Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Phosphoranes. II. Bis(dimethylamino)trifluoromethylfluorophosphoranes

DANIEL D. POULIN and RONALD G. CAVELL*

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Pyrolysis of $(CF_3)_3P[N(CH_3)_2]_2$ *in vacuo* at 100° yields $(CF_3)_2FP[N(CH_3)_2]_2$, and at 215° $(CF_3)F_2P[N(CH_3)_2]_2$ is formed. The difluorophosphorane (mp −17°) yields $CF_3P(O)[N(CH_3)_2]_2$ and $CF_3PO_3^{2-}$ upon alkaline hydrolysis. The ^{19}F nmr spectrum is temperature independent to −120° in keeping with a trigonal-bipyramidal structure with axial F substituents. The value of $^2J_{PF}$ (150 Hz) is typical of an equatorial CF_3 group. The monofluorophosphorane (mp +15°) yields CF_3H quantitatively and $CF_3PO_3^{2-}$ on alkaline hydrolysis. Acid hydrolysis gave some CF_3H but mainly $(CF_3)_2PO_2^-$ and $CF_3PO_3H^-$. Hydrogen chloride gave $(CF_3)_2PFCl_2$, $(CF_3)_2PCl_3$, and some unidentified compound. ^{19}F nmr spectra of the monofluorophosphorane are temperature dependent showing an averaged $^2J_{PF}$ coupling constant above room temperature and partially resolving to an equatorial ($^2J_{PF} = 125$ Hz) and an axial CF_3 group. Additional secondary processes complicate the spectrum so that the axial coupling was not completely resolved. Infrared and mass spectral data are reported for the new phosphoranes.

Introduction

The fluorophosphoranes $(CF_3)_3PF_2$, $(CF_3)_2PF_3$, and CF_3PF_4 decompose at ordinary temperatures by elimination of the CF_2 radical and form a series which leads ultimately to PF_5.[1] The only other trifluoromethylphosphorane whose thermal decomposition has been studied[2] is $(CF_3)_3P[OSi(CH_3)_3]_2$ which appeared to decompose by two major routes, the first leading to $(CF_3)_2P(O)OSi(CH_3)_3$, $(CH_3)_3SiF$, and CF_2 polymers (the latter two presumably arising from decomposition of the unknown $(CH_3)_3SiCF_3$) and the second giving $(CF_3)_3PO$ and $[(CH_3)_3Si]_2O$,[2] which is the reverse of the formation reaction. We report herein a study of the pyrolysis of $(CF_3)_3P[N(CH_3)_2]_2$[3] which yields $(CF_3)_2PF[N(CH_3)_2]_2$ and $CF_3F_2P[N(CH_3)_2]_2$ by successive difluorocarbene eliminations.

Experimental Section

Materials, Apparatus, and Techniques. All manipulations were carried out using standard vacuum techniques in a system constructed with Pyrex glass with stopcocks lubricated with Apiezon N grease. Involatile materials which remained in the reaction vessels were handled in a nitrogen atmosphere while aqueous solutions were handled in the air since it had been found by experience that such products were invariably air stable.

Materials. Trifluoromethyliodophosphines and $(CF_3)_3P$ were prepared from the reaction of CF_3I (Columbia Organic Chemical Co.) with red phosphorus at 220° for 48 hr.[4] The phosphorane $(CF_3)_3P[N(CH_3)_2]_2$ was prepared from $(CF_3)_3PCl_2$[4] and dimethylamine as described elsewhere.[3] Commercially available chemicals of "reagent" grade were used without further purification. Gaseous reagents were usually fractionated before use to remove any moisture or gross impurities.

