Preparation and Properties of Difluoro(difluorophosphinoamino)borane

By **David E. J. Arnold, E. A. V. Ebsworth,** and **David W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Aminodifluorophosphine and boron trifluoride react in the gas or liquid phase to give an adduct, which decomposes into difluoro(difluorophosphinoamino)borane, $BF_2[NH(PF_2)]$, which has been characterised by mass, photoelectron, n.m.r., and vibrational spectroscopy. With excess of $PF_2(NH_2)$, the adduct reacts further to give bis(difluorophosphino)amine, $NH(PF_2)_2$, and the ammonia–trifluoroborane adduct.

DURING the course of our work on secondary and tertiary difluorophosphine amines,[1] the use of boron trifluoride as a reagent for the removal of trimethylamine was investigated. It was found that the boron compound also reacted with aminodifluorophosphine to form an involatile white solid. Subsequent work has shown that this reaction proceeds in two stages, and, if care is taken, a new volatile compound can be isolated after the first stage. In this paper we describe the preparation, characterisation, and properties of this compound, difluoro(difluorophosphinoamino)borane, $BF_2[NH(PF_2)]$.

RESULTS AND DISCUSSION

Difluoro(difluorophosphinoamino)borane has been prepared by the gas- or liquid-phase reaction of $PF_2(NH_2)$ with BF_3, but the yield and purity of the product were found to depend on the experimental conditions and the ratio of reagents used. In particular, use of an excess of $PF_2(NH_2)$ led to the formation of the secondary amine, $NH(PF_2)_2$. The reaction can be described as adduct formation, followed by loss of hydrogen fluoride. The formation of the adduct as an intermediate was indicated

$$PF_2(NH_2) + BF_3 \longrightarrow PF_2(NH_2){\cdot}BF_3 \longrightarrow BF_2[NH(PF_2)] + HF \quad (1)$$

by the observation that on warming a mixture of the reagents from 77 to 209 K no volatile material was formed, although both starting materials and $BF_2[NH(PF_2)]$ are volatile at this temperature.

Although hydrogen fluoride appears in equation (1), its presence was not observed directly: neither was silicon tetrafluoride, the product of its action on glass. However, phosphorus trifluoride was a by-product in each preparation, and its formation can be rationalised in terms of reactions (2)—(4). The maximum yield of

$$PF_2(NH_2) + HF \longrightarrow PF_3 + NH_3 \quad (2)$$

$$NH_3 + HF \longrightarrow [NH_4]F \quad (3)$$

$$NH_3 + BF_3 \longrightarrow NH_3{\cdot}BF_3 \xrightarrow{HF} [NH_4][BF_4] \quad (4)$$

product that could be expected, therefore, is 67%, corresponding to the overall equation (5).

$$3PF_2(NH_2) + 3BF_3 \longrightarrow 2BF_2[NH(PF_2)] + PF_3 + [NH_4][BF_4] \quad (5)$$

Attempts were made to improve yields by carrying out reactions in the presence of hydrogen fluoride abstractors such as potassium fluoride and aluminium, but these were unsuccessful.

The order of the stabilities of adducts of BF_3 with ammonia and fluorophosphinoamines is: $NH_3{\cdot}BF_3 > (NH_2)PF_2{\cdot}BF_3 > NH(PF_2)_2{\cdot}BF_3 > N(PF_2)_3{\cdot}BF_3$. The primary amine adduct is undissociated at 209 K, whereas those of the secondary and tertiary amines are so weak that the amines may be separated from BF_3 by low-temperature fractional distillation.[1] The relative stabilities of the ammonia and aminodifluorophosphine adducts almost certainly accounts for the principal side reaction to reaction (1) that we observed. Equation (6) is the

$$PF_2(NH_2){\cdot}BF_3 + PF_2(NH_2) \longrightarrow NH(PF_2)_2 + NH_3{\cdot}BF_3 \quad (6)$$

simplest representation of the process. If the ratio of $PF_2(NH_2) : BF_3$ taken exceeds 2 : 1, this is the only reaction giving a volatile product. To maximise the yield of $BF_2[NH(PF_2)]$, an excess of BF_3, approximately threefold, must be used.

