Preparation and Chemical and Spectroscopic Properties of (Disilylamino)-difluorophosphine and Bis(difluorophosphino)silylamine

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The compounds $PF_2[N(SiH_3)_2]$ and $N(PF_2)_2(SiH_3)$ have been prepared by the reactions of $SiBrH_3$ and NMe_3 with $PF_2[NH(SiH_3)]$ and $NH(PF_2)_2$ respectively. Vibrational, n.m.r., mass, and photoelectron spectra have been recorded, and chemical properties have been studied. With diborane, $PF_2[N(SiH_3)_2]$ gives the adduct $PF_2[N(SiH_3)_2]\cdot BH_3$ and $N(PF_2)_2(SiH_3)$ gives both mono- and bis-(borane) adducts; n.m.r. spectra of the three borane adducts have been recorded. In reactions with HBr the P–N bonds are attacked preferentially, whereas in reactions with water the cleavage of the Si–N bonds takes place first.

WHEN chloro- or bromo-difluorophosphine reacts with ammonia in the gas or liquid phase the major volatile product is the primary amine, aminodifluorophosphine, and very small amounts of secondary and tertiary amines are formed.[1] Treatment of $PF_2(NH_2)$ with silyl bromide in the liquid phase leads to the formation of difluoro-(silylamino)phosphine, with replacement of just one of the amine hydrogen atoms,[2] although ammonia and halogenosilanes react rapidly to give the completely substituted product, trisilylamine.[3] The reluctance of (difluorophosphino)amines to undergo further substitution may be attributed to the low basicity of the nitrogen atoms, caused by a combination of inductive effects and possible delocalization of nitrogen lone-pair electrons into phosphorus $3d$ orbitals.

We have recently shown that by adding trimethyl-amine to the reaction systems, secondary and tertiary amines may be prepared, and we have used this technique to synthesize bis(difluorophosphino)amine and tris-(difluorophosphino)amine,[4] and several amines with both difluorophosphino- and germyl substituents.[5]

Tris(difluorophosphino)amine and trisilylamine are both unusually weak bases, and both molecules have been shown by electron-diffraction studies[6-8] to have planar M_3N skeletons. We have therefore synthesized the mixed amines (disilylamino)difluorophosphine and bis(difluorophosphino)silylamine by reaction of $SiBrH_3$ and NMe_3 with $NH(PF_2)_2$ and $PF_2[NH(SiH_3)]$ respectively, and have investigated some of their chemical and spectroscopic properties. We intend to determine their molecular structures, to see whether these molecules also have planar arrangements of the bonds to nitrogen, and also to study the conformations of the difluoro-phosphino-groups. Preliminary studies indicate that $PF_2[N(SiH_3)_2]$ does have a planar $PNSi_2$ skeleton.

RESULTS AND DISCUSSION

When difluoro(silylamino)phosphine and silyl bromide were mixed in the liquid phase at room temperature no reaction occurred, but with the addition of trimethyl-amine a rapid reaction took place, even at low temperatures, with the formation of white solid. The volatile products were a mixture of (disilylamino)di-fluorophosphine and $PF_2[NH(SiH_3)]$, with some silyl fluoride and bromide. The proportion of the disilyl-

amine was increased to close to 100% by treatment of the products of the first stage with a further excess of $SiBrH_3$ and NMe_3.

$$PF_2[NH(SiH_3)] + SiBrH_3 + NMe_3 \longrightarrow$$
$$PF_2[N(SiH_3)_2] + [NHMe_3]Br \quad (1)$$
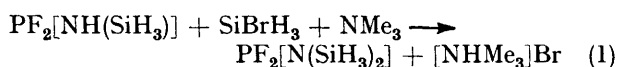
Similarly, bis(difluorophosphino)amine and $SiBrH_3$ did not react in the absence of base, but in the presence of NMe_3 a liquid-phase reaction occurred, even at low temperatures, giving a white solid which became orange-brown at room temperature. The main volatile product was bis(difluorophosphino)silylamine, with smaller amounts of $SiBrH_3$, $SiFH_3$, and trifluorophosphine.