Instrumental Techniques. Infrared spectra of gases were obtained using a 9-cm gas cell with potassium bromide windows. All spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. Gaseous samples were introduced *via* a heated inlet, low volatile liquids *via* a heated capillary, and solids by means of the direct probe. All nmr spectra were recorded with a Varian A-56/60, a Varian HA 100, or a Bruker HFX-90 spectrometer. Proton spectra were recorded at 60.0 MHz and fluorine spectra at 56.4 MHz using the A-56/60 instrument. In the case of the HA 100 instrument, proton spectra were recorded at 100 MHz and fluorine spectra at 94.1 MHz while for the Bruker the proton spectra were recorded at 90 MHz and the fluorine spectra at 84.67 MHz. Proton and fluorine spectra were routinely recorded on samples containing an approximate 10% solution of the compound in $CFCl_3$ or CF_2Cl_2. Nmr measurements for involatile products were obtained in solutions of CH_2Cl_2, $CHCl_3$, CD_3CN, or H_2O. Fluorine chemical shifts were measured relative to internal $CFCl_3$ solvent. In cases where other solvents were employed an external $CFCl_3$ (capillary) reference was used. Proton chemical shifts were measured relative to external tetramethylsilane (TMS) as a 5% solution in $CFCl_3$ in all cases. Each instrument was equipped with a variable-temperature controller which was established as accurate to within ±5° of the temperature indicated on the controller by calibration.

Prolysis of $(CF_3)_3P[N(CH_3)_2]_2$. (a) At 100°. $(CF_3)_3P[N(CH_3)_2]_2$[3] (0.520 g, 1.59 mmol) was heated for 2.5 hr at 100°. The major product, trapped at −45°, was a 75% yield of the phosphorane $(CF_3)_2FP[N(CH_3)_2]_2$ (0.329 g, 1.19 mmol). The more volatile products consisted of a mixture (0.071 g) of $(CF_3)_2PN(CH_3)_2$,[5,6] $(CF_3)_3P$,[4,6] CF_3H, $(CF_2)_3$ (ϕ_F 158.8 ppm, lit.[7] for neat liquid 160.9 ppm), and $(CF_2)_2$ (ϕ_F 134.1 ppm, lit.[8] 134.6 ppm as a 10% solution in $CFCl_3$) in the molar ratio 1:1.6:8.0:21:44 (by nmr spectroscopy). Thus the overall yield of $(CF_2)_n$ was 0.062 g (1.24 mmol of "CF_2," 78%). The nmr spectra of the brown involatile oil which remained in the reaction vessel showed that it contained a trace of $(CF_3)_2FP[N(CH_3)_2]_2$ and a product containing CF_3 and $N(CH_3)_2$ groups on P which had identical nmr parameters (ϕ_F 60.8 ppm, $^2J_{PF} = 116$ Hz, τ 6.95, and $^3J_{PH} = 11.4$ Hz) to a species that we have identified elsewhere[11] as the phosphonium ion, $(CF_3)_2P[N(CH_3)_2]_2^+$.

The monofluorophosphorane $(CF_3)_2PF[N(CH_3)_2]_2$ is a colorless solid melting at 15°. It is stable over a period of months at room temperature. Its spectroscopic properties are given in Tables I (ir), II (nmr), and III (mass spectroscopy). Some reactions are described below.

(b) **At 215°.** A sample of $(CF_3)_3P[N(CH_3)_2]_2$[3] (0.099 g, 0.30 mmol) was heated for 2 hr at 215°. The major product, collected at −96°, was a mixture (0.036 g) of the new phosphorane $(CF_3)F_2P[N(CH_3)_2]_2$ (0.033 g, 0.15 mmol) in a 50% yield and $(CF_3)_2PN(CH_3)_2$[5,6] (0.003 g, 0.01 mmol). Pure $(CF_3)_2FP[N(CH_3)_2]_2$ was obtained by careful refractionation of the crude product. The more volatile mixture (0.031 g) trapped at −196° contained CF_3H, $(CF_2)_3$,[7] and $(CF_2)_2$[8] in the molar ratio 1:2.4:2.7 (by nmr spectroscopy). The brown solid which remained in the reaction vessel did not dissolve in CD_3CN and was not identified.

The new difluorophosphorane $(CF_3)F_2P[N(CH_3)_2]_2$ melts at −17° forming a colorless liquid which is stable over long periods of time at room temperature. It was characterized by its spectroscopic properties (ir, Table I; nmr, Table II; mass spectroscopy, Table III) and by hydrolysis.

Reactions of $(CF_3)_2PF[N(CH_3)_2]_2$. (a) Alkaline Hydrolysis. Hydrolysis of $(CF_3)_2PF[N(CH_3)_2]_2$ (0.118 g, 0.43 mmol) with 0.5 ml of degassed 10% NaOH solution for 24 hr at room temperature gave CF_3H (0.033 g, 0.47 mmol). The ^{19}F nmr spectrum of the remaining aqueous solution indicated the presence of the $CF_3PO_3^{2-}$ ion.[9]

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(1) W. Mahler, *Inorg. Chem.*, 2, 230 (1963).

