapter 2, the reaction between $(Bu_3Sn)_2PCH_3$ & PF_2Br is described. $(PF_2)_2$ PCH_3 was the expected product: however PF_2PHCH_3 was detected instead.

Rn 3.6 Reaction of $(PF_2)_2$ P $SnBu_3$ with diborane :

It was considered interesting to see if borane would coordinate on the PF_2 groups of $(PF_2)_2PSnBu_3$.
Any reaction of this compound would have to be carried out 'in situ' after preparation from $(Bu_3Sn)_3$ P and PF_2Br.
The scheme is laid out below.

$$\begin{tikzcd}
(Bu_3Sn)_3P + 2PF_2Br \arrow[r] & (PF_2)_2 P Sn Bu_3 + 2 Bu_3Sn Br \arrow[d, "B_2H_6"] \\
 & (BH_3:PF_2)_2P Sn Bu_3
\end{tikzcd}$$

$(Bu_3Sn)_3$ P was first treated with PF_2Br in an n.m.r. tube and the reaction was allowed to proceed for a few minutes at -60°C. The tube was then frozen down and B_2H_6 was added.
The ^{31}P n.m.r.spectrum in the low frequency region was recorded. Centred on -108 ppm a triplet could be detected with separation 435HZ.

In the high frequency region a triplet of doublets was detected with the doublet splitting at 440HZ. The larger splitting (triplet) was 1246HZ.

The ^{19}F spectrum showed the presence of PF_3, PF_2Br, and $H_3B:F_2PH$. and two broad peaks centred on -75 ppm with a splitting of 1243HZ.

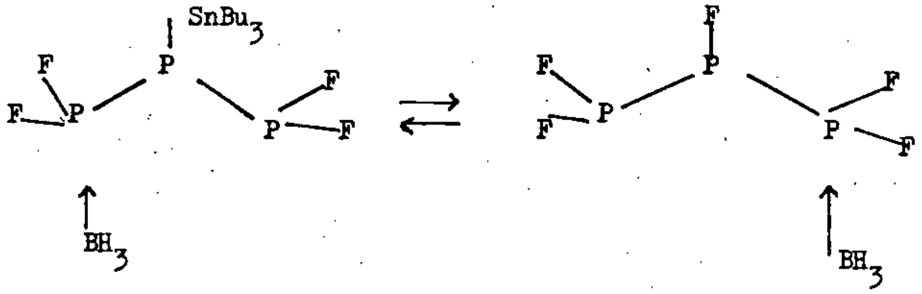
The value of $^1J(PF)$ agrees in both spectra as does the value for $^1J(PP)$ in the sets of phosphorus spectra. The observed values of 440 Hz & 435 HZ must be assumed to be the same coupling as the peaks were too poorly resolved to enable the computer to print out positions.

The coupling $^{2}J(PF)$ was not resolved in either the ^{31}P low frequency spectrum or in the ^{19}F spectrum.

If the low frequency ^{31}P spectrum is to be interpreted in 1st order terms then the fact that a triplet with ^{1}JPP of 440 HZ is observed means two chemically equivalent phosphorus nuclei. The structure $(BH_3:PF_2)_2$ $PSnBu_3$ is therefore postulated.

The coupling ^{1}JPP of the original phosphine is 360HZ and an increase of 80HZ to 440 HZ is consistent with the other borane adducts formed although the value of $^{1}J(PP)$ in $(Bu_3Sn)_2$-$PPF_2:BH_3$ is 100 HZ bigger, than that of the diphosphine.

It could be argued that only one BH_3 group is coordinated if some means of exchange can be envisaged eg.



This would account for the smaller increase in JPP referred to above.

Discussion of the n.m.r. spectra obtained from $(PF_2)_2PSnBu_3$ & $(PF_2)_3P$.

Solan and Timms in their communication stated that the spectra obtained for the tetra phosphine could be interpreted in terms of 1st order considerations, therefore these are now discussed with a view to making tentative identification of $(PF_2)_2PSnBu_3$ &$(PF_2)_3P$.

$(PF_2)_2PSnBu_3$ (referred to as P'P):

In this example the central phosphorus couples equally to the two phosphorus nuclei and would interact with the four fluorine nuclei. Hence, the expected spectrum for P would be a triplet of quintets with the couplings: $^1J(PP)$ & $^2J(PF)$ respectively.

The fluorophosphorus P^1 which resonates at higher frequency would show a pattern, in 1st order terms, of a wide triplet due to ^1JPF with a finer doublet splitting due to the adjacent phosphorus - long range interactions would complicate the structure of the spectra but a recognisable triplet of doublets might be expected. The ^{19}F spectrum would, on the same basis show a doublet of doublets with couplings to phosphorus of ^1JPF and $^2J(PF)$. It would be worthwhile comparing with the ^{31}P & ^{19}F spectra of P_2F_4.

$(PF_2)_3P$

Similarly the ^{31}P spectrum of the central phosphorus of $(PF_2)_3P$ would be expected to show a pattern of a quartet of septets. That of P' would again be a triplet of doublets considering first order interactions, similar to $(PF_2)_2PSnBu^n_3$.

Detailed examination of n.m.r. data:

Table 3:1 shows the n.m.r. parameters which were extracted from the spectra observed of the compounds $(PF_2)_2PSnBu_3$ & $(PF_2)_3P$.

$(PF_2)_3P$

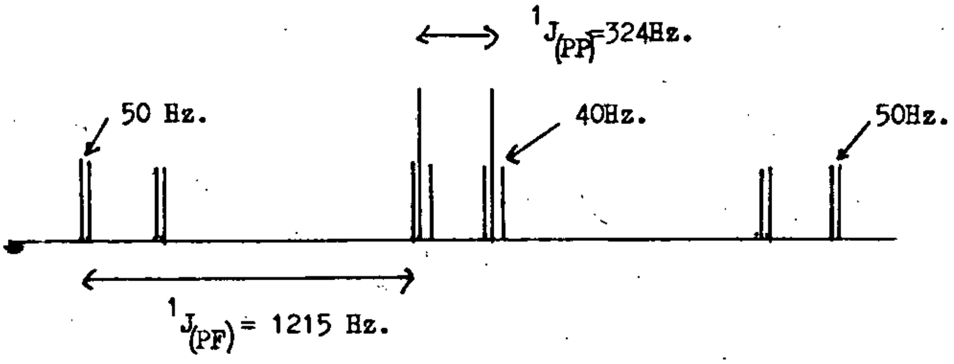
The correlation diagram which illustrates the system for $(PF_2)_3P$, $[H, SnBu_3, PF_2]$ indicates a value for δP which would range between 20 & 50 ppm. Solan & Timms indicated a difference $\Delta(\delta P, \delta P')$ of 245 ppm. The value δP^1 would therefore be between + 265 ppm at + 295 ppm.

It is important to have an idea where these resonances occur as spectral widths and offset values for the spectrometer have to be calculated to avoid 'fold back' from the resonances of other compounds, present in the n.m.r. tube, In the example PF_2Br, $(Bu_3Sn)_3P$ & PF_3 would all cause fold back.

The spectrum was readily recorded for the central phosphorus (P) and was a quartet of septets, i.e. $^1J(PP) = 324HZ$, $^2J(PF) = 61HZ$.

The resonances due to P^1 were observed 240 ppm to higher frequency from the central phosphorus resonances and the value of ^1JPP obtained for the low frequency spectrum, 324HZ, was corroborated in the high frequency spectrum. This took the form of a triplet of doublets, the central doublet showed a farther small triplet splitting of 40HZ while the outer lines showed doublet splitting of 50 Hz. This spectrum is illustrated in stick diagram format overleaf.

The ^{31}P n.m.r. spectrum, to high frequency of H_3PO_4 of $(PF_2)_3P$:



The ^{19}F spectrum showed a doublet of doublets which again corroborated the values of $^1J(PF)$ & $^2J(PF)$ observed in the phosphorus spectra. Lines of 2nd. order effects were also seen. The spin system to which this belongs is $(A(X)_2)_3M$ and was too complex for a computer analysis to be undertaken. Tracings of spectra are shown and experimental details are described in the experimental section.

$(PF_2)_2$ $PSnBu_3$

Use of the correlation diagrams gave an initial idea of where to find the central phosphorus resonance. A triplet of quintets is the expected pattern and this was indeed observed with the addition that the central peak of the cental quintet showed triplet splitting of 4.4HZ and the outermost lines of the central quintet were split into doublets with separation 9HZ. The value of $^1J(PP)$ at 360HZ was corroborated by measuring the P^1 resonance, which appeared at 334 ppm to higher frequency, at +301 ppm. The spectrum of the high frequency phosphorus nuclei proved more difficult to record at the spectral width required. The spectrum predicted to be a triplet of doublets, did indeed show this pattern, but 2nd. order effects were quite marked. Thevalue of $^{1}J(PP)$ corroborated the fact that the peaks came from the same compound.

The central doublet showed quintet splitting of 70HZ while the outer lines separated from the centre by $^{1}J(PF) = 1215Hz$. showed very complex patterns as can be seen.

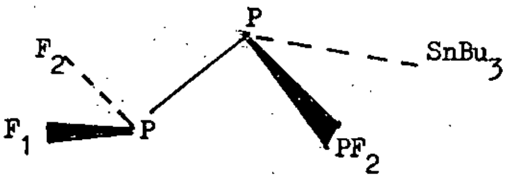
The ^{19}F spectrum shows a doublet of doublets with lines of lesser intensity.

From these lesser lines a value of $^{2}J(PP)$ can be deduced, this assumes the nuclei are not equivalent. Use of the spin system $(AX_2)_2$ shows which lines should be taken and a value of 195HZ was obtained, for this coupling constant.

In each example of the spectra of $(PF_2)_2PSnBu_3$ some 2nd. order effects were observed. A computer simulation was used to analyse the spectra, considered as a spin system $(AX_2)_2M$.

However it was not possible to reproduce the fine triplet splitting in the spectrum of P(Sn).

This means that the two fluorophosphine groups show inequivalence either in themselves as $PF_{\textcircled{1}}F_{\textcircled{2}}$ or to each other as $P_{\textcircled{1}}F_2$, $P_{\textcircled{2}}F_2$. This is illustrated below.



The diagram shows that the fluorines should be non-equivalent as F_1 is trans to tin, while F_2 is trans to the PF_2 group.

Again,spectra havebeen traced and are each presented with details of how they were recorded.

Table 3.1. lists the n.m.r. parameters of $(Bu_3Sn)_n P(PF_2)_{3-n}$

It was not possible to detect ^{117}Sn & ^{119}Sn satellites on the spectra of $(PF_2)_2PSnBu_3$ nor was it possible to record the ^{119}Sn spectrum of the compound. The feature common to the 4 phosphines in the series is δP and the gradation from -347 ppm in the case of $(Bu_3Sn)_3P$ to +24 ppm for $(PF_2)_3P$ is shown. This is by no means steady,as the correlation diagram D3.6 shows. The value of δP^1 for the fluorophosphine,also shows some variation from 322 to 264 ppm. The compound $(PF_2)_2$ P Sn Bu_3 has parameters nearer to $(PF_2)_3P$ for δP, δF & $^2J(PF)$; for δP^1, $^1J(PP)$ it is nearer to the parameters for $(SnBu_3)_2PPF_2$.

It is worthwhile considering the reasons for this, why the $(PF_2)_2$ - compound should be so similar to one as far as one parameter goes and then more similar to the other. There may be important changes in the structure and angles on the central phosphorus.

The series of compounds has generated some interesting spectra and it would be helpful to achieve a good analysis of the spectra by computer simulation. Comparison with other $(PF_2)_2$ PR would be interesting, if a way were to be found to prepare such derivatives.Obviously closer study of some of these complex systems would yield a range of spectra from which more accurate line positions could be defined. If cleaner ways are found to prepare these derivatives then the second order effects can be measured.

Chapter 4 :

Preparation and Properties of $(GeH_3)_2PPF_2$

N.M.R.tube experiments had shown the presence of diphosphines of the type PF_2-P , resulting from treatment of $(GeH_3)_3P$ with PF_2Br. The diphosphines were characterised by ^1H, ^{19}F and ^{31}P n.m.r. The reactions scheme used in the synthesis of $(GeH_3)_2PPF_2$ is given below.

$$(GeH_3)_3P + PF_2Br \longrightarrow (GeH_3)_2PPF_2 + GeH_3Br.$$

This reaction could be brought about either in solvent or as a direct reaction between the phosphines.

In the case of $(SiH_3)_2PPF_2$ the reaction was studied using both sets of conditions, but in each case $(SiH_3)_2PPF_2$ was not detected. The direct combination route rapidly led to the formation of PF_3 and SiH_3F; that in CCl_3F, as solvent, produced the same result only more slowly. In the germyl case however, isolation was relatively straight-forward.

Co-condensation of the two phosphines, followed by a simple fractionation, led to spectroscopically pure diphosphine. This diphosphine, having been isolated, was fully characterised and the study of its chemical reactions was undertaken.

Most of the reactions of the new diphosphine were carried out in sealed n.m.r. tubes with subsequent identification of products by, mainly ^{31}P, n.m.r. ,though I.R. was also used. The gas-phase structure of $(GeH_3)PPF_2$, determined by electron diffraction , is described in the following chapter.

4.1.

Preparation :

Experimental details are describedin chapter 6.

In the case of the germyl diphosphine, easy synthesis was found when the difluorophosphine was co-condensed with trigermyl phosphine. The products were later fractionated on a vacuum line, the byproduct, GeH_3Br being retained for farther $(GeH_3)_3P$ preparation.

4.2.

Molecular weights :

As the vapour pressure of the diphosphine at 293K is only 4mmHg measured on a spiral gauge, the accuracy in determining the molecular weight is ± 5% as the spiral accuracy is to 0.2 mmHg. The resultant molecular weight from several experiments was 247 which is within the experimental error calculated from the 251 theoretical molecular weight.

The transfer from vacuum line to bulb will result in some decomposition of the diphosphine over grease to PF_3, thus accounting for a consistently low reading.

4.3. Mass Spectra

As in the case of $(GeH_3)P^{(98)}$, complicated mass spectra arise, which are due to the germanium isotopic distribution and proton loss on ionization. The mass spectra are only of interest in as much as the parent ion was detected at low ionizing potential with the pattern expected of a molecule with two germanium atoms.

4.4.

Photo electron Spectrum :

The photoelectron spectrum was recorded and assignments were made of the peaks obtained in running the spectrum by comparison of the spectra of $(GeH_3)_3P$ itself and other difluorophosphines.$^{(99,100)}$ In the P.E. spectrumof $(GeH_3)_3P$ bands occur at 9.0, 10.4, 11.2-13.2 e.v., these were assigned on the basis of C_{3v} symmetry to a_1 class, P(3pz) for the lowest ionisation potential where there is a lone pair. The band at 10.4ev. is the GeP bonds level formed from the 3pxy of the central phophorus with the s and Pσ orbitals of germanium. The remaining band is due to the GeH bonds. (σ) at 11.2-13.2ev.

As far as $(GeH_3)_2PPF_2$ is concerned the 3 pz phosphorus electrons are shown at 9.4ev, the GeP bonds at 10.4 ev and the GeH bonds centred on 12.3ev.

For fluorophosphine compounds the spectrum of P_2F_4 serves as comparison. In this case two bands were formed for the P_{3P} lone pairs at 9.64 and 12.45ev centring on 11.0ev. This is the same as the ionization potential of the lone pair on phosphorus in PF_2H. In $(GeH_3)_2PPF_2$ this same level was found at 11.5ev and was thus assigned to the PF_2 lone pair. The P-P bonding level in P_2F_4 was assigned to theband at 14.4 ev; similarly the spectrum of $(GeH_3)_2PPF_2$ has a band at 15.0ev. which is thus assigned to the P-P bonding level. Fluorine lone pairs and P-F bonds occur, typically, between 15.8 and 19.4ev. consequently the band between 15.5ev. and 19.3ev was assigned as the $F_{2p\pi}$ and P-F levels. The spectral details are summarised below in a table.

Position of peaks	Assignments
9.4ev	P(Ge) 3pz
10.4ev	Ge-P σ
11.5ev	P(F) 3 pz
12.3ev	Ge-H σ
15.0ev	P-P σ
15.5-19.3ev	F lone pairs, P-F bonds

4.5 Vibrational Spectra:

I.R. spectra of $(GeH_3)_2PPF_2$ were obtained in both gaseous and solid states. Low frequency I.R. was also obtained using a solution of the diphosphine in pentane.

Raman spectra of the solid were obtained, and all the band position are given in table 4.2.

In the I.R. spectrum of the vapour 3 regions are easily distinguished.

1) The GeH stretch region of ca. 2,000 cm^{-1}
2) The GeH_3 deformation region of 867 cm^{-1}
3) The PF stretching region at 811 cm^{-1}

The distinction between bands due to PF stretching and those due to germyl deformation was made using the I.R. spectrum of the solid.

Assignments of the peaks were again made with the comparison of the spectra of trigermylphosphine [98] and some fluorophosphines. In trigermylphosphine the GeH stretches occur at 2062 and 2079 cm^{-1} in the infrared spectrum of the vapour. These bands are assigned to a_1 and e symmetry classes respectively in C_{3v} symmetry.

In the infra-red spectrum of $(GeH_3)_2PPF_2$ the germyl stretch occurs at 2083 cm^{-1}; the different modes are not resolved. The deformations of both phosphines are now considered.

The germyl deformations on $(GeH_3)_3P$ occurred at 872, 839, cm^{-1} 799 and 753 cm^{-1}. The germyl deformations in $(GeH_3)_2PPF_2$ occur at 867 cm^{-1}.

The rocking modes are now compared.

The germyl rock in $(GeH_3)_3P$ occurs at 516 cm^{-1} and 558 cm^{-1}. The spectrum of $(GeH_3)_2$ PPF_2 shows bands at 509 cm^{-1} and 562 cm^{-1}. When the spectrum of the crystalline diphosphine was recorded, these bands showed increased absorbance. This is also the case in $(GeH_3)_3P$, itself.

The P-F stretches are very strong and appear at 811cm^{-1}. The P-P stretch however, could not be distinguished from the remaining germyl and fluorophosphine rocks and wags, however in the Raman spectrum of liquid P_2F_4(2) a very strong and polarisable band, assigned to νPP occurred at 541 cm^{-1}. The Raman spectrum of solid $(GeH_3)_2PPF_2$ was recorded and a strong sharp band occurred at 447 cm^{-1}. This could well be due to νPP; the shift in frequency would be consistent with the P-P stretch involving heavier groups.

4.6. Nuclear Magnetic Resonance Spectra :

The ^{1}H, ^{19}F and ^{31}P n.m.r. spectra are described in chapter two of this work where $(GeH_3)_2PPF_2$ is treated as a member of the series PF_2PQ_2.

The proton spectrum is a $(\text{doublet})^2$ of triplets. The phosphorus spectrum consists of two sections.

To high frequency the proton decoupled spectrum is a triplet of doublets. With proton coupling retained each line shows sevenfold splitting.

To low frequency, the proton decoupled spectrum is a doublet of triplets. Again each line is split sevenfold when proton coupling is retained.

The fluorine spectrum is a doublet of doublets when protons are decoupled. Retention of proton coupling splits each line into seven.

The n.m. r. parameters are listed in Table 4.1. Signs of coupling constants were based on first finding the relative signs by spin tickling to a self consistent set. ^1JPF was then assumed to be negative (49),

Implications for structure :

The empirical formula $(GeH_3)_2PPF_2$ is easily satisfied when the molecular weight experiment and mass spectra are considered.

When the vibrational spectra and n.m.r. spectra are considered it can be seen that $(GeH_3)_2PPF_2$ bears close resemblance to $(GeH_3)_3P$ as far as the arrangement of germyl groups round the central phosphorus is concerned.

With the preliminary deductions, the structure of the diphosphine $(GeH_3)_2PPF_2$, was completed by a study of the structure in the gas phase by electron diffraction. This experiment and the processing of the data is discussed in Chapter five, with the results.

Reactions of the diphosphine are now described.

Chapter 4, Part 2

Some reactions of $(GeH_3)_2PPF_2$:

In chapter 2 some reactions of $(GeH_3)_2PPF_2$ were discussed with other diphosphines. This section deals with a variety of reactions which were attempted because the diphosphine was isolable. In deciding which reactions to investigate, a study must be made of the chemistry of germyl compounds, fluorophosphine derivatives and diphosphines. The introduction to this thesis covers all these topics.

The reactions which were undertaken were divided into 3 parts.

a) Cleavage of the P-P bond

b) Co-ordination of $(GeH_3)_2PPF_2$ to an organometallic compound.

c) Substitution.

Because of the facilities available and the fact that ^1H, ^{19}F + ^{31}P n.m.r. spectra would result from reactions, most of the reactions were carried out on an n.m.r. tube scale.

a) Cleavage of the P-P bond :

It is known that treatment of P_2F_4 with $(CH_3S)_2$ + $(CH_3Se)_2$ yielded the compounds PF_2SCH_3 and PF_2SeCH_3. In other words the P-P bond has been cleaved, Now, as $(GeH_3)_2PPF_2$ is not a symmetrical diphosphine the cleavage products if any could be of interest, Therefore reactions were carried out in which $(GeH_3)_2$-PPF_2 was treated with disulphides and diselenides.

RN 4.1. $(GeH_3)_2PPF_2 + (CH_3S)_2$

The diphosphine was treated with a dimethyldisulphide in a mole for mole ratio. After 2 days reaction at room temperature, PF_2-SCH_3 could be detected. $(GeH_3)_2PH$, GeH_3PH_2, $(GeH_3)_3P$ + $(GeH_3)_2S$ were also observed in the ^{31}P + ^{1}H n.m.r. spectra. As P_2F_4 reacted cleanly with $(CH_3S)_2$ then onemight have expected $(GeH_3)_2PPF_2$ to yield PF_2SCH_3 and $(GeH_3)_2P$-S-CH_3. This latter species was, however, not detected.

Rn 4.2. $(GeH_3)_2PPF_2 + (CH_3Se)_2$

In a similar way the diphosphine was treated with dimethyl diselenide. Within one hour's reaction time at room temperature PF_2-$SeCH_3$ had been detected. $(GeH_3)_3P$ + $(GeH_3)_2PH$ were also found among the products but as in case above, no sign of a compound, $(GeH_3)_2P$-$SeCH_3$, was detected anong the products by n.m.r. analysis.

The above two reactions had been devised to try and synthesise a species such as $(GeH_3)_2PYCH_3$ where Y = S or Se. Such a species may be subject to rearrangement and even oxidation of phosphorus to P(V) may occur.

Rn 4.3: $(GeH_3)_2PPF_2$ + $(CH_3C(O)S)_2$:

Treatment of the diphosphine with $(CH_3C(O)S)_2$ in an n.m.r. tube was carried out. After several weeks at room temperature the only fluorophosphine species present in any significant quantity was $(GeH_3)_2PPF_2$, under these conditions no reaction occurs.

b) Co-ordination of the diphosphine to organometallic compounds :

A brief attempt was made into the reaction of the diphosphine with some Mo, Fe + Pt systems.

i) Simple exchange reactions with Mo carbonyls.

Rn4.4. $(GeH_3)_2$ PPF_2 + N^+Me py $Mo(CO)_5I^-$

An equimolar mixture of the above was allowed to react in $CDCl_3$. It was hoped that when the N^+MepyI^- had been removed the diphosphine would be co-ordinated. However, even at - 50°C the only product observed was PF_3. A mauve oil separated out and no farther studies of this system was made.

Rn4.5. $(GeH_3)_2PPF_2$ + $Mo(CO)_4$ C_7H_8

The molybdenum carbonyl derivative was treated with $(GeH_3)_2PPF_2$ in a 1 : 2 ratio. The experiment, as before, was carried out in an n.m.r. tube and the reaction initially studied at - 60°C.

It was expected that norbornadiene would be replaced by the diphosphine, No change was detected at this temperature. However, after 4 hours at room temperature the peaks assigned to starting material, $(GeH_3)_2 PPF_2$, had broadened in the phosphorus spectrum and another, much broader PF_2-P type pattern, very poorly resolved, could be discerned.

This was purely transient as on examination of the ^{19}F spectrum the compound was not identifiable and GeH_3F, PF_3, + $(PF_2)_2O$ were detected. The colour of the solution had changed from brown to yellow but had remained clear. Repeated observation of the proton & phosphorus spectrum confirmed the presence of PF_3, PH_3, n.b.d., GeH_3F and unreacted $PF_2P(GeH_3)_2$.

ii) Insertion into a bridged species :

Rn. 4.6. $Fe_2(CO)_9$ + $(GeH_3)_2 PPF_2$

The iron carbonyl $Fe_2(CO)_9$ was chosen, as substrate, to see if $(GeH_3)_2 PPF_2$ would react in a way in which insertion took place. A one to one mixture of the above in deuterochloroform showed no sign of reaction after several months.

iii) Oxidative additions involving Pt lV derivatives.:

Rns 4.7 & 4.8:

Studies of reactions between Group $\overline{\text{lV}}$ hydride derivatives and PtH.X $(PEt_3)_2$ have been carried out by Ebsworth. (111). (X = Cl, I).

