Preparation and Properties of Difluorophosphino(tetrafluorophosphoranyl)amine

By **David W. H. Rankin*** and **John G. Wright**, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The compound $NH(PF_2)(PF_4)$ has been prepared from $PF_2[NH(SiH_3)]$ by reaction with PF_5. Vibrational, photoelectron, n.m.r., and mass spectroscopic data have been recorded, and interpreted in terms of the probable structure and conformation of the molecule. At low temperatures the phosphorus(v) group has chemically equivalent equatorial fluorine atoms but non-equivalent axial atoms, indicating restricted rotation about the P–N bond as well as restricted pseudo-rotation. At high temperatures, all four fluorine atoms are equivalent.

THE combination of phosphorus(III) and phosphorus(v) atoms in a single compound is well known, and examples have been reported in which the two phosphorus atoms are linked by oxygen,[1] sulphur,[1] or nitrogen.[2] In most of these cases, however, the P^V is four-co-ordinate, and the conjunction of three co-ordinate P^{III} with five-co-ordinate P^V is a much rarer phenomenon.

A number of fairly stable aminofluorophosphoranes are known,[3-5] and we have prepared a variety of secondary amines containing difluorophosphino-groups.[6-8] We therefore considered that the mixed-valence amine $NH(PF_2)(PF_4)$ should be accessible. It is well known that fluorosilane elimination provides a useful route to substituted fluorophosphoranes,[9,10] and so we have studied the reaction of $PF_2[NH(SiH_3)]$ with phosphorus pentafluoride, and have successfully prepared $NH(PF_2)(PF_4)$. While this work was in progress, the preparation of $NMe(PF_2)(PF_4)$ by a similar route was reported.[2]

RESULTS AND DISCUSSION

When equimolar amounts of $PF_2[NH(SiH_3)]$ and PF_5 were allowed to mix in the liquid phase at room temperature a rapid reaction occurred, giving fluorosilane and difluorophosphino(tetrafluorophosphoranyl)amine [equation (1)]. Trifluorophosphine, $PF_2(NPF_3)$, and a white

$$PF_2[NH(SiH_3)] + PF_5 \longrightarrow NH(PF_2)(PF_4) + SiFH_3 \quad (1)$$

solid were also formed, but in very small amounts, and yields of up to 95% of the desired product were obtained. Attempts to prepare the amine by direct reaction of $PF_2(NH_2)$ and PF_5 were unsuccessful, and an involatile white solid was the only significant product. The nature of this solid was not acertained, but reactions of $NH(PF_2)(PF_4)$ with HBr or HCl lead to the slow formation of similar white solids, and it seems probable that they are adducts, since both phosphorus atoms and the nitrogen atom are potential donor or acceptor sites.

Difluorophosphino(tetrafluorophosphoranyl)amine is a colourless, mobile, volatile liquid, stable in the gas and liquid phases at temperatures up to at least 375 K over several hours. At higher temperatures, $PF_2(NPF_3)$ is slowly formed, and a white solid is deposited. The decomposition reaction was accelerated markedly when samples were irradiated with green (488 nm) light during a laser Raman experiment, but samples were stable when a red (647 nm) laser was used. Hydrolysis of the amine took place rapidly, giving $O(PF_2)_2$, PF_3O, and a white solid.

Attempts to prepare other mixed-valence secondary amines have been unsuccessful. Reactions of $PF_2[NH(SiH_3)]$ with PF_3O, PF_3S, $PClF_2S$, and $PF_2I(S)$ have all been studied but in each case complete decomposition of the silylamine was observed, without any evidence for the occurrence of substitution reactions.

N.M.R. Spectra.—The ^{31}P, ^{19}F, and ^{1}H n.m.r. spectra provided unequivocal identification of $NH(PF_2)(PF_4)$. Samples labelled with ^{15}N were used throughout since ^{14}N quadrupolar coupling broadened lines in ^{31}P and ^{1}H spectra so much that many couplings could not be resolved.