(2) R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, 11, 2578 (1972).

(3) D. D. Poulin and R. G. Cavell, *Inorg. Chem.*, 13, 2324 (1974).

(4) F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1963).

(5) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

(6) K. J. Packer, *J. Chem. Soc.*, 960 (1963).

(7) M. G. Barlow, R. Fields, and F. P. Temme, *Chem. Commun.*, 1671 (1968).

(8) G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 87, 5356 (1965).

(9) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 10, 2720 (1971).

Table I. Infrared Spectra of $(CF_3)F_2P[N(CH_3)_2]_2$ and $(CF_3)_2FP[N(CH_3)_2]_2$[a]

$(CF_3)F_2P$ $[N(CH_3)_2]_2$	$(CF_3)_2FP[N(CH_3)_2]_2$	Assignment
3042 vw, sh	3040 vw, sh	ν(C–H)
2952 m	3010 vw	
2923 w, sh	2943 m	
2880 w	2920 w, sh	
2830 w	2879 w	
	2830 w	
1470 w	1467 w	$\delta(CH_3)$, $\nu_s(C_2\text{–}N)$
1297 m	1290 m	
1217 s	1224 m, sh	ν(C–F)
1176 vs	1195 vs	
	1154 vs, sh	
1131 vs	1135 vs	
1070 vw	1085 m	$\nu_{as}(C_2\text{–}N)$
1023 vs	1004 s	
	830 w	
811 s	755 m	ν(P–F)
771 m		
	727 w	$\delta_{as}(CF_3)$
673 s	662, 678 s, doublet	$\nu_{as}(N_2\text{–}P)$
609 w	609 vw	
541 m	502 vw	$\delta_{as}(CF_3)$

[a] All values in cm^{-1}. Abbreviations: ν, stretching; δ, deformation; s, strong; m, medium; w, weak; v, very; sh, shoulder; as, antisymmetric; s, symmetric.

Table II. Nmr Parameters of Trifluoromethylaminofluorophosphoranes (ϕ, ppm; J, Hz)

	Temp, °C	$\phi_{CF_3}{}^a$	$\phi_F{}^a$	$\tau_H{}^b$	$^2J_{PF}$	$^3J_{HP}$	$^5J_{HF}$	$^1J_{FP}$	$^4J_{FH}$	$^3J_{FF}$	$^4J_{FF}$
$(CF_3)_2PF[N(CH_3)_2]_2$	+40	58.2		7.43	~88[f]	11.6	0.60				
			32.6					792	3.1		
	−90[d]	61.4			125.5[g]					6.0	21.5
		56.2			*c*						
		49.6			*c*						
	+75[e]	59.9			86					16	
$CF_3PF_2[N(CH_3)_2]_2$	+40	68.6		7.44	150[g]	10.1	~0			17.8	
			58.9					794	2.7		

[a] *Vs.* CCl_3F; positive values represent resonances to high field of standard. [b] *Vs.* TMS; τ 10.0. [c] Complex multiplet, not assignable. [d] Obtained on a CF_2Cl_2 solution. [e] Obtained on a C_6F_6 solution. [f] Approximate separation of two components of a broad multiplet. [g] Assigned to equatorial CF_3 group.

(b) **Acid Hydrolysis.** Hydrolysis of $(CF_3)_2FP[N(CH_3)_2]_2$ (0.084 g, 0.31 mmol) with 0.5 ml of degassed distilled H_2O initially adjusted to pH ~1 at room temperature for 24 hr gave CF_3H (0.006 g, 0.09 mmol). The ^{19}F nmr spectrum of the remaining aqueous solution indicated the presence of $(CF_3)_2PO_2^-$ and $CF_3PO_3H^-$ ions in the ratio of 2:1.[9]

(c) **Reaction of the Monofluorophosphorane with Hydrogen Chloride.** A sample of $(CF_3)_2FP[N(CH_3)_2]_2$ (0.202 g, 0.73 mmol) was allowed to react with an excess of anhydrous HCl (0.587 g, 21.9 mmol) for 10 min at room temperature. Vacuum fractionation of the volatile products gave a mixture (0.019 g) trapping at −116° which contained $(CF_3)_2PCl_3$[10,11] and $(CF_3)_2FPCl_2$[12] in the ratio 1:5 (by nmr spectroscopy) and a mixture (0.528 g) of mainly HCl with at least two additional unidentified compounds which also trapped at −196°.