These studies involve the formation of a six co-ordinated Pt species initially followed by rearrangement to four co-ordinate platinum and the liberation of hydrogen.

Reactions between the trans Pt species and $(GeH_3)_2PPF_2$ were investigated by ^{31}P n.m.r. In every case, whether with equimolar proporitons of reactants or with an excess of the phosphine, decomposition began at the melting point of the solvent. PF_3 + PH_3 were found and orange-red solids resulted. The systems were not investigated farther.

c) Substitution reactions :

Rn 4.9. $(GeH_3)_2PPF_2 + PF_2I$

Several substitution schemes have already been described in chapter 2, namely treatment with HCl and SiH_3I.

In addition to these, PF_2I was used in a reaction with $(GeH_3)_2PPF_2$ to prepare $(PF_2)_2PGeH_3$ as GeH_3I would be the co-product.

An equimolar mixture of PF_2I & the diphosphine was allowed to react in an n.m.r. tube. No change was found after several days though the amount of PF_3, always present as PF_2I readily decomposed, was found to increase after prolonged standing at room temperature.

In addition to these classified reactions some miscellaneous reactions were studied.

Rn 4.10. $(GeH_3)_2PPF_2 + BF_3$

Vigorous reaction occurred on warming a mixture of these two substrates to room temperature, PF_3 was the only product to be detected and as a pale yellow solid separated out farther ^{31}P study was impossible.

This reaction should be repeated using the variable temperature facility of the n.m.r. spectrometer to enable any BF_2 species to be examined.

Rn 4.11. $(GeH_3)_2PPF_2 + PF_5$

This reaction was not as vigorous as in the case above but PF_3 was the only product to be identified. Yellow solids appeared and as above the system was not farther investigated.

Rn 4.12 & 4.13. $(GeH_3)_2PPF_2 + S$, $(GeH_3)_2PPF_2 + Se$

These reactions involved an n.m.r. study of mixtures of phosphine with an excess of either sulphur or selenium. Carbon disulphide was used as a solvent with the required deuterated solvent.

After several months reaction at room temperature several changes occurred.

$HPF_2{=}S$ was detected in the case of sulphur treatment. It is likely that sulphur has reacted with the germyl protons on prolonged decomposition. In the selenium case no HPF_2Se was detected.

Conclusion

Of all the reactions described above only those involving the disulphides and diselenides proved to be clean. These were the only reactions where an identifiable postulated product did in fact result. Attempts were made to identify the co-product in reaction with $(MeS)_2$ or $(MeSe)_2$.

The reaction could be extended to other biphosphine derivatives and is worthy of farther study.

A reaction scheme of all the reactions described both here and above has been drawn up, and appears in a table(4.3)

Chapter 5 :

The Determination of the Gas Phase Molecular Structure of $(GeH_3)_2$-PPF_2 by Electron Diffraction.

Introduction

From the spectroscopic data, already discussed on $(GeH_3)_2PPF_2$ a lot may be deduced about the molecular structure. As this is the first diphosphine of its type to be isolated it is necessary to compare it with a) germyl phosphine derivatives and b) other PF_2 compounds. It can be expected that the bonds about the germyl phosphorus will be arranged in a similar way to those of $(GeH_3)_3P$ (95). The angle Ge-P-Ge is 95.4°.

In Rankin's study of $PF_2N(CH_3)_2$ (108) non bonded interactions between F and H are discussed. A most recent study of the structure of PF_2-S-GeH_3 found the shortest F-H distance to be 271 pm - as the sum of Van der Waal's radii is 255 pm (109), a weak hydrogen fluorine contact is possible.

It is already known from consideration of the n.m.r. data that $(GeH_3)_2$ PPF_2 showed no temperature dependence when ^{1}JPP was considered.

5.1. Molecular Model and Refinement :

The model chosen for the refinement of the data obtained from the photographic plates, was that for $PF_2Z(MH_3)_2$ which can cater for any angle at Z.

An example of the type of molecule is PF_2NMe_2 whose structure was determined by Rankin (105) in 1971. In this model, where it is assumed that both the PF_2 and Z $(MH_3)_2$ groups have planes of symmetry, the structure may be defined by eight parameters: the angles of $F\text{-}\hat{P}\text{-}Z$, $F\text{-}\hat{P}\text{-}F$, $M\text{-}\hat{Z}\text{-}P$, $M\text{-}\hat{Z}\text{-}M$ together with the three bonded distances of the skeleton F_2PZM_2. Farther, a dihedral angle is defined as that between the planes bisecting the angles $F\text{-}\hat{P}\text{-}F$ and $M\text{-}\hat{Z}\text{-}M$, and each including the P-Z bond. The hydrogen atoms on M are fixed by the M-H bond length and the Z-M-H angle. Local C_{3v} symmetry was assumed for the ZMH_3 groups.

For $(GeH_3)_2PPF_2$, there are the four independent distances: PF, PP, P Ge, GeH and 6 angles $Ge\text{-}\hat{P}\text{-}Ge$, $Ge\text{-}\hat{P}\text{-}P$, $F\text{-}\hat{P}\text{-}F$, $F\text{-}\hat{P}\text{-}P$, $P\text{-}\hat{Ge}\text{-}H$ & dihedral (defined above)

Refinement :

The radial distribution curve P(R)/R is shown on figure (p 144) and this shows the state of refinement used to evaluate the bond lengths and angles. The peak at about 160 pm corresponds to the P-F bonded distance in the same area. At about 220 pm the P-P and P-Ge bonded distances appear and are not resolved.

Clearly, when the peaks overlap it is not possible to refine all the distances, with their amplitudes of vibration, consequently many refinements were attempted by fixing some amplitudes or tying others together in some fixed ratio.

The best refinement was one in which both the P-F & PGe amplitude was free to refine, while the P-P and GeH amplitudes were fixed.

Peaks which appear beyond 240 pm are due to the various non-bonded atom pairs. Their positions depend on the independent distances and the six angles which define the structure. Two of the F-Ge non bonded distances had their amplitude tied and the non bonded distance amplitude, allowed to refine and with the tying ratio of 1:1, resulted in the two distances being equal. It was found necessary however, to fix the amplitude of the shortest non bonded F-Ge distance.

The P-F non-bonded distances had their amplitude refined freely as had the P.Ge and Ge.Ge non bonded distances.

It was necessary to fix all the other amplitudes to typical values (106). By consulting, again, the P(R)/(R) plots, non bonded distances are clearly shown, at 300 pm, 350 pm and 470 pm, these compared to P..F + P..Ge, Ge.Ge, F.Ge, and 2x F..Ge respectively. At about 400 pm there is another peak in the curve which is the remaining F..Ge non bonded distance.

All the angles, except P-Ge were left free to refine, however the dihedral angle was first determined by means of an "R factor Loop" in order to get an approximate value before farther refinement was carried out. P-Ge-H was first allowed to refine but it was found becessary to fix it.

As the F..F and F.P non bonded distances were similar, their amplitudes and the angles F-P-F, F-P-P were clearly correlated although, as was said, it was found necessary to fix the amplitude for F...F.

As so many parameters were refined, there were inevitably strong correlations between the parameters and these are listed in the least squares correlation matrix. (Table 5.3.) Allowance is made for this in the quoted errors for the parameters listed in table 5.2. The errors include random errors obtained in the least squares analysis, with an allowance for systematic errors, e.g. wavelength and camera height.

In the final refinement, the R factors were $R_G = 0.14$, $R_D = 0.11$ where these R factors have been defined (105). Details concerning the experiment and data reduction/refinement stages are described in the experimental section in Chapter 6.

Results and Discussion:

The parameter of obvious interest in a discussion concerning diphosphines is the P-P bond. For comparison with $(GeH_3)_2PPF_2$

r(P-P) is listed for several other simple diphosphines, below, in picometres.

	compound	r(P-P)		Reference
(e.d.)	P_2F_4	228.1	± .003	(88)
"	$P_2(CH_3)_4$	219.2	± 0.9	(94)
"	P_2H_4	221.9	±0.4	(93)
"	$P_2(CF_3)_4$	218.2	+0.8	(88)
"	$P_2F_2(GeH_3)_2$	217.7	+0.8	this work
(μ wave	$P_2F_2H_2$	221.8	∓3.8	(96)
(X ray)	P_2I_4	221.0	±6.0	(107)

As was mentioned in the introduction the length of the P-P (with the exception of P_2F_4 in this case) is fairly constant. The variation in this range is from 218 pm to 222 pm, some 2% variation.

The angles at the phosphorus attached to fluorine was also worthy of comparison with other fluorophosphines These are listed in a table below.

Compound	$\widehat{PPF}$	$\widehat{FPP}$	Reference
P_2F_4	95.4(3)	99.1(4)	(88)
PF_2PH_2	97.2(± 1.6)	98.2(±1.2)	(96)
$PF_2P(GeH_3)_2$	98.9(± 0.8)	98.5(±1.6)	This work

In $(GeH_3)_3P$ the angle Ge-P-Ge was found to be 95.4° and in $(GeH_3)_2PPF_2$ the angles Ge-P-Ge and Ge-P-P are 98.6° and 95.7° respectively. It would be worthwhile to compare these angles with other diphosphines as well as with $(GeH_3)_3P$ itself. $(GeH_3)_2PPF_2$ shows the smallest variation in comparison with the two angles and the angle $X\hat{P}X$ in PX_3 (which is not listed)

PF_2PX_2	$P\hat{P}X$	$X\hat{P}X$
P_2F_4	95.4(3)	99.1(4)
$P_2(CH_3)_4$	101.1(7)	99.6(10)
P_2H_4	95.2(6)	91.3(14)
$P_2(CF_3)_4$	106.7(7)	103.8(8)
$PF_2\ PH_2$	90.3 ±0.4	93.2 ± 1.0°
$PF_2P(GeH_3)$	95.7 ± 0.9	98.6 ± 1.1
P_2I_4	93.6	102.2

Lastly, the presence or otherwise of F..H interactions has to be considered. The shortest F...H bond was found to be 320.9 pm, which puts it well above the distance calculated from the sum of the Van der Waal's radii of 255 pm. It must therefore be assumed that these interactions play little part in establishing the conformation of the molecule.

Chapter 6

Experimental Section

1. Synthetic Methods:

The volatile compounds were handled in a standard Pyrex-glass vacuum system, fitted with greased ground-glass and "Sovirel" polytetrafluoroethylene taps. Apiezon N and L greases were used on glass taps and joints. Off-line experiments were conducted with detachable apparatus fitted with "Sovirel" taps. The amounts of volatile compounds and molecular weights were calculated from gas volumes, assuming Boyle's Law. Materials were fractionated at convenient temperatures using slush baths of liquid nitrogen or solid carbon dioxide in a suitable solvent (110)

Solvents for n.m.r. tube reactions were commercially available and purified as follows.

CCl_3F, C_6D_6, $CDCl_3$ and T.M.S. were spectroscopically pure; C_6H_6 was distilled off sodium; CD_2Cl_2 and CH_2Cl_2 were distilled through molecular sieve. Other solvents were pure enough for use or were purified by standard methods.

Ammonia and diethyl ether were stored over sodium wire, then distilled; dimethyl ether was distilled off $LiAlH_4$ and then fractionated on the vacuum line.

Starting materials for reactions were prepared as outlined below. Checks for purity were made by both infra red and n.m.r. spectroscopy.

All other compounds were either commercial products, or were prepared by standard methods. The reader is referred to "Inorganic Syntheses";

The range of alkyl tin phosphines was prepared the standard way, with the addition of the alkyl tin chloride to a mixture of PH_3 and triethylamine. The resultant phosphine was extracted into ether, filtered and dried on a vacuum line.

Compound	Preparation	Reference
(1) Cl_2PNMe_2	$PCl_3 + HNMe_2$	112
(2) F_2PNMe_2	(1)+ SbF_3	112
(3) F_2PX	(2) + HCl,HBr or HI	112
(4) GeH_3Br	$GeH_4 + HBr + AlBr_3$	113
(5) SiH_3Br	$PhSiCl_3 + LiAlH_4$, then HBr	114
(6) SiH_3Cl	(5) + $HgCl_2$ (streaming)	115
(7) $(SiH_3)_3P$	(5) + KPH_2	116
(8) PH_3	H_3PO_3 + heat	117
(9) AsH_3	$As_2O_3 + KBH_4$	118
(10) B_2H_6 / B_2D_6	KBH_4 /KBD_4 + $H_3(D_3)PO_4$	119
(11) $(R_3Sn)_3P$		120
(12) $MoC_7H_8(CO)_4$		121
(13) Me-Se-Se-Me	Me_2SO_4 + Se + NaOH	122
(14) Me_2PPMe_2	($Me_2P(S)$ $)_2$ + Fe	123
(15) Me_2PH	" + $LiAlH_4$	124
(16) $LiPMe_2$	(15) + BuLi	125
(17) Me_3SiPMe_2	(16) + Me_3SiCl	125

Where other materials mentioned in the text have been used, reference has already been made concerning their preparation in the introduction. However variations in preparation of some of the methyl and dimethyl phosphine derivatives were made to (a) adapt their use to the n.m.r. tube scale requirement and (b) take account of the commercially available reagents at the time.

2. Instrumentation.:

Infra-red spectra were recorded on a Perkin-Elmer 225 grating spectrometer (4000 - 200 cm^{-1}), or a Beckmann RIIC FS720 interferometer (400 - 50 cm^{-1}), using gas cells equiped with CsI windows, a solid/condensation cell with CsI windows , and a solution cell fitted with polythene windows (for the Beckmann). Raman spectra were obtained using a Cary 83 spectrophotometer with argon-ion 488 nm. laser excitation. Mass spectra were recorded with a double focussing A.E.I. MS 902 spectrometer.Ultra violet photoelectron spectra were recorded on a Perkin-Elmer PS16 spectrometer having He(I) excitation (21.22 eV).
N.m.r. spectra were recorded on Varian Associates HA100 and deuterium locking XL100 spectrometers. (126,127). Both spectrometers were fitted with variable temperature control,and the facility to carry out double resonance experiments in the case of the HA100, came from use of a Schlumberger FS/30 frequency generator which was monitored to ensure consistency (128). Various modifications to the XL100 permitted direct observation of many 'rarer' nuclei.

Electron diffraction data were collected photographically on Kodak plates, using Balzer's KD.G2 instrument, with a rotating sector, at the University of Manchester Institute of Science and Technology.(129) . The electron wavelength was determined directly by measurement of the accelerating voltage and also from the diffraction patterns of benzene. Nozzle to plate distances of 250, 500 and 1000mm were used with the samples maintained at room temperature. A Joyce-Loebl automatic microdensitometer was used to convert the data to digital form. The data was then handled by established methods and programmes on the ICL computer at the Edinburgh Regional Computing Centre. (130,131,132). Distances

quoted are r_a values which correspond to the centre of gravity of peaks in the radial distribution curve $P(R)/R$ (133,134).
Errors in distances, amplitudes of vibration and angles have been increased to allow for systematic errors (133). Davis has givem a general account of procedures adopted in the electron diffraction study of gases (135).

3. Experimental details :

All reactions were carried out under vacuum in clean apparatus which was streamed with silyl halide to remove traces of moisture. Many of the reactions were followed in 5mm n.m.r. tubes which were filled under vacuum with condensible material , or filled in a dry, nitrogen filled glove bag with solid or non- volatile material. The n.m.r. tube was then sealed with a gas-torch at a previously formed constriction. It was often necessary to pre-heat n.m.r. tubes in acetone/carbon dioxide, after removal from liquid nitrogen storage . This reduced the risk of broken tubes when the spinner, for insertion into the probe, was fitted.
The experimental details of the reactions described in the text follow on the next page.

Chapter 1 Experimental section :

Reaction 1.1. $(SiH_3)_3P$+ GeH_3Br

0.2 m mole of $(SiH_3)_3P$ was treated with 0.3 m mole of GeH_3Br, in an n.m.r. tube. C_6D_6 and TMS were used as solvents After 5 minutes reactions at -10°C the ^{31}P spectrum was recorded. Resonances due to $(GeH_3)_3P$ and $(SiH_3)_3P$ were observed, those due to the intermediates postulated. After several days' reaction at room temperature the spectrum showed no sign of $(SiH_3)_3P$, only a shift in distribution of the intermediates to the germyl side. Some $(SiH_3)_2PH$ was detected with the consequent formation of $(GeH_3)_2PH$ and GeH_3PH SiH_3.

Reaction 1.3. $(Me_3Si)_3P$ + GeH_3Cl

a) n.m.r. tube scale

0.5 m mole of $(Me_3Si)_3P$ was syringed into an n.m.r. tube in a glove bag filled with dry nitrogen. The n.m.r. tube was transferred to the vacuum line and 1 m mole of GeH_3Cl was distilled into it. The solvent used was $CDCl_3$.

At -50°C only $(Me_3Si)_3P$ was detected when the ^{31}P spectrum was measured and at room temperature $(GeH_3)_3P$ was predominant.

b) Preparative scale

As $(Me_3Si)_3P$ is involatile, it has to be syringed. 1 millilitre weighs 0.941 grammes, therefore, as its molecular weight is 250, then 1 m mole has a volume, at room temperature, of 0.23 millilitres.

4 m moles of $(Me_3Si)_3P$ were treated with GeH_3Cl (13 m moles) in an ampoule fitted with a greaseless tap. The ampoule was allowed to warm to room temperature and the volatile products were fractionated. $(GeH_3)_3P$ was held in a trap at -46°C while Me_3SiCl passed through. I.R.& ^{31}P n.m.r. spectroscopy confirmed the products of reaction.

Reaction 1.4.

$(Me_3Si)_2PH + GeH_3Br$

$(Me_3Si)_2PH$ was prepared the standard way (reference 31) from treatment of $(Me_3Si)_3P$ with water. The water was added to dried ether and a solution of $(Me_3Si)_3P$ in ether was added to this. All reactions at this stage were carried out in a glove bag filled with dry nitrogen; the solution of phosphine, by this time in an ampoule fitted with a greaseless tap, was transferred to the vacuum line for distillation.

0.3 m mole of $HP(Me_3Si)_2$ was treated with 0.3 m mole of GeH_3Br. The solvents used were TMS and C_6D_6 in a 4:1 ratio. The n.m.r. spectra were recorded at -20°C. A wide range of phosphines was detected.

Reaction 1.5.

$(Me_3Si)_3P + SiH_3Br$

0.5 m mole of phosphine were treated with 1 m mole of SiH_3Br in an n.m.r. tube using $CDCl_3$ as solvent. The ^{31}P spectra were recorded at - 50°C and the presence of $(Me_3Si)_3P\ SiH_3$, $Me_3Si\ P(SiH_3)_2$ + $(SiH_3)_3P$ was observed.

Reaction 1. 6 $(Bu_3Sn)_3P + GeH_3Cl$

0.5 m mole of phosphine was weighed out in an n.m.r. tube and the tube was pumped on a vacuum line for 4 hours. 1 m mole of GeH_3Cl was added and $CDCl_3$ was the solvent.

^{31}P spectra were recorded at -50°C. This experiment was repeated with CD_2Cl_2 as solvent.

Reaction 1.7 $(Bu_3Sn)_3P + SiH_3Br$

0.3 m mole of $(Bu_3Sn)_3P$ was treated in an n.m.r. tube with 0.5 m mole of SiH_3Br. $CDCl_3$ was the solvent. The spectra were initially recorded at - 60°C.

Reaction 1.8 $(Bu_3Sn)_3P + Me_3SiCl$

0.3 m mole of phosphine was treated with 0.5 m mole Me_3SiCl in an n.m.r. tube with $CDCl_3$ as solvent. Observation of the reaction commenced at - 60°C.

Reaction 1.9 $(Me_3Sn)_3P + GeH_3Cl$

0.3 m mole of $(Me_3Sn)_3P$ was treated with 0.6 mmole of GeH_3Cl in an n.m.r. tube. $CDCl_3$ was the solvent used. The ^{31}P spectrum was initially recorded at - 60°C.

Reaction 1:10 $(Me_3Sn)_3P + SiH_3Br$

0.3 m mole of $(Me_3Sn)_3P$ was treated with 0.6 m mole of SiH_3Br in an n.m.r. tube, $CDCl_3$ was the solvent used and the ^{31}P spectrum was recorded at -60°C, initially.

Appendix Reactions

Preparation of $(Bu^n_3Sn)_3P$:

$$3\ Bu_3SnCl\ +\ PH_3\ \xrightarrow[Et_3N]{}\ (Bu_3Sn)_3P\ +\ 3\ Et_3NH^+Cl^-$$

A 200 ml. ampoule, fitted with a greaseless tap, was evacuated and then 9.1g of Et_3N and 29.2g of Bu_3SnCl was added. The ampoule was frozen in liquid nitrogen and pumped down on the vacuum line. 23 m mole of PH_3 were then condensed into the ampoule, which was then removed and allowed to warm to room temperature. A white solid was observed to precipitate on warming and after several minutes more Et_3N was added. The ampoule was then opened to air and the phosphine was extracted into ether. The solution was filtered on a sinter and the ether removed on a rotary evapotator. The phosphine was pumped on a vacuum line and was analysed by I.R. and n.m.r. spectroscopy. A yield of 85% was achieved subsequently if the PH_3 was added in stages to excess with ether, though this gave problems with disposal.

Reaction of $(Bu_3Sn)_3P$ + HCl:

The phosphine was treated with 0.45 m mole of HCl (a 1:1 mixture) gas by vacuum distillation in an n.m.r. tube. The ^{31}P and ^{119}Sn n.m.r. spectra showed the presence of $(Bu_3Sn)_3P$,$(Bu_3Sn)_2PH$, $(Bu_3Sn)PH_2$ & PH_3.

Chapter 2 reactions PREPARATIONS OF P-P :

Scheme 1

$$Q_3P + PF_2Br \dashrightarrow Q_2PPF_2 + Q\,Br$$

$Q = SiH_3, Me_3Si, Me_3Sn, Bu_3Sn, GeH_3$

Rn 2.1 $(SiH_3)_3P + PF_2Br$

i) 0.5 m mole of $(SiH_3)_3P$ was treated with 1.5 mole of PF_2Br in a dry ampoule fitted with a greaseless tap. The reactants having been condensed into the ampoule were allowed to react at - 64°C. It was noticed that a yellow orange solid had started to form. Fractionation of the volatile products at this stage, followed by infra- red analysis clearly showed $(SiH_3)_3$ P, PF_2Br + SiH_3F with no trace of SiH_3Br or the expected product $(SiH_3)_2PPF_2$.

On recombination of the $(SiH_3)_3P$ and PF_2Br into the ampoule and allowing farther reaction time up to seven days at room temperature, it was observed that a considerable amount of a red-orange solid had appeared and that the only volatile products detected by I.R. spectroscopy were some SiH_3F and some PF_3. It was also observed during the operation of the high vacuum equipment that non-condensible gas (H_2) had been produced.

ii) 1 m mole of $(SiH_3)_3$ P + PF_2Br were added separately by condensation to an ampoule containing $CFCl_3$(2mls).

The ampule was allowed to warm to -64°C and a yellowish solid started to appear. Fractionation of the volatile products at -64°C, followed by IR spectrometry showed the presence of SiH_3F with unreacted $(SiH_3)_3P$. However other reactions yielding decomposition products resulted as the vacuum line was by this time showing a deposit of a yellow/red solid.

iii) 1.5 m mole of $(SiH_3)_3P$ was similarly treated with 2.5 m mole of PF_2Br in 'Arcton' as solvent. On warming to room temperature there was considerable effervescence and a solid(yellow /green in colour) appeared after 10 minutes. However examination of the fraction, remaining at -64°C, showed the presence of $(SiH_3)_3P$ and $(SiH_3)_3$ PPF_2 breakdown products , i.e. SiH_3F + PF_3 + yellow/solid on IR spectroscopic analysis.

iv) An n.m.r. tube reaction .

$(SiH_3)_3P$ (0.4 m mole) + PF_2Br (1.0 m mole) were added to an n.m.r. tube containing $CFCl_3$ + TMS in an 80% / 20% ratio.

As decsribed in Arnolds thesis (Ref. 49) $(SiH_3)_2PPF_2$ was detected by its n.m.r. spectra.