$$NH(PF_2)_2 + SiBrH_3 + NMe_3 \longrightarrow$$
$$N(PF_2)_2(SiH_3) + [NHMe_3]Br \quad (2)$$
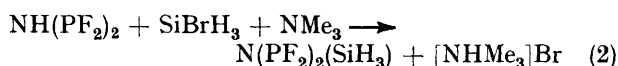
Both of the new amines were stable at room temperature in the liquid or gas phase for periods of at least 1 h, but in the presence of the trimethylammonium salts slow decomposition occurred, giving $SiFH_3$ [and some PF_3 from $N(PF_2)_2(SiH_3)$] and involatile products. Both compounds reacted explosively with air.

N.M.R. Spectra.—The ^1H, ^{19}F, and ^{31}P n.m.r. spectra of $PF_2[^{15}N(SiH_3)_2]$ and $^{15}N(PF_2)_2(SiH_3)$ were recorded. Use of ^{15}N-labelled samples was necessary since ^{14}N quadrupolar broadening of lines in ^{31}P (and to a lesser extent in ^1H) spectra was such that small couplings would not have been resolved. Double-resonance experiments for $PF_2[^{15}N(SiH_3)_2]$ enabled $\delta(^{15}N)$ and signs of coupling constants [relative to $^1K(^{31}P^{19}F)$, assumed to be negative] to be determined.

The spectra of $PF_2[^{15}N(SiH_3)_2]$ were all first order, indicating that rotation about the P–N bond was rapid at the temperature of the experiments (223 K). The ^{19}F and ^{31}P spectra of $^{15}N(PF_2)_2(SiH_3)$, being the A and X parts of an $[A[X]_2]_2MQ_3$ spin system, were second order. With ^1H decoupling, these simplify to a pair of $[A[X]_2]_2$ sub-spectra, which could be easily analysed. N.m.r. parameters for both compounds are given in Table 1.

The observed chemical shifts and coupling constants are in general close to the values expected, and provided positive identification of the compounds. The observation of clearly resolved coupling to ^{14}N in the ^{31}P spectra of both of these compounds is surprising, and must mean

TABLE 1

N.m.r. parameters for $PF_2[^{15}N(SiH_3)_2]$ and $^{15}N(PF_2)_2(SiH_3)$

Parameter	$PF_2[^{15}N(SiH_3)_2]$ [a]	$^{15}N(PF_2)_2(SiH_3)$ [b]
$\delta(^1H)$/p.p.m.	4.42	4.39
$\delta(^{19}F)$ [c]/p.p.m.	−51.6	−62.3
$\delta(^{31}P)$ [d]/p.p.m.	155.7	150.0
$\delta(^{15}N)$ [e]/p.p.m.	7.1	n.s.
$^1J(^{31}P^{19}F)$/Hz	−1 237	−1 255
$^1J(^{31}P^{15}N)$/Hz	+77.5 [d]	74.6 [f]
$^1J(^{29}Si^1H)$/Hz	228	232
$^2J(^{19}F^{15}N)$/Hz	−2.6	3.2
$^2J(^{15}N^1H)$/Hz	−3.8	3.5
$^2J(^{31}P^{29}Si)$/Hz	25	7
$^2J(^{31}P^{31}P')$/Hz		367.6
$^3J(^{31}P^1H)$/Hz	+9.3	3.5
$^3J(^{29}Si^{19}F)$/Hz	7.5	11.6
$^3J(^{31}P^{19}F')$/Hz		+24.9
$^4J(^{19}F^1H)$/Hz	+2.9	3.7
$^4J(^{19}F^{19}F')$/Hz		3.7
$^4J(^{19}F^{19}F'')$/Hz		8.0

Relative signs of coupling constants were determined, where they are explicitly given; n.s. = not studied. Chemical shifts are positive to high frequency.

