Preparation and Properties of Diaminodifluorophosphorane

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Diaminodifluorophosphorane, $PF_2H(NH_2)_2$, has been prepared by the reaction of chlorodifluorophosphine and ammonia, and has been characterised spectroscopically. Its vibrational spectra can be interpreted in terms of C_{2v} symmetry, with a trigonal-bipyramidal structure with axial fluorine atoms. N.m.r. spectra are consistent with this structure, and show that the amino-groups rotate rapidly at room temperature, but are slowed on cooling. Signs and magnitudes of coupling constants for $PF_2H(^{15}NH_2)_2$ are reported.

IN the course of work on the preparation of $BF_2[NH(PF_2)]$,[1] it became necessary for us to obtain samples of aminodifluorophosphine, $PF_2(NH_2)$, which were completely free of the secondary amine, $NH(PF_2)_2$. In order to obtain these, the usual preparative reaction, mixing chloro- or bromo-difluorophosphine and ammonia in the gas phase,[2,3] was carried out with an excess of ammonia present. A novel compound, subsequently identified as diaminodifluorophosphorane, was detected amongst the products. We have now shown that this compound, formed by the addition of ammonia to $PF_2(NH_2)$, can be prepared in fairly high yield. In considering its structure, a number of interesting questions come to mind concerning the coplanarity of the three bonds to a nitrogen, the preferred orientation of the amino-groups, and the extent to which rotation about P–N bonds is restricted. We report here the results of our investigations into the properties of this compound, and our answers to the questions, insofar as we have been able to determine them.

RESULTS AND DISCUSSION

The preparation of diaminodifluorophosphorane involves the formal oxidative addition of ammonia to a phosphorus(III) species [equation (1)]. Similar oxidative

$$PF_2(NH_2) + NH_3 \longrightarrow PF_2H(NH_2)_2 \quad (1)$$

additions, involving alkylamines or alcohols, have been reported,[4,5] in each case giving a phosphorus(V) hydride as the product. In the present study, it was found that isolation of $PF_2(NH_2)$ as an intermediate is not essential, and that the desired product could be obtained in a single step from chlorodifluorophosphine [equation (2)]. The

$$PClF_2 + 3NH_3 \longrightarrow PF_2H(NH_2)_2 + [NH_4]Cl \quad (2)$$

compound obtained in this way is a colourless liquid, melting at 270 K, and with a vapour pressure of 6 Torr at 292 K.† It was characterised spectroscopically.

The reaction leading to the formation of $PF_2H(NH_2)_2$ could be reversed in two ways. Firstly, reaction with $PClF_2$ and trimethylamine gave $PF_2(NH_2)$ [equation (3)].

$$PF_2H(NH_2)_2 + PClF_2 + NMe_3 \longrightarrow 2PF_2(NH_2) + [NMe_3H]Cl \quad (3)$$

Hydrogen chloride also removed ammonia. If insufficient hydrogen chloride was used to complete the reaction, $PClF_2$ and not $PF_2(NH_2)$ was found in the reaction products, indicating that the second stage [equation (5)] was more rapid than the first [equation (4)].