Rn 2.2 $(GeH_3)_3P$ + PF_2Br

i) 0.15 m mole $(GeH_3)_3P$ and 0.3 m mole PF_2Br were allowed to react at room temperature after condensation into an n.m.r. tube containing the following solvents $CFCl_3$, C_6H_6 and C_6D_6.

Over a period of 21 days the formation of $(GeH_3)_2PPF_2$ was observed with its co-product GeH_3Br. No farther substitution was detected as exhaustive ^1H, ^{31}P + ^{19}F n.m.r. showed PF_2Br (unreacted), $GeH_3)_2PPF_2$, GeH_3Br, and a little PF_3 as the contents. No trace of GeH_3F was detected.

ii)The preparation of $(GeH_3)_2PPF_2$ is described in the section under chapter 4 experimental details.

Rn. $(Me_3Si)_3P$ + PF_2Br.

0.070g of $(Me_3Si)_3P$(0.3 m mole) was weighed into a nitrogen filled n.m.r. tube, in a glove bag. The n.m.r. tube was then pumped for 1 hour on the vacuum line. 1 m mole of PF_2Br was condensed after addition of C_6D_6. $(Me_3Si)_2PPF_2$, $(PF_2)_2O$ and PF_3 were detected in the ^{31}P and ^{19}F spectra while Me_3SiBr was detected from the ^1H spectrum after ca. 10 minutes reaction at room temperature.

3) Rn 2.3 $(Me_3Si)_3P$ + PF_2Cl, PF_2Br.

0.5 m mole of $(Me_3Si)_3P$ was added to an n.m.r. tube into which C_6D_6 was later condensed. 0.5 m mole of PF_2Cl were then added.

After 10 mins. at room temperature, the contents of the n.m.r. tube were examined by ^{31}P n.m.r. and $(Me_3Si)_2PPF_2$ was detected by its n.m.r. parameters.

Rn 2.4 $(Bu^n{}_3Sn)_3P + PF_2Br$

i) $(Bu^n{}_3Sn)_3P$ prepared + purified (see details under Appendix experimental details for Chapter 1) was weighed out (0.23g= 0.25 m mole) and syringed into an n.m.r. tube fitted with a B10 cone. The tube was then evacuated and pumped for 2 hours.
Benzene & d^6 benzene were added as solvents and 0.8 m mole of PF_2Br was added to the tube. On warming the tube after sealing, a red solid was observed to form with rapid effervescence. The ^{31}P n.m.r. spectrum showed the presence of PF_3, with a little $(PF_2)_2O$, as the main product.

ii) 0.845 g (0.95 m mole) of $(Bu_3Sn)_3P$ was syringed into an ampoule fitted with a greaseless tap. 3 m moles of PF_2Br were then condensed into the ampoule which was allowed to warm to -23°C. An orange/brown solid was observed. The volatile products were fractionated through a trap in a slush bath at - 96°C. No volatile products were observed at this temperature however the trap at -196°C contained PF_3 (2.0 m mole.)

iii) 0.5 m mole of $(Bu_3Sn)_3P$ was treated with 0.3 m mole of PF_2Br in a n.m.r. tube. Deuterochloroform was the solvent used. Use of variable temperature ^{31}P n.m.r. enabled the spectrum of $(Bu_3Sn)_2PPF_2$ to be recorded at - 60°C. It was possible to store this compound in solution at this temperature for several hours without appreciable decay to PF_3 and polymeric solids although a yellowish deposit was eventually observed.

Reactions were carried out using different ratios of PF_2Br to phosphine and these are described in the experimental detail section of Chapter 3 reactions.

Rn 2.5 $(Me_3Sn)_3P + PF_2Br$

i) 0.35 g (0.7 m mole) of $(Ne_3Sn)_3P$ was added to an n.m.r. tube by a similar method to that above. The solvent selected was d^8toluene and 0.8 m mole of PF_2Br was added. In order to prevent ice forming on the outside walls of the n.m.r. tube it was necessary to warm the tube to - 78°C before fitting a spinner to enable the n.m.r. operation to be recorded at - 100°C.

The compound $(Me_3Sn)_2 PPF_2$ was detected and most of its parameters established from spectra were therefore recorded.

Other ratios of $(Me_3Sn)_3P$ and PF_2 Br are described under the section dealing with Chapter 3 experimental details.

Scheme 2 $R_2PQ + PF_2Br \longrightarrow R_2PPF_2 + Q\ Br$

$R = CH_3 \quad Q = Me_3Si.$

Rn 2.6 $(Me_3Si)\ P\ (CH_3)_2 + PF_2\ Br$:

i) 0.5 m mole of $Me_3SiP(CH_3)_2$ was treated with 0.5 m mole PF_2Br in an n.m.r. tube containing d^2 CD_2Cl_2. The solvent was condensed on to the phosphine and the tube warmed to permit mixing. A farther layer of solvent was added before the PF_2Br was condensed into the tube. On recording the ^{31}P spectrum of the contents of the tube at -80°C no peaks could be attributed to known compounds with the exception of PF_3 and $(PF_2)_2O$.

ii) The above experiment was repated with d^8 toluene as the solvent and great care was taken in inserting the tube into spinner and variable temperature spectrometer. The tube was warmed to -60°C and the spectrum of $(CH_3)_2PPF_2$ was recorded. This arrangement had to be repeated to collect the data for all the n.m.r. parameters as the tube was of only limited use, even at -60°C, as $(CH_3)_2$ PPF_2 was found to be very unstable.

Rn 2.6 (a) $KPMe_2$ + PF_2Cl

$KPMe_2$ 0.4 m mole was treated with PF_2Cl(0.5 m mole) using an n.m.r. tube filled with benzene as solvent, in an initial attenpt to make $PF_2P(CH_3)_2$. No reaction at room temperature was apparent until after 8 weeks the tube was farther examined and was found to contain PH_3 and PF_2Cl with a yellow solid.

Scheme 3

$$Q_2PPF_2 + MX \dashrightarrow QM\ PPF_2 + Q\ Cl$$

i) $M=H$, $Q=GeH_3$, $X = Cl$

ii) $M=SiH_3$ $Q = GeH_3$ $X = I$

iii) $M = GeH_3$ $Q = SiH_3$ $X = Br$

Rn 2.7 $(GeH_3)_2\ PPF_2$ + HCl :

0.2 m mole of $(GeH_3)_2\ PPF_2$ were dissolved in a 20% C_6D_6/TMS and treated with 0.2 m mole of HCl. The tube was warmed to - 60°C and the spectrum showed the formation of GeH_3PH-PF_2 with some unreacted $PF_2P(GeH_3)_2$. A yellow solid was observed to appear on continued storing at this temperature. The products found on warming to room temperature were $(GeH_3)_2PH$ and $(GeH_3)_3P$ indicating some disproportionation. PH_3 was also detected.

Rn 2.8 $(SiH_3)_2PPF_2$ + GeH_3Br:

Step A: Preparation of $(SiH_3)_2PPF_2$,see above.

Step B: Rn of $(SiH_3)_2PPF_2$ with GeH_3Br

The contents of an n.m.r. tube containing $(SiH_3)_2PPF_2$ were distilled into another n.m.r. tube; this was done by placing the n.m.r. tube into an ampoule so that the tap of the ampoule just covered the sealed end of the tube, previously scored. On rotation of the tap the seal breaks and the contents of the tube, in this case $(SiH_3)_2PPF_2$,SiH_3F, PF_2Br + some $(SiH_3)_3P$ were distilled into another tube. As 0.2 m mole of $(SiH_3)_3P$ had been used in step A it was decided to add 0.3 m mole of GeH_3Br. The 'mixed' silyl/germyl type was detected by ^{31}P n.m.r. spectroscopy.

Rn $(Me_3Si)_3P + H_2O \longrightarrow (Me_3Si)_2O + 2\,(Me_3Si)_2PH$

Rn 2.9 $(Me_3Si)_2PH + PF_2Cl$:

$(Me_3Si)_3P$ is not volatile under vacuum at room temperature so it has to be added to the n.m.r. tube using a syringe. 0.3 m mole was added to an ampule fitted with a greaseless tap and an n.m.r. tube on the side arm. 0.15 m mole of H_2O were added after dissolving the phosphine in dry Et_2O, in a glove bag. The Et_2O was removed by pumping on the ampoule which had to be cooled with ice. The n.m.r. solvents were distilled into the side arm n.m.r. tube and the $(Me_3Si)_2$ PH formed was also condensed and dissolved. PF_2 Cl (0.3 m mole) was added. The tube was warmed to room temperature and the P spectrum was recorded. $(Me_3Si)_2 PPF_2$ was the only diphosphine observed and on allowing the tube to remain at room temperature a yellowish solid appeared while the n.m.r. spectrum showed an increase in the amount of (Me_3Si) PH2. and the appearance of $(Me_3Si)_3P$.

Rn $(Bu^n{}_3Sn)_3P + HCl \dashrightarrow (Bu^n{}_3SnCl + (Bu^n{}_3Sn)_2 PH$

Rn 2.10 2 $(Bu^n{}_3Sn)_2$ PH + 3 PF_2Br :

0.5 m mole of $(Bu_3Sn)_3$ P was syringed into an n.m.r. tube and treated with 0.5 m mole of dry HCl gas, the latter was condensed into the tube with the solvent CD_2Cl_2. The tube was warmed and cooled until no pressure was detected at room temperature. The PF_2Br was then condensed (0.75 m mole) and the tube sealed. On warming to -60°C only $PF_2P(SnBu_3)_2$ was detected as the diphosphine. Warming the tube gradually to room temperature resulted in a red solid forming with PF_3 + $(PF_2)_2O$ observed, in the spectrum as well.

Scheme 4

$$RPQ_2 + 2\ PF_2Br \xrightarrow{H_2O/HBr} RPH.PF_2 + 2Q\ Br + (PF_2)_2O$$

$$R = CH_3 \qquad Q = SnBu_3$$

Rn 2.11 $CH_3P(SnBu^n{}_3)_2 + PF_2Br$

i) 0.33 m mole of $CH_3.P(SnBu^n{}_3)_2$ was added to an n.m.r. tube by syringe, d^8 toluene was added, 0.7 m mole of PF_2Br was added. Observation of the ^{31}P n.m.r. spectrum showed mainly PF_3, $(PF_2)_2O$, however on repeatedly resetting the offset lines to shift "fold back" the species $PF_2PH.CH_3$ was detected. The reagents were then checked. PF_2Br was fractionated several times to remove all traces of HBr and the phosphine was pumped for 4 hours to remove traces of water. Repetition of this experiment yielded no $PF_2H.CH_3$, only PF_3 and a red solid.

Rn 2.12. $(Bu_3Sn)_2PMe + 2\,GeH_3Cl \dashrightarrow (GeH_3)_2PMe + 2\,Bu_3SnCl$.

then.

Rn $(GeH_3)_2PMe + PF_2Br$:

0.65 m mole $(Bu_3Sn)_2PCH_3$ + 1.3 m moles GeH_3Cl were condensed into an ampoule. After 30 minutes at room temperature the volatile contents were distilled into an n.m.r. tube and were treated with 1 m mole of PF_2Br. Warming to - 60° showed the presence of $PF_2PH.CH_3$.

The formation of borane adducts is next detailed. Di borane was prepared and stored under a vacuum, at liquid nitrogen temperatures. The same care has to be taken with it as was taken with the derivatives of silane discussed earlier.

Experimental Section for the borane adduct section of Chapter 2 .

Reactions of Q Q' P-PF_2

Rn 2.13 $(GeH_3)_2PPF_2 + B_2H_6$

0.2 m mole of $(GeH_3)_2$ PPF_2 was treated with 0.2 m mole of B_2H_6 in an n.m.r. tube using a 50/50 mixture of T.M.S. and d^6 benzene as solvents.

On warming to room temperature the n.m.r. spectra of the P,F,H nuclei were recorded and, the parameters obtained for BH_3: PF_2 P $(GeH_3)_2$. This experiment was repeated with B_2D_6 to establish the reason for $H_3B:PF_2H$ formation.

Rn 2.14 $(Bu_3Sn)_2P$ PF_2 + B_2H_6

0.46 m mole of $(Bu_3Sn)_3P$ was treated with 0.4 m mole PF_2Br in an n.m.r. tube using $d^2CD_2Cl_2$ as solvent. 0.2 m mole of B_2H_6 were then added and the tube was sealed. The n.m.r. spectra showed a boron adduct attributed to $BH_3:PF_2P(SnBu_3)_2$. Slightly less PF_2Br was added compared with tin phosphine to ensure no $(PF_2)_2PSnBu_3$ could form.

Rn 2.15 PF_2 $P(CH_3)_2$ + B_2H_6

0.5 m mole of Me_3Si $P(CH_3)_2$ was treated with 0.5 m mole of PF_2Br in an n.m.r. tube using d^8 toluene to dissolve the silyl phosphine and as a buffer between the fluorophosphine and solution. The tube, still attached to the vacuum line was warmed to - 78°C for 5 minutes and then cooled to - 196°C. 0.25 m mole of B_2H_6 was then added. On recording the spectrum at -80°C. A boron adduct of a diphosphine, attributed to $BH_3{:}PF_2$-$P(CH_3)_2$ was observed and although it was as unstable as the parent diphosphine, nevertheless some n.m.r. parameters were obtained.

Rn 3.1.

i) The $(Bu_3Sn)_3P$ was treated with 3 m moles of PF_2Br in an ampoule fitted with a greaseless tap. The ampoule was allowed to warm to - 23°C and the contents were observed to effervesce and turn a reddish colour. Fractionation through a trap at -96°C into one at -196°C yielded only one product which was identified by its I.R. spectrum as PF_3, although decomposition in the traps was observed.

ii) This experiment was repeated in an n.m.r. tube using solvent. 0.25 m mole $(Bu_3Sn)_3P$ was treated with 0.8 m.mole PF_2Br using a 20% d^6 benzene/benzene mixture as solvent. The tube, after sealing, was allowed to warm to room temperature and quickly a red/brown deposit was formed, virtually solidifying the contents of the n.m.r. tube. The ^{31}P n.m.r. spectrum showed PF_3, with some $(PF_2)_2O$, as the only product.

iii) $(Bu_3Sn)_3P + PF_2Br$ 1:2.2.

0.45 m mole of $(Bu_3Sn)_3P$ was treated with 1 m mole of PF_2Br in an n.m.r. tube using $CDCl_3$ as the solvent. Warming the tube to -60°C resulted in a yellowish tinge with no solid appearing. The ^{31}P n.m.r. was recorded showing the presence of $(PF_2)_3P$ + $(PF_2)_2P\ SnBu_3$ with PF_3 + $(PF_2)_2O$.

iv) .25 g $(Bu_3Sn)_3P$ (0.3 m mole) was treated with 1.2 m mole of PF_2Br in an n.m.r. tube using $CDCl_3$ as the solvent. The spectrum of ^{31}P was recorded and resonances attributed to $(PF_2)_3P$ from the literature were observed. (Ref 47).

R n 3.2 $(Me_3Sn)_3P + PF_2Br$

i) $(Me_3Sn)_3P$, 0.4 m mole, was treated with PF_2Br, 1.3 m mole, in an n.m.r. tube using $d^2CD_2Cl_2$ as the solvent The ^{19}F n.m.r. spectrum was recorded at $- 100^oC$ and showed only the formation of $(PF_2)_3P$; even at this temperature with relatively short reaction times, due to the sensitivity of ^{19}F compared with ^{31}P to accumulate data, no sign of intermediates namely $(PF_2)_2PSnMe_3$ or $(PF_2)P(SnMe_3)_2$ was observed.

ii) $(Me_3Sn)_3P$, 0.6 m mole, was treated with PF_2Br, 0.9 m mole in an n.m.r. tube with d^2 CD_2Cl_2 as the solvent. Recording the spectrum of this system at $- 100^oC$ showed the presence of PF_3 even at low temperatures.

R n 3.3:

$3\ PF_2Br + (Bu^n{}_3Sn)_3P \dashrightarrow (PF_2)_3P + 3\ Bu^n{}_3SnBr$

1.5 g of tin phosphine (1.7 m mole) was treated with 5 m mole of PF_2Br in an ampoule fitted with a greaseless tap The reaction was held at $- 64^oC$ for a few minutes. It was noted that a yellow solid was being precipitated. The contents were then fractionated through a trap at -46^oC into one at -196^oC. The glass ampule itself was held at $- 23^oC$. PF_3 and a little PF_2Br was all that remained in the volatile fractions. However a yellow/green deposit had been left on the glassware after the condensed fractions were fractionated. The ampoule had an orange solid left behind, which was not identified.

No farther attempts were made to isolate $(PF_2)_3P$ by this route, though a low temperature fractionation apparatus should be employed to purify the tetraphosphine.

Rn 3.4 $3PF_2Cl + PH_3 + 3Et_3N$

i) 1.5 m mole PF_2Cl_2 was condensed into an ampoule, fitted with a greaseless tap, and treated with an equimolar amount of Et_3N and 0.5 m mole of PH_3. The mixture was allowed to warm slowly, and a yellowish/brown solid formed rapidly. The volatile products were removed and were found to be PF_3.

ii) 0.9 m mole of PF_2Cl was condensed into an n.m.r. tube and treated with an equimolar amount of Et_3N and 0.3 m mole of PH_3. $CDCl_3$ was added between condensations as the solvent. When the tube was warmed to -60°C a brown solid was observed to form and the ^{31}P n.m.r. spectrum showed only the presence of PF_3+PF_2Cl. At room temperature only PF_3 was observed.

Rn 3.5 Route to $(PF_2)_2PH$:

0.5 m mole $(Bu_3Sn)_3P$ was treated with HCl(0.5 mole) in an n.m.r. tube using $d^2CD_2Cl_2$ as the solvent. The tube was allowed to warm to room temperature until little pressure could be detected in the vacuum system which would indicate that the HCl had been used up. 0.75 m mole PF_2Br was then added. $PF_2P(SnBu_3)_2$ was the only product detected in the diphosphine series at -60°C and PF_3 was all that remained apart from a red solid at room temperature.

Rn. 3.6. $(PF_2)_2PSnBu_3 + B_2H_6$: (1:1 ratio)

0.5 m mole of phosphine was treated with 1 m mole of PF_2Br in an n.m.r. tube. CD_2Cl_2 was the solvent. The tube was allowed to warm to -60°C, then diborane was added. PF_3,PF_2Br and $H_3B:PF_2H$ were found with $(BH_3:PF_2)_2PSnBu_3$.

Chapter 4, part 1, Preparation of $(GeH_3)_2PPF_2$.

The reaction described in experiment 2.4. was attempted on a preparative scale.

$$(GeH_3)_3P + PF_2Br \longrightarrow (GeH_3)_2PPF_2 + GeH_3Br.$$

1 m mole of $(GeH_3)_3P$ was condensed into an ampoule fitted with a greaseless tap. 2 m mole of PF_2Br were then condensed into the ampoule. It is very important at this stage to ensure that HBr is absent from the PF_2Br ; fractionation through a trap held at −120°C will suffice.

The ampoule was allowed to warm to room temperature for ten minutes. The products of reaction were then fractionated on the vacuum line. As an excess of PF_2Br is used then theoretically no unreacted $(GeH_3)_3P$ should remaim. Consequently GeH_3Br has to be separated. Fractionation through a trap held at −46°C allowed GeH_3Br to pass through, while the diphosphine was held. This reaction gives a high yield based on $(GeH_3)_3P$.

Caution:

As $(GeH_3)_3P$ was prepared from treatment of $(Me_3Si)_3P$ with GeH_3Cl, it is imperative that GeH_3Cl is free from HCl. Chapter 2 deals with reactions of diphosphines with HX.

Chapter 4 ,Pt. II , Experimental Details,

Reaction 4.1. $(GeH_3)_2PPF_2+(MeS)_2$:

$(GeH_3)_2PPF_2$ (0.2 m mole) was treated with $(MeS)_2$ (0.3 m mole) in an n.m.r tube with $CDCl_3$ as the solvent. The $(MeS)_2$ was obtained commercially and was purified by vacuum distillation to remove water, The ^{31}P n.m.r. spectrum was recorded at -50° and at room temperature but no change was observed, in the segment to high frequency. After 2 days reaction this segment was re-recorded and the spectrum showed the presence of PF_2SCH_3 , identified by its chemical shift and coupling constant J PF. The low frequency segment of the phosphorus spectrum indicated that $(GeH_3)_3$ P had been formed (it was not previously there), with smaller amounts of $(GeH_3)_2PH$ and $(GeH_3)PH_2$. The ^{19}F spectrum confirmed the presence of PF_2SCH_3 and some PF_2H was also detected..The proton spectrum indicated that some $(GeH_3)_2S$ had also formed in the n.m.r. tube.

Rn 4.2

$(GeH_3)_2PPF_2$ + $(MeSe)_2$

$(GeH_3)_2$ PPF_2 (0.2 m mole) was treated with 0.2 m mole of $(MeSe)_2$ which had been freshly prepared and which had also been purified by vacuum distillation to separate water and polyselenides. The colourof $(MeSe)_2$ is orange red and on warming the tube to room temperature the colour became less intense over a period of 45 minutes. The proton spectrum quickly verified the presence of PF_2SeCH_3 and some other Germyl phosphines. The phosphorus spectrum of the reactants and products was recorded and from it the presence of PF_2SeCH_3 was confirmed from the section of the spectrum to high frequency of phosphoric acid. The low frequency spectrum howver was complex with $(GeH_3)_2PH$ + $(GeH_3)_3P$ being identified as the major components. No other lines of significance were confirmed and it was not possible to detect a line with Se satellites.

Rn 4.3 $(GeH_3)_2PPF_2 + (AcS)_2$

A sample of $(AcS)_2$ was obtained and dried on molecular sieve. The S reactant was pumped and approximately 0.2 m mole was weighed into an n.m.r. tube in a dried nitrogen filled glove bag. The equivalent amount of $(GeH_3)_2PPF_2$ was added , in this case .21 m mole, and the reaction was allowed to proceed at room temperature for several days. No observable change took place which could be detected by n,m.r. spetroscopy.

Reactions with Molybdenum Carbonyls :

Rn 4.4 $(GeH_3)_2PPF_2 + N^+Me\ C_5H_5Mo\ (CO)_5I^-$

0.2 m mole of the molybdenum compound was treated with 0.2. m mole of $(GeH_3)_2$ PPF_2 in an n.m.r. tube. The solvent used with $CDCl_3$. A mauve oil was observed separating from the $CDCl_3$ but only PF_3 was detected, by ^{31}P n.m.r. spectroscopy.

Rn 4.5, $Mo(CO_4)$ norbornadiene + $(GeH_3)_2\ PPF_2$

0.15 m mole of the molybdenum carbonyl was weighed into an n.m.r. tube and the solid was dissolved in $CDCl_3$, 0.3. m mole of $(GeH_3)_2PPF_2$ was added and the tube was sealed in the usual way.

^1H n.m.r. showed the presence of norbornadiene and as the solution gradually changed colour from brown to dark green. GeH_3F was detected in the ^1H spectrum and some complex broad band structure was also detected in the phosphorus spectrum resembling the ($,PF_2P$)pattern in the same area as $(GeH_3)_2\ PPF_2$ which was still there in quantity. After prolonged standing at room temperature, $(GeH_3)_2\ PPF_2$ eventually decayed to PF_3, $(GeH_3)_3P$ + $(GeH_3)_2\ PH$.

Rn 4.6, $(GeH_3)_2\ PPF_2$ + Fe $(CO)_9$

0.2. m mol of $Fe_2(CO)_9$ was added to an n.m.r. tube and carefully pumped for a few minute on a vacuum line. The solvent $CDCl_3$, was added before an equivalent amount of $(GeH_3)_2\ PPF_2$ was added. That reaction was followed by n.m.r. and none was found to take place as the $(GeH_3)_2PPF_2$ remained as the only product identifiable by n.m.r.

Coordination type reactions with Pt systems

Rn. 4.7.

$(GeH_3)_2\ PPF_2$ + HPt $(PEt_3)_2$ Cl (trans)

0.15 m mole of $HPt(PEt_3)_2$ Cl was treated with .15 m mole of $(GeH_3)_2PPF_2$ in an n.m.r. tube.

d^8 toluene was used as the solvent on the first attempt .

The spectrum was recorded with the n.m.r. tube at - 60°C but as H_2 gas was evolved there was poor resolution and after the reaction subsided a red/orange solid could be observed in the tube. The free phosphines, detected, were PF_3 + PH_3 before the tube contents solidified and resolution was totally lost.

This experiment was repeated in $CDCl_3$ with much the same result.

