Preparation and Nuclear Magnetic Resonance Spectra of Aminodifluorophosphorane

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Aminodifluorophosphorane has been prepared by the reaction in solution of difluorophosphine and ammonia. N.m.r. spectra indicate that the fluorine atoms are in axial positions and that the amino-group atoms lie in a plane perpendicular to the equatorial plane. At 215 K there is no evidence for rotation about the P–N bond or for fluxional behaviour. The compound is thermally unstable, and has not been isolated.

THE oxidative addition of primary amines to substituted difluorophosphines has been used as a means of preparing phosphoranes which have P–H bonds,[1] and it has also been shown [2] that ammonia may act as the formal oxidising species in the preparation of diaminodifluorophosphorane. There have been no reports of such oxidative-addition reactions with unsubstituted difluorophosphine to give difluorodihydrophosphoranes. There is, however, a report of the addition of alcohols and alkyl thiols to difluorophosphine, giving dihydrophosphoranes: [3] the products were reported to be very unstable. The only other known phosphoranes with more than one P–H bond are PF_3H_2 and PF_2H_3, and there is a marked decrease in the stability of the fluorophosphoranes as the number of hydrogen atoms increases.[4,5]

We have now studied the oxidative addition of ammonia to difluorophosphine to give aminodifluorophosphorane. This is a simple compound which may be expected to have a high degree of symmetry, and to be suitable for detailed spectroscopic analysis. Its stability, however, is such that we have been unable to isolate it, and we report here the results of a limited study of its n.m.r. spectra, recorded at low temperatures.

RESULTS AND DISCUSSION

When ammonia and difluorophosphine were allowed to mix in solution a rapid reaction took place. Large amounts of an orange-red solid were formed, and further precipitation of solid occurred subsequently, even while spectra were being recorded at 215 K. N.m.r. spectra of the solution indicated that a simple addition reaction was occurring, followed by decomposition, which gave trifluorophosphine as the only soluble product (Scheme).

$$\begin{aligned} PF_2H + NH_2 &\longrightarrow PF_2H_2(NH_2) \longrightarrow \\ &PF_3 + \text{insoluble solids} \end{aligned}$$

SCHEME

The product of the reaction was unequivocally identified by the ^1H, ^{19}F, and ^{31}P n.m.r. spectra of samples made using $^{15}NH_3$. The ^{31}P spectrum was first order, and consisted of a triplet (754 Hz) of triplets (599 Hz) of doublets (41 Hz) of triplets (13 Hz). The first and last of these splittings were removed by ^1H noise decoupling. The ^1H spectrum had two groups of resonances, of equal area. The higher-frequency group, assigned to the hydrogen atoms bound to phosphorus, showed first-order couplings to ^{31}P, ^{19}F, and ^{15}N, giving a total of 12 lines, but long-range NH coupling was not resolved. The other group of proton resonances, and the ^{19}F spectrum, showed two and three first-order splittings respectively, giving sets of identical second-order subspectra. These were not completely resolved, but nevertheless indicated that the fluorine and amino-hydrogen atoms formed an $[AX]_2$ spin sub-system, and partial analysis of the spectra gave values for the two different FH couplings, and upper limits for the FF and HH couplings.

N.m.r. parameters [a] for $PF_2H_2(^{15}NH'_2)$

$\delta(^1H)$	$+6.90$	$^2J(^{19}F^{15}N)$	13.2
$\delta(^1H')$	$+2.05$	$^2J(^{15}N^1H)$	4.7
$\delta(^{19}F)$	-57.5 [b]	$^2J(^{31}P^1H')$	13.0
$\delta(^{31}P)$	-57.3 [c]	$^2J(^1H'^1H')$ [d]	<1
$^1J(^{31}P^1H)$	754.4	$^2J(^{19}F^{19}F)$ [d]	<1
$^1J(^{31}P^{19}F)$	598.6	$^3J(^{19}F^1H')$ [d]	17.2
$^1J(^{15}N^1H')$	88	$^3J(^{19}F^1H')$ [d]	21.5
$^1J(^{31}P^{15}N)$	41.1	$^3J(^1H^1H')$	<0.5
$^2J(^{19}F^1H)$	89.6		

[a] Recorded at 215 K in CCl_3D–$SiMe_4$ (95 : 5); δ values in p.p.m., J in Hz. [b] Derived by analysis of incompletely resolved $[AX]_2$ sub-spectra. [c] Relative to CCl_3F. [d] Relative to 85% H_3PO_4.

The n.m.r. parameters are listed in the Table. The ^1H and ^{31}P chemical shifts and the large $^1J(^{31}P^1H)$ are all consistent with the phosphorane formulation.[2,4,6] The one-bond P–F coupling is amongst the smallest reported, and indicates that the fluorine atoms occupy the axial positions of the trigonal-bipyramidal structure,[7] while the large value for $^1J(^{15}N^1H)$ implies a large *s*-orbital contribution to the N–H bonds,[8] and hence that the PNH_2 group is probably planar. Finally, the magnetic non-equivalence of the amino-protons and of the fluorine atoms, combined with the magnetic equivalence of the phosphorane protons, implies that the plane of the amino-group is aligned perpendicular to the equatorial plane, giving the molecule overall C_{2v} symmetry, and that at 215 K there is restricted rotation about the P–N bond. Thus the behaviour of the amino-group with respect to rotation in this compound parallels that found for other aminofluorophosphoranes.[2,9]

EXPERIMENTAL

Volatile materials were handled using a conventional Pyrex-glass vacuum line fitted with greaseless taps.

Difluorophosphine was prepared by the reaction of difluoroiodophosphine, phosphine, and mercury.

N.M.R.-tube Preparation of $PF_2H_2(NH_2)$.—Typically, [^{15}N]ammonia (0.5 mmol) was thoroughly mixed with CCl_3D and a trace of $SiMe_4$ in an n.m.r. tube. Difluorophosphine (0.5 mmol) was then condensed into the tube, which was then sealed. The solution was then warmed briefly to 270 K, with the formation of substantial amounts of an orange-red solid. Spectra were recorded at 215 K, but decomposition continued at this temperature, and several samples were required for a complete set of spectra to be obtained. Spectra were recorded using Varian Associates XL100 and HA100 spectrometers.

Attempted Isolation of $PF_2H_2(NH_2)$.—Ammonia (0.5 mmol) and PF_2H (0.5 mmol) were condensed together in a glass ampoule and warmed rapidly. On melting they formed a yellow solid which became orange and then brown. After 1 min the volatile materials present were fractionated, but PF_3 (0.3 mmol) was the only product isolated.

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