Preparation and Spectroscopic Properties of Amines containing Germyl and Difluorophosphino-groups

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The compounds $PF_2[NH(GeH_3)]$, $PF_2[N(GeH_3)_2]$, $PF_2[N(GeH_3)(SiH_3)]$, and $N(GeH_3)(PF_2)_2$ have been prepared from the appropriate primary and secondary difluorophosphinoamines by reaction with germyl halide and trimethylamine. The compounds are all much more stable than trigermylamine, but decompose at room temperature by elimination of GeH_2. Vibrational, photoelectron, n.m.r., and mass spectroscopic data have been recorded, and are interpreted in terms of the probable conformations adopted by the fluorophosphino-groups.

ALTHOUGH trisilylamine is easily prepared [1] and stable at room temperature, the germyl analogue is extremely unstable. Early attempts to prepare it were unsuccessful,[2] and it has subsequently been shown that trigermylamine can be prepared in the gas phase, but that decomposition takes place in a few minutes in the gas phase, and even more rapidly in the liquid phase.[3] The process appears to involve elimination of GeH_2 as a yellow solid, leaving ammonia, which in turn catalyses the decomposition. In contrast, other germanium–nitrogen compounds, such as germyl isocyanate,[4] isothiocyanate,[4] azide,[5] and digermyl carbodi-imide,[6] are reasonably stable in the gas and liquid phases, although there is evidence that these, too, decompose by elimination of GeH_2,[4] as does digermyl ether.[7]

In this paper we describe the preparation and characterisation of four germylamines, stabilised to some extent by the presence of difluorophosphino-substituents on nitrogen. Their properties are compared with those of analogous silylamines [8,9] and simple difluorophosphino-amines.[10,11]

RESULTS AND DISCUSSION

Aminodifluorophosphine and germyl bromide or iodide react to a small extent (1—2%) in the liquid

[1] A. Stock and C. Somieski, *Ber.*, 1921, **54**, 740.

[2] L. M. Dennis and R. W. Work, *J. Amer. Chem. Soc.*, 1933, **55**, 4486.

[3] D. W. H. Rankin, *J. Chem. Soc. (A)*, 1969, 1926.

[4] T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, *Canad. J. Chem.*, 1962, **40**, 739.

[5] S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc. (A)*, 1968, 1420.

[6] S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc. (A)*, 1968, 1423.

[7] T. D. Goldfarb and S. Sujishi, *J. Amer. Chem. Soc.*, 1964, **86**, 1679.

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

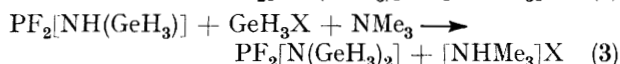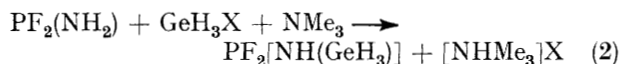[9] E. A. V. Ebsworth, D. W. H. Rankin, and J. G. Wright, unpublished work.

[10] D. W. H. Rankin, *J. Chem. Soc. (A)*, 1971, 783.

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

phase, and to an even smaller extent in the gas phase, to give difluoro(germylamino)phosphine [equation (1); X = Br or I]. The small yields contrast with those

$$3PF_2(NH_2) + 2GeH_3X \longrightarrow$$
$$2PF_2[NH(GeH_3)] + PF_2X + [NH_4]X \quad (1)$$
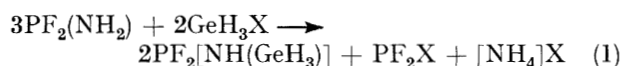
obtained in the analogous reaction of $PF_2(NH_2)$ with silyl bromide.[8] However, if the reaction is allowed to proceed in the presence of trimethylamine much greater yields are obtained, and replacement of another hydrogen atom by a germyl group also occurs [equations (2) and (3); X = Br or I]. By changing the reaction conditions, particularly the proportions of $PF_2(NH_2)$ and

$$PF_2(NH_2) + GeH_3X + NMe_3 \longrightarrow$$
$$PF_2[NH(GeH_3)] + [NHMe_3]X \quad (2)$$

$$PF_2[NH(GeH_3)] + GeH_3X + NMe_3 \longrightarrow$$
$$PF_2[N(GeH_3)_2] + [NHMe_3]X \quad (3)$$

GeH_3X taken, the relative amounts of germylamines formed can be varied, and pure samples of each compound can be obtained after a lengthy fractionation procedure.