$$PF_2H(NH_2)_2 + HCl \longrightarrow PF_2(NH_2) + [NH_4]Cl \quad (4)$$

$$PF_2(NH_2) + 2HCl \longrightarrow PClF_2 + [NH_4]Cl \quad (5)$$

N.M.R. Spectra.—Hydrogen-1, ^{19}F, and ^{31}P n.m.r. spectra observed directly, and various double-resonance experiments, gave the parameters for $PF_2H(^{15}NH_2)_2$ given in Table 1. The ^{31}P spectrum was a doublet of triplets of triplets of quintets, due to coupling with the single hydrogen atom, two fluorines, two nitrogens, and four equivalent hydrogens. At 273 K, the ^{19}F spectrum consisted of a doublet (^{31}P) of doublets (^{1}H) of quintets (^{1}H) of triplets (^{15}N), the equivalence of the amino-protons showing that rotation about the P–N bonds was rapid. This was confirmed by the proton spectrum, in which the resonance due to the amino-protons was a doublet (due to the ^{15}N to which they were bonded) of triplets (^{19}F) of doublets (^{31}P). The couplings $^{3}J(^{1}HPN^{1}H)$, $^{3}J(^{15}NPN^{1}H)$, and $^{4}J(^{1}HNPN^{1}H)$ were not observed and so the spectrum was of the first order. The resonance due to the hydrogen bound to phosphorus was observed as a doublet (^{31}P) of triplets (^{19}F) of triplets (^{15}N). The proton spectrum at 233 K did show changes

TABLE 1

N.m.r. parameters for $PF_2H(^{15}NH'_2)_2$[a]

$\tau(^{1}H)$	2.77 p.p.m.
$\tau(^{1}H')$	7.11 p.p.m.
$\delta(^{15}N)$ [b]	28.6 p.p.m.
$\delta(^{19}F)$ [c]	−51.2 p.p.m.
$\delta(^{31}P)$ [d]	−63.4 p.p.m.
$^{1}J(^{31}P^{1}H)$	836.0 Hz
$^{1}J(^{31}P^{19}F)$	−619.1 Hz
$^{1}J(^{31}P^{15}N)$	−45.0 Hz
$^{1}J(^{15}N^{1}H')$	−85.0 Hz
$^{2}J(^{19}F^{1}H)$	109.1 Hz
$^{2}J(^{19}F^{15}N)$	−14.0 Hz
$^{2}J(^{31}P^{1}H')$	11.8 Hz
$^{2}J(^{15}N^{1}H)$	−8.3 Hz
$^{3}J(^{19}F^{1}H')$	19.7 Hz [e]
$\lvert ^{3}J(^{1}H^{1}H')\rvert$	<0.5 Hz
$\lvert ^{3}J(^{15}N^{1}H')\rvert$	<0.5 Hz
$\lvert ^{4}J(^{1}H'^{1}H')\rvert$	<0.5 Hz

[a] Solution of 0.4 mmol in 0.5 cm³ of C_6D_6–$CHCl_3$(2 : 3) at 273 K. [b] To high frequency of external $[NMe_4]I$. [c] To high frequency of external CCl_3F. [d] To high frequency of external 85% H_3PO_4. [e] Average value, fast rotation (see text).

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† 1 Torr = (101 325/760) Pa, 1 eV ≈ 1.60 × 10^{-19} J.

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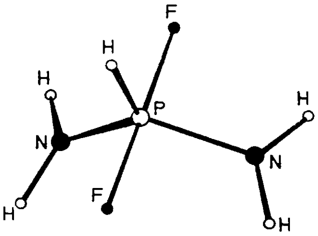
that indicated that P–N bond rotation was slowed. In particular, the outer lines of triplets caused by coupling with the fluorine atoms remained sharp, but the inner line broadened and showed signs of splitting. A similar effect was observed in the ^{19}F spectrum. Thus the two hydrogens on one nitrogen atom were no longer magnetically equivalent with respect to the fluorine atoms, which, from their various parameters, were considered to be in axial positions of the phosphorus trigonal bipyramid. The preferred orientation of the amino-group is therefore likely to be one in which the hydrogens lie relatively close to the fluorine atoms, with the possibility of weak H · · · F interactions stabilising this conformation (I). The barrier to rotation seems to be somewhat lower than in $PF_3(NH_2)_2$,[6] which has a ^{19}F n.m.r. spectrum at 233 K showing sharp lines, indicating that the rotation process is slow relative to the n.m.r. time scale at that temperature.