Rn 4.8 $(GeH_3)_2PPF_2$ + $HPt(PEt_3)_2I$ (trans)

0.15 m mole of $PF_2P(GeH_3)_2$ was treated with 0.15 m mols $HPt(PEt_3)_2I$. The platinum - iodide compound as in the case of the chloride had previously been preweighed into an n.m.r. tube and then pumped on a vacuum line. CD_2Cl_2 was the solvent. A bright red solid appeared on warming and with the liberation of H_2, the only products observed and identified by their n.m.r. spectrum were PF_3 and PH_3.

Substitution reactions

Rn 4.9 $(GeH_3)_2$ PPF_2 + PF_2I

0.2. m mole of $(GeH_3)_2-PPF_2$ was treated with 0.2 m mole of PF_2I. The reaction was carried out in an n.m.r. tube with $CDCl_3$ as the solvent. No change was observed save gradual decomposition.

Experimental details of the miscellaneous reactions

Rn 4.10 $(GeH_3)_2$ PPF_2 + BF_3

0.15 m mole of $(GeH_3)PPF_2$ was treated with 0.15 m mole BF_3 in an n.m.r. tube using TMS & benzene as the solvents.

Warming the tube to room temperature resulted in the contents effervescing with the formation of a pale yellow solid. The only identifiable product in the ^{31}P spectrum was PF_3.

Rn 4.11 $(GeH_3)_2PPF_2 + PF_5$

0.15 m mole of $(GeH_3)_2PPF_2$ was treated with 0.15 m mole PF_5, in an n.m.r. tube using TMS and benzene as the solvents. On warming, a gradual clouding of the clear solution was observed. The colour of the precipitate changed from white to yellow in 30 minutes. The only product identified was PF_3 and some unreacted $(GeH_3)_2PPF_2$.

Reactions with Sulphur and Selenium :

Rn 4.12. $(GeH_3)_2PPF_2 + S$ (in CS_2)

0.15 m.mol of $(GeH_3)_2PPF_2$ was treated with 1.50 m mole of Sulphur (yellow flowers). As CS_2 had previously been chosen as the solvent, it had to be added last as there is a greater risk of fracturing an n.m.r. tube with the freezing down of this solvent than there is with the freezing/remelting of benzene, Therefore, benzene ,TMS and the $(GeH_3)_2PPF_2$ were vacuum distilled into the tube before CS_2 was added. The solvents were added in equal amounts.

No change was observed until months later when some HPF_2S was observed in the system with $(PF_2)_2O + PF_3$.

Reaction 4.13 $(GeH_3)_2PPF_2 + Se$.

A similar method to that outlined above was used when 0.45 m mole of Se was added to 0.15 m mole of the diphosphine. After several months, at room temperature, only decomposition products of $(GeH_3)_2PPF_2$ were found, namely PF_3 and $(PF_2)_2O$.

CONCLUSIONS AND FUTURE WORK

Certain of the preceding chapters have been ended with a conclusion, related to that section. However the work as a whole requires some summing up.

Of all the diphosphines of the type PF_2PQQ' which were prepared, only $(GeH_3)_2PPF_2$ was found to be isolable. The reasons for this are not clear although the ease with which the silyl derivative forms SiH_3F does point at least to structural differences within the molecule as being in part responsible. Therefore it would be useful to persevere with the isolation of $(SiH_3)_2PPF_2$ so that its structure could be determined. It is possible to distil this species and given a large amount of $(SiH_3)_3P$, reasonable quantities of diphosphine could be prepared.

The instability of the species $(CH_3)_2PPF_2$ is surprising; another route to its preparation , from say, $(CH_3)_2PGeH_3$ should be attempted.

More routes to the $(PF_2)_2PQ$ type compounds could be explored. If the tin phosphine, $(Bu_3Sn)_2PH$ could be purified, then treatment with PF_2Br may result in, at least, an opportunity to observe its n.m.r. spectrum.

Investigations of the chemistry of the tri-alkyl germanium phosphines should be made. For instance; why should the reaction with PF_2Br stop when one group has been exchanged in the case of trigermylphosphine and continue till full exchange has occurred in the case of the tri-alkyl tin phosphines ? Perhaps there is an alkyl germyl derivative which results in the formation of a stable and isolable bis (PF_2) species.

Once reactions with PF_2X have been studied, there remains the reactions of $PFBr_2$.

Reactions with $PFBr_2$ are likely to be somewhat more complicated and ^{31}P and ^{19}F n.m.r. spectroscopy would prove useful at sorting out the reaction of:

$$PFBr_2 + 2\,(GeH_3)_3P \xrightarrow{?} (P(GeH_3)_2)_2PF$$

With the tin phosphines the reaction scheme appears to be endless and even treatment of $(GeH_3)_2PPF_2$ with $PFBr_2$ could result in removal of a germyl group.

If more use is made of the tin phosphines as a preparative route then some studies of the polymeric systems should be made. In this work polymeric residues were never farther investigated. Solids are an anathema to any vacuum line chemist.

The cleavage of the diphosphine by disulphides and diselenides should be farther investigated, as should reactions of P_2F_4 with a selection of disulphides and diselenides.

Finally another route to the formation of the tetraphosphine- $(PF_2)_3P$ should be attempted, and its structure determined by electron diffraction. This would illustrate what part,crowding , by the (PF_2) moiety plays in the determination of the structure.

REFERENCES

1. H. Ritter, Annalen, (1855), 95 ,208.
2. R.W. Rudolph, R.C.Taylor and R.W. Parry, J. Amer. Chem. Soc (1966) 88 , 3729.
3. J.P. Albrand, S.P. Anderson, H. Goldwhite and L. Huff, Inorg. Chem., (1975), 14 , 570.
4. R.W. Rudolph, and H.W. Schiller, J. Amer. Chem. Soc. (1968), 90 ,3581.
5. M. Baudler and A. Zarkadas, Chem. Ber., (1971), 104 ,3519.
6. R.K. Harris, E.M. M^{c}Vicker and M. Fild, Chem. Comm., (1975) 886.
7. M. Baudler, M. Hallab, A. Zarkadas and E. Tolls, Chem. Ber., (1973) 106,3962.
8. F.W. Bennet, H.J. Emeléus and R.N. Haszeldine, J. Chem. Soc., (1953)1565
9. H.W. Schiller and R.W. Rudolph, Inorg.Chem.,(1971) 10,2500.
10. H.L. Hodges,L.S. Su and L.S. Bartell, Inorg. Chem.,(1975), 14, 599.
11. J.E. Drake and C. Riddle, Quart. Rev.,(1970),24,263.
12. M.A. Finch and C.H. v Dyke, Inorg. Chem., (1975) 14, 134.
13. S. Cradock, E.A.V. Ebsworth and H.F. Jessep, J. Chem. Soc.,Dalton, (1972) 359.
14. S. Cradock, EA.V. Ebsworth, D.W.H. Rankin and W.J. Savage,J.C.S. Dalton, (1976) 1661.
15. K.G. Sharp, Chem. Comm., (1977) 564.
16. R.Demuth, Z. Naturforsch.,(1974),296,42.
17. G. Fritz, H. Schäfer,R. Demuth and J. Grobe, Z. Anorg. Chem.,(1974) 407, 287.
18. G. Fritz and H. Schäfer, Z. Anorg. Chem.,(1974),406,169.
19. A.R. Dahl, C.A. Heil and A.D. Norman, Inorg. Chem., (1975), 14,1095.
20. S. Cradock, E.A.V. Ebsworth,W.J. Savage and R.A. Whiteford, Trans. Faraday Soc.,(1971),55,934.
21. C. Glidewell, P.M. Pinder, A.G. Robiette and G.M. Sheldrick, J.C.S. Dalton(1972) 1402.

22. H. Sshumann, Angew. Chem.,Int. Ed., (1969),8, 937.

23. W. Kuchen and H. Buchwald, Chem. Ber.,(1959),92,227.

24. A.B. Bruker, L.D. Balshova, L.Z. Soborovski, Dokl. Akad. Nauk. USSR, (1960),135, 843.

25. F. Glockling and K.A. Hooton, Proc. Chem. Soc., (1963), 143.

26. H. Schumann, H. Kopf and M. Schmidt, J. Organometallic Chem.,(1964),2 159.

27. G. Fritz, Angew. Chem., (1966), 5, 53.

28. H. Schumann, P. Schwabe, and O. Stelzer, Chem. Ber.(1969),102 ,2900.

29. G. Fritz and G. Becker, Z. Anorg. Allg. Chem., (1970), 372,196.

30. G.W. Parshall and R.V. Lindsey, J. Amer. Chem. Soc., (1959), 81,6273.

31. H. Bürger and U. Goetze,J. Organometallic Chem.,(1968) 12, 451.

32. G. Fritz, H. Schäfer and W. Hölderich, Z. Anorg. Allg. Chem. (1974) 407 266.

33. G. Fritz and H. Schäfer, Z. Anorg. Allg. Chem. (1974),407,295.

34. H. Schumann and H. Benda, Chem. Ber.,(1971),104, 333.

35. H. Schumann and L. Rösch, Chem. Ber. (1974),107, 854.

36. H. Schumann and W.W. du Mont, Chem. Ber.,(1975)108, 2261.

37. W.W. du Mont and H. Schumann, Angew. Chem., (1975)14,368.

38. H. Schumann, W.W. du Mont and B. Wöbke, Chem. Ber., (1976), 109,1017.

39. J.F. Nixon, Adv.Inorg. Chem. Radiochem.,(1970),13,363.

40. R. Schmutzler, Adv. Fluorine Chem.(1965) 5, 31.

41. R. Schmutzler and O. Stelzer,MTP Intl. Rev. Science- Main Group Elements Group V and VI, Ed. H.J. Emeléus,Series1,Vol.2,61.

42. H. Moissan, Compt. Rendues (1884),99, 655.

43. J.S. Harman and D.W.A. Sharp, J. Chem. Soc.(A),(1970), 1935.

44. D.W.H. Rankin, J. Chem. Soc. (A),(1971), 783.

45. F.A. Johnson and R.W. Rudolph, J. Chem. Phys., (1967), 47, 5449.

46. R.W. Rudolph and H.W. Schiller,J. Amer. Chem. Soc, (1968), 90, 3581.

47. D. Solan and P.L. Timms,Chem. Comm.,(1968), 1540.

48. D.E.J. Arnold,E.A.V. Ebsworth, H.F. Jessep and D.W.H. Rankin, J.C.S. Dalton(1972),1681.

49. D.E.J. Arnold, Ph.D. Thesis, Edinburgh 1976.

50. J. Wright, Private Communication.

51. R.W. Rudolph,R.C. Taylor and R.W. Parry, J. Amer. Chem. Soc. (1966)88,3729.

52. L.F. Centofani and R.W. Parry, Inorg. Syn.,(1970),12,281.

53. G.N. Bockerman and R.W. Parry, J. Fluorine Chem.,(1976)7, 1.

54. D.E.J. Arnold,E.R. Cromie and D.W.H. Rankin, J.C.S. Dalton

55. E.R. Cromie, Private Communication.

56. M.L. Hodges and R.W. Rudolph, Inorg. Chem., (1972), 11, 2845.

57. E.R. Lory and D.M. Ritter, Inorg. Chem.(1971),10, 937.

58. E.R. Lory, R.F. Porter and S.H. Bauer, Inorg. Chem.,(1971),10, 1072.

59. R.T. Paine and R.W. Parry, Inorg. Chem.,(1972), 11,1237.

60. S. Fleming and R.W. Parry, Inorg. Chem.,(1972),11,1.

61. H.G. v Schnering and H. Menke, Z. Anorg. Allg. Chem.,(1973) 395, 223.

62. H.G. v Schnering and H. Menke, Z. Anorg. Allg. Chem.,(1976) 422, 219.

63. H.G. v Schnering and H. Schmidt, Angew. Chem., Internat. Ed., (1967) 6, 356.

64. P. Royen and K. Hill, Z. Anorg. Allg. Chem.,(1936),229, 97 and 112.

65. D.E.C. Corbridge, Topics in Phosphorus Chemistry, (1966) 3, 63-363.

65. D.S. Payne, Topics in Phosphorus Chemistry,(1967),85-144.

67. J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper and Row,(1976)

68.H. Niebergall and B. Langenfeld, Chem. Ber.,(1962),95, 64.

69. A.B. Burg and J.E. Griffiths, J. Amer. Chem. Soc., (1960),82, 3514.

70 A.B. Burg, J. Amer. Chem. Soc.,(1961), 83, 2226.

71. K. Issleib and F. Krech, Z. Anorg. Allg. Chem.,(1964),328, 21.

72. Topics in Phosphorus Chemistry, ed. J.R. v Wazer, pub. New York 1967 Wiley Interscience.

73. R.K. Harris, Quart. Rev.,(1976),5, 1.

74. R. Freedman,H.D.W. Hill& R. Kaptein, J. Mag. Res. ,(1972),7, 327.

75. G. Engelhardt, Z. Anorg. Allg. Chem.,(1972), 387, 52.

76. G. Fritz and H. Schäfer, Z. Anorg. Allg. Chem.,(1974),409,137.

77. H. Schumann, H.J. Kroth and L. Rösch.,Z. Naturforsch., (1974),29b,608.

78. Chemical Society, Annual Reports (A), (1975),129.

79. R.K. Harris, E. M^{c}Vicker and M. Fild, Chem. Comm.,(1975), 886.

80. S. Aime, R.K. Harris, E. M^{c}Vicker and M. Fild, Chem. Comm.,(1974),426.

81. A. M^{c}Farlane and W. M^{c}Farlane, Chem. Comm.,(1975),582.

82. E. Fluck and K. Issleib, Chem. Ber., (1965), 98,2674.

83. S.L. Mannatt, D.D. Elleman, A.H. Cowley and A. Burg, J. Amer. Chem. Soc., (1967), 89, 4544.

84. R.W. Rudoph and R.A. Newmark, J. Amer. Chem. Soc.,(1970), 92, 1195.

85. E.G. Finer and R.K. Harris, Mol. Phys., (1967),13, 65.

86. R.M. Lynden-Bell, Trans. Faraday Soc.,(1961),57, 888.

87. L.O. Brockway and F.T. Wall, J. Amer. Chem. Soc.,(1934), 56, 2373.

88. H.L. Hodges, L.S. Su and L.S. Bartell, Inorg. Chem.,(1975),14, 599.

89. C. Glidewell, P.M. Pinder, A.G. Robiette and G.M. Sheldrick, J.C.S. Dalton,(1972), 1402.

90. D.W. Rankin and S.J. Cyvin, J.C.S. Dalton, (1972),1277.

91. D.E.J. Arnold, E.A.V. Ebsworth, H.F. Jessep and D.W.H. Rankin. J.C.S. Dalton,(1972), 1681.

92. G. Glidewell, D.W.H. Rankin and A. Robiette, J. Chem. Soc.(A).,(1970), 2935.

93. B. Beagley,J.J. Monaghan,A.R. Conrad,J.M. Freeman, B.G. Norton, G.C. Holywell, J. Mol. Structure,(1972), 11, 371.

94. A. M^{c}Adam, B. Beagley and T.G. Hewitt, Trans. Faraday Soc.,(1970),66,2732.

95. D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and T.G. Hewitt. J. Inorg. Nuc. Chem.,(1969), 31, 2351.

96. R. Kuczkowski, H.W. Schiller and R.W. Rudolph, Inorg. Chem.(1971),10,2505.

97. J.D. Witt, J.W. Thompson and J.R. Durig, Inorg. Chem.(1973),12,811.

98. S. Cradock, E.A.V. Ebsworth, G. Davidson and L.A. Woodward,J. Chem. Soc. (A),(1967),1229.

99. S. Cradock, E.A.V. Ebsworth, W.J. Savage, R.A. Whiteford, J.C.S. Faraday 2, (1972), 68, 934.

100. S. Cradock, D.W.H. Rankin, ibid., p 940.

101. I.N. Shlyk, G.M. Bogolyubov, A.A. Petrov, Dokl. Akad. Nauk. USSR, (1967) 176(6),1327-30 (Chem. Abs., 69, 19261)

102. R. Foster and K.Cohn, Inorg. Chem., (1972), 11, 2590.

103. A.W. Burt, private communication.

104. G. Hunter, private communication.

105. G.C. Holywell, D.W.H. Rankin, B. Beagley and J.M. Freeman, J. Chem. Soc. (A), (1971), 785.

106. S.J. Cyvin, Mol. Vibns. and Mean Square Amplitudes, Universitet Forlagets Oslo, Elsevier Amsterdam(1968).

107. Y.C. Leung and J. Waser, J. Phys. Chem.,(1956), 60, 539.

108. D.W.H. Rankin, J.C.S. Dalton, In the Press.

109. L. Pauling, "The Nature of the Chemical Bond", 3rd. Edition, Cornell University Press,Ithaca N.Y., (1960),p 260.

110. G. Brauer, "Handbook of Preparative Inorganic Chemistry", Academic Press London, 1963 and 1965, Vols. I and II, and references therein.

111. J.E. Bentham, S. Cradock and E.A.V. Ebsworth, J. Chem. Soc (A), (1971), 587.

112. J.G. Morse, K. Cohn, R.W. Rudolph and R.W. Parry, Inorg. Synth., (1967), 10 ,147.

113. L.M. Dennis and P.R. Judy, J. Amer. Chem. Soc. , (1929), 51 2321.

114. G. Fritz and D. Kummer, Z. Anorg. Chem.,(1961), 308, 105.

115. E.A.V. Ebsworth, J.R. Hall., M.J. Mackillop, D.C. M^c^Kean, N. Sheppard and L.A. Woodward, Spectrochim. Acta, (1958), 13, 202.

116. F. Amberger and H.D. Boetters, Chem. Ber., (1964), 97 .,1999.

117. F.A. Cotton and G.W. Wilkinson, Advanced Inorganic Chemistry, 3rd. Ed. Wiley-Interscience , London.

118. G. Brauer, ' Handbook of Preparative Inorganic Chemistry', Academic Press, London, 1963 and 1965, Vols. I & II, and references

119. Inorganic Syntheses, XI, p15.

120. Chem. Ber. (1969) 2900.

121. M.A. Bennett, L. Pratt and G.W. Wilkinson, J. Chem. Soc. (1961) 2037.

122. A. Bird and D. Challenger, J. Chem. Soc. (1942) 570-4.

123. Inorganic Synthesis, XV,p 187.

124. " " , XI,p 157.

125. Chem. Ber. (1968) 1852-6.

126. T.C. Farrar and E.D. Becker, 'Pulse and Fourier Transform N.M.R.', Academic Press, London and New York, 1971.

127. W. M^{c}Farlane and R.F.M. White, ' Techniques in High Resolution Nuclear Magnetic Resonance Spectroscopy', Butterworths, London, 1972.

128. A. Charles and W. M^{c}Farlane, Mol. Phys., (1968), 14 ,299.

129. B. Beagley, A.H. Clark and T.G. Hewitt, J. Chem. Soc. (A), (1968), 658.

130. G.C. Holywell, D.W.H. Rankin, B.Beagley and J.M. Freeman, J. Chem. Soc. (A),(1971), 785.

131. D.W.H. Rankin, Ph.D. Thesis, Cambridge, 1969.

132. D.M. Bridges, G.C. Holywell, D.W.H. Rankin and J.M. Freeman, J. Organometallic Chem., (1971), 32, 87.

133. H.M. Seip, 'Molecular Structure by Diffraction Methods', ed. G.A. Sim and L.E. Sutton, The Chemical Society, London, 1973, Vol. 1, and references.

134. A.G. Robiette, as above.

135. M.I. Davis, 'Electron Diffraction in Gases', Marcel Dekker Inc., New York, 1971.

CORRELATION DIAGRAMS

The corners of each triangle in the diagram represents Q_3P. Points along the edges represent Q_2PQ' and QPQ'_2, while the centre of each triangle represents the compound $QQ'PQ''$.
Q,Q',Q'' are defined by the system on each diagram.
Chemical shift is measured on the horizontal axis.
Chemical shifts of known derivatives have been marked at the relevant position. Those numbers in parentheses represent the chemical shifts of compounds which had not been prepared.

CORRELATION DIAGRAM D.3.1:

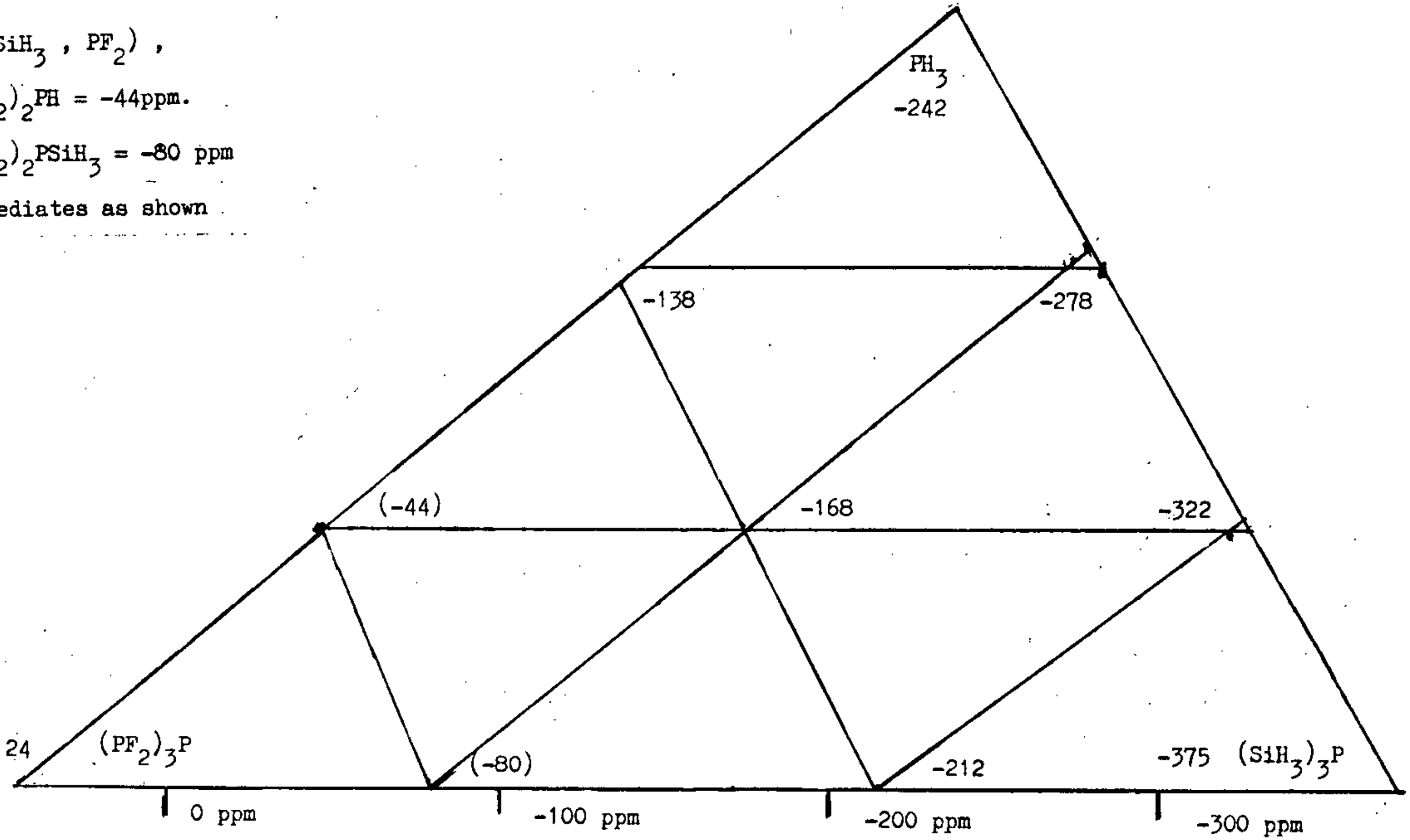
Phosphorus chemical shifts.

System (H, SiH_3 , PF_2) ,

Predict $(PF_2)_2PH$ = -44ppm.