Bis(difluorophosphino)amine does not react directly with germyl iodide in either the gas or the liquid phase, but, on addition of NMe_3, bis(difluorophosphino)germyl-amine is rapidly formed. The formation of difluoro-

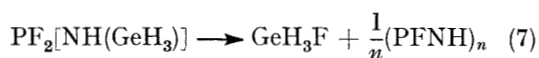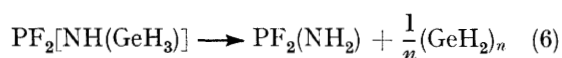$$NH(PF_2)_2 + GeH_3I + NMe_3 \longrightarrow$$
$$N(GeH_3)(PF_2)_2 + [NHMe_3]I \quad (4)$$
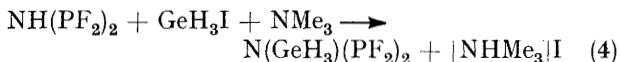
[germyl(silyl)amino]phosphine from difluoro(silylamino)-phosphine and GeH_3I in the presence of NMe_3 by a similar reaction has been established.

$$PF_2[NH(SiH_3)] + GeH_3I + NMe_3 \longrightarrow$$
$$PF_2[N(GeH_3)(SiH_3)] + [NHMe_3]I \quad (5)$$
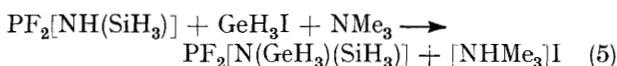
Stability.—Trigermylamine, the other known germyl-amine, decomposes within a few minutes in the gas phase, unless diluted with an inert gas, and cannot be condensed and revaporised at all.[3] In contrast, the germylamines described here, although less stable than their silyl analogues, are sufficiently stable to be handled by conventional vacuum-line procedures, although in all cases decomposition is faster in glassware not scrupulously dry and clean.

Difluoro(germylamino)phosphine is the least stable of these amines, decomposing completely in the gas phase in *ca.* 1 h at room temperature, and in *ca.* 10 min at 305 K, and having a half-life in the liquid phase at 209 K of *ca.* 15 min. The decomposition involves formation of an involatile yellow solid, the volatile products being mainly $PF_2(NH_2)$, with small amounts of germyl fluoride, monogermane, and digermane. Thus the main route involves GeH_2 elimination, with loss of GeH_3F being of secondary importance. In this respect

$$PF_2[NH(GeH_3)] \longrightarrow PF_2(NH_2) + \frac{1}{n}(GeH_2)_n \quad (6)$$

$$PF_2[NH(GeH_3)] \longrightarrow GeH_3F + \frac{1}{n}(PFNH)_n \quad (7)$$

$PF_2[NH(GeH_3)]$ resembles trigermylamine, rather than $PF_2[NH(SiH_3)]$ whose decomposition gives silyl fluoride.[8] Its instability is such that it is extremely difficult to obtain pure samples, and the spectroscopic data for this compound are therefore incomplete.

(Digermylamino)difluorophosphine is more stable than the monogermyl species, showing no sign of decomposition after 4 h in the gas phase at room temperature. In the liquid phase at 227 K, solid material could be observed after 10 min, and n.m.r. spectra of solutions indicated that the main route involved GeH_2 elimination, giving $PF_2[NH(GeH_3)]$, and then $PF_2(NH_2)$ as in reaction (6).

$$PF_2[N(GeH_3)_2] \longrightarrow PF_2[NH(GeH_3)] + \frac{1}{n}(GeH_2)_n \quad (8)$$
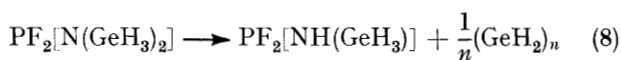
The reason for the extra stability of the digermyl species is not clear: it may be associated with the absence of a N–H bond, or it may reflect reduced basicity of the tertiary amine. The stability of difluoro[germyl(silyl)-amino]phosphine could not be studied, as pure samples were not obtained, but it seemed to be about as stable as the digermyl compound.