[a] Recorded at 223 K for solutions in CCl_3D–$SiMe_4$ (3 : 1). [b] Recorded at 238 K for solutions in CCl_3D–$SiMe_4$ (3 : 1). [c] Relative to CCl_4F. [d] Relative to 85% H_3PO_4. [e] Relative to $[NMe_4]I$. [f] $^1J(^{31}P^{14}N)$ was observed to be ca. 50 Hz.

that the electric-field gradients at the nitrogen atoms are fortuitously small. Both compounds are likely to have trigonal-planar arrangements of the bonds to nitrogen, and it is particularly noteworthy that replacement of a silyl by a difluorophosphino-group does not seem to have a large effect on the linewidths of the ^{31}P resonances. The ^{31}P spectra of other aminodifluorophosphines usually have broad resonances, with no, or poorly resolved, ^{14}N splittings.

It has been suggested [5,9] that some two- or three-bond couplings to three-co-ordinate ^{31}P depend on conformation, with large couplings to nuclei that are cis to the phosphorus lone pair of electrons. For $N(PF_2)_2(SiH_3)$, $^3J(^{31}P^1H)$ and $^2J(^{31}P^{29}Si)$ are both very small (3.5 and 7 Hz respectively), and we therefore consider that the conformation adopted by this molecule is probably the same as that proposed for $N(GeH_3)(PF_2)_2$,[5] with the PF_2 groups turned towards the MH_3 group, as has been observed for $NMe(PF_2)_2$,[10] which also has a very small $^3J(^{31}P^1H)$.[11] For $PF_2[N(SiH_3)_2]$ the values of these two couplings are substantially larger (9.3 and 25 Hz respectively), and we suggest that these are the averages of large and small values for nuclei cis and trans to the phosphorus lone pair, and therefore that there is free exchange (on the n.m.r. time scale) between the two equivalent conformations in which the phosphorus lone pair eclipses one of the N–Si bonds.

The large value of $^2J(^{31}P^{31}P)$ for $N(PF_2)_2(SiH_3)$ is also consistent with the proposed conformation.[12] This coupling constant was found to decrease with increasing temperature (Table 2), consistent with increasing amplitudes of torsional vibrations about the P–N bonds. Other coupling constants change little with temperature, the most significant change observed being of $^3J(^{31}P^{19}F)$, from 27.8 Hz at 293 K to 22.8 Hz at 203 K.

Infrared Spectra.—Details of the gas- and solid-phase i.r. spectra of the two amines are given in Table 3. The assignments of group frequencies given in the Table are very tentative, since the molecules must have low symmetry, and there will be considerable mixing of vibrations, particularly between those of the PF_2 groups and the so-called 'skeletal' vibrations. However, there are bands in the regions normally associated with the stretching and deformation vibrations of silyl and difluorophosphino-groups, and the spectra are generally similar in appearance to those of their germyl analogues.

Mass Spectra.—Details of the mass spectra of the two amines are given in Table 4. There are at least two breakdown routes for $PF_2[N(SiH_3)_2]$, one involving loss of a silyl group, followed by either HF or a second silyl group, and the other involving loss of a PF_2 group first. In the spectrum of $N(PF_2)_2(SiH_3)$ the parent-ion peak is very weak indeed, and it appears that SiH_2 is eliminated to give $[NH(PF_2)_2]^+$, which can then lose H, F, HF (metastable ion peak observed), PF_2, or PF_3. An alternative route involves initial loss of a PF_2 group, giving $[N(PF_2)(SiH_3)]^+$.

Photoelectron Spectra.—He(I) u.v. photoelectron spectra were recorded, and details are given in Table 5. Assign-

TABLE 2

Temperature variation of $^2J(^{31}P^{31}P)$ in $N(PF_2)_2(SiH_3)$ *

T/K	Coupling (Hz)
203	397.0
233	375.6
263	354.2
293	333.2

* Recorded for solutions in CCl_3D–$SiMe_4$ (3 : 1).