$(PF_2)_2PSiH_3$ = -80 ppm

Other intermediates as shown



CORRELATION DIAGRAM D 3.2:

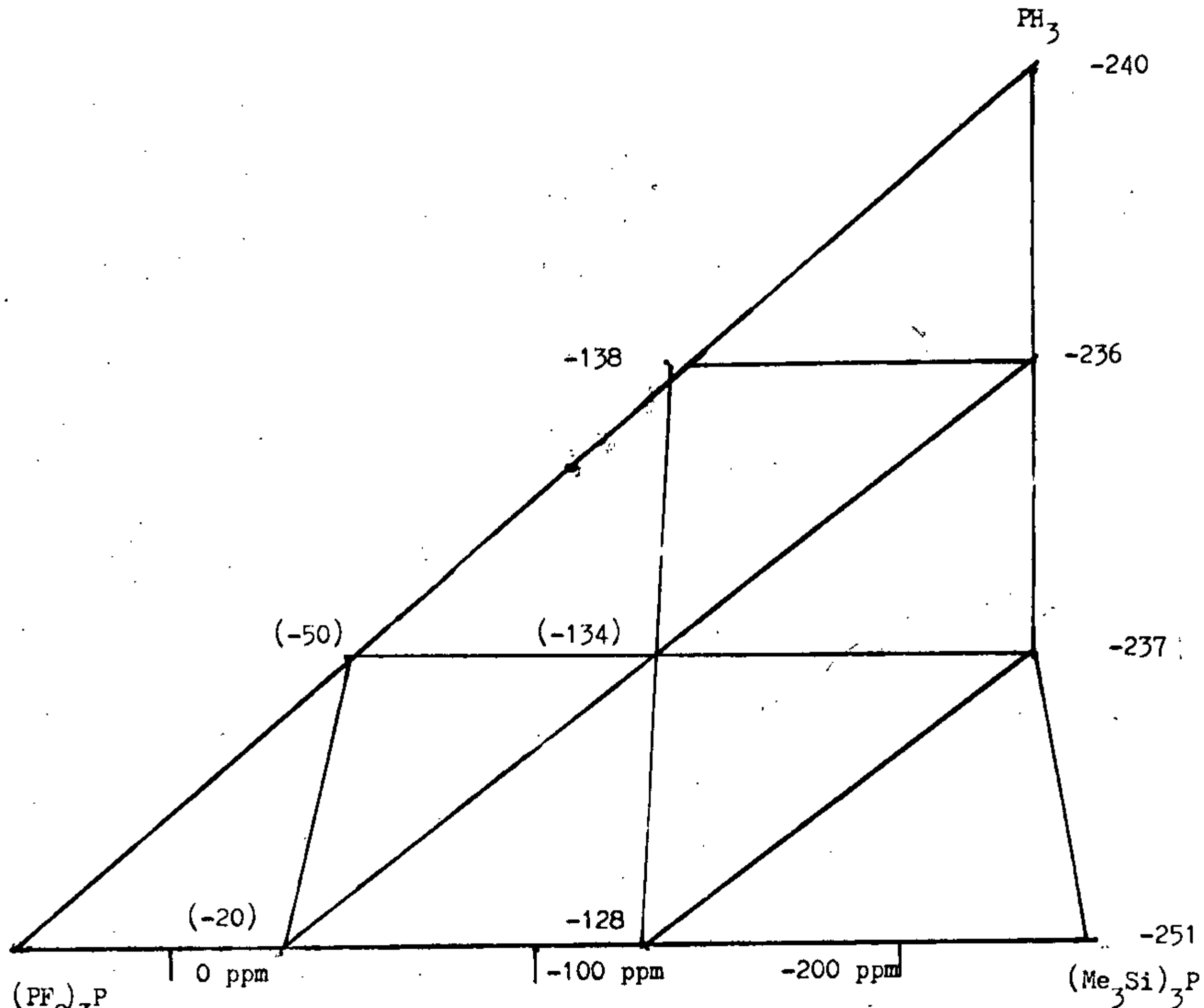
Phosphorus chemical shifts

System (H, $SiMe_3$, PF_2)

Predict $(PF_2)_2PH$ = -50 ppm.

$(PF_2)_2PSiMe_3$ = -20 ppm.

$PF_2PH.SiMe_3$ = -134 ppm.



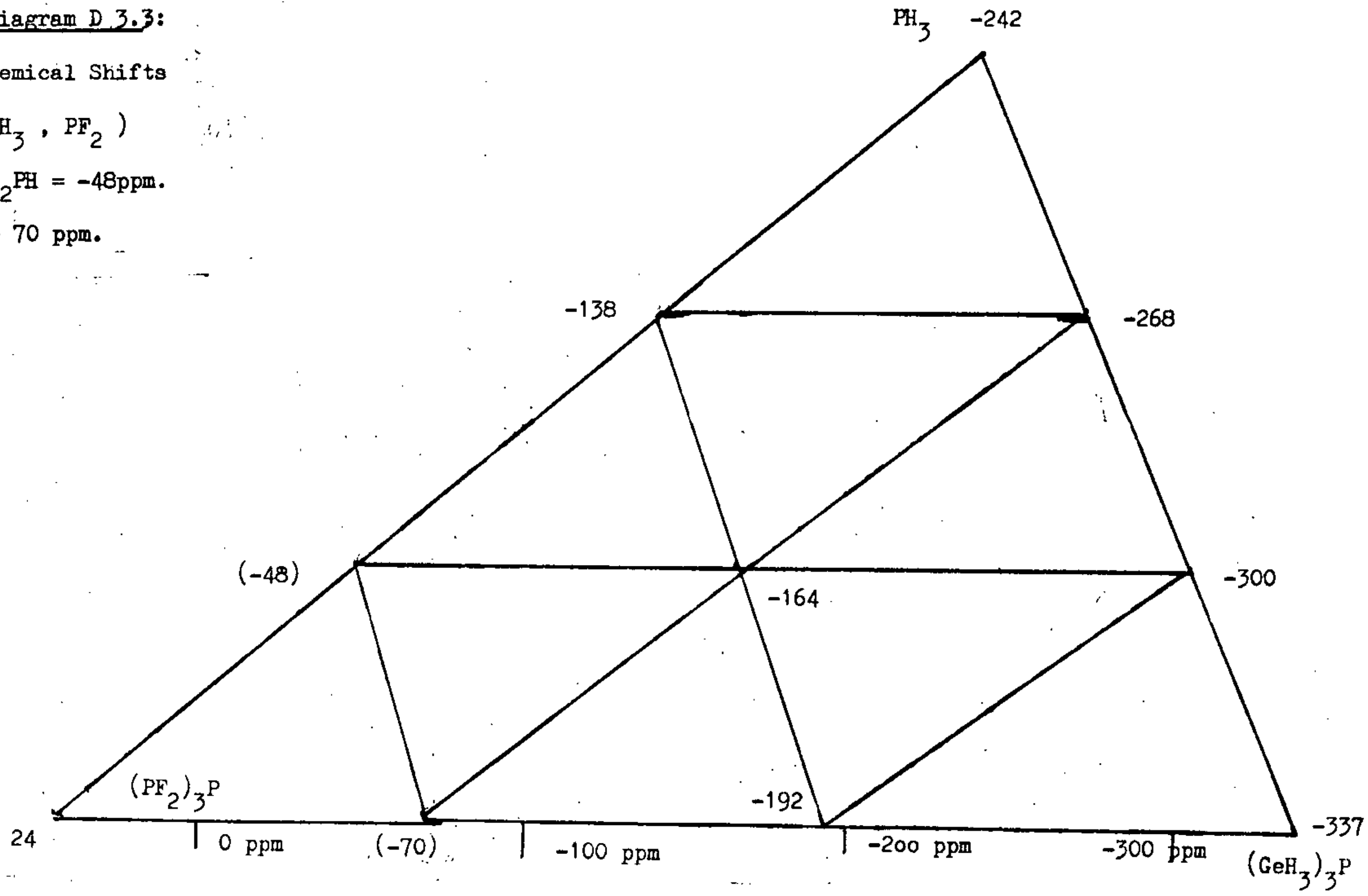
Correlation Diagram D 3.3:

Phosphorus Chemical Shifts

System (H, GeH_3 , PF_2)

Predict $(PF_2)_2PH$ = -48ppm.

$(PF_2)_2PGeH_3$ = -70 ppm.



CORRELATION DIAGRAM D 3.4:

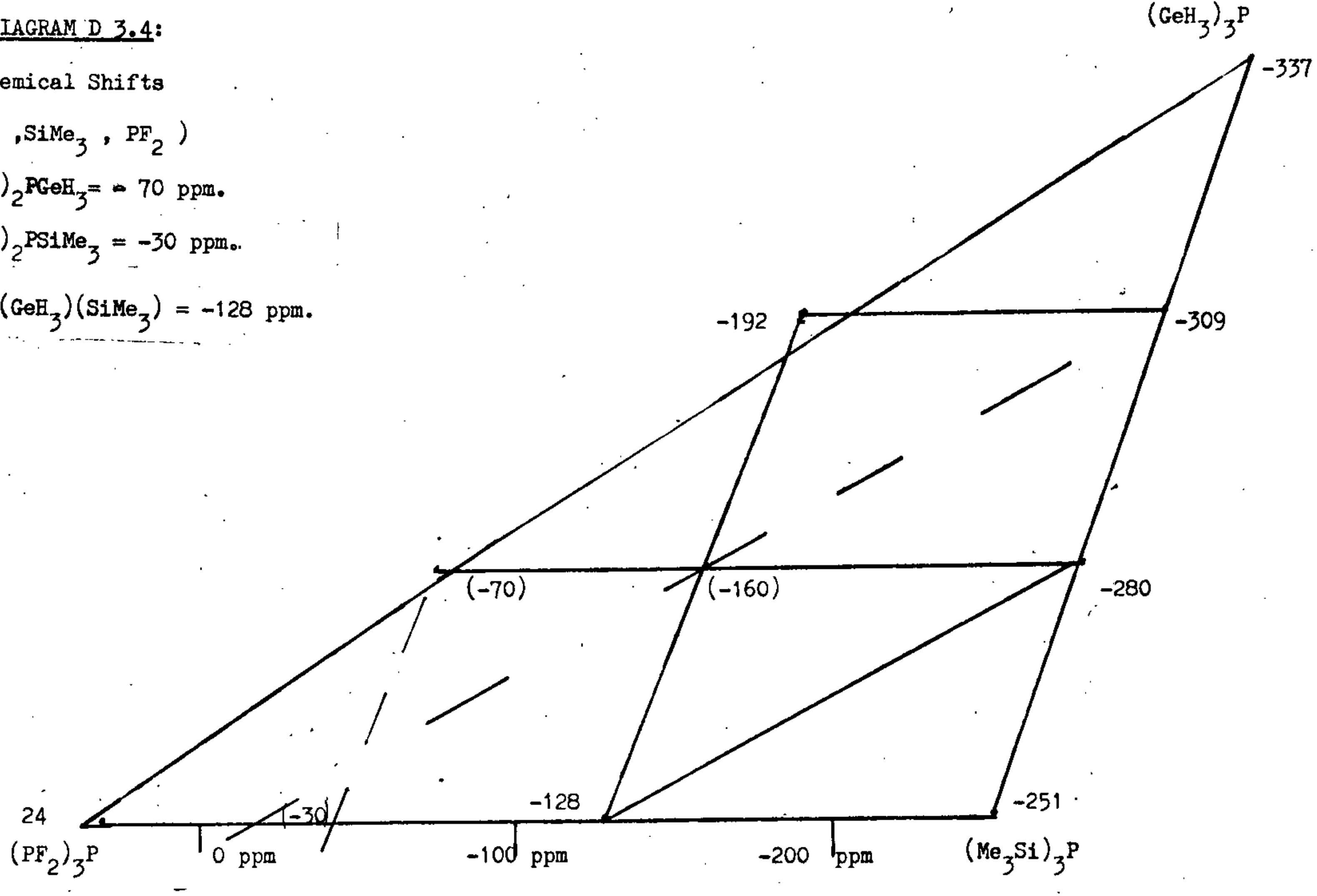
Phosphorus Chemical Shifts

System (GeH_3 , $SiMe_3$, PF_2)

Predict $(PF_2)_2PGeH_3$ = - 70 ppm.

$(PF_2)_2PSiMe_3$ = -30 ppm.

$PF_2P(GeH_3)(SiMe_3)$ = -128 ppm.



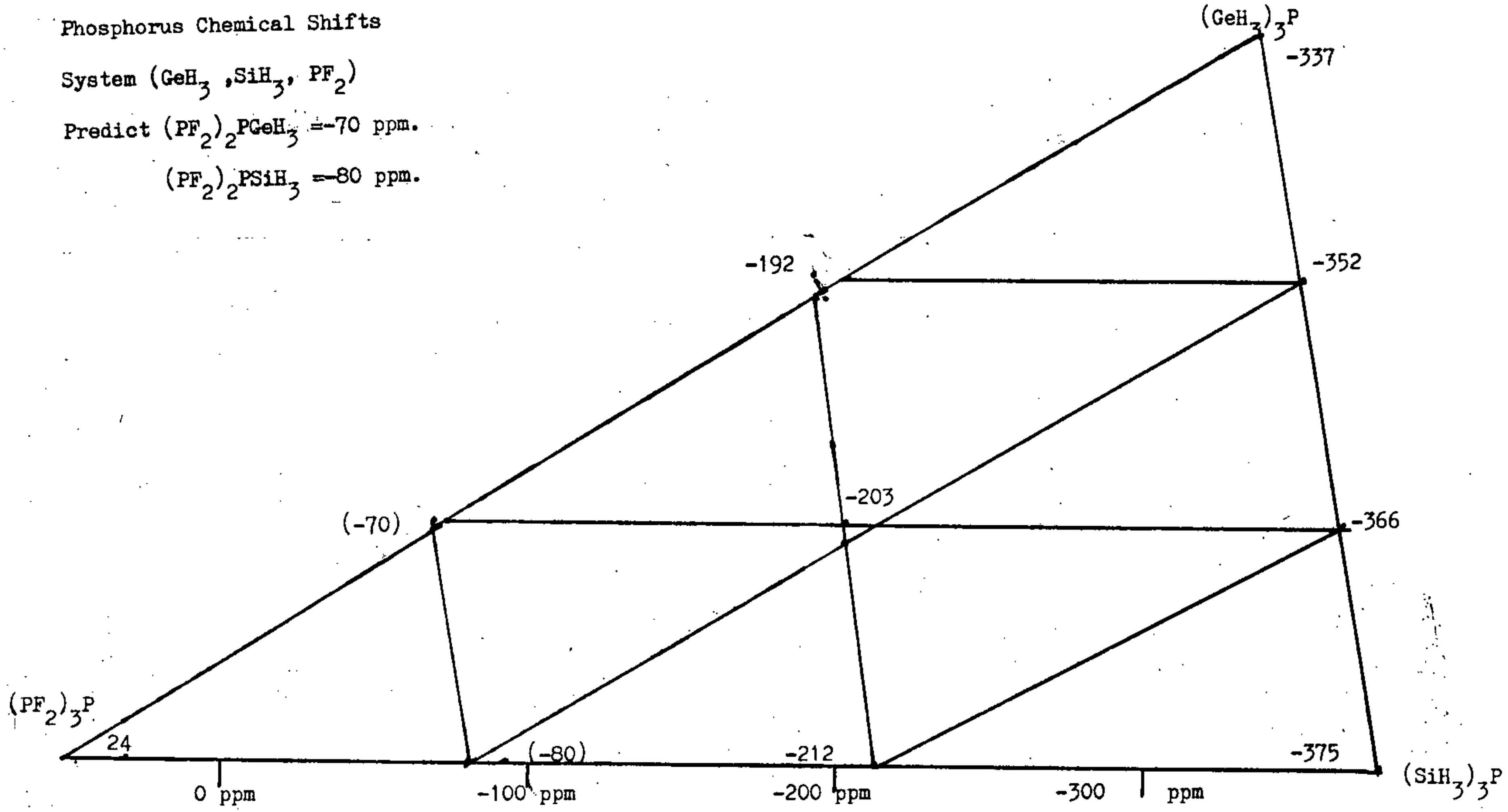
CORRELATION DIAGRAM D 3.5 :

Phosphorus Chemical Shifts

System (GeH_3, SiH_3, PF_2)

Predict $(PF_2)_2PGeH_3$ = -70 ppm.

$(PF_2)_2PSiH_3$ = -80 ppm.

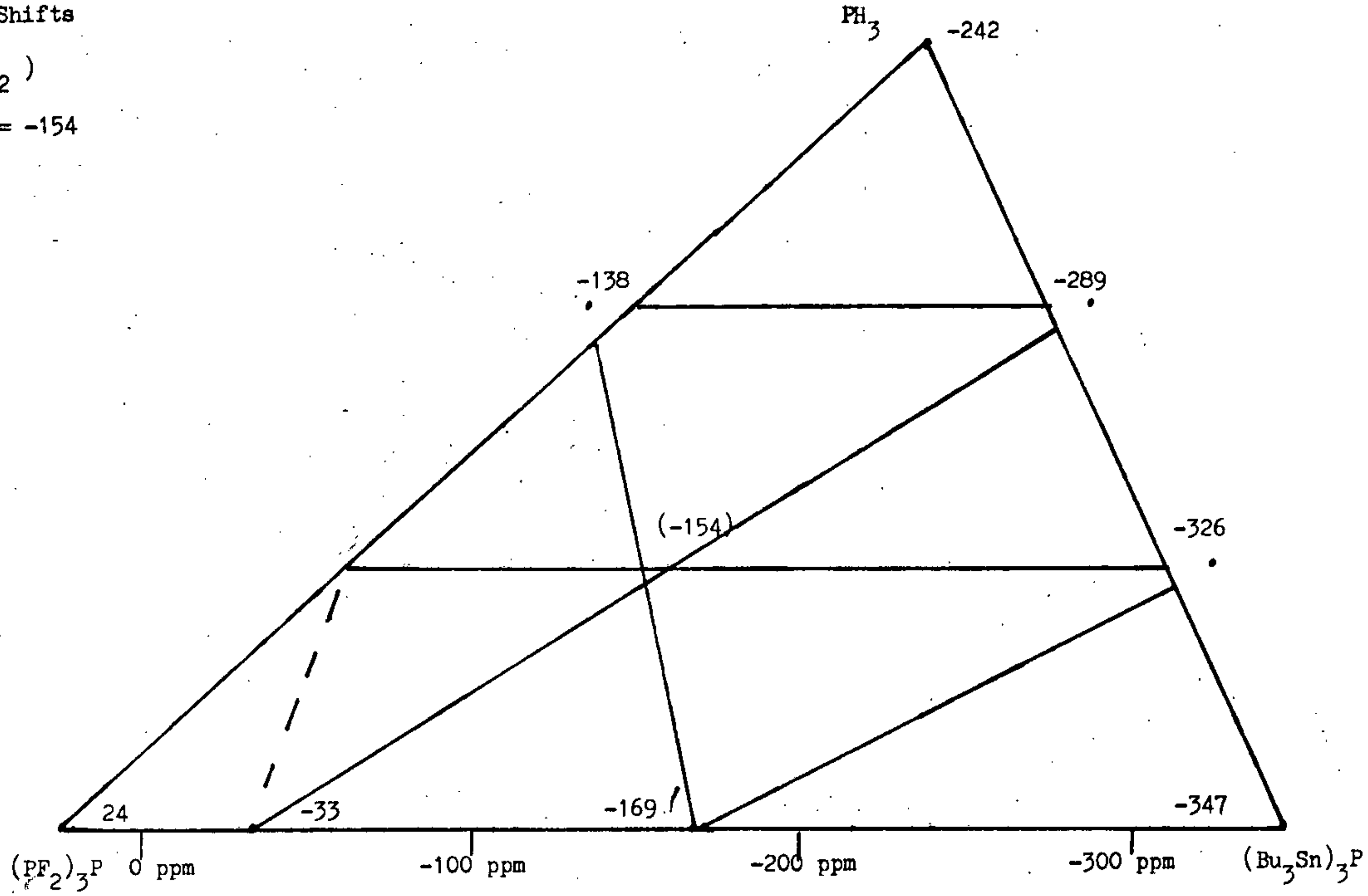


CORRELATION DIAGRAM D 3.6:

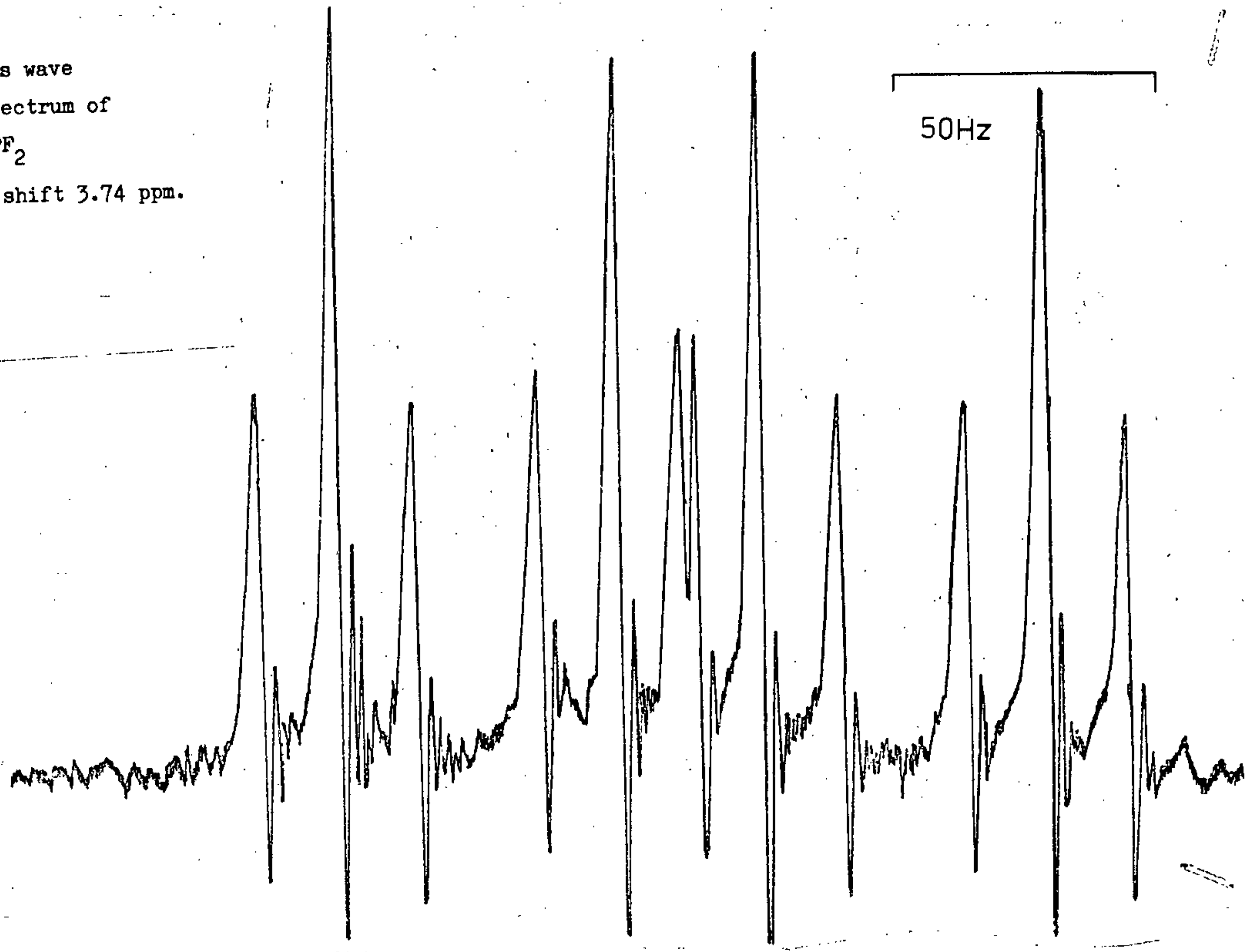
Phosphorus Chemical Shifts

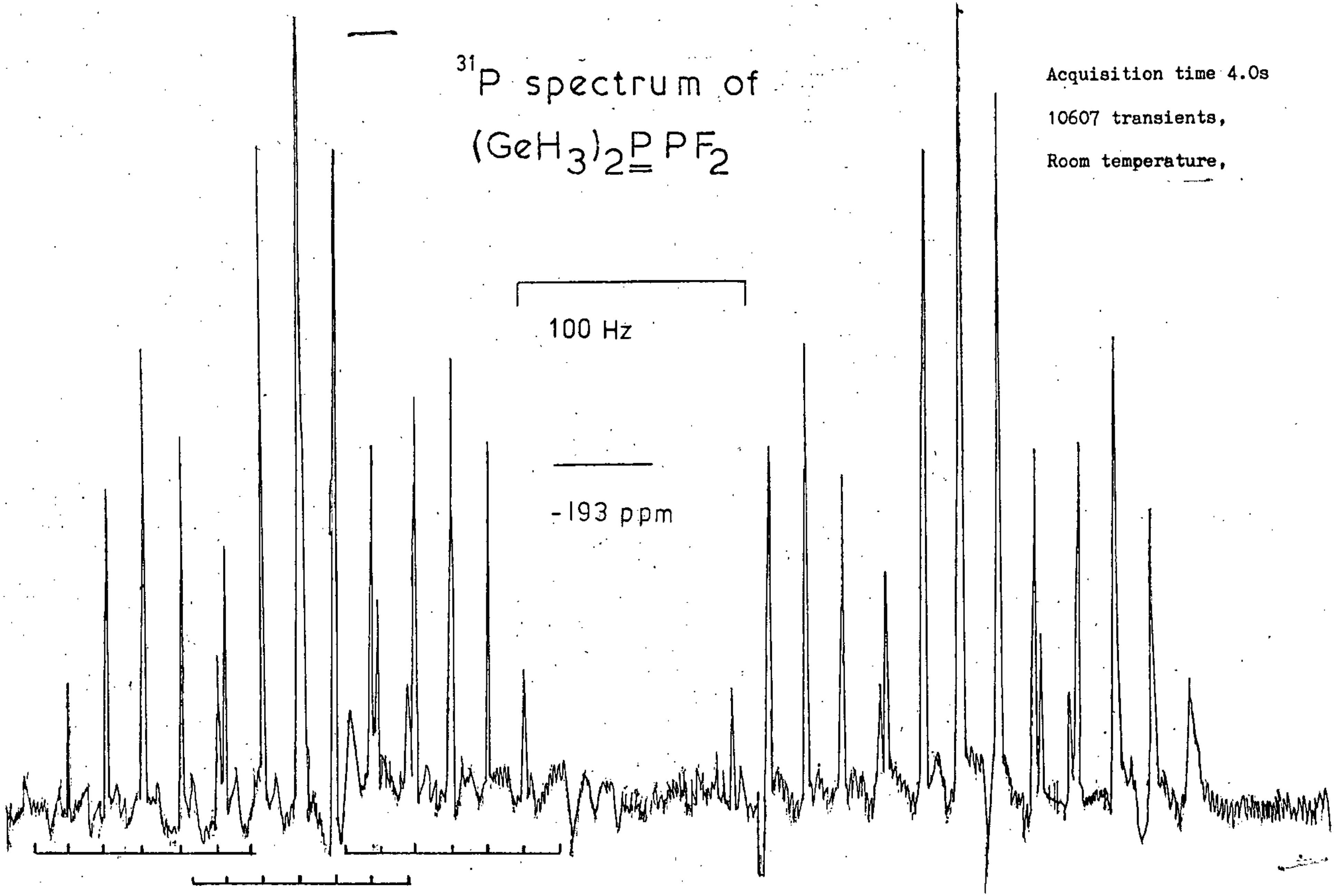
System (H, $SnBu_3$,PF_2)

Predict $PF_2PH.SnBu_3$ = -154



Continuous wave
proton spectrum of
$(GeH_3)_2PPF_2$
Chemical shift 3.74 ppm.