At low temperatures, the ^{19}F spectra contained four sets of resonances, all of first order, with relative intensity 2 : 2 : 1 : 1, which could be assigned, on the basis of multiplicities (Table 1) and magnitudes (Table 2) of couplings, to the fluorine atoms F′, F_a, F_b, and F_e (Figure). The observation of three chemically distinct types of fluorine in the PF_4 group implies that not only is pseudo-rotational exchange between axial and equatorial sites slow on the n.m.r. time scale, but also that rotation about the P–N bond is restricted, so that the two axial

TABLE 1

Couplings and multiplicities in n.m.r. spectra of $^{15}NH(P'F'_2)(PF_4)$

Nucleus	Low temperature	High temperature
^{31}P	$3 \times 2 \times 2 \times 2 \times 2 \times 3 \times 2$ $F_e\ F_a\ F_b\ N\ P'\ F'\ H$	$5 \times 2 \times 2 \times 3 \times 2$ $F\ N\ P'\ F'\ H$
$^{31}P'$	$3 \times 2 \times 2 \times 2 \times 2 \times 2$ $F'\ F_b\ N\ P\ F_a\ H$	$3 \times 2 \times 5 \times 2 \times 2$ $F'\ N\ F\ P\ H$
$^{19}F_a$	$2 \times 3 \times 2 \times 2 \times 2$ $P\ F_e\ P'\ N\ H$	$2 \times 2 \times 3 \times ?$ * $P\ P'\ F'$
$^{19}F_b$	$2 \times 2 \times 3 \times 2 \times 3 \times 2$ $P\ P'\ F_e\ H\ F'\ N$	
$^{19}F_e$	$2 \times 2 \times 2$ $P\ F_a\ F_b$	
$^{19}F'$	$2 \times 2 \times 2 \times 2 \times 2$ $P'\ P\ F_b\ N\ H$	$2 \times 2 \times 5 \times 2 \times 2$ $P'\ P\ F\ N\ H$
^{1}H	$2 \times 2 \times 3 \times 2 \times 2 \times 2$ $N\ F_a\ F'\ F_b\ P\ P'$	

* Fully resolved high-temperature spectra were not obtained.

TABLE 2

N.m.r. parameters [a] of $^{15}NH(PF_2)(PF_4)$

Parameter		Parameter	
$\delta(^{1}H)$/p.p.m.	5.40 [b]	$^{2}J(^{19}F_a-^{19}F_b)$/Hz	<0.2
$\delta(^{31}P)$/p.p.m.	−71.3	$^{2}J(^{19}F_a-^{19}F_e)$/Hz	88.2
$\delta(^{31}P')$/p.p.m.	138.9	$^{2}J(^{19}F_b-^{19}F_e)$/Hz	79.7
$\delta(^{19}F_a)$/p.p.m.	−48.3	$^{2}J(^{19}F_a-^{15}N)$/Hz	11.5
$\delta(^{19}F_b)$/p.p.m.	−41.8	$^{2}J(^{19}F_b-^{15}N)$/Hz	3.9
$\delta(^{19}F_e)$/p.p.m.	−73.4	$^{2}J(^{19}F_e-^{15}N)$/Hz	<0.2
$\delta(^{19}F')$/p.p.m.	−61.2	$^{2}J(^{19}F'-^{15}N)$/Hz	3.4
$\delta(^{15}N)$/p.p.m.	60	$^{3}J(^{31}P-^{19}F')$/Hz	16.1
$^{1}J(^{31}P-^{19}F_a)$/Hz	801.7	$^{3}J(^{31}P'-^{19}F_a)$/Hz	±14.7
$^{1}J(^{31}P-^{19}F_b)$Hz	766.5	$^{3}J(^{31}P'-^{19}F_b)$/Hz	∓209.2
$^{1}J(^{31}P-^{19}F_e)$/Hz	965.5	$^{3}J(^{31}P'-^{19}F_e)$/Hz	<0.2
$^{1}J(^{31}P'-^{19}F')$/Hz	1 256.7	$^{3}J(^{19}F_a-^{1}H)$/Hz	1.0
$^{1}J(^{31}P-^{15}N)$/Hz	69.5	$^{3}J(^{19}F_b-^{1}H)$/Hz	31.0
$^{1}J(^{31}P'-^{15}N)$/Hz	84.0	$^{3}J(^{19}F_e-^{1}H)$/Hz	<0.2
$^{1}J(^{15}N-^{1}H)$/Hz	80.7 [b]	$^{3}J(^{19}F'-^{1}H)$/Hz	6.3
$^{2}J(^{31}P-^{31}P')$/Hz	14.7	$^{4}J(^{19}F_a-^{19}F')$/Hz	<0.2
$^{2}J(^{31}P-^{1}H)$/Hz	1.0 [b]	$^{4}J(^{19}F_b-^{19}F')$/Hz	14.0
$^{2}J(^{31}P'-^{1}H)$/Hz	1.0 [b]	$^{4}J(^{19}F_e-^{19}F')$/Hz	<0.2

[a] In CD_2Cl_2–$SiMe_4$ at 223 K, except where indicated otherwise. [b] Measured at 187 K in $CDCl_3$.

fluorine atoms are chemically non-equivalent. Similarly, the ^{31}P spectra run at low temperatures showed two sets of resonances, with chemical shifts as expected for PF_4N and PF_2N species. These resonances were split by the other spinning nuclei in the molecule, with one of them showing coupling to all the seven other groups of nuclei, giving 288 lines in all. The ^{1}H spectrum also showed six couplings to the single proton.