Bis(difluorophosphino)germylamine was the most stable compound of the group, remaining unchanged in the gas phase at 305 K for 10 h. Only on prolonged standing in the liquid phase at 209 K did solid materials appear, associated with the formation of $NH(PF_2)_2$: again, loss of GeH_2 is the important breakdown process.

$$N(GeH_3)(PF_2)_2 \longrightarrow NH(PF_2)_2 + \frac{1}{n}(GeH_2)_n \quad (9)$$
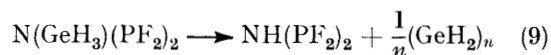
The simplest explanation of the observed relative stabilities of the germylamines is that the process is base catalysed, and therefore autocatalytic, with the rates of decomposition being dependent on the amine basicity, which is influenced by the electron-withdrawing character of the substituents, whether by inductive means or by $(p \rightarrow d)$ π bonding. Decomposition certainly takes place faster in the presence of NMe_3, and it has been noted that the rate of decay of $N(GeH_3)_3$ accelerates as the more basic ammonia is produced.[3] However, the relative stabilities may also be influenced by intra-molecular H–F interactions: in the most probable conformation of $N(GeH_3)(PF_2)_2$, for instance, there would be four short H–F interactions stabilising one GeH_3 group, whereas there would be only two such interactions stabilising two germyl groups in PF_2-$[N(GeH_3)_2]$.

N.M.R. Spectra.—N.m.r. parameters for the four germylamines are given in Table 1. Spectra of the compounds with only one PF_2 group were all first order, implying that rotation about P–N bonds must be rapid on the n.m.r. time scale. Complications were introduced by fortuitously equal coupling constants, particularly in the case of $PF_2[^{15}NH'(GeH_3)]$ for which $^2J(^{15}N^1H)$ and $^3J(^{31}P^1H)$ are both 4.6 Hz, and $^3J(^1H^1H')$ and $^4J(^{19}F^1H)$ are both 2.3 Hz. Samples enriched with ^{15}N (*ca.* 95%) were necessary for good ^{31}P spectra to be obtained; in each case, when unenriched samples were used, broad

resonances were observed due to ^{31}P–^{14}N coupling. The proton-decoupled ^{31}P and ^{19}F spectra of $^{15}N(GeH_3)$-$(PF_2)_2$ were second order, representing the A and M parts of an $[A(M)_2]_2X$ spin system.

Chemical shifts for ^{15}N, and signs of coupling constants for $PF_2[^{15}N(GeH_3)_2]$, relative to $^{1}J(^{31}P^{19}F)$, assumed to be negative, were determined by heteronuclear double-

bond is eclipsed by the phosphorus lone pair, as has already been suggested [12] for $PCl_2(NMe_2)$. This hypothesis is supported by the observation that $^{3}J(^{31}P^{1}H)$ is even smaller (2.0 Hz), in $N(GeH_3)(PF_2)_2$. This compound probably exists in the conformation in which the fluorine atoms are close to the GeH_3 group, so that the phosphorus lone pairs are *trans* to the N–Ge bond

TABLE 1

N.m.r. parameters [a]

Parameter	PF₂[¹⁵NH′(GeH₃)]	PF₂[¹⁵N(GeH₃)₂]	¹⁵N(GeH₃)(PF₂)₂	PF₂[N(GeH₃)(SiH′₃)]
δ(¹H)/p.p.m.	4.82	4.92	4.98	4.95
δ(¹H′)/p.p.m.	n.o.			4.35
δ(¹⁹F)/p.p.m.	−55.2	−45.8	−60.6	−48.5
δ(³¹P)/p.p.m.	155.1	158.0	149.8	155.5
δ(¹⁵N)/p.p.m.[b]	7.7	−1.4	91.4	n.s.
¹J(³¹P¹⁹F)/Hz	1 200	−1 218	−1 239	1 225
¹J(³¹P¹⁵N)/Hz	73.5	+82.5	74.0	n.s.
²J(¹⁵N¹H)/Hz	4.6	−4.4	3.5	n.s.
²J(¹⁹F¹⁵N)/Hz	5.6	2.7	4.0	n.s.
²J(³¹P¹H′)/Hz	32.7			
²J(³¹P³¹P′)/Hz			431[c]	
³J(³¹P¹H)/Hz	4.6	+9.4	2.0	n.o.
³J(¹⁹F¹H′)/Hz	16.3			
³J(¹H¹H′)/Hz	2.3			
³J(³¹P¹⁹F′)/Hz			+15.7	
⁴J(¹⁹F¹H)/Hz	2.3	+2.9	3.5	n.o.
⁴J(¹⁹F¹⁹F′)/Hz			n.o.	
⁴J(¹⁹F¹⁹F″)/Hz			n.o.	