Alkaline Hydrolysis of $CF_3PF_2[N(CH_3)_2]_2$. Hydrolysis of $(CF_3)F_2P[N(CH_3)_2]_2$ (0.025 g, 0.11 mol) with 0.3 ml of degassed 10% NaOH solution for 48 hr gave no CF_3H. Nmr spectra of the remaining aqueous solution indicated the presence of $CF_3P(O)[N(CH_3)_2]_2$ (by comparison of the nmr parameters with those of an authentic sample[3]) and the $CF_3PO_3^{2-}$ ion[9] in the ratio 1:1:5 and a species giving rise to a singlet in the ^{19}F nmr spectrum at ϕ_F 121.3 ppm which is either[13] F^- or HF_2^-.

Results and Discussion

Pyrolysis Reactions. The thermal decomposition of trifluoromethylphosphoranes leading to the formation of difluorocarbene has been observed for $(CF_3)_3PF_2$, $(CF_3)_2PF_3$, and CF_3PF_4. In the absence of a trapping agent, the CF_2 radical forms both the dimer C_2F_4 and the trimer C_3F_6 in varying proportions depending on the pyrolysis conditions.[1]

The pyrolysis of $(CF_3)_3P[N(CH_3)_2]_2$ proceeded similarly. After 2.5 hr at 100°, the compounds $(CF_3)_2FP[N(CH_3)_2]_2$, $(CF_2)_3$,[7] and $(CF_2)_2$[8] were produced according to the eq 1 and 3.

$$(CF_3)_3P[N(CH_3)_2]_2 \rightarrow (CF_3)_2FP[N(CH_3)_2]_2 + CF_2 \quad (1)$$

$$(CF_3)_3P[N(CH_3)_2]_2 \rightarrow (CF_3)F_2P[N(CH_3)_2]_2 + 2CF_2 \quad (2)$$

$$nCF_2 \rightarrow (CF_2)_n \quad n = 2, 3 \quad (3)$$

At 215° for 2 hr pyrolysis of $(CF_3)_3P[N(CH_3)_2]_2$ gave $(CF_3)F_2P[N(CH_3)_2]_2$, $(CF_2)_3$, and $(CF_2)_2$ according to eq 2 and 3. As in the previous case, $(CF_3)_2PN(CH_3)_2$ and CF_3H were again present in very small amounts. In both cases the difluorocarbene produced forms dimeric and trimeric products. At the higher pyrolysis temperature both dimeric (C_2F_4) and trimeric (C_3F_6) fluorocarbons are found in roughly equal proportions but at lower temperatures the dimeric species dominated, being present in a twofold molar ratio relative to the trimeric product. Total yields of the difluorocarbene polymers corresponded well with the yield of $(CF_3)_2FP[N(CH_3)_2]_2$ or $CF_3PF_2[N(CH_3)_2]_2$ although the relative amounts of the dimer and trimer varied somewhat between different preparations. Also found in the products were small amounts of $(CF_3)_2PN(CH_3)_2$,[5,6] $(CF_3)_3P$,[4,6] and CF_3H which arise from unknown secondary decomposition pathways.

Attempts to prepare $(CF_3)F_2P[N(CH_3)_2]_2$ by heating $(CF_3)_2FP[N(CH_3)_2]_2$ for 10 days at 100° resulted in the recovery of unchanged starting materials. Heating $(CF_3)_2FP[N(CH_3)_2]_2$ for 2 days at 200° gave large amounts of black involatile solid which did not dissolve in CD_3CN and a small amount of unidentified volatile material. Heating $(CF_3)_3P[N(CH_3)_2]_2$ for 48 hr at 200° gave only large amounts of black involatile solid and small amounts of CF_3H and other unidentified volatile products but no detectable amount of the third member of the series $F_3P[N(CH_3)_2]_2$, which, although known,[14] may not be stable under the conditions used.