Properties of $BF_2[NH(PF_2)]$.—The compound is sufficiently stable in the gas phase to allow study of its spectroscopic properties, but in the liquid phase there is rapid decomposition, yielding BF_3, PF_3, and a white solid. On gently heating this solid, $BF_2[NH(PF_2)]$ was regenerated, with more BF_3 and PF_3, and eventually some involatile white material remained. In this behaviour, $BF_2[NH(PF_2)]$ resembles aminodifluoroborane.[2] As both compounds have both Lewis-acid and Lewis-base properties, it is possible that the first solid formed is a cyclic or polymeric adduct of the compound with itself, $\{BF_2[NH(PF_2)]\}_n$. The involatile solid, formed by loss of PF_3 and BF_3, is probably a polymer, consisting of -NH-PF- and -NH-BF- units. The instability of the compound in the liquid phase made a study of some properties impossible, and characterisation was therefore rendered more difficult than is usually the case. The molecular weight in the gas phase [Found: 132.2. Calc. for HBF_4NP: 132.8] and the exact mass of the parent ion [Found: 132.9874. Calc. for $^{1}H^{11}B^{19}F_4{}^{14}N^{31}P$: 132.9876] were in agreement with the proposed formulation.

Other details of the mass spectrum are given in Table 1. Initial breakdown of the parent ion can involve loss of

---

[1] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975, 889.

[2] F. J. Lovas and D. R. Johnson, *J. Chem. Phys.*, 1973, **59**, 2347.

hydrogen or fluoride, or possibly larger units. There is little evidence from the spectrum to indicate whether the fluorine loss is preferentially from phosphorus or from boron.

Vibrational Spectra.—The i.r. and Raman spectra of $BF_2[NH(PF_2)]$ (Table 2) provide good evidence for the suggested identity of the compound. In particular: bands at 3 400 and 1 205 cm^{-1} imply that there is a secondary amine present; bands between 1 400 and 1 500 cm^{-1} suggest the presence of a species containing fluorine bound to three-co-ordinate boron; and absorptions between 800 and 900 cm^{-1}, and below 500 cm^{-1}, are consistent with a fluorophosphinoamine rather than a phosphorus(v) species.

TABLE 1

Mass spectrum [a] of $BF_2[NH(PF_2)]$

m/e	Relative abundance	Assignment [b]
133	92	$^{11}M^+$
132	17	$^{10}M^+$, $[^{11}M - H]^+$
131	1	$[^{10}M - H]^+$
114	5	$[^{11}M - F]^+$
113	4	$[^{10}M - F]^+$, $[^{11}M - HF]^+$
112	<1	$[^{10}M - HF]^+$
94	8	$[^{11}M - HF_2]^+$
93	2	$[^{10}M - HF_2]^+$
88	10	$[PF_3]^+$
84	5	$[NH(PF_2)]^+$
69	100	$[PF_2]^+$
68	4	$[^{11}BF_3]^+$
67	1	$[^{10}BF_3]^+$
65	12	$[NH(PF)]^+$
64	2	$[N(PF)]^+$
50	6	$[PF]^+$
49	10	$[^{11}BF_2]^+$
48	2	$[^{10}BF_2]^+$
46	17	$[NH(P)]^+$
45	2	$[NP]^+$, $[^{11}BF(NH)]^+$
44	<1	$[^{10}BF(NH)]^+$, $[^{11}BF(N)]^+$
31	1	$[P]^+$
20	1	$[HF]^+$

[a] Recorded at an ionising voltage of 70 eV. [b] $^{11}M = {}^{11}BF_2[NH(PF_2)]$, $^{10}M = {}^{10}BF_2[NH(PF_2)]$.

The highest possible point group for $BF_2[NH(PF_2)]$ is C_s, in which case there would be 12 a' and 6 a'' vibrational modes. The only practical difference between C_s and C_1 point groups is that in the latter case all modes would be polarised in the Raman spectrum, instead of just the a' modes of a C_s molecule. By analogy with other BF_2N compounds,[2,3] the $BF_2(NHP)$ unit is expected to be planar, while the maximisation of H · · · F interactions [4,5] would make one P–F bond also lie in the plane, giving overall C_1 symmetry. However, the spectra can be interpreted in terms of, and are consistent with, the higher symmetry, and any distortion caused by rotation of PF_2 or BF_2 groups has little effect on the spectra.