Relative signs of coupling constants were determined where they are explicitly given; n.o. = not observed, n.s. = not studied.
[a] Recorded at 223 K for solutions in $CDCl_3$–$SiMe_4$ (1 : 1). [b] Relative to $[NMe_4]I$. [c] Varies from 405 Hz at 303 K to 442 Hz at 193 K.

resonance experiments, while observing ^{1}H spectra. Signs of coupling constants for $^{15}N(GeH_3)(PF_2)_2$ were derived from the analysis of second-order spectra.

Chemical shifts for ^{1}H, ^{19}F, ^{31}P, and ^{15}N are all in the ranges expected. Comparison of parameters reported here with those for the simple difluorophosphino-amines [11] shows that replacement of an amino-hydrogen atom by a germyl group leads to a high-frequency shift of ^{31}P and ^{19}F resonances, but a low-frequency shift of ^{15}N resonance. Replacement of a hydrogen atom by a PF_2 group shifts the resonances in the opposite directions, with the effect on the ^{15}N resonance being much more pronounced, *ca.* 80 p.p.m. The Ge*H* resonances shift to higher frequency with increasing electonegativity of the substituents at N.

Most coupling constants are also as expected, but a few of them call for comment. The value of 32.7 Hz for $^{2}J(^{31}P^{1}H)$ in $PF_2[NH(GeH_3)]$ compares with 18.8 Hz in $PF_2[NH(SiH_3)]$[8] and 18.6 Hz in $PF_2(NH_2)$.[10] We suggest that this coupling constant is largest when the phosphorus lone pair eclipses the N–H bond, and therefore that the germyl compound exists in solution predominantly in conformations in which the fluorine atoms are close to the germyl group. In the same compound $^{3}J(^{31}P^{1}H)$ is small (4.6 Hz) compared with values for $PF_2[NH(SiH_3)]$ and $PF_2[N(GeH_3)_2]$, and it may be that this coupling is at a maximum when the N–Ge or N–Si

(Figure). This conformation also means that two lone pairs are fairly close to each other, giving a large temperature-dependent $^{2}J(^{31}P^{31}P)$ coupling, as is found in
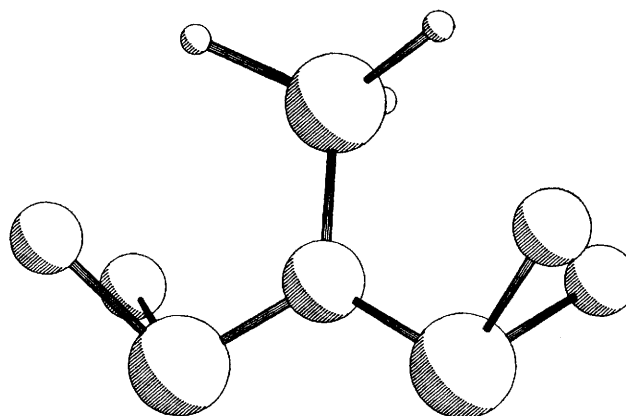
Probable conformation of $N(GeH_3)(PF_2)_2$

$NMe(PF_2)_2$ [13,14] and other bis(difluorophosphino) compounds.

The coupling constants in $PF_2[NH(SiH_3)]$,[8] PF_2-$[N(SiH_3)_2]$, and $N(PF_2)_2(SiH_3)$ [9] can also be interpreted in this way. In the first two compounds the intermediate values of $^{3}J(PH)$ are regarded as averages of a

[12] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.

[13] J. F. Nixon, *J. Chem. Soc. (A)*, 1969, 1087.
[14] E. Hedberg, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, 1974, **96**, 4417.

large and a small value because of the mixture of conformations. In $N(PF_2)_2(SiH_3)$ the small value for $^3J(PH)$ is due to the predominant conformation. This interpretation implies that the values normally observed for $^2J(PH)$ and $^3J(PH)$ in compounds like these are weighted averages of large and small couplings associated with the two extreme configurations of the lone pairs.