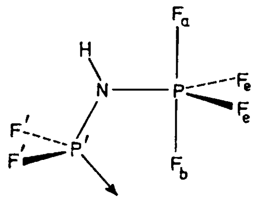

FIGURE Probable structure of $NH(PF_2)(PF_4)$ showing axis of phosphorus lone pair of electrons

A variable-temperature n.m.r. study was initiated, using samples dissolved in a mixture of CD_2Cl_2 and $SiMe_4$. These samples had sharp low-temperature-limiting ^{19}F and ^{31}P spectra at 223 K, but on warming above this temperature line broadening due to exchange processes was observed, particularly in the ^{19}F spectrum. The three groups of phosphoranyl fluorine resonances had coalesced by 293 K, but the spectra had still not reached the high-temperature limit at 353 K, the highest temperature considered safe for sealed tubes containing these solvents. The study was then repeated using $CDCl_3$ as solvent, and it was found necessary to go to lower temperatures than were needed in the earlier experiments, in order to achieve the limiting spectra. The implication of this is that external factors, such as the nature of the solvent, do have some influence on the rate of the intramolecular rearrangements.

The PF_2 group fluorine resonances were sharp at 187 K, poorly resolved at 215 K, and had reached the high-temperature limit by 231 K. The PF_4 group phosphorus resonances were still well resolved at 218 K, but were broad at 298 K, and did not reach their high-temperature form until *ca.* 320 K. The PF_4 group fluorine resonances, with chemical shifts differing by up to 3 kHz, were sharp at 187 K, showing signs of broadening at 215 K, and between 240 and 290 K were a band some 5 kHz wide, barely distinguishable from the baseline. By 299 K a pair of broad resonances in the mean position could be observed, at 329 K further structure was resolved, and at 374 K, the highest temperature considered safe, the resonances were approaching the high-temperature limit, although the smallest couplings could still not be resolved.

The collapse of the three PF_4 fluorine sets of resonances into a single set, but with retention of couplings to other nuclei, indicates that an intramolecular rearrangement is taking place. There is no evidence for the axial fluorines exchanging with each other prior to the onset of axial–equatorial exchange, and it is therefore clear that rotation about the P–N bond cannot commence before pseudorotation. We attribute the resistance to both these processes to an interaction between the hydrogen atom and one of the axial fluorine atoms, which is possible if the molecule adopts the depicted conformation (Figure). Equivalent interactions have been proposed to account for similar resistance to rearrangement in other aminofluorophosphoranes.[11,12]

The observed n.m.r. parameters are listed in Table 2: most of them are fully consistent with those reported for related compounds, in particular $NMe(H)(PF_4)$ [4] and $NMe(PF_2)(PF_4)$.[2] It has been noted [13,14] that $^{1}J(^{31}P-^{15}N)$ is positive for phosphorus(III) compounds, but in phosphorus(V) compounds the coupling is much smaller and may be negative. The two values recorded here are therefore probably of opposite sign, being +84.0 and −69.5 Hz for $J(P'N)$ and $J(PN)$ respectively. The value of $^{2}J(PP')$ (14.7 Hz) is much smaller than those recorded for amines with two phosphorus(III) substituents,[7,15,16] where there is the possibility of interaction between the two phosphorus lone pairs of electrons.