Moreover, the spectra are entirely consistent with there being only one conformer present in the gas phase. This is in marked contrast with $SiH_3[NH(PF_2)]$ [5] and $NH(PF_2)_2$,[1] but is not surprising when the possibilities for H · · · F interactions are considered. Delocalisation of nitrogen lone-pair electrons into a boron $2p$ orbital may also play a part, by reducing phosphorus–nitrogen lone pair–lone pair interactions. Thus the bands at 3 400 and 1 205 cm^{-1}, shifting to 2 530 and 1 055 cm^{-1} on deuteriation, are assigned to the N–H stretch and N–H in-plane deformation of a secondary amine. Other assignments in Table 2 are very much more tentative, and assume considerable mixing of simple bond-stretching and deformation co-ordinates. The bands between 1 400 and 1 500 cm^{-1} are related to the B–F antisymmetric stretches of $^{11}BF_3$ and $^{10}BF_3$, but with the degeneracy lifted by replacement of one fluorine by nitrogen. The ' symmetric ' BF_2N vibration (890 cm^{-1} in BF_3) is then assumed to mix with the P–N stretch, expected in the same region, to give bands at 952 and 678 cm^{-1}. Other bands in this region are the P–F stretches, and another NH deformation which appears at 780 cm^{-1} on deuteriation. Assignment of deformations is more difficult: our suggestions are based on work on $BF_2(NMe_2)$ [6] and on our own earlier work on $NH(PF_2)_2$ and $N(PF_2)_3$.[1]

TABLE 2

Vibrational spectra (cm^{-1}) of $BF_2[NH(PF_2)]$

I.r. (gas)		Raman (solid)	Assignment
$BF_2[NH(PF_2)]$	$BF_2[ND(PF_2)]$	$BF_2[NH(PF_2)]$	
3 400m	2 530m	3 386m	$\nu(NH)$, $\nu(ND)$
1 494 s			$\nu_{asym}[BF_2(N)]$
1 489			
1 485			
1 446 vs	1 445vs		
1 441			
1 404vs	1 415vs, br	1 410w, br	
1 355w	1 359w		
1 205m	1 055m		$\delta(NH)$, $\delta(ND)$
		995w	$\delta(NH)$
952m	954w	961w, br	$\nu(BNP)$
851 s		877s	$\nu(PF)$
848	860s		
845		842vs	
809vs	814s	786m	
		772m	
	780s		$\delta(ND)$
678m	672m	659w, br	$\nu(BNP)$
592m	590w	604w, br	$\delta[BF_2(N)]$
541m	530w		
508w			$\delta(PF_2)$
434w		434w	$\tau(BF_2)$
396m, br	395m	401m	
356w		331m	
296w, br	290w	294m	
		260w	$\delta(BNP)$
		156w	$\tau(PF_2)$

vs = Very strong, s = strong, m = medium, w = weak, and br = broad.

N.m.r. Spectra.—Determination of n.m.r. parameters was made unusually difficult by the instability of the compound in the liquid phase or in solution, and by

---

[3] A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. Beagley, D. W. J. Cruickshank, J. J. Monaghan, B. J. Aylett, and I. A. Ellis, *Chem. Comm.*, 1968, 909.

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

[5] D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.

[6] A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J. Chem. Soc.*, 1964, 995.

broadening of spectral lines by quadrupolar nuclei. Satisfactory broad-band decoupling of ^{11}B with the equipment available to us was not possible; use of ^{15}N-substituted $BF_2[NH(PF_2)]$ did resolve the problems due to ^{14}N. The parameters quoted in Table 3 are fully consistent with the suggested structure. In particular, the ^{19}F chemical shifts confirm the presence of a fluorophosphinoamine, and of fluorine bonded to three-co-ordinate boron.[7] No significant temperature dependence of the spectra was noted.