(I)

The signs of coupling constants given in Table 1 were determined on the assumption that $^1K(^{31}P^{19}F)$ is negative.[7,8] The coupling constants are more remarkable for their similarity to corresponding values for $PF_2(NH_2)$ [9] than for their differences. A small value for $^1J(^{31}P^{19}F)$ reflects the relatively small *s*-orbital contribution to axial P–F bonds, and in the same way a negative value for $^1J(^{31}P^{15}N)$ [*i.e.* positive ^1K(PN)] is found in the phosphorus(V) compound, whereas it is positive in phosphorus(III) compounds.[9,10] In comparing our value of −45 Hz for this coupling with reported values of −81.5 and −53.2 Hz for phosphorus(V)–nitrogen coupling constants in $PF_3(^{15}NH_2)_2$ and $PF_2(N{=}PF_3)$ respectively,[11] it is worth noting that the size of the constant depends not only on the nature of the co-ordination of phosphorus and nitrogen but also on the nature of the ligands. Thus replacing one fluorine of $PF_3(NH_2)_2$ by a hydrogen has a greater effect on the P–N coupling constant than has reducing the co-ordination numbers of P and N to 4 and 2.

Mass Spectra.—Details of mass spectra run with ionising voltages of 70 and 13 eV are given in Table 2. The most remarkable feature of these is the low abundance of the parent ion, particularly relative to ions formed by loss of one ligand (H, F, or NH_2) from the parent. This behaviour has been noted for other aminofluorophosphoranes [12,13] and fluorophosphoranes,[14] and it has been suggested that the stability of phosphonium ions is responsible. However, in the present case, it is not possible to say whether the ions involved are phosphonium or ammonium ions, formed by transfer of hydrogen from phosphorus to nitrogen. Certainly such a transfer eventually takes place, as prominent peaks at *m/e* 52.5 and 55.4 can be assigned to the processes involving loss of NH_3, as shown in Table 2. Other strong peaks at *m/e* 85 and 82 (the latter being the strongest in the spectrum at 13 eV) indicate that loss of NH_3 and HF from the parent ion, whether in a single reaction, or by separate loss of two ligands, are steps in other important breakdown routes.

TABLE 2

Mass spectra of $PF_2H(NH_2)_2$

	Relative abundance		
m/e	at 70 eV	at 13 eV	Assignment
102	1	3	$[PF_2H(NH_2)_2]^+$
101	13		$[PF_2(NH_2)_2]^+$, $[PF_2H(NH_2)(NH)]^+$
86	100	37	$[PF_2H(NH_2)]^+$
85	80	22	$[PF_2(NH_2)]^+$, $[PF_2H(NH)]^+$
84	5		$[PF_2(NH)]^+$, $[PF_2HN]^+$
83	25	1	$[PF_2N]^+$, $[PFH(NH_2)_2]^+$
82	16	100	$[PF(NH_2)_2]^+$, $[PFH(NH_2)(NH)]^+$
81	4		$[PF(NH_2)(NH)]^+$, $[PFH(NH)_2]^+$
78	1	6	$[PFN_2]^+$
69	42		$[PF_2]^+$
67	1		$[PFH(NH_2)]^+$
66	44	3	$[PF(NH_2)]^+$, $[PFH(NH)]^+$
65	4		$[PF(NH)]^+$, $[PFHN]^+$
62	2	3	$[P(NH_2)(NH)]^+$, $[PH(NH)_2]^+$
50	3		$[PF]^+$
47	1		$[P(NH_2)]^+$, $[PH(NH)]^+$
46	21		$[P(NH)]^+$, $[PHN]^+$
45	2		$[PN]^+$
33	1		$[NF]^+$
31	1		P^+
20	3		$[HF]^+$
16	3		$[NH_2]^+$

Metastable ions

49.7 $[PF_2(NH_2)]^+ \longrightarrow HF + [PF(NH)]^+$
52.5 $[PFH(NH_2)_2]^+ \longrightarrow NH_3 + [PF(NH_2)]^+$
55.4 $[PF_2H(NH_2)]^+ \longrightarrow NH_3 + [PF_2]^+$

Vibrational Spectra.—In Table 3 are listed bands observed in the i.r. spectra of solid and gas phases, and the Raman spectra of liquid and solid phases, of $PF_2H(NH_2)_2$ and $PF_2D(NH_2)_2$. In addition, samples were prepared using NH_3 and $PF_2(ND_2)$, and ND_3 and $PF_2(NH_2)$. Although some scrambling occurred, the spectra of these products provided some extra information which was of help in assignment of the other spectra.