The couplings between the three types of fluorine nucleus of the PF_4 group and nuclei separated from them by two or more bonds are of particular interest. For the equatorial fluorine nuclei each of the four relevant couplings (to ^{15}N, ^{1}H, $^{31}P'$, and $^{19}F'$) is too small to be resolved. Of the two axial fluorine nuclei, the one labelled F_a couples more strongly than F_b to ^{15}N (11.5 and 3.9 Hz respectively), whereas F_b has the stronger coupling to ^{1}H (31.0 and 1.0 Hz), $^{31}P'$ (209.2 and 14.7 Hz), and $^{19}F'$ (14.7 and 0 Hz). We interpret these in terms of the presumed structure of the molecule (Figure), in which one axial fluorine atom lies close to the hydrogen atom, and the PF_2 group adopts a conformation which allows close contact between its two fluorine atoms and the proton, as observed in other aminofluorophosphines.[8,17,18] In this structure, the phosphorus lone pair of electrons is directed towards one of the axial fluorine atoms, and it may be expected that there should be very strong interaction between these two atoms. This might well give rise to the extraordinarily large coupling $^{3}J(^{31}P'-^{19}F_b)$, and to the large $^{4}J(^{19}F_b-^{19}F')$. It is interesting that the fluorine nucleus with the largest three-bond coupling to phosphorus (presumed to be *cis*) also has the largest coupling to the proton, which must therefore be *trans*. However, the variation of ^3J(FCCH) in fluoroethanes has been studied,[19,20] and shows a maximum for a dihedral angle of 180°, with a smaller maximum at 0°, and minima at 90 and 270°. The observed set of values suggest that there is a similar relationship for ^3J(FPNH). We have interpreted couplings in several other molecules in terms of orientations of groups relative to a phosphorus lone pair. For example, in $PF_2[NH(GeH_3)]$,[16] in which the proton is probably *cis* to the lone pair, $^2J(^{31}P-^1H)$ is large (32.7 Hz); in $PF_2[NH(SiH_3)]$ and $PF_2(NH_2)$, which have N–H bonds approximately orthogonal to the phosphorus lone pairs, these couplings are *ca.* 18 Hz.[8,17,21] In the present case, the proton is probably *trans* to the lone pair, and $^2J(^{31}P'-^1H)$ is an order of magnitude smaller than usual.

The parameters involving the PF_4 group nuclei in the high-temperature spectra were close to the means of the values determined at low temperatures (Table 3). In the case of $^3J(^{31}P'-^{19}F)$, however, the weighted mean value is 56.0 Hz, compared with an observed value of 49 Hz. This implies either that one or more of these couplings is highly temperature dependent, or that the values of the couplings to F_a and F_b are of opposite sign. If the latter is assumed, the mean coupling becomes 48.6 Hz, in excellent agreement with the observed value.

TABLE 3

Temperature dependence of n.m.r. parameters [a]

	Low temperature				High temperature
Parameter	F_a	F_b	F_e	Weighted mean	
$\delta(^{19}F)$/p.p.m.	−48.3	−41.8	−73.4	−59.2	−59.4
$^1J(^{31}P-^{19}F)$/Hz	801.7	766.5	965.5	874.8	875
$^2J(^{19}F-^{15}N)$/Hz	11.5	3.9	<0.2	7.7	n.r.
$^3J(^{31}P'-^{19}F)$/Hz	14.7	209.2	<0.2	56.0/48.6 [b]	49
$^3J(^{19}F-^1H)$/Hz	1.0	31.0	<0.2	8.0	n.s.
$^4J(^{19}F-^{19}F')$/Hz	<0.2	14.0	<0.2	3.5	4.9

[a] In $CD_2Cl_2-SiMe_4$ at 220 and 333 K; n.r. = not resolved, n.s. = not studied. [b] Depending on the relative signs of $J(P'F_a)$ and $J(P'F_b)$.

Vibrational Spectra.—Details of i.r. spectra of the gas and solid phases, and Raman spectra of the liquid phase, are given in Table 4. We have not attempted to make detailed assignments since the results for a molecule with nine atoms of comparable mass, and at best one element of symmetry, would be meaningless in the absence of a complete vibrational analysis, and a derived potential-energy distribution. It should be noted, however, that the spectrum includes bands in the regions associated with stretching and deformation vibrations of PF_4X and PF_2X groups. On ^{15}N substitution there are shifts of bands from 1 030 to 1 022, 911 to 903, and 784 to 775 cm^{-1}, which indicates that these modes include substantial contributions from the two P–N stretches.

Of particular importance are the N–H stretch and deformation modes. In the gas phase, only one band is seen in each of the regions associated with these vibrations, indicating that there is probably only one gas-phase conformer of this compound. In this respect it differs from $PF_2[NH(SiH_3)]$ [8] and $PF_2[NH(GeH_3)]$.[16] In the solid phase, the stretching mode is shifted to lower frequency and splits into two, while the deformation is shifted to slightly higher frequency. These changes suggest that hydrogen bonding is of greater significance in the solid than in the gas phase, presumably involving intermolecular contacts. We hope to be able to study these interactions by determining the structure of this compound in the crystalline phase.