TABLE 3

Infrared spectra (cm⁻¹)

$PF_2[N(SiH_3)_2]$ Gas	$PF_2[N(SiH_3)_2]$ Solid	$N(PF_2)_2(SiH_3)$ Gas	$N(PF_2)_2(SiH_3)$ Solid	Assignment
2 212s (sh)			2 230m	ν(SiH)
2 189s	2 185s	2 220ms	2 218m	
			2 199m	
			2 178m	
1 930vw		1 946vw		
1 900vw		1 907vw		
		1 638vw		
1 014m	1 034s			
1 004m	1 000mw		992m	
990s (sh)	958s	963 ⎱ vs	964s	δ(SiH₃)
970s	927s	954 ⎰	935 (sh)	ν(skeletal)
			918vs	
926vs	893vs	936vs	886 (sh)	
822 ⎱ s (sh)				
815 ⎰ s	819m	830vs	838m	ν(PF₂)
808	791s	817vs	814s	
795s			790vs	
			774 (sh)	
734mw	751s	751w	736m	ρ(SiH₃)
	730s (sh)	713w	705w	
674w	685w	656w	660w	ν(skeletal)
529w	532 ⎱ 523 ⎰ w	548w		
			478w	
		465m	462m	δ(PF₂)
			447w	
			431w	
			408w	
368 ⎱ 362 ⎰ vw	357m	362m	367s	δ- or ω-(PF₂)
325mw	326 ⎱ m 319 ⎰ w (sh)	291 ⎱ 282 ⎰ w	348 (sh) 357m	ω- or ρ-(PF₂)

TABLE 4

Mass spectra

Relative abundance

m/e	$PF_2[N(SiH_3)_2]$	$N(PF_2)_2(SiH_3)$	Assignment
183		0.2	$[N(PF_2)_2(SiH_3)]^+$
153		73	$[NH(PF_2)_2]^+$
152		41	$[N(PF_2)_2]^+$
145	59		$[PF_2\{N(SiH_3)_2\}]^+$
134		10	$[NH(PF_2)(PF)]^+$
133		34	$[N(PF_2)(PF)]^+$
115	20		$[NH(PF_2)(SiH_3)]^+$
114	100	24	$[N(PF_2)(SiH_3)]^+$
113	85		$[N(PF_2)(SiH_2)]^+$
112	59	8	$[N(PF_2)(SiH)]^+$
94	56		$[PF(NSiH_2)]^+$
93	7		$[PF(NSiH)]^+$
92	18		$[PF(NSi)]^+$
88		6	$[PF_3]^+$
85	21	9	$[PF_2(NH_2)]^+$
78	21	7	$[O(SiH_3)_2]^+$
77	34	60	$[NH(SiH_3)_2]^+$, $[PH(NSiH_3)]^+$
76	56	24	$[N(SiH_3)_2]^+$, $[P(NSiH_3)]^+$
75	27	33	$[N(SiH_3)(SiH_2)]^+$, $[P(NSiH_2)]^+$
74	19	5	$[N(SiH_2)_2]^+$, $[P(NSiH)]$
73	20	15	$[N(SiH_2)(SiH)]^+$, $[P(NSi)]^+$
72	17	6	$[N(SiH)_2]^+$
70	25		$[NSi_2]^+$
69	33	100	$[PF_2]^+$
65		66	$[PF(NH)]^+$
50	4	8	$[PF]^+$, $[SiFH_3]^+$
49	22	23	$[SiFH_2]^+$
48	8	14	$[SiFH]^+$
47	22	7	$[SiF]^+$
46	59	48	$[PNH]^+$, $[NH(SiH_3)]^+$
45	15		$[PN]^+$, $[NSiH_3]^+$
42	9		$[NSi]^+$
31		12	$[SiH_3]^+$
29	8		$[SiH]^+$
28	8	5	$[Si]^+$

Only ions of abundance $>5\%$ of that of the most abundant ion are included.