Characterization of the Phosphoranes. The alkaline hydrolysis of $(CF_3)_2FP[N(CH_3)_2]_2$ gave 1 molar equiv of CF_3H and 1 molar equiv of $CF_3PO_3^{2-}$ according to eq 4. Di-

$$2(CF_3)_2FP[N(CH_3)_2]_2 + 5OH^- + H_2O \rightarrow 2CF_3PO_3^{2-} + 4(CH_3)_2NH + 2CF_3H + HF_2^- \quad (4)$$

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(10) H. J. Emeleus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 563 (1955).

(11) D. D. Poulin and R. G. Cavell, unpublished results.

(12) J. F. Nixon, *J. Inorg. Nucl. Chem.*, **31**, 1615 (1969).

(13) R. Haque and L. W. Reeves, *J. Amer. Chem. Soc.*, **89**, 250 (1967).

(14) R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, **3**, 753 (1964).

Table III. Mass Spectra of $(CF_3)_2FP[N(CH_3)_2]_2$ and $(CF_3)F_2P[N(CH_3)_2]_2$

	Rel intens[a]		
m/e	$(CF_3)_2FP$-$[N(CH_3)_2]_2$[b]	CF_3PF_2-$[N(CH_3)_2]_2$	Assignment
257	0.5[c]		$C_6F_6H_{12}N_2P$
238	1.2		$C_6F_5H_{12}N_2P$
232	9.5[d]		$C_4F_7H_6NP$
226		0.7[e]	$C_5F_5H_{12}N_2P$
207	1.2	0.5[f]	$C_5F_4H_{12}N_2P$
195	1.4		$C_4F_5H_7NP$
194	26.4		$C_4F_5H_6NP$
182	7.4	9.9[g]	$C_3F_5H_6NP$
178	1.1		$C_3F_5H_2NP$
169	2.1		C_2F_6P
160	1.6		$C_3F_4H_3NP$
157	1.8	4.4	$C_4F_2H_{12}N_2P$
153		1.1	$C_4F_2H_8N_2P$
151		1.7	$C_4F_2H_6N_2P$
144	2.0		$C_3F_3H_6NP$
137		0.6	$C_4FH_{11}N_2P$
133		0.5	$C_4FH_7N_2P$
132	5.5	18.7	$C_2F_3H_6NP$
126	1.0		$C_4F_2H_{12}N_2$
121		1.4	$C_3FH_7N_2P$
119		5.1	CF_4P
117		5.1	CF_3H_3NP
116		0.6	CF_3H_2NP
112		1.8	$C_2F_2H_5NP$
110	1.0		$C_2F_2H_3NP$
105		1.4	C_3FH_5NP
103		9.6	CF_3H_3P
101		14.4	CF_3HP
94	6.5	7.6	C_2FH_6NP
86		1.5	CF_2H_5P
85		3.8	CF_2H_4P
84		4.0	CF_2H_3P
83		1.8	CF_2H_2P
82		4.1	CF_2HP
69	6.4	3.3	CF_3, PF_2
66		4.5	CFH_4P
58	2.1		$C_2H_6N_2$
51	1.2		FHP
49		3.7	H_4NP
47		5.1	H_2NP
44	3.0	3.5	C_2H_6N
43	1.6	2.6	C_2H_5N
42	6.5	12.0	C_2H_4N
35		3.6	FH_2N
32	5.2		PH
31	0.7	3.2	CF

[a] Intensities are expressed relative to the total ionization defined as Σ_n(intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. [b] Parent ion not observed. [c] The identity of this peak was established by mass measurement: Calcd for $C_6F_6H_{12}N_2P$, *m/e* 257.0640; found, *m/e* 257.0644. [d] Identity established by mass measurement: calcd for $C_4F_7H_6NP$, *m/e* 232.0125; found, *m/e* 232.0118. [e] Identity established by mass measurement: calcd for $C_5F_5H_{12}N_2P$, *m/e* 226.0656; found, *m/e* 226.0656. [f] Identity established by mass measurement: calcd for $C_5F_4H_{12}N_2P$, *m/e* 207.0672; found, *m/e* 207.0666. [g] Identity established by mass measurement: calcd for $C_3F_5H_6NP$, *m/e* 182.0157; found, *m/e* 182.0154.

methylamine was present in the hydrolysate and no P-N-$(CH_3)_2$ species were observed.