^{31}P spectrum of $(GeH_3)_2\underline{\underline{P}}PF_2$

Acquisition time 4.0s

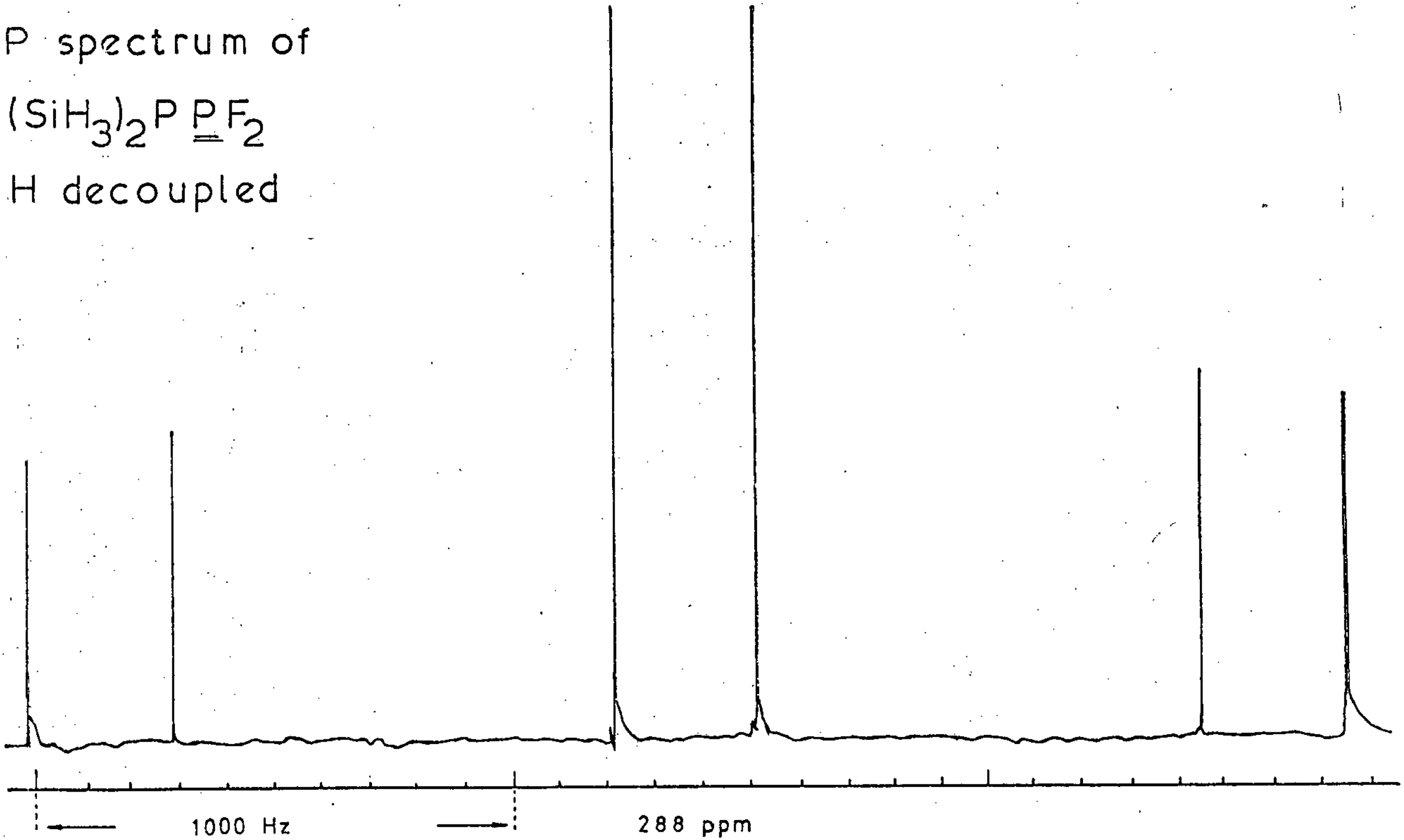
10607 transients,

Room temperature,

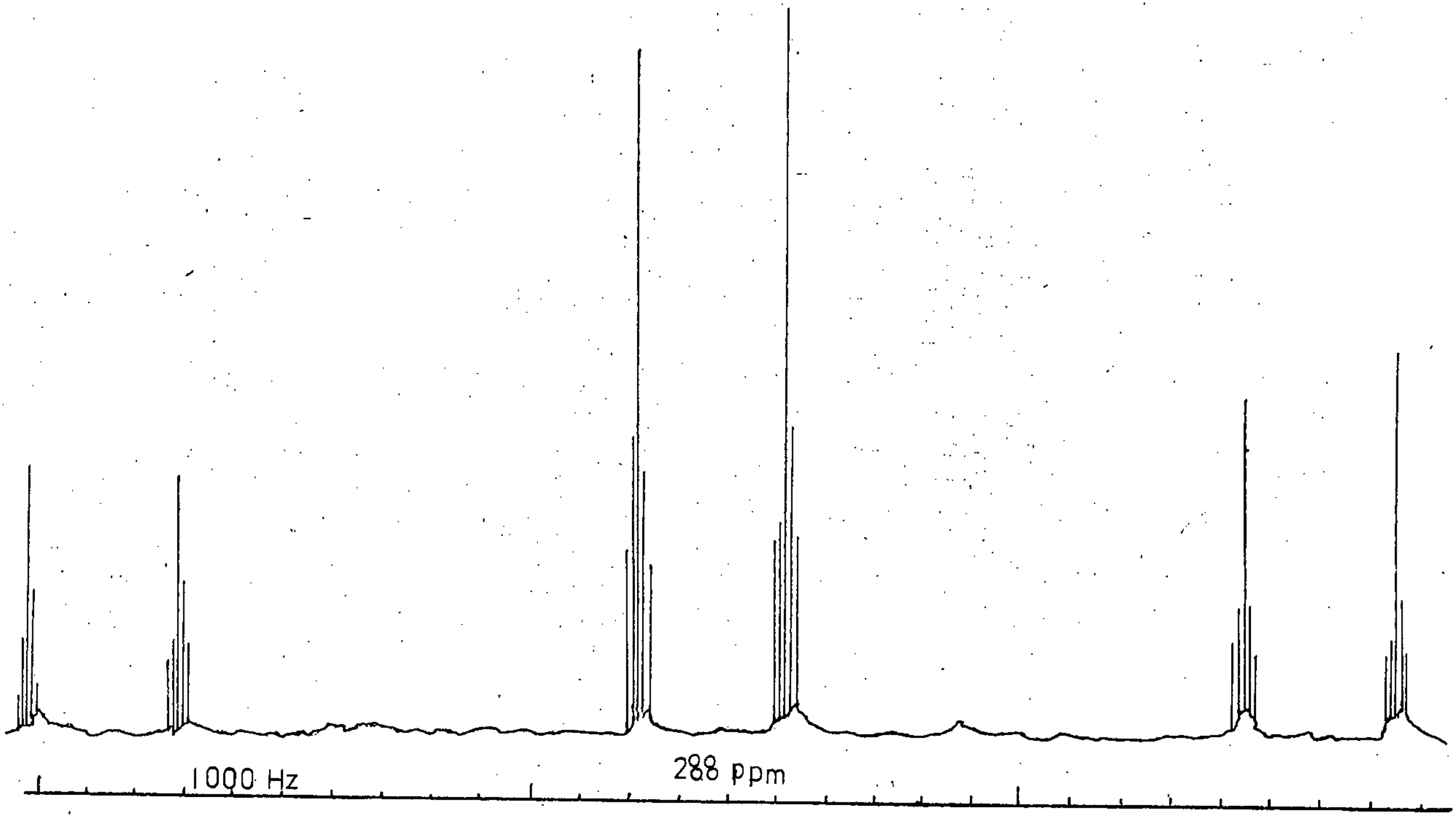
P spectrum of

$(SiH_3)_2P\underline{\underline{P}}F_2$

H decoupled



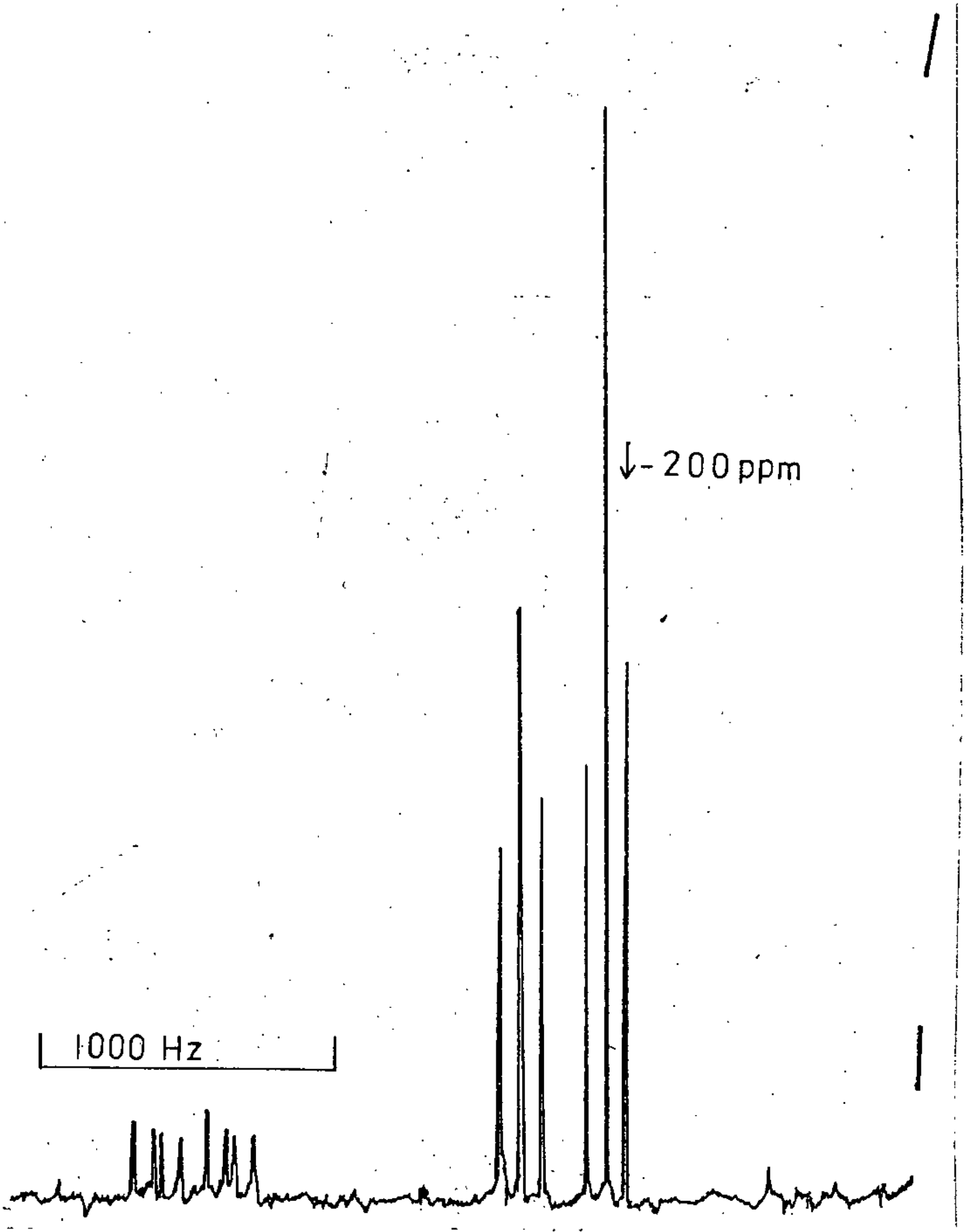
H coupling retained



^{31}P spectrum of $(GeH_3)_2PPF_2$ and $(GeH_3)HPPF_2$:

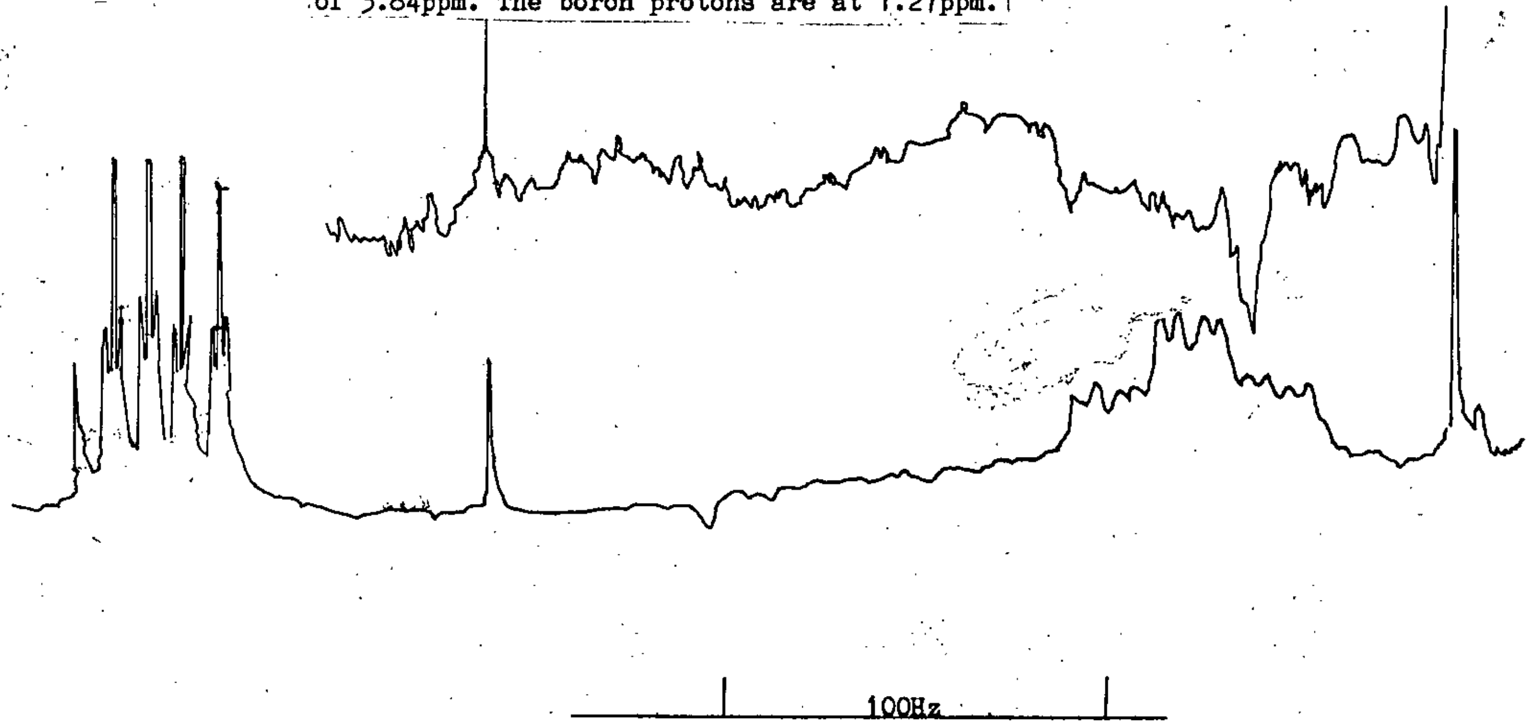
Proton decoupled, section to low frequency showing the phosphorus bonded to germanium.

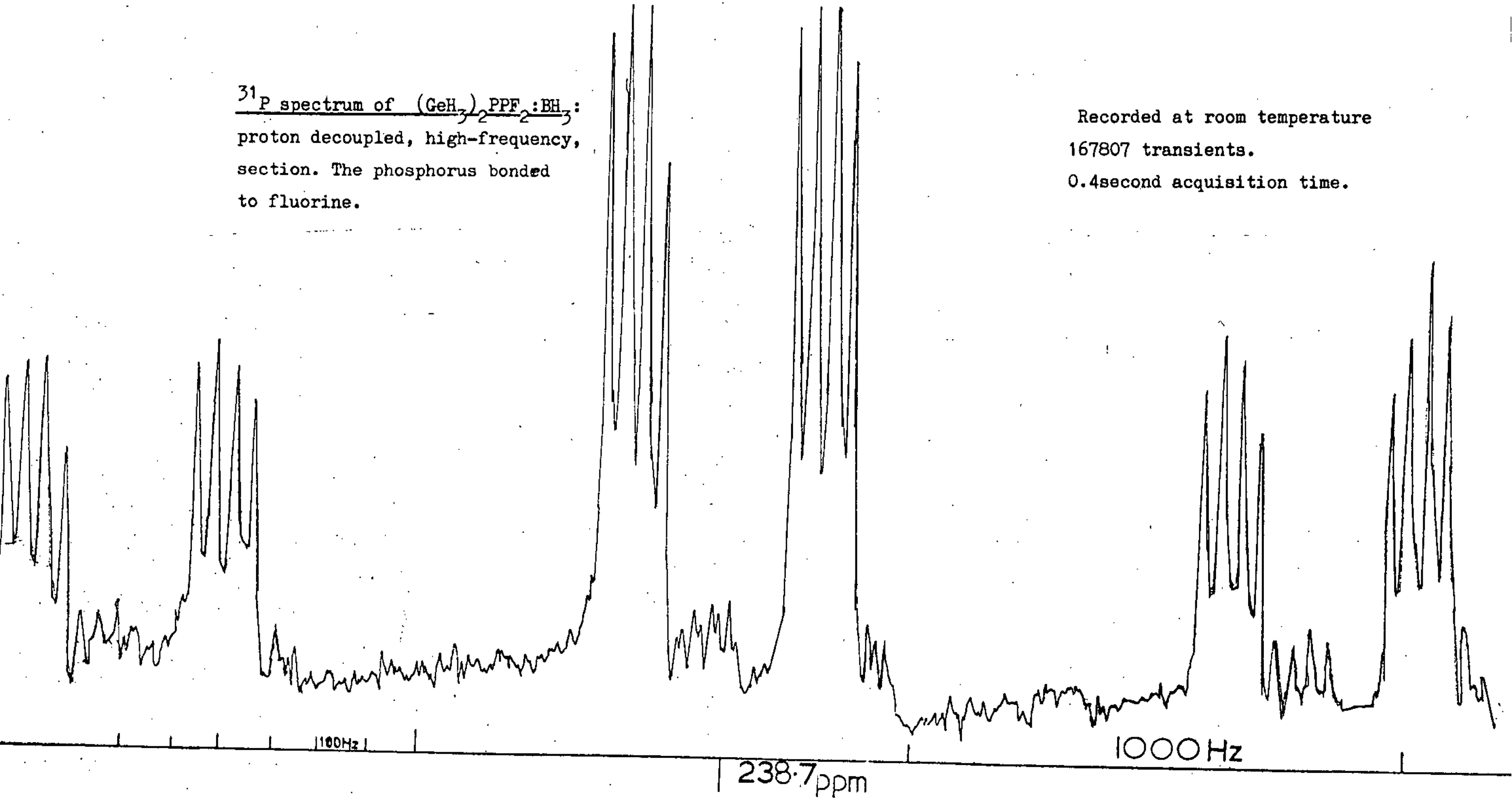
Recorded at room temperature.



^{1}H spectrum of $(GeH_3)_2PPF_2$

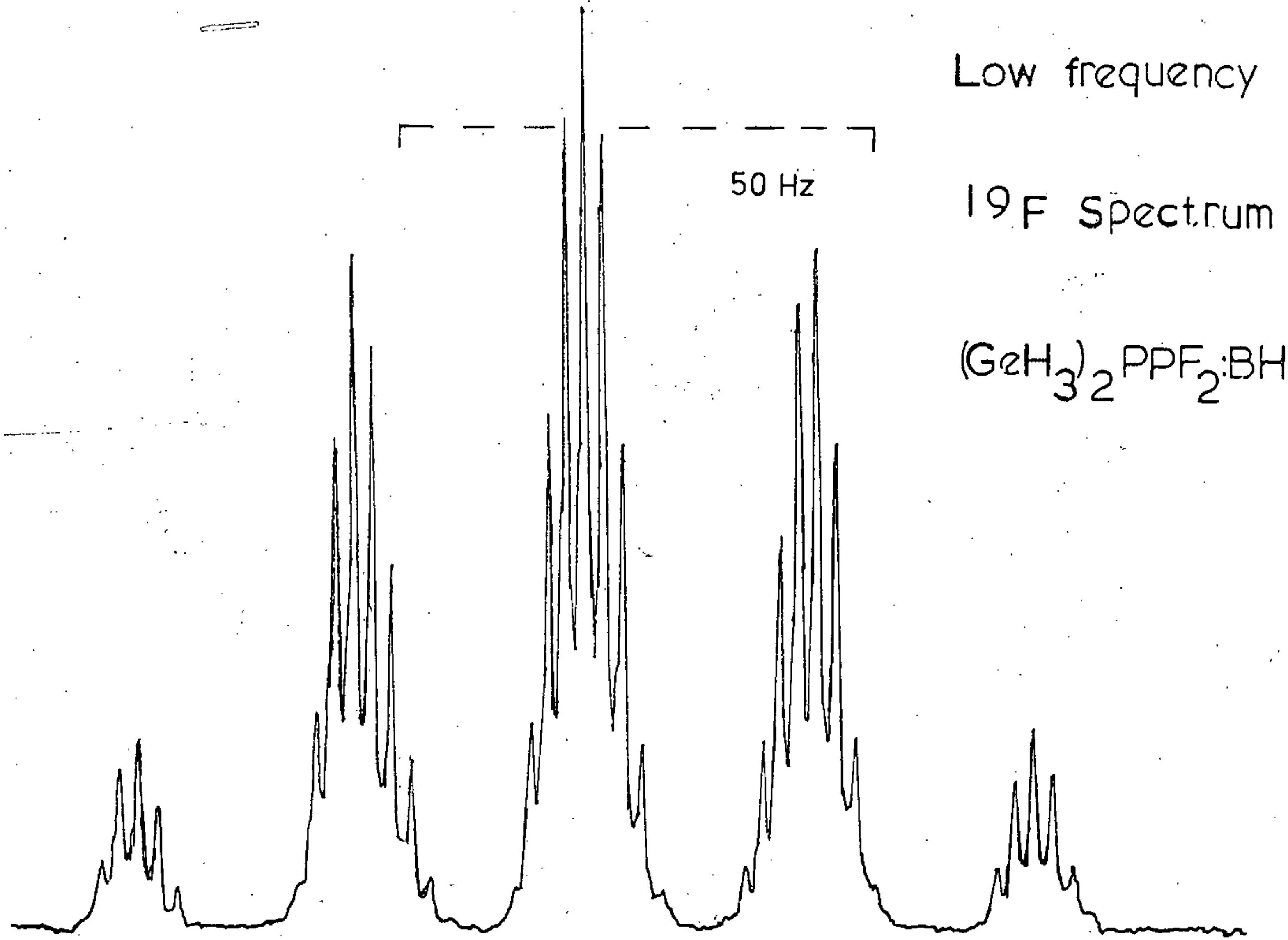
four seconds acquisition time, 17 transients, recorded at 25°C. The lower spectrum shows effect of boron decoupling, while the non decoupled spectrum to the top shows no distinguishable borane protons. The germyl protons appear to the left, at a chemical shift of 3.84ppm. The boron protons are at 1.27ppm.





