Synthesis of a Silylamino-substituted Phosphorane

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Summary The synthesis of $Me_3Si(Me)NPF_4$, the first silylamino-substituted phosphorane, is described; variable temperature ^{19}F n.m.r. data indicate that the molecule is fluxional, with the silylamino group occupying an equatorial site of a trigonal bipyramid in the ground state.

THE growing interest in Si–N–P compounds relates to questions of bonding and stereochemistry as well as to their potential utility in chemical synthesis. To date two-,[1] three-,[2–4] and four-[3,5] co-ordinate phosphorus compounds featuring the Si–N–P linkage have been reported. However, five-co-ordinate species have eluded isolation owing to the ready elimination of silyl halides. We now report the first synthesis of such a compound.

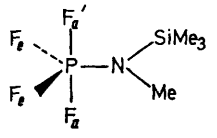
An equimolar mixture of $Me_3SiN(Me)PF_2$[2b,6] and SF_4 was allowed to warm from −196 to −78 °C and was maintained at this temperature for 2 days. Fractionation of the volatile material afforded a *ca.* 20% yield of $Me_3SiN(Me)PF_4$ (**1**), in a trap maintained at −45 °C. Compound (**1**) is a colourless liquid which decomposes above 0 °C to yield Me_3SiF and $(MeNPF_3)_2$;[7] its characterisation was based, therefore, upon mass spectrometric and n.m.r. data.

The mass spectrum of (**1**) consisted of a low-intensity parent peak at *m/e* 209, and anticipated fragmentation peaks at *m/e* 194 [$Me_2SiN(Me)PF_4^+$], 164 [$SiN(Me)PF_4^+$], and 107 [PF_4^+].

At 0 °C the ^1H n.m.r. spectrum of (**1**) comprised an *N*-methyl doublet of quintets at τ 7·29, with J_{PNCH} 18·5, and J_{FPNCH} 2·0 Hz, and an Me_3Si singlet at τ 9·76. The relative areas of the N–Me and Me_3Si resonances were 1 : 3, respectively. At 0 °C the ^{19}F n.m.r. spectrum (94·2 MHz; $CHFCl_2$ solution; CCl_3F reference) of (**1**) consisted of a doublet at 59·2 p.p.m. with J_{PF} 862 Hz. Upon cooling a coalescence was observed at −90 °C, followed by the emergence of six triplets (each with poorly resolved quartet fine splitting) in a 1 : 1 : 1 : 1 : 2 : 2 intensity ratio at −120 °C. The following assignments were made by comparison with ^{19}F n.m.r. data for other tetrafluorophosphoranes:[8]

$\delta(F_e)$ 71·6 p.p.m., $J(PF_e)$ 942·6 Hz, $J(F_aPF_e)$ 69·2 Hz;
$\delta(F_a)$ 56·6 p.p.m., $J(PF_a)$ 816·7 Hz, $J(F_ePF_a)$ 74·6 Hz;
$\delta(F_a')$ 38·9 p.p.m., $J(PF_a')$ 746·7 Hz, $J(F_ePF_a')$ 64·4 Hz.

Collectively these data establish for (**1**) the trigonal bipyramidal ground-state geometry shown.



(1)

However, the present data do not permit unequivocal assignments for the F_a and F_a' resonances. *A priori* one can consider three stereochemical processes for (**1**), *viz.*, pyramidal nitrogen inversion, N–P rotation, and fluorine positional interchange. However, careful scrutiny of the ^{19}F dynamic n.m.r. spectra reveals that no distinction can be made between these processes. The experimental free energy of activation is estimated to be 7·4 kcal mol^{-1}.

A final noteworthy feature is the fact that the reaction of $Me_3SiN(Me)PF_2$ with SF_4 proceeds *via* oxidative fluorination rather than Si–N cleavage.

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