Hydrolysis in an acidic medium (pH ~1) gave 0.30 molar equiv of CF_3H, 0.30 molar equiv of $CF_3PO_3H^-$, and 0.70 molar equiv of $(CF_3)_2PO_2^-$. The formation of additional amounts of CF_3H and the $CF_3PO_3H^-$ ion presumably arises from subsequent slow hydrolysis of $(CF_3)_2PO_2^-$ by acid in the solution. Similar behavior was noted during the hydrolysis of $(CF_3)_3P[N(CH_3)_2]_2$.[3]

Alkaline hydrolysis of $CF_3PF_2[N(CH_3)_2]_2$ gave no CF_3H, and a mixture of $CF_3PO_3^{2-}$ and $CF_3P(O)[N(CH_3)_2]_2$[3] was found in the solution. The formation of $CF_3P(O)[N(CH_3)_2]_2$ indicates the resistance of the P-N linkage to hydrolysis in this compound. A similar result was observed in the case of hydrolysis of $CF_3P[N(CH_3)_2]_3^+$ which gave only $OP[N(CH_3)_2]_3$.[15]

The reaction of $(CF_3)_2FP[N(CH_3)_2]_2$ with excess HCl proceeded in very low yield to form $(CF_3)_2FPCl_2$. This compound was identified by comparison of its ir spectrum with that reported in the literature.[12] The ^{19}F nmr spectrum at room temperature showed a doublet of doublets (ϕ_F 77.0 ppm, $^2J_{FP} = 184$ Hz, $^3J_{FF} = 14$ Hz), but the compound was present in a too small quantity to allow observation of the fluorine atom signal which would be split into a doublet of septets. Also produced in this reaction were small amounts of $(CF_3)_2PCl_3$ and several other unidentified species.

Infrared Spectra of Fluorophosphoranes. The ir spectrum of $(CF_3)_2FP[N(CH_3)_2]_2$ (Table I) showed the expected CF_3 and CH_3 absorptions and also showed peaks at 1085 and 1004 cm^{-1}, 755 cm^{-1}, and a doublet at 678 and 662 cm^{-1} which were attributed to asymmetric C_2N stretching, P-F stretching, and asymmetric N_2P stretching vibrations, respectively. The relatively low P-F stretching frequency is compatible with an axial fluorine substituent.[16]

The ir spectrum of $(CF_3)F_2P[N(CH_3)_2]_2$ (Table I) shows bands due to CF_3 and $N(CH_3)_2$ groups. Absorptions appearing at 1023, 811 and 770, and 673 cm^{-1} can be assigned to asymmetric C_2N stretching, P-F stretching, and asymmetric N_2P stretching vibrations, respectively.

Mass Spectra. The compound $(CF_3)_2PF[N(CH_3)_2]_2$ does not show a parent ion in the mass spectrum, a property typical of pentacoordinate phosphorus compounds.[17] The ions at *m/e* 232 and 257 were found by accurate mass measurement to be the $C_4F_7H_6NP^+$ and $C_6F_6H_{12}N_2P^+$ ions whose formation can be explained by the loss of $N(CH_3)_2$ and F, respectively, from the unobserved parent $(CF_3)_2FP[N(CH_3)_2]_2$.

The compound $CF_3PF_2[N(CH_3)_2]_2$ shows a weak parent ion at *m/e* 226, identified as such by mass measurement. The ions at *m/e* 207 and 182 were identified as $C_5F_4H_{12}N_2P^+$ and $C_3F_5H_6NP^+$, respectively, by mass measurement. The formation of these two ions can be explained by the loss of F and $N(CH_3)_2$, respectively, from the parent $(CF_3)F_2P[N(CH_3)_2]_2$. The complete data are given in Table III.

Nmr Spectroscopy of Fluorophosphoranes and Substitutional Preferences of Groups. (a) The Difluorophosphorane. This compound presents the simplest nmr spectrum of the two fluorophosphoranes considered herein since the two fluorine atoms, being more electronegative than the CF_3 group, are expected[16] to occupy the axial positions of the trigonal-bipyramidal framework, constraining the CF_3 and $N(CH_3)_2$ groups to the equatorial plane. As expected, therefore, the spectrum is essentially temperature independent; however at low temperatures changes in chemical shift and the possibility of restricted rotation of the $N(CH_3)_2$ groups allow the second-order character, in part evident at room temperature, to become more prominent and complicate the spectrum. The CF_3 groups however do not appear to be involved in a pseudorotatory exchange process as in the case of the monofluorophosphorane (*vide infra*) or $(CF_3)_3P[N(CH_3)_2]_2$,[3] and all principal features of the spectrum are obtainable from the room-temperature spectrum.