Vibrational Spectra.—Details of the vibrational spectra of the three amines that were isolated and purified are given in Table 2. The compounds must all have low symmetry, and, as the conformations adopted are uncertain, assignments of bands to particular vibrational modes must be tentative. Assignments given in Table 2 are based on typical vibrational frequencies of compounds containing GeH_3 or PF_2 groups. Skeletal modes are

therefore suggest that this conformer is relatively stable, a conclusion contradicting our interpretation of the n.m.r. coupling constants. Perhaps the i.r. intensities do not reflect the relative populations of the two conformers; perhaps the solid-phase form of PF_2-$[NH(SiH_3)]$ is not equivalent to either of the conformers found in the gas phase. These uncertainties can only be removed by studies of the gas- and solid-phase structures of the compounds involved.

Mass Spectra.—Because of the extreme susceptibility of these compounds to hydrolysis, satisfactory mass spectra were impossible to obtain with our equipment. However, the identities of $PF_2[N(GeH_3)_2]$ and $N(GeH_3)$-$(PF_2)_2$ were confirmed by observation of parent ions, and some of the ions formed by breakdown of the parent.

TABLE 2

Vibrational spectra (cm^{-1})

$PF_2[NH(GeH_3)]$ (I.r., gas)	$PF_2[N(GeH_3)_2]$ (I.r., gas)	N(GeH$_3$)(PF$_2$)$_2$		Assignment
		I.r., gas	Raman, solid	
3 444m				} ν(NH)
3 380w				
2 111s	2 120s	2 138s	2 162m	} ν(GeH$_3$)
2 096 (sh)	2 107s		2 139vs	
1 225s				} δ(NH)
1 190m				
	1 005s	961s	955m	ν(PN)
842s	862s	868s	860s	} ν(PF$_2$), δ(GeH$_3$)
			840m	
811vs	820vs	812vs	792w	
	774s			ν_{sym}(Ge$_2$N)? ν_{asym}(P$_2$N)?
			770m	
642m	655m	641m	648m, br	} ρ(GeH$_3$)
		610m	630m, br	
530w		572w	584m, br	} ν(GeN)?
			571m, br	
435w	450m	465ms	422s	δ(PF$_2$) ν_{asym}(Ge$_2$N)?
	393w			
	308vw	362ms	391s	} ω(PF$_2$)
		313w		
	270w	296w	280w	ρ(PF$_2$)
			262m	
			231vs	} δ(GeNP$_2$) and τ(PF$_2$)
			153w	
			124w	

s = Strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad. Gas-phase spectra were obtained at 298 K, solid-phase spectra at 77 K.

even more uncertain, since there are no similar compounds that could be used for reference purposes, and the extents of coupling between these vibrations and those of the PF_2 groups are also unknown.

Of particular importance are the bands associated with N–H stretching and deformation in the gas-phase i.r. spectrum of $PF_2[NH(GeH_3)]$. In each region two bands are observed, the higher-frequency band being several times more intense than the lower-frequency one. In the spectrum of the analogous silyl compound there are two bands in each region, but the members of each pair are of approximately equal intensity.[8] From studies of the vibrational spectra of the solid phase and of conformers found in the gas phase, it was deduced that the higher-frequency vibration of each pair was associated with a conformation in which the fluorine atoms are close to the amino-hydrogen atom. The intensities of the bands in the spectrum of the germyl compound

The most important route involved elimination of GeH_2, but loss of a PF_2 group also occurred.

TABLE 3

He(I) u.v. photoelectron spectra

Ionisation potential (eV)

$PF_2[N(GeH_3)_2]$	N(GeH$_3$)(PF$_2$)$_2$	Assignment
10.5	10.8	N 2p_z
11.3	11.0	} P 3p_z
	11.6	
12.5	12.4	GeH$_\sigma$
13.2	13.1	GeN$_\sigma$
15.1	15.5	PN$_\sigma$
16.5	16.0	} F 2p_π
	16.8	
17.6	17.4	} PF$_\sigma$
	18.3	

Photoelectron Spectra.—He(I) u.v. photoelectron spectra were recorded for the two most stable amines, $PF_2[N(GeH_3)_2]$ and $N(GeH_3)(PF_2)_2$, and details are given in Table 3, with assignments made by comparison with

observed ionisation potentials for other compounds.[11,15,16] The nitrogen $2p$ ionisation potentials were smaller than those in the simple fluorophosphinoamines [11] but larger than that in $N(GeH_3)_3$.[15]

EXPERIMENTAL

All the volatile compounds were handled using a Pyrex-glass vacuum system, equipped with 'Sovirel' greaseless taps. Before the easily hydrolysed fluorophosphinoamines could be prepared, all the glassware had to be carefully dried, by allowing silyl chloride vapour to fill the system for a few minutes. Aminodifluorophosphine,[10] difluoro-(silylamino)phosphine,[8] bis(difluorophosphino)amine,[11] and germyl halides [17,18] were prepared by published methods.