The observation of bands of A, B, and C shape in the spectra of gas-phase samples was consistent with the

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evidence from n.m.r. spectra that the molecule preferentially adopts a structure with C_{2v} symmetry. Assignments have therefore been based on this assumption. The normal modes of vibration are then distributed according to $\Gamma_{\text{vib.}} = 8a_1 + 4a_2 + 6b_1 + 6b_2$.

Bands occurring at *ca.* 3 500 cm^{-1}, shifting to *ca.* 2 500 cm^{-1} on deuteriation, are assigned to NH stretching modes. In each spectrum there were two groups of bands, separated by *ca.* 100 cm^{-1}. Polarisation measurements indicate that the lower group includes the a_1 NH stretch; the b_2 mode, which also involves symmetric stretching of NH_2 groups, is likely to be at a similar frequency. If this is so, then the band in the i.r. spectrum in the gas phase should be made up of components with B and C band shapes. On this basis, the a_1 band is estimated to occur at 3 476 cm^{-1}, with the b_2 band centred at 3 468 cm^{-1}. Similarly, the higher-frequency region will contain the a_2 and b_1 modes. In Raman spectra of the solid phases of $PF_2H(NH_2)_2$ and $PF_2D(ND_2)_2$, two bands were observed in this region. The bands also observed in the i.r. spectra of solids are assigned to the b_1 modes. Bands at *ca.* 1 570 and 1 240 cm^{-1}, shifting to 1 410 and 1 090 cm^{-1} on partial deuteriation, and to 1 200 and 935 cm^{-1} on complete deuteriation, are assigned to deformations (scissors and rocking) of the NH_2 groups, by analogy with other amino-compounds such as hydrazine.[15] In each case, there will be a_1 and b_2 components, but no splitting was observed.

TABLE 3

Vibrational spectra (cm^{-1})

$PF_2H(NH_2)_2$				$PF_2D(ND_2)_2$				
I.r.(s)	Raman (s)	Raman (l)	I.r.(g)	I.r.(s)	Raman (s)	Raman (l)	I.r.(g)	Assignment
3 518 3 508 } s	3 531 w	3 546 w, dp	3 587 m, A	2 630 m	2 642 w	2 645 w, dp	2 678 m	$\nu(NH_2)$ or $\nu(ND_2)$ [a]
	3 516 w		3 476 3 471 3 464 } m, C, B		2 628 w			
3 417 s	3 416 m	3 440 m, p		2 500 m	2 502 w	2 515 m, p	2 451 m	
2 502 m	2 518 m	2 522 m, p	2 504 m, ?C	1 820 m	1 822 w	1 815 m, p	1 825 w, ?C	See text
2 428 m	2 448 m	2 450 m, p	2 437 m, C	1 780 m	1 785 w	1 775 m, p	1 786 m, C	$\nu(PH)$ or $\nu(PD)$
1 569 s	1 586 1 571 } w, br	1 580 w, dp	1 564 1 557 } s	1 210 m	1 194 w	1 185 w, p	1 204 s	$\delta(NH_2)$ or $\delta(ND_2)$ [b]
1 241 w	1 234 w	1 249 m, dp	1 240 w					$\rho(NH_2)$ [b]
1 029 s			1 017 1 010 } s, B	950 s	900 w	905 w	935 s	$\rho(ND_2)$, $\nu_{asym}(PN_2)$
	935 m	930 m, dp			840 m		854 s	$\omega(NH_2)$
882 m	884 vvs	889 vs, p	879 w, C	840 s	821 s	825 s, p	829 vw	$\nu_{sym}(PN_2)$
							816 vw	
			844 836 } vw					$\delta(PH)$
			782 m, A					$\omega(NH_2)$
					697 m	695 m, dp		$\omega(ND_2)$
676 s, br			730 s, A	660 vvs			716 s, A	$\nu_{asym}(PF_2)$
612 vw	616 vw, br		658 m, A					$\delta(PH)$
	591 vw, br			610 w				
548 vw	561 w, br	561 m, p	582 w, C	545 m	541 m	555 m, p	580 w, C	$\nu_{sym}(PF_2)$
503 w	506 m	516 m, dp	519 m, ?A	495 s	489 m	500 m, dp	505 m	$\delta(PF_2N_2)$
	461 m	454 m, dp						$\tau(NH_2)$
			437 w					
	446 w		420 m, br		445 w			$\delta(PF_2N_2)$
397 w	407 m		383 m, C		401 w			$\delta(PF_2N_2)$
350 vw			359 m, ?A					$\tau(NH_2)$
			308 ms, C		298 w			$\delta(PF_2N_2)$
	240 m	248 m, dp			221 m	230 m, dp		$\tau(PF_2N_2)$
	120 w							