^{31}P spectrum of (GeH$_3$)$_2$PPF$_2$:BH$_3$: proton decoupled, high-frequency, section. The phosphorus bonded to fluorine.

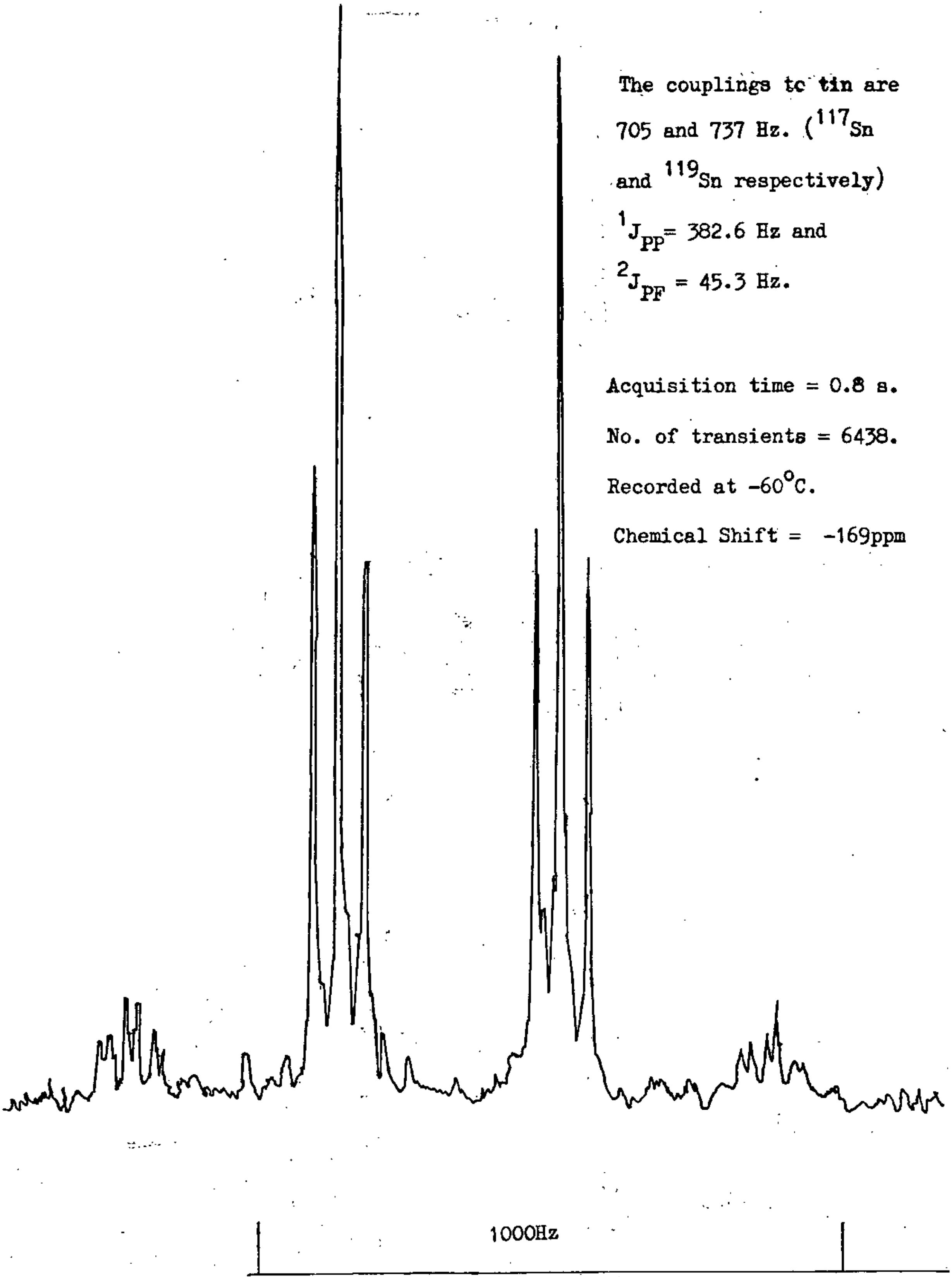
Recorded at room temperature
167807 transients.
0.4second acquisition time.



Low frequency half of the ^{19}F Spectrum of $(GeH_3)_2PPF_2{:}BH_3$

^{31}P spectrum of $(Bu_3Sn)_2PPF_2$:

This is the spectrum of the phosphorus bonded to tin and shows the expected doublet of triplet pattern. The tin couplings are all resolved.



The couplings to tin are 705 and 737 Hz. (^{117}Sn and ^{119}Sn respectively)

$^1J_{PP}$= 382.6 Hz and

$^2J_{PF}$ = 45.3 Hz.

Acquisition time = 0.8 s.

No. of transients = 6438.

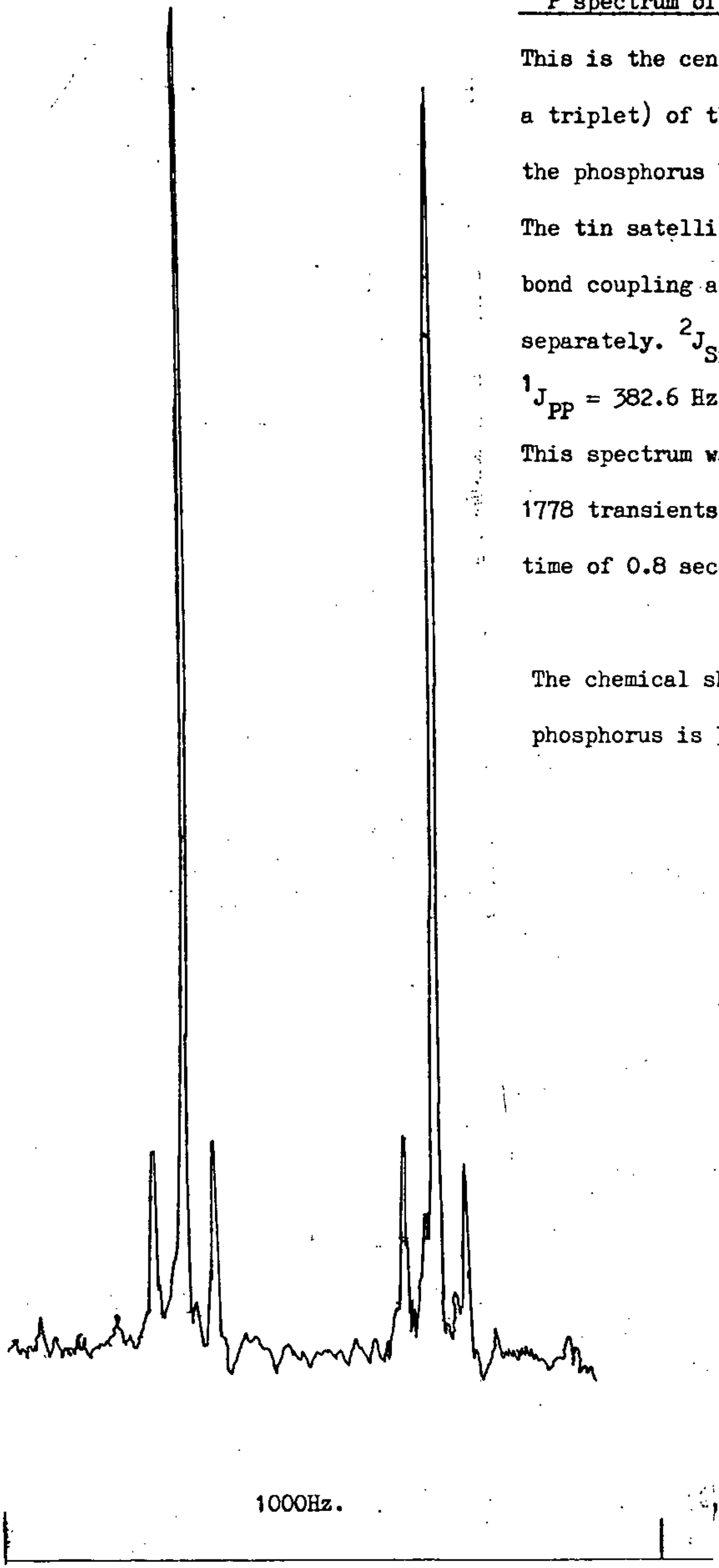
Recorded at -60°C.

Chemical Shift = -169ppm

^{31}P spectrum of $(Bu_3Sn)_2PPF_2$:

This is the central doublet (of a triplet) of the spectrum of the phosphorus bonded to fluorine. The tin satellites of the two bond coupling are not resolved separately. $^{2}J_{SnP} = 92$ Hz. $^{1}J_{PP} = 382.6$ Hz. $^{1}J_{PF} = 1188$Hz. This spectrum was obtained after 1778 transients with an acquisition time of 0.8 seconds.

The chemical shift of this phosphorus is 322 ppm.



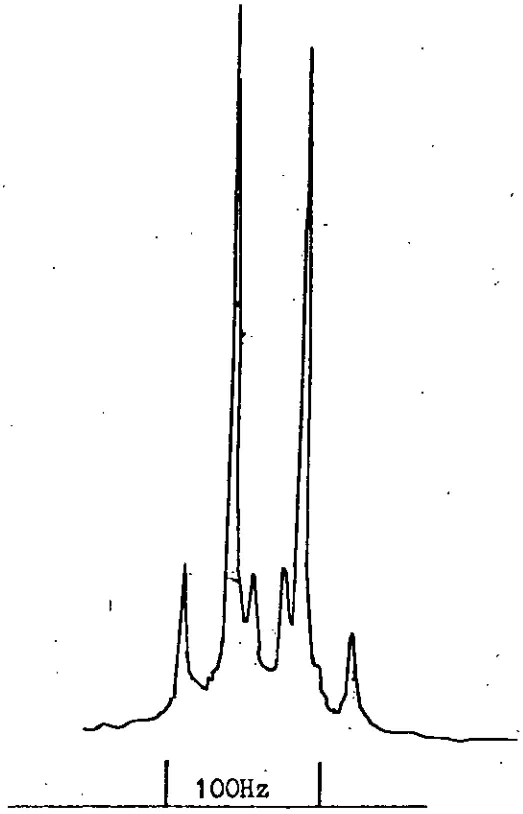
^{19}F spectrum of $(Bu_3Sn)_2PPF_2$

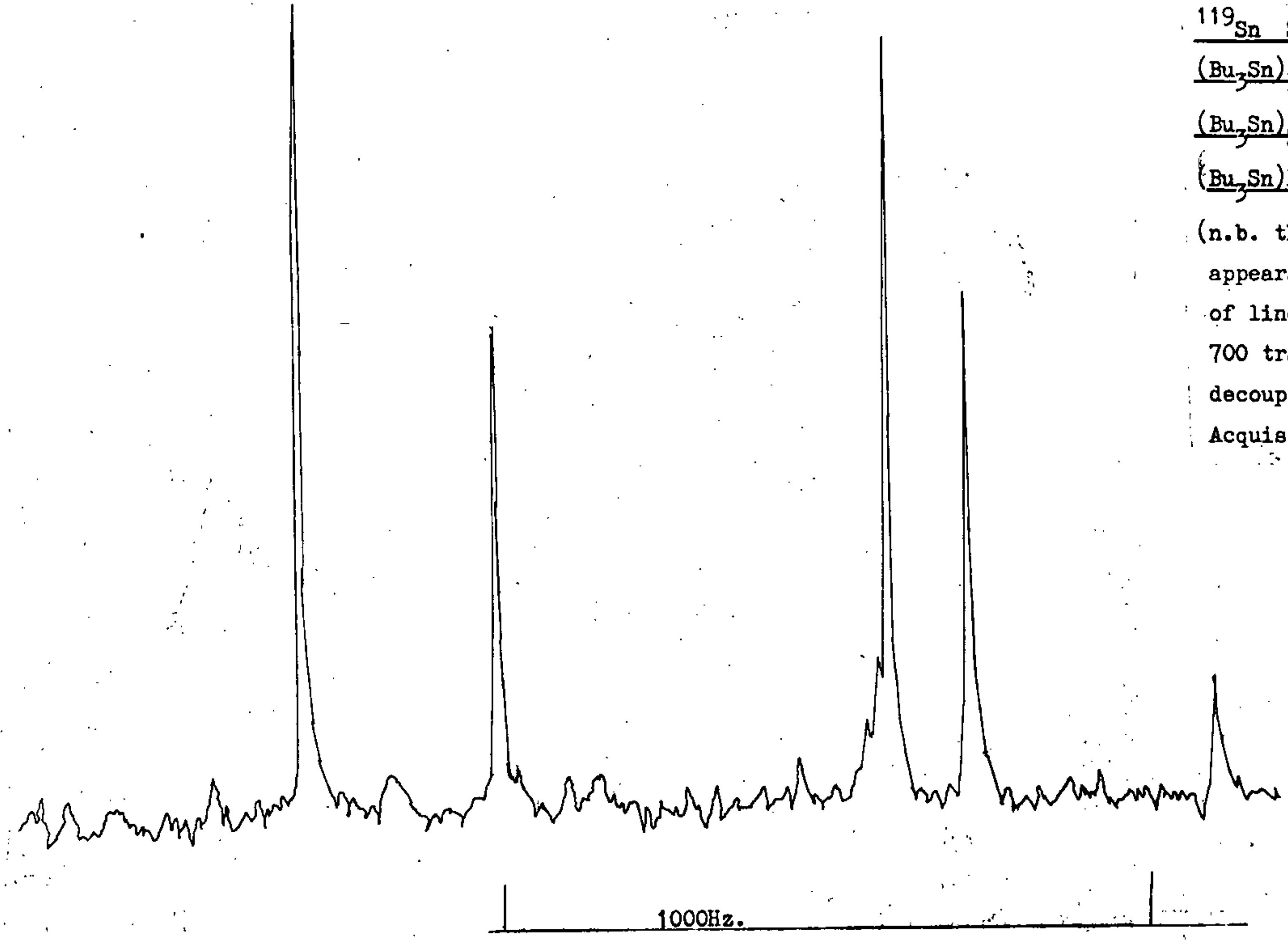
This shows half of the spectrum to higher frequency.

The satellites due to ^{117}Sn and ^{119}Sn are not separately resolved.

The value of $^3J_{SnF}$ is 65 Hz, $^2J_{PF} = 45.3$ Hz and the large separation due to the one bond coupling of phosphorus to fluorine is 1188Hz.

This spectrum was obtained after 200 transients with an acquisition time of 1.6 seconds.





^{119}Sn Spectrum of
$(Bu_3Sn)_3P$ lines 1 and 3
$(Bu_3Sn)_2PH$ lines 2 and 4
$(Bu_3Sn)PH_2$ line 5.
(n.b. the other line appears on the shoulder of line 3)
700 transients, proton decoupled. Pulse delay 50s. Acquisition time 0.8s.

^{119}Sn spectrum of $PF_2P(SnBu_3)_2$:

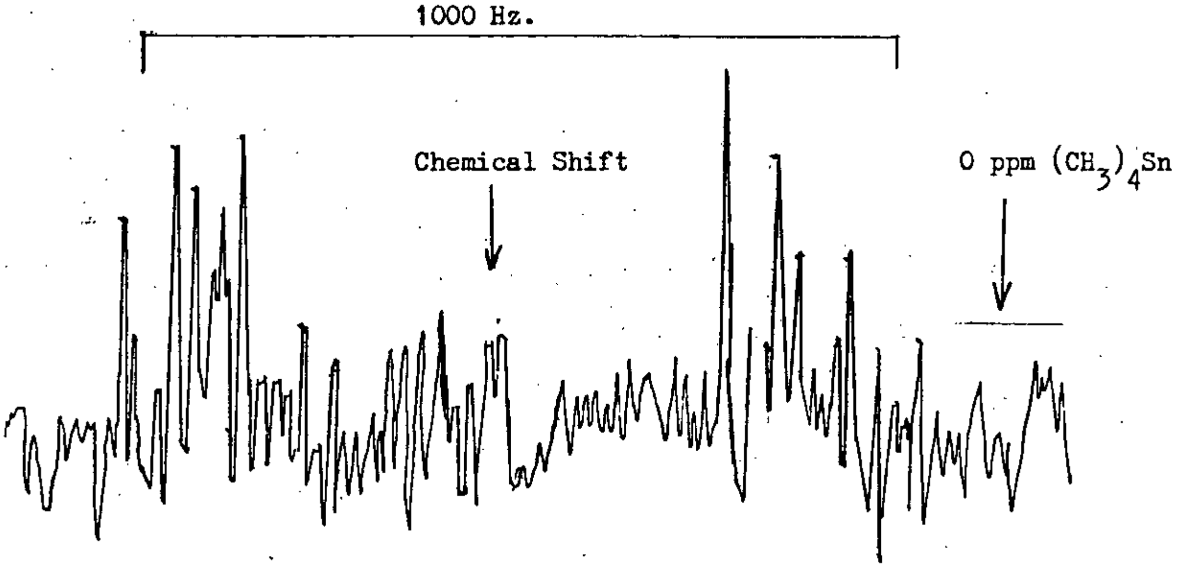
Recorded at -60°C.

proton decoupled,

154 transients,

Acquisition time 0.4 seconds, pulse delay = 30 seconds.

Chemical shift 18ppm, $(CH_3)_4Sn$ taken as 0ppm.



^{19}F spectrum of a mixture of $(PF_2)_3P$ and $(PF_2)_2PSnBu_3$

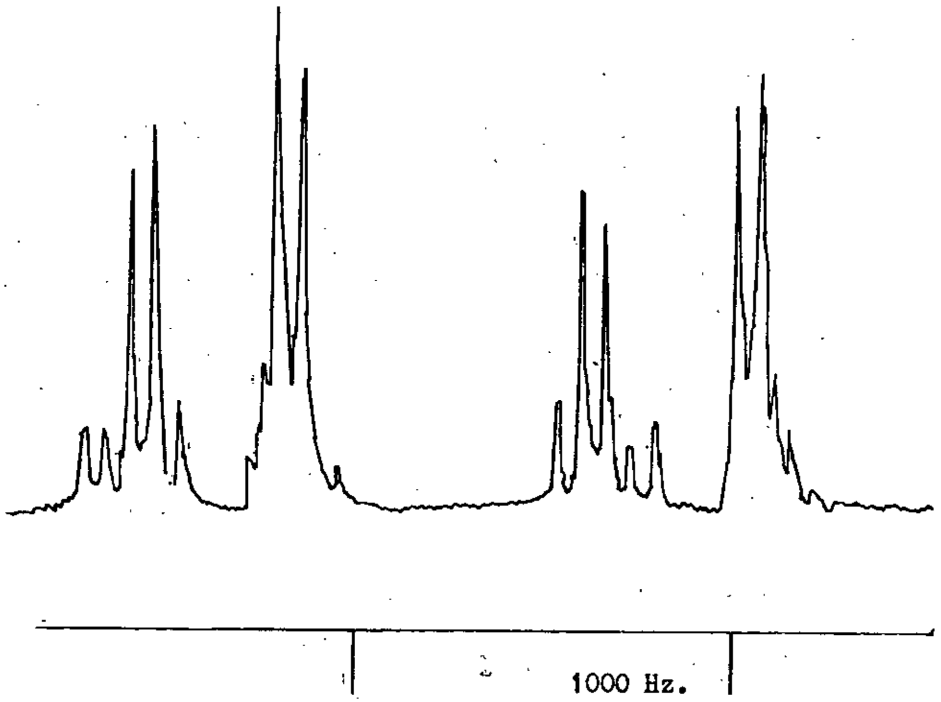
Recorded at -60°C on a F.T. spectrometer.

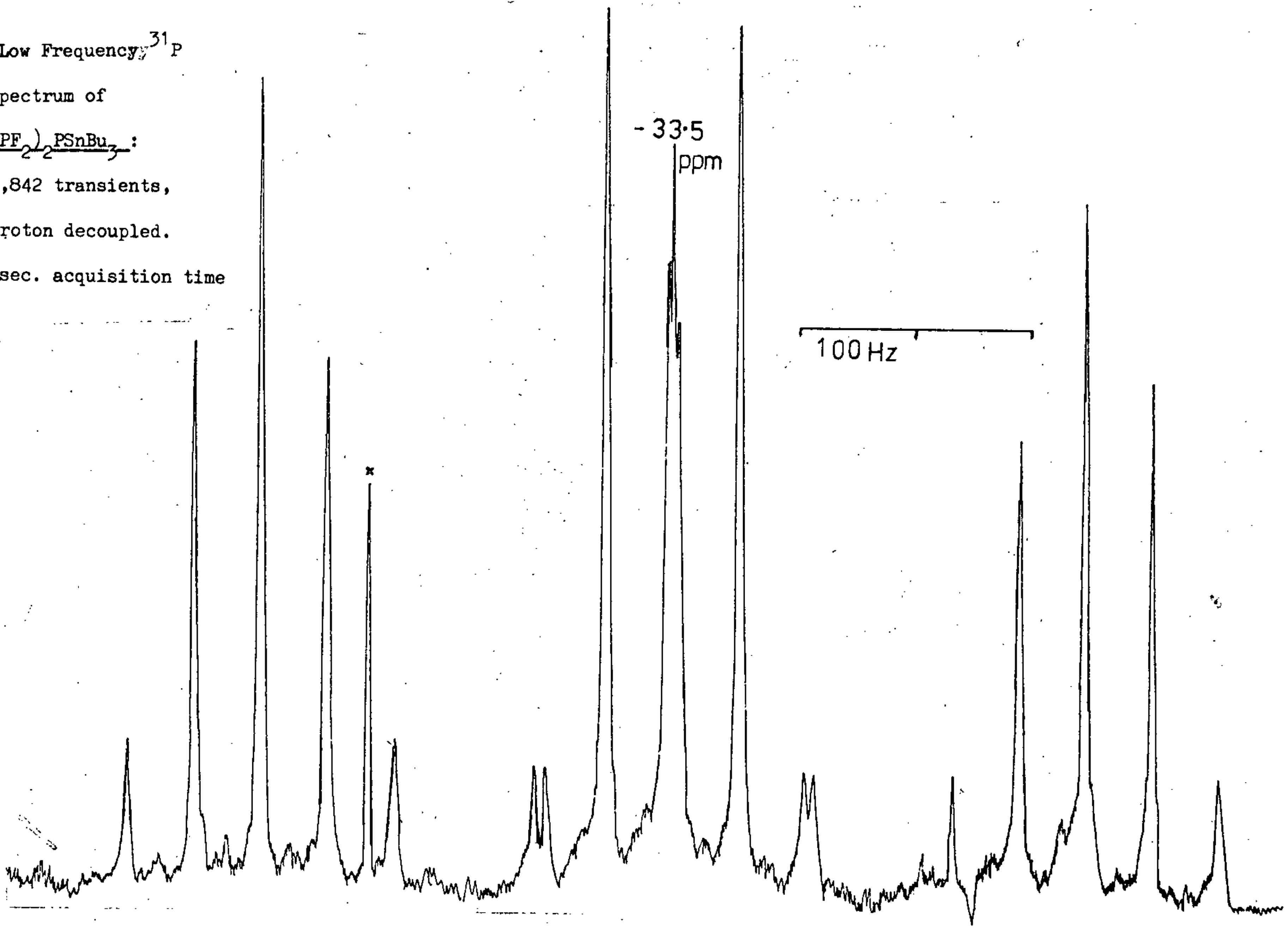
proton decoupled,

127 transients

Acquisition time 0.4 seconds.