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(15) D. D. Poulin and R. G. Cavell, in preparation.

(16) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963).

(17) T. A. Blazer, R. Schmutzler, and I. K. Gregor, *Z. Naturforsch. B*, 24, 1081 (1969).

The room-temperature ^{1}H nmr spectrum of $CF_3PF_2[N(CH_3)_2]_2$ shows a doublet of triplets arising from methyl group protons coupling to phosphorus ($^3J_{PH}$ = 10.4 Hz) and to the two fluorine atoms ($^4J_{FH}$ = 2.7 Hz) bound to phosphorus. The absence of any fine structure in the expansion of this doublet of triplets indicates that the magnitude of coupling between the fluorine atoms on the CF_3 group and the protons in the $N(CH_3)_2$ substituents is below the resolution of the instrument. Typical values for this coupling $^5J_{FH}$ were obtained from other related compounds[3,6] ranging from 0.60 to 1.09 Hz.

The room-temperature ^{19}F nmr spectrum of $CF_3PF_2[N(CH_3)_2]_2$ appears as a doublet of triplets and a doublet of broad multiplets in the intensity ratio of 3:2, respectively. The signal of intensity 3 arises from the CF_3 group which is coupled to phosphorus ($^2J_{PF}$ = 150 Hz) and to the fluorine atom ($^3J_{FF}$ = 17.8 Hz) while the signal of intensity 2 arises from the two directly bound fluorine atoms coupled to phosphorus ($^1J_{PF}$ = 794 Hz), to the CF_3 group, and to the two $N(CH_3)_2$ groups. The latter two couplings should split each component of the doublet into a quartet of 13-line multiplets, but the low intensity and width of these signals did not permit sufficient resolution to confirm this. The doublet of triplets arising from the CF_3 group showed some asymmetry in peak height and intensity, a feature which was particularly evident in the triplet nearest the fluorine atom signal. Although attempts to compute a spectrum showing the same intensity features as that observed were unsuccessful, it seems likely that the asymmetry results from a second-order spectrum of the A_2B_3X type in which the chemical shift difference between CF_3 and F bound to P is sufficiently small to cause partial second-order effects similar to the behavior of the $(CF_3)_2PF_4^-$ ion.[18] Further study of the system is in progress.

It is important to note that $^2J_{PF}$ is rather large (150 Hz) in this compound in keeping with the suggestion[3,20] that equatorial CF_3 groups will be characterized by large values of $^2J_{PF}$ and axial CF_3 substituents by small values of this coupling constant. Since F is definitely more apicophilic[19,20] than CF_3 on simple considerations of electronegativity, this difluorophosphorane should exhibit characteristics of exclusive equatorial CF_3 substitution.

(b) The Monofluorophosphorane. With only one fluorine substituent and with the tendency of the two alkylamino substituents (possibly as a result of their strong π-bonding tendencies) to occupy preferentially equatorial positions[3,19,20] of the trigonal-bipyramidal framework, the CF_3 groups must occupy both axial and equatorial locations at ordinary temperatures and this is reflected in the temperature dependence of the nmr spectra of this monofluorophosphorane.

The room-temperature ^{1}H nmr spectrum (Figure 1) of $(CF_3)_2FP[N(CH_3)_2]_2$ shows a doublet of doublets of septets arising from the coupling of the protons to a phosphorus atom ($^3J_{PH}$ = 11.6 Hz), to a fluorine atom ($^4J_{FH}$ = 3.1 Hz), and to six equivalent fluorine atoms ($^5J_{FH}$ = 0.6 Hz) thus confirming the presence of two CF_3 groups and one F atom on phosphorus. The ^{1}H nmr spectrum remained unchanged on cooling the sample to −70° indicating that the $N(CH_3)_2$ groups were magnetically equivalent to this temperature.