TABLE 5

He(I) photoelectron spectra

Ionization potential/eV

$PF_2[N(SiH_3)_2]$	$N(PF_2)_2(SiH_3)$	Assignment
10.8		N $2p_z$, P $3p_z$
	11.2	N $2p_z$
	11.7 } 12.2 }	P $3p_z$
12.3 } 12.7 }	13.5	SiH$_\sigma$
13.7	14.3	SiN$_\sigma$
15.2	15.6	PN$_\sigma$
16.7	16.1 } 16.8 }	F $2p_\pi$
17.8	17.5 } 18.4 }	PF$_\sigma$

ments were made by comparison with observed ionization potentials for other aminodifluorophosphines [4,5,13] and silylamines.[14] The spectra are generally very similar to those of the germyl analogues, in peak positions and areas. We therefore assign both nitrogen and phosphorus lone-pair levels of $PF_2[N(SiH_3)_2]$ to 10.8 eV,*

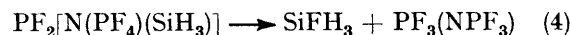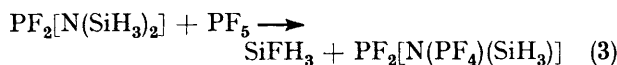* Throughout this paper: 1 eV $\approx$ 1.60 $\times$ 10^{-19} J.

and conclude that the axes of the two lone pairs must be orthogonal. This is consistent with the conformation proposed on the basis of n.m.r. coupling constants. No conclusions may be drawn concerning the conformation of $N(PF_2)_2(SiH_3)$, since three distinct bands are seen in the 10—12.5 eV region.

It should be noted that the nitrogen lone-pair ionization potentials of these silylamines are *ca.* 0.4 eV larger than those of their germyl analogues,[5] this difference being close to that between the potentials of trisilyl- and trigermyl-amines.[14]

Reactions with HBr *and Water.*—When equimolar amounts of $N(PF_2)_2(SiH_3)$ and HBr were allowed to react in an n.m.r. tube the products were $PBrF_2$, $SiBrH_3$, a white solid, and unchanged amine. Since $NH(PF_2)_2$ is known not to react rapidly with HBr,[4] it follows that a P–N bond must have been broken first to give $PF_2[NH(SiH_3)]$, which is known to react further.[2] Similarly, reaction of equimolar amounts of PF_2-$[N(SiH_3)_2]$ and HBr gave $PBrF_2$ and $SiBrH_3$ in a ratio of *ca.* 2:1, with disilylamine and unchanged tertiary amine. In this case also the P–N bond appears to be attacked preferentially.

In contrast to this, however, $PF_2[N(SiH_3)_2]$ reacted with water to give $PF_2[NH(SiH_3)]$, $PF_2(NH_2)$, PF_3, $O(PF_2)_2$, $O(SiH_3)_2$, SiH_4, $SiFH_3$, all identified by n.m.r. spectroscopy, and solid products, while $N(PF_2)_2(SiH_3)$ gave the same products, with $NH(PF_2)_2$ instead of $PF_2[NH(SiH_3)]$. The initial reaction in both cases is therefore cleavage of an Si–N bond.

Exchange Reactions of $PF_2[N(SiH_3)_2]$.—When PF_2-$[N(SiH_3)_2]$ was treated with $PBrF_2$ at room temperature slow decomposition took place, and although a little $SiBrH_3$ was formed no $N(PF_2)_2(SiH_3)$ or $N(PF_2)_3$ was observed. Similarly, there was no reaction with PF_3O, nor between PF_3O and $N(PF_2)_2(SiH_3)$. With PF_5, however, a rapid reaction occurred, giving $PF_2(N=PF_3)$, identified by its n.m.r. parameters. Presumably, this is formed by a substitution reaction, followed by elimination of $SiFH_3$ [equations (3) and (4)]. A reaction

$$PF_2[N(SiH_3)_2] + PF_5 \longrightarrow$$
$$SiFH_3 + PF_2[N(PF_4)(SiH_3)] \quad (3)$$

$$PF_2[N(PF_4)(SiH_3)] \longrightarrow SiFH_3 + PF_3(NPF_3) \quad (4)$$

analogous to the first part of this has been observed for $PF_2[NH(SiH_3)]$ and PF_5.[15]

Reaction of $PF_2[N(SiH_3)_2]$ *with Sulphur.*—The oxidation of $PF_2(NMe_2)$ to $PF_2(NMe_2)(S)$ by sulphur can be achieved, but the reaction takes *ca.* 5 d at 420 K. The analogous oxidation reaction of $PF_2[N(SiH_3)_2]$ was attempted, but complete decomposition of the amine occurred within 24 h at 360 K, and no phosphorus(v) products were observed.