p = Polarised and dp = depolarised; A, B, and C refer to band shapes.

[a] Stretches of NHD groups were observed at 3 490 and 2 580 cm^{-1} (Raman, liquid) and 3 531 and 2 608 cm^{-1} (i.r., gas). [b] Deformations and rocking vibrations of NHD groups were observed at 1 425 and 1 090 cm^{-1} (Raman, solid), 1 090 cm^{-1} (Raman, liquid), and 1 406 and 1 095 cm^{-1} (i.r., gas).

The lower-frequency region presents rather more problems, and assignments are necessarily tentative. The gas-phase i.r. spectrum of $PF_2H(NH_2)_2$ had four bands with a C band shape, two of which were also seen as polarised lines in the liquid-phase Raman spectrum. Equivalent lines were seen in the Raman spectra of $PF_2D(ND_2)_2$. Those at 879 and 582 cm^{-1} lie in the ranges expected for symmetrical P–N [16] and P–F [17] stretches respectively, leaving those at 383 and 308 cm^{-1} as the two a_1 skeletal deformation modes. Of the other skeletal modes, the asymmetric P–N stretch is probably at 1 014 cm^{-1}, where a B band-shape absorption was observed. This shifted on deuteriation, at least to 935 cm^{-1}, but mixing with the b_2 rock of the ND_2 groups complicated the spectra of $PF_2D(ND_2)_2$ in this region. An A-shape band at 730 cm^{-1}, observed in all i.r. spectra and in no Raman spectra, is likely to be the asymmetric P–F stretch; being an asymmetric stretch of an almost linear PF_2 group, its absence from the Raman spectra is

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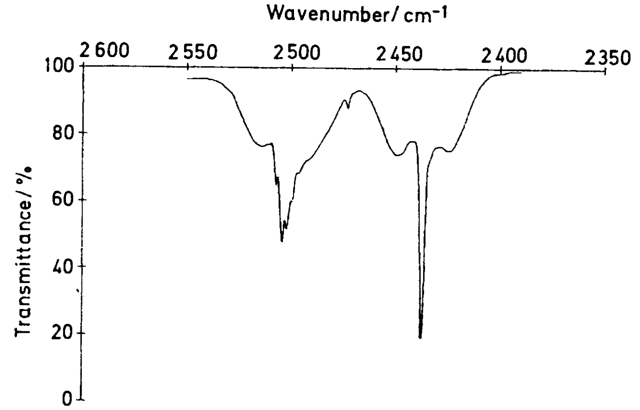
not surprising. The remaining skeletal modes are a_2 and b_1 deformations. Bands observed only in Raman spectra, at 248 cm^{-1} (liquid phase), are assigned to the a_2 mode, while those at 519 cm^{-1} (i.r. gas phase, A band shape) represent the b_1 vibration.