TABLE 4

Vibrational spectra (cm^{-1}) of $NH(PF_2)(PF_4)$

I.r. (gas)	I.r. (solid)	Raman (liquid)	Assignment
3 413m	3 353m	3 410s, br	ν(NH)
	3 303m	3 340mw	
1 328s	1 342s		δ(NH)
1 030vs	1 051s	1 005w	$\nu(PF_{e2})$ ν(PN)
990vs	1 002s	993vw	
911s	909s	921w,br	
886vs	854s	885m,br	$\nu(P'F'_2)$
833vs		836s,br	
818 (sh)	819vs	810m,br	
784s	780vs	789s	ν(P'N)
	740 (sh)	755m	
	686m		$\nu(PF_{a2})$ $\delta(PF_{e2}N)$
614m	622vw	635m	
565ms	558m	572w	
541m	539m		
515m	516m	518w	
	482w	494w	deformations and torsions
	469w	446w	
445m	442w	440w	
	427w	433w	
	418w	414w	
393m	397m	402m	
358w		359w	
350w	350w		
324vw	323w	333w,br	
295vw	301w		
274vw		276s	
		226m	
188w			
162w		155mw,br	

s = Strong, m = medium, w = weak, v = very, br = broad, and sh = shoulder.

Mass Spectra.—In Table 5 are listed the ions observed in mass spectra of $NH(PF_2)(PF_4)$, run with ionising voltages of 70 and 16 eV.* These data indicate that the parent ion can dissociate in several ways. At low ionising voltage the $[PF_3(NH)]^+$ ion gives the strongest peak in the spectrum, and at 70 eV a metastable ion peak is observed corresponding to the formation of this ion by elimination of PF_3 from the parent. This ready elimination of PF_3 is easily rationalised in terms of the proposed structure, in which the phosphorus atom of the PF_2 group lies close to one fluorine atom of the PF_4 group. The $[PF_3(NH)]^+$ ion subsequently eliminates NH.

The parent ion can also lose one or two fluorine atoms and a hydrogen atom, to give the ions $[NH(PF_2)(PF_3)]^+$, $[NH(PF_2)_2]^+$, and $[N(PF_2)(PF_3)]^+$, and peaks observed at *m/e* 134.3, 151.0, and 135.1 are assigned to the processes

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

TABLE 5

Mass spectra of $NH(PF_2)(PF_4)$

m/e	Relative abundance at 70 eV	Relative abundance at 16 eV	Assignment
191	2	3	$[NH(PF_2)(PF_4)]^+$
172	13		$[NH(PF_2)(PF_3)]^+$
171	54	72	$[N(PF_2)(PF_3)]^+$
153		17	$[NH(PF_2)_2]^+$
152	43		$[N(PF_2)_2]^+$
107	79		$[PF_4]^+$
104	54	14	?$[PF_3(NH_2)]^+$, $[PF_3O]^+$
103	85	100	$[PF_3(NH)]^+$
88	18	11	$[PF_3]^+$
85	48		?$[PF_2(NH_2)]^+$, $[PF_2O]^+$
69	100		$[PF_2]^+$
66.5	5		$[N(PF)(PF_2)]^{2+}$
65	10	11	$[PF(NH)]^+$
46	14		$[P(NH)]^+$
44	1		$[PF_3]^{2+}$

Metastable ions

55.5w	$[NH(PF_2)(PF_4)]^+ \longrightarrow PF_3 + [PF_3(NH)]^+$
75.2w	$[PF_3(NH)]^+ \longrightarrow NH + [PF_3]^+$
115.6w	$[NH(PF_2)_2]^+ \longrightarrow HF + [N(PF)(PF_2)]^+$
134.3w	$[NH(PF_2)(PF_3)]^+ \longrightarrow HF + [N(PF_2)_2]^+$
135.1m	$[N(PF_2)(PF_3)]^+ \longrightarrow F + [N(PF_2)_2]^+$
151.0w	$[NH(PF_2)_2]^+ \longrightarrow H + [N(PF_2)_2]^+$

m = Medium and w = weak.

in which these ions lose HF, H, and F respectively, in each case giving $[N(PF_2)_2]^+$. Fairly strong peaks due to $[PF_4]^+$ suggest that cleavage of a P–N bond of the parent ion is also significant. Similar easy loss of one ligand from aminofluorophosphoranes has been noted several times.[3,4,12]