Reactions with Diborane.—When $PF_2[N(SiH_3)_2]$ and diborane were allowed to warm to room temperature in solution in CCl_3H an immediate and quantitative reaction occurred. The product, which was stable at room temperature in solution, was unequivocally identi-

TABLE 6

N.m.r. parameters for borane adducts of $PF_2[N(SiH_3)_2]$ and $N(PF_2)_2(SiH_3)$

Parameter	$PF_2[^{15}N(SiH'_3)_2]\cdot BH_3$ [a]	$PF_2[N(P'F'_2)(SiH'_3)]\cdot BH_3$ [b]	$N[PF_2(BH_3)]_2(SiH'_3)$ [b]
$\delta(^1H)$/p.p.m.	0.78	n.o.[c]	n.o.[c]
$\delta(^1H')$/p.p.m.	4.47	n.o.[c]	n.o.[c]
$\delta(^{19}F)$ [d]/p.p.m.	-60.2	-64.4	-60.7
$\delta(^{19}F')$ [d]/p.p.m.		-60.2	
$\delta(^{31}P)$ [e]/p.p.m.	135.1	130.7	128.9
$\delta(^{31}P')$ [e]/p.p.m.		142.6	
$^1J(^{31}P^{19}F)$/Hz	1 209	1 205	1 250 [f]
$^1J(^{31}P'^{19}F')$/Hz		1 288	
$^1J(^{31}P^{15}N)$/Hz	40.9	n.s.	n.s.
$^1J(^{31}P^{11}B)$/Hz	72.4	55	n.o.[c]
$^1J(^{29}Si^1H')$/Hz	212	n.o.	n.o.
$^1J(^{11}B^1H)$/Hz	101	100	100
$^2J(^{31}P^1H)$/Hz	16	n.o.	n.o.
$^2J(^{15}N^1H')$/Hz	4.2	n.s.	n.s.
$^2J(^{31}P^{31}P')$/Hz		118	<10
$^3J(^{19}F^1H)$/Hz	16	17	16
$^3J(^{31}P^1H')$/Hz	6.9	n.o.	n.o.
$^4J(^{19}F^1H')$/Hz	2.1	n.o.	n.o.

n.o. = Not observed, n.s. = not studied.   Chemical shifts are positive to high frequency.

[a] Solution in CCl_3D at 303 K.   [b] Solution in CCl_3D at 223 K.   [c] Not resolved, see text.   [d] Relative to CCl_3F.   [e] Relative to 85% H_3PO_4.   [f] $|^1J(PF) + {}^3J(PF')|$; $^3J(PF) < 5$ Hz.

fied from n.m.r. spectra as an adduct, with a borane group co-ordinated to the phosphorus atom.   The ^{31}P spectra were particularly useful, since couplings to ^{19}F,

$$2PF_2[N(SiH_3)_2] + B_2H_6 \longrightarrow 2PF_2[N(SiH_3)_2]\cdot BH_3 \quad (5)$$

^{11}B, ^{15}N, and two types of protons could be observed. Couplings to the quadrupolar ^{11}B nuclei were clearly resolved in ^1H and ^{31}P spectra, but the resonances were broad and some small couplings could not be observed. With the ^{14}N species the ^{31}P spectrum was very poorly resolved, and ^{15}N substitution was essential so that the multiplicities of the resonances, and hence the identity of the species, could be reliably established.   No attempt was made to isolate the adduct.

Several reactions of $N(PF_2)_2(SiH_3)$ with diborane were carried out, using different ratios of reagents.   Spectra were recorded at 223 K, after briefly warming the mixture to room temperature, and two different complexes were detected in each case.   Neither was stable at room temperature.