Four sets of resonances, from the left numbers one and three are due to $(PF_2)_2SnBu_3$. Numbers two and four, those due to $(PF_2)_3P$.



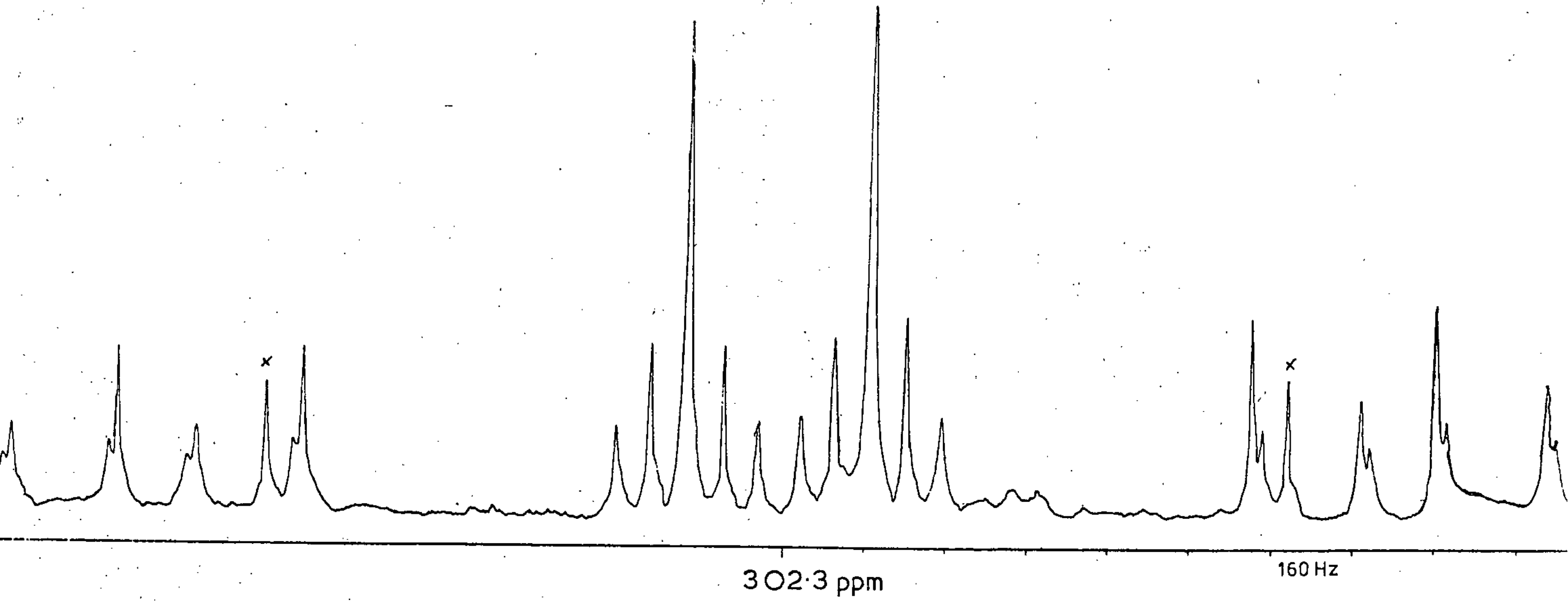


Low Frequency ^{31}P
spectrum of
$(PF_2)_2PSnBu_3$:
2,842 transients,
proton decoupled.
2sec. acquisition time

HIGH FREQUENCY spectrum of ^{31}P in $(PF_2)_2PSnBu_3$

Recorded at -60°C , 11,273 transients.

0.4 seconds acquisition time.

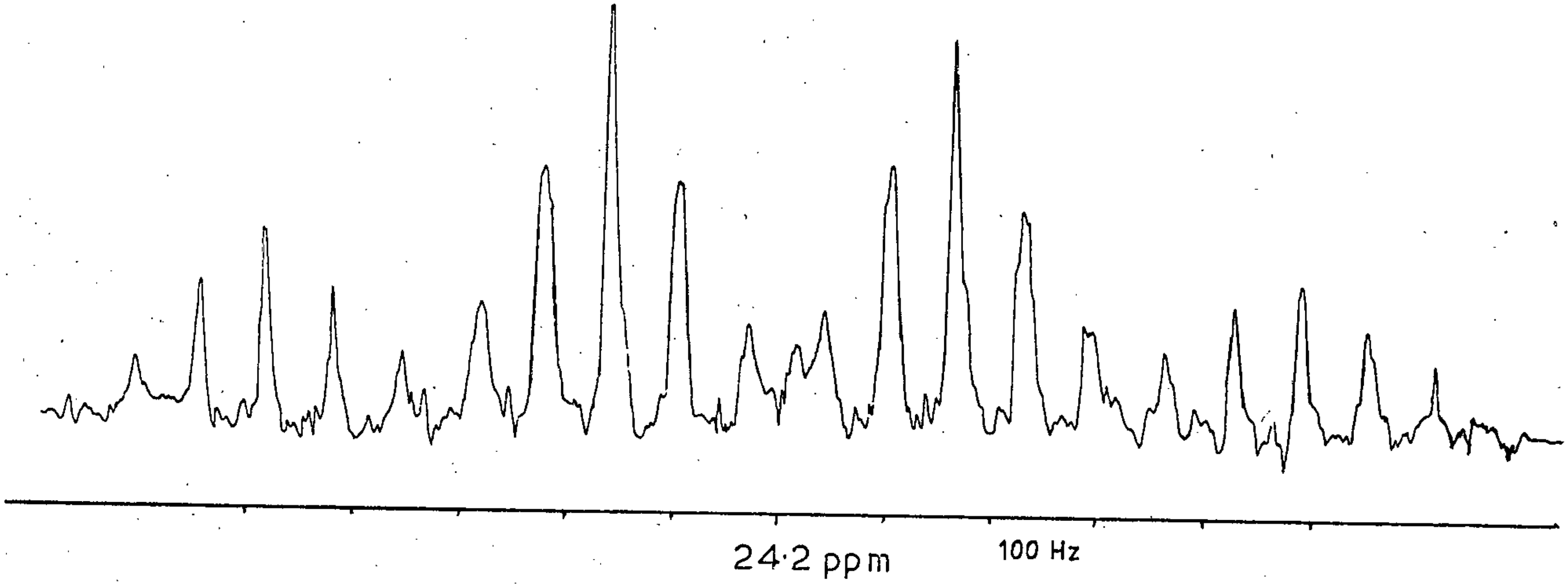


Low frequency part of ^{31}P nmr spectrum of $P(PF_2)_3$

Recorded at -60°C.

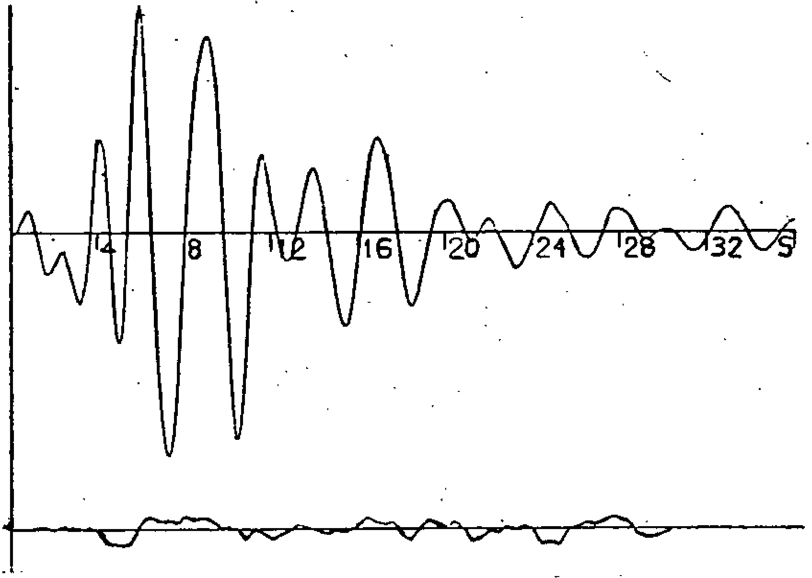
13,668 transients,

0.4 s, acquisition time.



Electron Diffraction Data for $(GeH_3)_2PPF_2$:

250 mm Intensity data



Radial distribution plot P(R)/R:

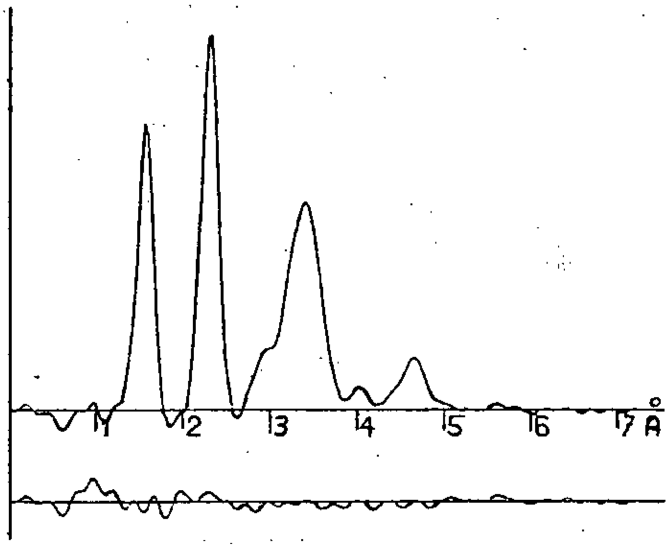


Table 1.1:

Receptivity of nuclei in n.m.r.:

Nucleus, $I = \frac{1}{2}$ X	Natural abundance C_X	Gyromagnetic Ratio γ_X	Receptivity D
^{1}H	99.8	26.7519	1.000
^{19}F	100	25.167	0.8335
^{31}P	100	10.829	0.0664
^{117}Sn	7.67	-9.530	3.47×10^{-3}
^{119}Sn	8.63	-9.971	4.50×10^{-3}

γ_X has units 10^7 rad $T^{-1}s^{-1}$

Receptivity is defined as $D = \left|\gamma_X^3\right| C_X/99.8\ \gamma_H{}^3$

(after Harris)

Table 1.2

N.m.r. data for some Trinbutyl tin phosphines:

Compound	δ P ppm	δ Sn ppm	^1J(SnP)/Hz	Others
$(Bu_3Sn)_3P$	-347.4	36	918, 877	^2J(SnSn) = 281 Hz.
$(Bu_3Sn)_2PPF_2$	-169	18	737, 705	^2J(FSn)= 92Hz, ^3J(SnF)= 65Hz
$(Bu_3Sn)_2PH$	-326	30	727, 700	^1J(HP)= 158Hz.
$(Bu_3Sn)_2PCH_3$	-226	18.5	830, 793	^2J(SnSn)= 320Hz, ^2J(HP)=5Hz
Bu_3SnPH_2	-289	17	500	^1J(HP)=170Hz.

Notes

(a) Chemical shifts for tin relative to $(CH_3)_4Sn$.

(b) Where two tin couplings are entered, that for ^{119}Sn is entered first

(c) These chemical shift data were obtained at room temperature with the exception of those from $(Bu_3Sn)_2PPF_2$, which were obtained at -60°C.

Table 2.1: **Summary of routes to PF_2PQQ':**

(a) $Q_3P + PF_2Br \dashrightarrow PF_2\,PQ_2 + QBr$

(i) $(SiH_3)_3P + \text{xs. } PF_2Br \xrightarrow[\text{9 days}]{\text{R.T.}} (SiH_3)_2PPF_2$

(ii) $(GeH_3)_3P$ " $\xrightarrow[\text{10 mins.}]{\text{R.T.}} (GeH_3)_2PPF_2$

(iii) $(Me_3Si)_3P$ " $\xrightarrow[\text{1 hour}]{\text{R.T.}} (Me_3Si)_2PPF_2$

(b) $Q_2PQ' + PF_2Br \dashrightarrow PF_2PQ_2 + Q'Br$

$Me_2PSiMe_3 + PF_2Br \xrightarrow[\text{30 s}]{-60^{\circ}C} (CH_3)_2PPF_2$

(c) $Q_2PPF_2 + Q'X \dashrightarrow PF_2PQ'_2$ or $PF_2PQQ' + QBr$

(i) $(SiH_3)_2PPF_2 + GeH_3Br \xrightarrow[\text{1 hour}]{\text{R.T.}} GeH_3.P(SiH_3)PF_2$

$+ (GeH_3)_2PPF_2$

(ii) $(GeH_3)_2PPF_2 + SiH_3I \xrightarrow[\text{30 mins}]{\text{R.T.}} (SiH_3)_2PPF_2$

(iii) $(GeH_3)_2PPF_2 + HCl \xrightarrow[\text{30 mins.}]{\text{R.T.}} (GeH_3)PHPF_2$

Table 2.2 N.m.r. data for diphosphines of type PF_2PQQ':

Compound	δ $\underline{P}_{(F)}$	δ $\underline{P}_{(Q)}$	δ $\underline{F}$	$^2\underline{J}$ (PF)	$^1\underline{J}$ (PF)	$^1\underline{J}$ (PP)	$^2J(F_1F_2)$
$(SiH_3)_2PPF_2$	288.6	-211.8	-82.9	+69.8	-1224	-301.0	
$(SiH_3)GeH_3PPF_2$	290.3	-202.7	-82.8	+69.6	-1222	-299.0	
$(GeH_3)_2PPF_2$	291.5	-192.8	-82.4	+68.6	-1214	-295.7	
$(Me_3Si)_2PPF_2$	314.0	-128.7	-85.2	60.7	1196	381	
$(Bu_3Sn)_2PPF_2$	322	-169.0	-71.0	45.3	1188	382.6	
$(Me_3Sn)_2PPF_2$	326	-160	n.o.	48	1188	380	
$(CH_3)_2PPF_2$	294	-53.5	-81.8	72	1178	250	
$(GeH_3)PHPF_2$	291	-164	-80.2	91	1203	250	
			-93.8	65	1191		192 Hz.
$(SiH_3)PHPF_2$	291	-168	n.o.	78	1200	255	
			n.o.	n.o.	n.o.		n.o.
$(CH_3)PHPF_2$	291	-91	-99	88	1177	235	n.o.
			n.o.	65	n.o.		

Notes.

(a) Other n.m.r. parameters are listed for $(GeH_3)_2PPF_2$ and $(CH_3)_2PPF_2$ elsewhere.

(b) Where the fluorines on phosphorus have beem chemically inequivalent, values for F_1 and F_2 have been shown, where values were obtained.

(c) A negative sign before a coupling constant means that the relative signs for that compound were measured specifically.

Table 2.3: $^{1}J(PP)$ in Diphosphines:

Diphosphine	$^{1}J(PP)$/Hz.	
P_2H_4	-108.2	
PMe_2PMe_2	-179.7	
PF_2PH_2	-211	
P_2F_4	-227.4	
CH_3PHPF_2	235	
$(CH_3)_2PPF_2$	250	
GeH_3PHPF_2	250	
SiH_3PHPF_2	255	Ref. 49
$(GeH_3)_2PPF_2$	-295.7	
$(SiH_3)(GeH_3)PPF_2$	-299.0	
$(SiH_3)_2PPF_2$	-301	
$(Me_3Sn)_2PPF_2$	380	
$(Me_3Si)_2PPF_2$	381	
$(Bu_3Sn)_2PPF_2$	382.6	
$(PF_2)_2PSnBu_3$	360	
$(PF_2)_3P$	323	
$S{=}PF_2PMeH$	308	Ref. 55
$Se{=}PF_2PMeH$	320	"
$S{=}PF_2PMe_2$	-350	"
$BH_3{:}PF_2P(GeH_3)_2$	-375	
$BH_3{:}PF_2P(SnBu_3)_2$	487	
$(BH_3{:}PF_2)_2PSnBu_3$	440.	

Note: Relative signs are given where they have been measured.

Table 2.4 : N.M.R. data for borane adducts:

Compound	$\delta P_{(F)}$	$\delta P_{(M)}$	δF	δB	$\delta H_{(M)}$	$\delta H_{(B)}$	$^{2}J_{(PF)}$	$^{1}J_{(PF)}$	$^{1}J_{(PP)}$
$BH_3:PF_2P(GeH_3)_2$	238.7	-207,2	-71.5	-63	3.84	1.27	31	-1210	-375
$BH_3:PF_2P(SnBu_3)_2$	248	-215	-56	n.o.	-	n.o.	40	1186	487
$BH_3:PF_2P(CH_3)_2$	206	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	1130	194
$(BH_3:PF_2)_2PSnBu_3$	223	-108	-75	n.o.	-	n.o.	n.o.	1246	440.

Note (a) The identity of the last two species is by no means certain, as mentioned in the text.

(b) Additional couplings for $BH_3:PF_2P(GeH_3)_2$ are available: $J_{(BP_{(F)})}$ =40 Hz.

	Z=Ge	Z=B
$J_{(FH_{(Z)})}$	2.0	23.5
$J_{(P_{(F)}H_{(Z)})}$	9.2	10.7
$J_{(P_{(Ge)}H_{(Z)})}$	18.0	5.5

Table 3.1: N.m.r. parameters of phosphines, $(Bu_3Sn)_nP(PF_2)_{3-n}$

Compound	$\delta^{119}Sn$	$\delta P_{(F)}$	$\delta P_{(centre)}$	δF	$^2J_{(PF)}$	$^1J_{(PF)}$	$^1J_{(PP)}$	Other
$(Bu_3Sn)_3P$	36	-	-347	-	-	-	-	see t. 1.2
$(Bu_3Sn)_2PPF_2$	18	322	-169	-71	45.3	1188	382.6	"
$(Bu_3Sn)P(PF_2)_2$	n.o.	301	-33	-85.1	59	1186	360	$^3J_{(PP)}$ = 195Hz.
$P(PF_2)_3$	-	264	+24	-89.2	61	1215	324	

Table 4.1: N.M.R. data for $(GeH_3)_2PPF_2$ and $(SiH_3)_2PPF_2$ (49)

	Ge	**Si**
δH	3.80 ppm	3.82 ppm
$\delta P_{(F)}$	291.5 ppm	288.7 ppm
$\delta P_{(Ge)}$	-192.8 ppm	-211.7 ppm
δF	-82.4 ppm	-84.3 ppm
$^1J(PF)$	-1214 Hz	-1225 Hz
$^2J(PF)$	68.6 Hz	70 Hz
$^1J(PP)$	-295.7 Hz	-301 Hz
$^2J(PH)$	16.5 Hz	17.0 Hz
$^3J(PH)$	10.9 Hz	9.1 Hz
$^4J(FH)$	3.1 Hz	2.5 Hz

Table 4.2: Vibrational Spectra for $(GeH_3)_2PPF_2$

Vapour(IR)	Solid(IR)	Solution(IR) in pentane	Solid(R)	Assignment.
2083 s	2080 s		2063 s	ν GeH
867 s				
851,sh	860 s		867 vs	δ GeH_3
838,833 dbt.				
795 s				
757,748 dbt.				
811 vs	770 vs		813 w	
			767 m	ν PF_2
			667,653 w	
562 m	560 s			ρ GeH_3
509 w	520 m			ρ GeH_3
486 w				
444 m	450 m		447 m	
390 m	384 m	378 s	392 w	ν P-Ge
	350 w		368 m	
			344 w	
			325 s	
		266 m	280,268, 251 w	
		236 s	239 s	
		214		
			163, 153 m	
		110 m		
		86 m		

Table 4.3: Summary of reactions of $(GeH_3)_2PPF_2$:

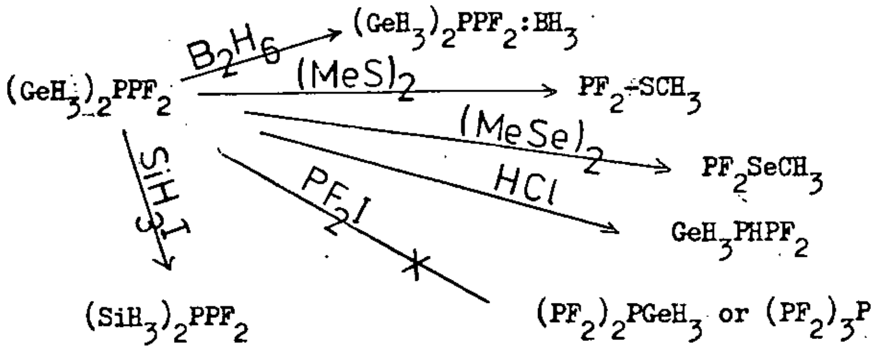


Table 4.4.: Some Physical Properties of $(GeH_3)_2PPF_2$

(1) Colourless liquid at 293K.

(2) Vapour pressure; 5 ± 1 torr at 293K.

(3) Can be contained in a trap held at 227K, under vacuum.

(4) Molecular weight; 247± 5% g mol^{-1}. (observed)
251 g mol^{-1}(calculated).

Table 5.1

Weighting functions, correlation parameters and scale factors :

Camera Height mm.	Δs	s_{min}	s_1	s_2	s_{max} nm^{-1}	p/h	Scale factor
250.1419	0.400	6.800	9.000	26.000	30.000	0.4632	0.744 ± 0.024
500.1555	0.200	2.600	4.500	13.500	15.600	0.4980	0.826 ± 0.021
999.8169	0.100	1.000	2.000	6.750	7.700	0.4998	0.956 ± 0.033

The value of the wavelength was 5.660 pm.

Table 5.2

Molecular parameters for $(GeH_3)_2PPF_2$:

(a) Independent distances		Distance/pm	Amplitude/pm
r_1	P-F	158.1 ± 0.5	3.9 +0.7
r_2	P-P	217.7 ± 0.8	5.0 (fixed)
r_3	P-Ge	232.0 ± 0.4	5.2 + 0.4
r_4	Ge-H	151.2 ± 1.4	8.0 (fixed)

(b) Dependent distances

d1	F..P	288.0 ± 4.0	10.9 + 1.2
d2	F..Ge	462.7 ± 4.2	14.6 + 1.0
d3	F..Ge	407.0 ± 6.6	16.6 + 3.1
d4	F..Ge	328.7 ± 3.0	15 (fixed)
d5	F..Ge	462.3 ± 3.3	14.6 (tied to u_6)
d6	F..F	239.5 ± 3.7	7.5 (fixed)
d7	P..Ge	333.6 ± 2.6	15.2 + 3.0
d8	Ge..Ge	351.9 ± 3.0	13.6 + 1.3
d9	P..H	316.4 ± 1.4	12.0 (fixed)
shortest (P..H)		332.0 ± 3.2	16.0 (fixed)
shortest (F..H)		320.9 ± 3.1	20.0 (fixed)
shortest (Ge..H)		375.5 ± 2.9	20.0 (fixed)
shortest (H..H)		246.9 ± 2.5	20.0 (fixed)

(c) Independent Angles (degrees)

> 1 (Ge-P-Ge)	98.6 ± 1.1
> 2 (Ge-P-P)	95.7 ± 0.9
> 3 (F-P-F)	98.5 ± 1.6
> 4 (F-P-P)	98.9 ± 0.8
> 5 (P-Ge-H)	109.5 (fixed)
> 6 (Dihedral)	156.1 ± 2.4

Table 5.3: $(GeH_3)_2PPF_2$:Least-squares Correlation Matrix (x 1000):

r1	r2	r3	r4	<1	<2	<3	<4	<6	u1	u3	u5	u6	u7	u11	u12	k1	k2	k3	
1000	-85	-78	-611	190	142	31	-267	-124	-113	-4	34	158	-62	-85	-3	233	173	83	r1
	1000	435	60	169	-276	-212	-134	168	-306	274	57	-69	31	-152	-139	-399	-392	-230	r2
		1000	87	-29	-366	-609	116	494	-218	524	191	-36	-40	8	-50	-310	-350	-236	r3
			1000	-210	-100	-115	218	151	198	-16	-108	-191	18	194	70	-333	-169	13	r4
				1000	-304	-49	67	-241	-101	27	13	86	-51	-884	-666	24	-109	-171	<1
					1000	591	-321	-736	229	-295	59	108	-463	563	774	369	498	428	<2
						1000	-435	-807	313	-606	-236	148	-8	93	163	526	574	598	<3
							1000	180	-57	128	146	-269	17	-215	-106	-237	-396	-368	<4
								1000	-245	458	76	-140	327	23	-248	-457	-475	-327	<6
									1000	-76	-25	79	0	131	131	455	337	214	u1
										1000	211	36	-59	22	4	-5	-176	-157	u3
											1000	-42	-68	1	112	91	-103	-247	u5
												1000	-155	13	3	242	299	220	u6
													1000	-243	-450	19	-167	-297	u7
														1000	848	29	258	349	u11
															1000	119	288	341	u12
																1000	550	269	k1
																	1000	439	k2
																		1000	k3