This leaves only the NH_2 wagging and torsion vibrations, and P–H vibrations. On the basis of its appearance only in Raman spectra, we propose that the a_2 wagging mode is at *ca.* 930 cm^{-1} in $PF_2H(NH_2)_2$ and 695 cm^{-1} in the deuteriated compound (both liquid-phase frequencies), while the a_2 torsion is at 454 cm^{-1}. The latter vibration was not observed in spectra of the deuteriated species. The b_1 wag and torsion of the NH_2 group occurred at rather lower frequencies, A-shape bands in the i.r. spectrum being at 782 and 359 cm^{-1}. The P–H deformations are then assigned to the remaining bands, at 658 cm^{-1} (A shape, b_1 mode) and 840 cm^{-1} (b_2 mode).

The final problem involves the P–H stretching vibration, expected between 2 300 and 2 460 cm^{-1} in five-co-ordinate phosphorus compounds. In the i.r. spectra (solid and gas phases) of $PF_2H(NH_2)_2$ and $PF_2D(ND_2)_2$ there were two bands in the revelant regions, and two bands were also observed in the Raman spectra. Both were polarised in the liquid phase. Both gas-phase i.r. absorptions had an approximate C band shape, but the lower-frequency band was more intense and had a shape more like the other C bands in the spectrum (see Figure). We therefore assign the lower frequency to the P–H stretch, leaving the upper one as either a P–H stretch of a second conformer or a combination band with its intensity enhanced by Fermi resonance. There is no other evidence for the existence of two conformers, and it is unlikely that merely changing the orientation of NH_2 groups would result in a 70 cm^{-1} shift in P–H stretching frequency. One is left with Fermi resonance as an explanation, with a similar effect occurring fortuitously in the spectra of both deuteriated and undeuteriated species. However, no binary combinations of a_1 symmetry fall into the correct regions, the nearest being $\delta(NH_2) + \nu_{sym}(PN_2)$ (at 1 560 + 879 = 2 439 cm^{-1}) and $\delta(ND_2) + \nu_{sym}(PF_2)$ (at 1 204 + 580 = 1 784 cm^{-1}). Moreover, similar doubling of the P–H stretches has been observed for HPF_4 and DPF_4,[14,18] and for $PF_2H(NRH)_2$ (R = Me, Et, and Bu^n).[5] One is therefore forced to the conclusion that the Fermi resonance is enhancing the intensity of a band of third or higher order, being a combination of vibrational modes belonging solely to the PF_2HX_2 skeleton.



P–H Stretching region of the i.r. spectrum of gaseous $PF_2H(NH_2)_2$

Photoelectron Spectrum.—The most important feature of the He(I) photoelectron spectrum of $PF_2H(NH_2)_2$ (Table 4) is the pair of bands of roughly equal intensity at 10.7 and 11.4 eV. These can only be due to ionisation from the nitrogen lone-pair levels, which would be of a_1 and b_2 symmetry in the C_{2v} model we have proposed. The magnitude of their separation, 0.7 eV, indicates that the lone pairs cannot be considered as being localised, each on a single nitrogen atom. Thus if a second conformer, differing in the orientation of its NH_2 groups, were present it would be most unlikely that its lone-pair levels would have exactly the same energy as the first conformer's. We therefore take the presence of only two bands, and those of equal intensity, as adding weight to our argument that $PF_2H(NH_2)_2$ has but one gas-phase conformer of significant abundance.