The complex that was formed first was identified by n.m.r. spectroscopy as the mono(borane) species, $PF_2[N(PF_2)(SiH_3)]\cdot BH_3$.   The ^{31}P spectrum contained two sets of resonances, both apparently first order, each with coupling to two ^{19}F nuclei and to each other, with one set showing coupling to a ^{11}B nucleus.   The ^{19}F spectrum similarly contained two sets of resonances, one of which showed coupling to three protons, but these resonances were second order and were not fully analysed. The second-order features indicate that the two fluorine atoms on one phosphorus atom are not magnetically equivalent, which implies that rotation about the P–N bond is restricted.

The second complex formed was the major ultimate product, even when excess of amine was used in the reaction.   It was identified as the bis(borane) complex, $N[PF_2(BH_3)]_2(SiH_3)$.   Both ^{19}F and ^{31}P n.m.r. spectra of this species showed that there was only one type of PF_2 group present, with couplings to co-ordinated BH_3

groups, but both spectra were second-order centro-symmetric patterns, as would be expected for $[PF_2(BH_3)]_2$ spin systems.   With broadening due to ^{14}N and ^{11}B, the spectra were exceedingly complex, and a full analysis was not attempted.

Proton n.m.r. spectra of the complexes contained resonances that could be assigned to silyl and co-ordinated borane groups, but since the complicated patterns of the two species present in every sample overlapped the chemical shifts and coupling constants could not be determined reliably.

The preferred formation of a complex containing two co-ordinated borane groups is of interest, since other systems with two PF_2 groups, such as P_2F_4,[16] $O(PF_2)_2$,[17] $S(PF_2)_2$,[18] and $Se(PF_2)_2$,[12] have only accepted a single borane.   In the cases of P_2F_4 and the sulphur and selenium compounds this may be attributed to steric factors, but it seems unlikely that the same could be true for the oxygen compound which has a wide angle at oxygen when uncomplexed.[19]   Our preliminary studies of other amines with two PF_2 groups indicate that these also can co-ordinate to two borane groups.[20]

N.m.r. parameters for the three borane complexes are given in Table 6.   They are in general fully consistent with those reported for related compounds.   The measured values of $^1J(^{31}P^{11}B)$ are somewhat smaller than those in alkyl(difluorophosphino)amine complexes,[21] while $\delta(^1H)$ is somewhat larger,[22] and this implies that the phosphine basicity is reduced by the silyl sub-stituents.

The coupling $^1J(^{31}P^{15}N)$ in $PF_2[N(SiH_3)_2]\cdot BH_3$ (41 Hz) is intermediate in magnitude between those in phos-phorus(III) and four-co-ordinate phosphorus(V) com-pounds.   We conclude that the sign of this coupling is probably positive, as in phosphorus(III) compounds.

The two-bond phosphorus–phosphorus coupling is also interesting, changing from ca. 350 Hz in complexed $N(PF_2)_2(SiH_3)$ to 118 Hz in the mono(borane) complex, and to <10 Hz in the bis(borane) species.   This change

is consistent with the idea that large $^2J(^{31}P^{31}P)$ couplings are found in systems in which two phosphorus lone pairs of electrons can interact.

EXPERIMENTAL

All volatile compounds were handled in a Pyrex-glass vacuum line, equipped with 'Sovirel' poly(tetrafluoroethylene) taps. All glass apparatus was dried by allowing contact with silyl chloride vapour for a period of several minutes. Silyl bromide,[23] $PF_2[NH(SiH_3)]$,[2] $NH(PF_2)_2$,[4] and diborane [24] were prepared by standard literature methods.

Proton n.m.r. and double-resonance experiments were carried out using a Varian Associates HA100 spectrometer, modified [25] to accept a second radiofrequency derived from a Schlumberger FS30 frequency synthesizer. Fluorine-19 and ^{31}P spectra were obtained using a Varian Associates XL100 spectrometer with deuterium lock and Gyrocode decoupler. Infrared spectra were recorded in the range 200—4 000 cm^{-1} on Perkin-Elmer 225 and 457 spectrometers, using cells equipped with KBr or CsI windows. Mass spectra were obtained using an A.E.I. MS902 spectrometer operating at 70 eV ionizing voltage, and u.v. photoelectron spectra using a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation.