Photoelectron Spectrum.—He(I) u.v. photoelectron spectra were recorded for $NH(PF_2)(PF_4)$ and for $PF_2(NPF_3)$, and details are given in Table 6, with assignments made by comparison with observed ionisation potentials for other compounds.[7,12,22] For each of the compounds studied, the phosphorus lone-pair ionisation potential is greater than in other related aminofluorophosphines, and the nitrogen lone-pair ionisation potential is similarly large, particularly for $NH(PF_2)(PF_4)$. This may simply reflect the electron-withdrawing properties of the groups with three or four fluorine atoms. In the case of $PF_2(NPF_3)$, the nitrogen lone-pair level will be mixed to some extent, depending on the P–N–P angle, with the P=N π-bonding level. The latter has not been assigned, but may give rise to part of the band at 12.6 eV.

TABLE 6

He(I) u.v. photoelectron spectra

Ionisation potential (eV) $NH(PF_2)(PF_4)$	Ionisation potential (eV) $PF_2(NPF_3)$	Assignment
11.6	11.2	N $2p$
12.7	12.6	P $3p$, ? P–N π
15.6	16.3	P–N σ, N–H σ
16.2 17.4	17.6	F $2p$ π
17.8	18.0 18.6	P–F σ
18.6		

EXPERIMENTAL

All volatile compounds were handled using a Pyrex glass vacuum line, fitted with Sovirel greaseless taps. Difluoro(silylamino)phosphine was prepared from aminodifluorophosphine and bromosilane,[8] and phosphorus pentafluoride was obtained by heating a diazonium hexafluorophosphate *in vacuo*.

N.m.r. spectra were recorded on Varian Associates XL100 and HA100 spectrometers, the latter modified to accept a second frequency, derived from a Schlumberger FS30 frequency synthesizer. Vibrational spectra were obtained using Perkin-Elmer 225 and 557 and Beckmann-RIIC FS270 i.r. spectrometers, covering the ranges 200—4 000 and 50—400 cm^{-1} respectively, and a Cary 82 Raman spectrometer, with 647.1-nm Kr laser excitation. For mass spectra, an A.E.I. MS902 spectrometer was used, and for photoelectron spectra, a Perkin-Elmer PS16 spectrometer, with He(I) (21.22 eV) excitation.

Preparation of Difluorophosphino(tetrafluorophosphoranyl)amine.—A glass ampoule (40 cm^3) fitted with a greaseless tap was dried by allowing gaseous bromosilane to stand in it for a few minutes. Then $PF_2[NH(SiH_3)]$ (1.00 mmol) and PF_5 (1.10 mmol) were condensed into the ampoule, and allowed to warm to room temperature for 15 s. The products were separated by fractional condensation *in vacuo*. The major products were fluorosilane (1.00 mmol) and *difluorophosphino(tetrafluorophosphoranyl)amine* (0.93 mmol, 93%, almost involatile at 195 K), with small amounts of $PF_2(NPF_3)$, PF_3, and a white solid.

Reaction of $PF_2(NH_2)$ *with* PF_5.—Phosphorus pentafluoride (0.2 mmol) and $PF_2(NH_2)$ (0.3 mmol) were warmed together to room temperature in a glass ampoule. A white solid was formed, and the only volatile material recovered was unchanged $PF_2(NH_2)$ (0.1 mmol).

Reactions between $NH(PF_2)(PF_4)$ *and* HX (X = Cl *or* Br).—In a typical experiment, $NH(PF_2)(PF_4)$ (0.3 mmol) and HCl (0.9 mmol) were allowed to mix in an n.m.r. tube, with C_6D_6 as solvent. After *ca.* 10 min at room temperature, white solids were seen to be slowly forming. N.m.r. spectra showed unchanged amine to be present, with only a trace amount of $PClF_2$.

Attempted Preparations of $NH(PF_2)(PF_2O)$ *and* $NH(PF_2)(PF_2S)$.—Equimolar amounts of $PF_2[NH(SiH_3)]$ and PF_3O, PF_3S, $PClF_2S$, or $PF_2I(S)$ were condensed into an n.m.r. tube, with a mixture of $CDCl_3$ and $SiMe_4$ as solvent. The reaction mixture was monitored by ^{19}F or ^{31}P n.m.r. spectroscopy as it was warmed to room temperature or above. In no case was any reaction observed, other than the slow decomposition of the starting amine by elimination of $SiFH_3$.

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