TABLE 4

He(I) photoelectron spectrum of $PF_2H(NH_2)_2$

Ionisation potential/eV	Assignment
10.7 11.4	N 2*p*
12.9	P–H σ
13.9	P–N σ
14.5	P–N σ, N–H σ
16.5	F 2*p*
17–18	P–F σ

The average nitrogen lone-pair ionisation potential is similar to that found for $PF_2(NH_2)$,[19] while the fluorine lone-pair and P–F bonding levels agree with those in PF_5.[20] The P–H bonding level at 12.9 eV lies close to the upper level of PH_3.[21]

EXPERIMENTAL

Manipulations of volatile compounds were carried out in a Pyrex vacuum line, fitted with Sovirel greaseless taps. Chlorodifluorophosphine was prepared by a standard method.[22] [$^2H_3$]Ammonia was prepared by repeated dissolution of [ND_4]Cl in [$^2H_2$] water, followed by addition of CaO; $^{15}NH_3$ (95% enrichment) was obtained commercially.

^{1}H N.m.r. and double-resonance experiments were made on a Varian Associates HA100 spectrometer, modified [23] to accept a second radiofrequency derived from a Schlumberger FS30 frequency synthesiser. Fluorine-19 and ^{31}P

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spectra were obtained using a Varian Associates XL100 spectrometer, with deuterium lock and Gyrocode decoupler. For mass spectra, an A.E.I. MS902 spectrometer, with ionising voltages of 70 and 13 eV, was used, while for vibrational spectra use was made of a Cary 83 Raman spectrometer, with 488-nm argon-ion laser excitation and a Perkin-Elmer 225 grating i.r. spectrometer. Using cells equipped with caesium iodide windows, the range from 200 to 4 000 cm^{-1} was studied. Spectra were also obtained for the range 50—400 cm^{-1}, using a Beckmann-RIIC FS720 interferometer and a gas cell fitted with Polythene windows, but no additional absorptions were observed. U.v. photoelectron spectra were obtained using a Perkin-Elmer PS16 spectrometer, with He(I) (21.22 eV) excitation.

Preparation of Diaminodifluorophosphorane.—From $PF_2(NH_2)$ *and* NH_3. Aminodifluorophosphine (2.0 mmol) and NH_3 (2.0 mmol) were condensed into an ampoule (100 cm^3) fitted with a greaseless tap, and allowed to warm to room temperature. A white solid was formed. After 600 s the volatile products were removed and separated by fractional condensation *in vacuo*. Diaminodifluorophosphorane (0.49 mmol, 25%), *M* 101.4 (calc. for $H_5F_2N_2P$, 102.0), *M* (mass spectrum) 102.015 74 (calc. for $^1H_5{}^{19}F_2{}^{14}N_2{}^{31}P$, 102.015 84) was retained in a trap held at 227 K.

From $PClF_2$ *and* NH_3. Ammonia (8.4 mmol) was allowed to expand at room temperature from a bulb (100 cm^3) into another bulb (1 l) containing $PClF_2$ (2.8 mmol). A white solid was formed immediately. After 180 s the volatile products were condensed out, this process taking up to an hour. Separation of products yielded $PF_2H(NH_2)_2$ (1.17 mmol, 42%), retained at 227 K; $PF_2(NH_2)$ (0.1 mmol) was retained at 177 K, and PF_3 and unchanged ammonia (0.3 mmol) were stopped by a trap held at 77 K.

Reactions of $PF_2H(NH_2)_2$.—*With* $PClF_2$. The compound $PF_2H(NH_2)_2$ (0.4 mmol) was allowed to react in the gas phase with $PClF_2$ (2.8 mmol) and NMe_3 (1.4 mmol) for 300 s. The products were $PF_2(NH_2)$ (0.8 mmol), unchanged $PClF_2$, and a white solid.

With HCl. The compound $PF_2H(NH_2)_2$ (0.2 mmol) and HCl (0.2 mmol) were condensed together and warmed to room temperature. The products were $PClF_2$ (*ca.* 0.05 mmol), unchanged $PF_2H(NH_2)_2$ (0.10 mmol), and a white solid. No $PF_2(NH_2)$ was detected.

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