Preparations.—(Disilylamino)difluorophosphine.—In a typical experiment, NMe_3 (2.4 mmol) was condensed into a glass ampoule (40 cm^3) containing a mixture of PF_2-$[NH(SiH_3)]$ (2.2 mmol) and $SiBrH_3$ (2.5 mmol). After briefly warming the reagents to room temperature the products were fractionated, and the portion volatile at 177 K was discarded, leaving 2.0 mmol of an 85 : 15 mixture of $PF_2[N(SiH_3)_2]$ and $PF_2[NH(SiH_3)]$. This mixture was then treated with more portions of $SiBrH_3$ (1.0 mmol) and NMe_3 (0.8 mmol), and on fractionation it yielded (disilylamino)difluorophosphine (1.7 mmol, 77%), volatile at 195 K but retained at 177 K.

In the same way $PF_2[^{15}N(SiH_3)_2]$ was prepared from $PF_2[^{15}NH(SiH_3)]$, which was made from $PF_2(^{15}NH_2)$, which in turn was obtained from $^{15}NH_3$.

Bis(difluorophosphino)silylamine. Trimethylamine (1.0 mmol) was condensed into a glass ampoule (40 cm^3) containing a mixture of $NH(PF_2)_2$ (0.8 mmol) and $SiBrH_3$ (1.2 mmol). The reagents were warmed to room temperature for 15 s, with the formation of first white and then orange-brown solids. Fractionation of the volatile products yielded bis(difluorophosphino)silylamine (0.7 mmol, 87%), involatile at 177 K but volatile at 195 K.

Similarly, $^{15}N(PF_2)_2(SiH_3)$ was prepared from $^{15}NH(PF_2)_2$, which was made from $^{15}NH_3$ and $PBrF_2$ in the usual manner.

Reactions of $PF_2[N(SiH_3)_2]$ *and of* $N(PF_2)_2(SiH_3)$.—*With HBr.* The reactions were carried out in CCl_3D solution in n.m.r. tubes and were monitored by ^1H and ^{31}P n.m.r. spectroscopy. In a typical experiment, $PF_2[N(SiH_3)_2]$ (0.3 mmol) and HBr (0.3 mmol) were allowed to react at room temperature, with the formation of $PBrF_2$, $SiBrH_3$, and a white solid.

With water. These reactions were also carried out in n.m.r. tubes. The amounts of water introduced were not accurately measured, but small quantities could be added either by passing the amine through glass tubing which had previously been in contact with water vapour, or by using CCl_3D solvent which had not been carefully dried before use.

With $PBrF_2$. In an n.m.r. tube, $PF_2[N(SiH_3)_2]$ (0.25 mmol) and $PBrF_2$ (0.6 mmol) were allowed to stand at room temperature for 24 h. Proton and ^{31}P n.m.r. spectra showed that decomposition was taking place, with no displacement of silyl by PF_2 groups.

With sulphur. When sulphur (0.075 g) was heated with $PF_2[N(SiH_3)_2]$ in CCl_3D solution, ^1H and ^{31}P n.m.r. spectra showed that decomposition of the amine occurred, without the formation of any phosphorus(v) species.

With PF_5. Equimolar quantities of $PF_2[N(SiH_3)_2]$ and PF_5 were allowed to react in CCl_3D solution in an n.m.r. tube. The tube was warmed to room temperature for a few minutes, and ^{31}P n.m.r. spectra were then recorded at 223 K. These indicated that $PF_2(NPF_3)$ had been formed.

With PF_3O. When PF_3O was warmed to room temperature with $PF_2[N(SiH_3)_2]$ or $N(PF_2)_2(SiH_3)$ in CCl_3D solution, no reaction occurred other than the slow decomposition of the amine.

With B_2H_6. Reactions between $PF_2[N(SiH_3)_2]$ or $N(PF_2)_2(SiH_3)$ and B_2H_6 were carried out in CCl_3D solution in n.m.r. tubes. Samples were warmed to room temperature to allow reaction to occur, and spectra were then recorded at room temperature or at 223 K, depending on the stability of the products.

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