Infrared spectra were recorded on Perkin-Elmer 225 and 457 spectrometers, using cells equipped with KBr or CsI windows. Raman spectra were obtained using a Cary 83 instrument, with argon-ion 488-nm laser excitation, mass spectra using an A.E.I. MS902 spectrometer operating at 70 eV ionising voltage,* and u.v. photoelectron spectra using a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation. N.m.r. spectra were recorded on Varian Associates XL100 and HA100 spectrometers, the latter modified to accept an irradiation frequency provided by a Schlumberger FS30 frequency synthesiser.

Preparations—$PF_2[NH(GeH_3)]$ *and* $PF_2[N(GeH_3)_2]$. A mixture of germyl iodide (1.1 mmol), aminodifluorophosphine (1.0 mmol), and trimethylamine (1.0 mmol) was warmed to room temperature for 20 s, yellow-brown solids being rapidly formed. Repeated fractionation yielded *difluoro(germylamino)phosphine* (0.25), retained at 209 K, *(digermylamino)difluorophosphine* (*ca.* 0.1) retained at 227 K, unchanged $PF_2(NH_2)$ (0.4), and a mixture of mono- and di-germane (0.3 mmol).

In an experiment designed to maximise the yield of the digermylamine, GeH_3I (2.2 mmol) and $PF_2(NH_2)$ (1.0 mmol) were mixed, in a glass ampoule (40 cm³), and NMe_3 (2.2 mmol) was added in three stages, the ampoule being warmed to room temperature for a few seconds after each addition.

Repeated fractionation yielded $PF_2[N(GeH_3)_2]$ (0.3), PF_2-$[NH(GeH_3)]$ (0.15), $PF_2(NH_2)$ (0.35), NMe_3 (0.05), and Ge_2H_6 (0.05 mmol).

$N(GeH_3)(PF_2)_2$.—Bis(difluorophosphino)amine (1.8 mmol) and GeH_3I (2.0 mmol) were mixed in a glass ampoule (40 cm³) and NMe_3 (2.0 mmol) was added in two portions, the reagents being warmed to room temperature for *ca.* 15 s after each addition. Yellow-brown solids were rapidly formed. Fractionation yielded *bis(difluorophosphino)-germylamine*, retained at 209 K, GeH_3I (0.3, retained at 227 K), $NH(PF_2)_2$ (0.6), NMe_3 (0.1), and GeH_4 (0.35 mmol). The recovered starting materials were again treated with more GeH_3I (1.0 mmol) and NMe_3 (0.9 mmol), and the products were fractionated again. The total yield of the desired product after purification was 0.5 mmol, *ca.* 30% based on $NH(PF_2)_2$ taken.

Reaction of $PF_2[NH(SiH_3)]$ *with* GeH_3I.—Difluoro-(silylamino)phosphine (0.4 mmol) and GeH_3I (0.4 mmol) were mixed in a glass ampoule (40 cm³) and NMe_3 (0.4 mmol) was then added. After warming the reagents to room temperature for *ca.* 15 s the volatile products were immediately distilled into an n.m.r. tube. N.m.r. spectra confirmed the presence of *difluoro[germyl(silyl)amino]phosphine*, together with small amounts of $PF_2[NH(SiH_3)]$, $NH(PF_2)_2$, $PF_2(NH_2)$, and $N(GeH_3)(PF_2)_2$. No attempt was made to isolate a pure sample of the amine since the impurities present would all be of similar volatility.

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

[15] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.
[16] S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. W. Whiteford, *J.C.S. Faraday II*, 1972, 934.
[17] M. F. Swiniarski and M. Onyszchuk, *Inorg. Synth.*, 1974, **15**, 157.
[18] S. Cradock *Inorg. Synth.*, 1974, **15**, 161.