TABLE 3

N.m.r. parameters [a] for $BF_2[^{15}NH(PF'_2)]$

$\tau(^1H)$/p.p.m.	5.56 (5)
$\delta(^{19}F)$ [b]/p.p.m.	−62 (1)
$\delta(^{19}F')$ [b]/p.p.m.	−116 (1)
$\delta(^{31}P)$ [c]/p.p.m.	150 (1)
$^1J(^{31}P^{19}F)$/Hz	1 240 (10)
$^1J(^{31}P^{15}N)$/Hz	70 (10)
$^1J(^{15}N^1H)$/Hz	77 (1)

[a] Recorded at 273 K in C_6D_6–$CHCl_3$. Estimated standard deviations are given in parentheses. [b] To high frequency of external CCl_3F. [c] To high frequency of external 85% H_3PO_4.

Photoelectron Spectrum.—Details of the spectrum are given in Table 4. Assignment of the first two bands as nitrogen and phosphorus lone-pair levels is based on earlier results for fluorophosphine–nitrogen compounds.[1,8] Table 5 gives these two ionisation potentials for several amines with PF_2 or BF_2 groups. It can be seen that both lone-pair levels depend mainly on the number of fluorine-containing substituents, and that replacement of PF_2 by BF_2 has little effect. This may only reflect the electronegativities of the two groups. The only other possibility is that the extent of overlap of the nitrogen lone-pair orbital with the vacant boron 2*p* orbital is matched by the overlap of the nitrogen lone-pair and vacant phosphorus 3*d* orbitals.

TABLE 4

Photoelectron spectrum of $BF_2[NH(PF_2)]$

Vertical i.p.*	Assignment
11.5	N lone pair
12.3	P lone pair
15.3	N–P, N–H, B–N bonding
15.9	
16.6	
17.2	F lone pairs
18.0	P–F bonding
ca. 18.7 (br)	B–F bonding

* ±0.1 eV.

TABLE 5

Ionisation potentials of some amines [a]

Compound	N lone pair	P lone pair	Ref.
$PF_2(NMe_2)$	9.6	10.5	8
$BF_2(NMe_2)$	9.7		*b*
$PF_2(NH_2)$	10.9	11.5	8
$NH(PF_2)_2$	11.3	12.1	1
$BF_2[NH(PF_2)]$	11.5	12.3	This work

[a] Vertical i.p. ±0.1 eV. [b] H. Bock and W. Fuss, *Chem. Ber.*, 1971, **104**, 1687.

EXPERIMENTAL

Volatile compounds were handled in a Pyrex glass vacuum line fitted with Sovirel greaseless taps. The purities of the starting materials, prepared by standard methods or purchased, were checked spectroscopically. Spectra were recorded using: an A.E.I. MS902 mass spectrometer, operating with an ionising voltage of 70 eV; * a Perkin-Elmer 225 grating i.r. spectrophotometer, in the range 200—4 000 cm^{-1}, with cells equipped with caesium iodide windows; a Cary 83 Raman spectrometer with argon-ion (488-nm) laser excitation; a Varian Associates XL100 n.m.r. spectrometer operating at 100 (^1H), 94 (^{19}F), or 40.5 MHz (^{31}P); and a Perkin-Elmer PS16 photoelectron spectrometer with He(I) (21.22 eV) excitation.

Preparation of Difluoro(difluorophosphinoamino)borane.—Boron trifluoride (3.0 mmol) was allowed to expand from a glass bulb (100 cm^3) into a bulb (2 l) containing aminodifluorophosphine (1.0 mmol). A cloud of white solid was formed, which settled slowly on to the walls of the vessel. After 15 min, the contents were condensed into the vacuum line and separated by fractional condensation. The component retained at 177 K (0.8 mmol) was $BF_2[NH(PF_2)]$ (*ca.* 90%) contaminated with $NH(PF_2)_2$. Further separation of these was not possible. A mixture (1.8 mmol) of BF_3 and PF_3 was retained at 77 K. The proportion of $NH(PF_2)_2$ impurity in the product varied unpredictably, 90% purity being typical, but not the highest that was obtained.

We thank Dr. S. Cradock for his assistance in recording and interpreting the photoelectron spectrum.

[5/1526 *Received, 1st August*, 1975]

---

* 1 eV ≈ 1.60 × 10^{-19} J.

[7] C. H. Dungan and J. R. Van Wazer, 'Compilation of Reported ^{19}F N.M.R. Chemical Shifts,' Wiley–Interscience, New York, 1970, and refs. therein.

[8] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.