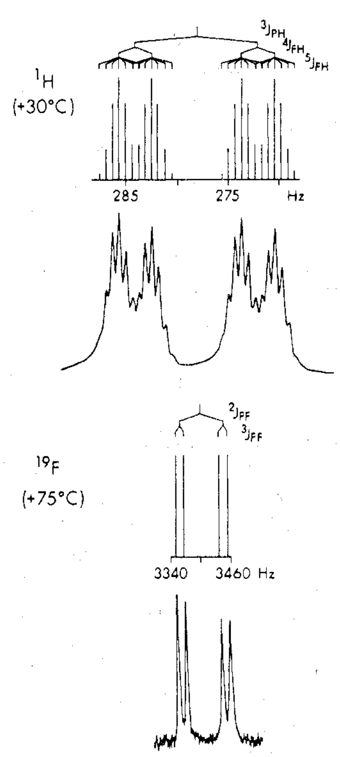

Figure 1. Averaged ^{1}H spectra and CF_3-region ^{19}F spectra of $(CF_3)_2PF[N(CH_3)_2]_2$. The upper spectrum, obtained at +30° on a CCl_3F solution at 60 MHz, shows the coupling of the amino methyl protons to all other magnetic nuclei in the molecule as indicated by the stick diagram calculated with values given in Table II. The lower spectrum was obtained at +75° on a C_6F_6 solution at 56.4 MHz and shows the averaged coupling of the CF_3 groups to phosphorus and to the single fluorine bound to phosphorus as indicated by the stick diagram. Values used are given in Table II.

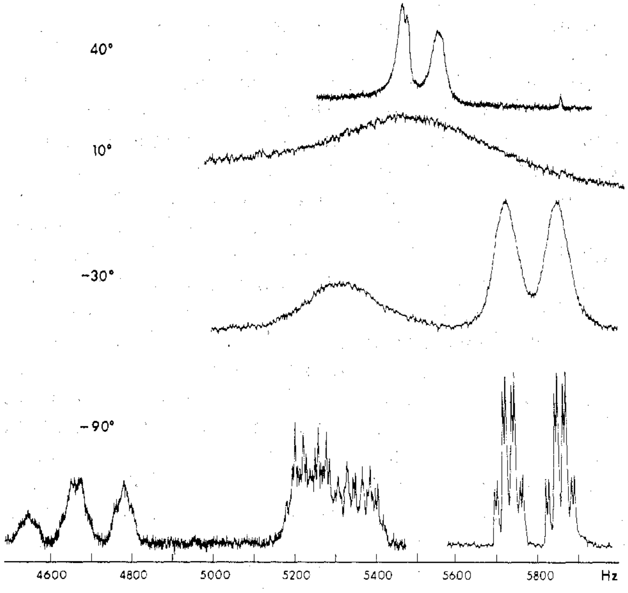

Figure 2. Temperature dependence of the CF_3 portion of the spectrum of $(CF_3)_2PF[N(CH_3)_2]_2$ obtained at 94.1 MHz on an approximately 1:1 $CFCl_3$-CF_2Cl_2 solution. The scale gives cycles to high field of the CCl_3F standard and the spectra are discussed in the text.

The room-temperature ^{19}F nmr spectrum of $(CF_3)_2FP[N(CH_3)_2]_2$ (Figure 2, 40°) shows a broad doublet with a coupling ($^2J_{FP}$ = 88 Hz) due to the CF_3 signals. A second broad doublet with a major coupling $^1J_{FP}$ of 790 Hz (φ 32.6 ppm) which had one-sixth of the intensity of the first doublet was also observed at lower field and is not shown in

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(18) E. O. Bishop, P. R. Carey, J. F. Nixon, and J. R. Swain, *J. Chem. Soc. A*, 1074 (1970).

(19) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, 4, 288 (1971).

(20) R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J. Chem. Soc., Chem. Commun.*, 19 (1974).

Figure 2. It was apparent that at room temperature an average $^2J_{PF}$ is observed, presumably as a result of a psuedorotatory process since the more electronegative fluorine atom would be expected[16] to occupy preferentially the axial environment requiring the CF_3 groups to occupy both axial and equatorial positions. Heating to 75° increased the rate of the averaging process and resulted in a sharpening of the broad doublet arising from the CF_3 substituents such that a doublet of doublets (Figure 1), which are assigned to the averaged coupling of CF_3 fluorine atoms to the phosphorus atom and the unique fluorine atom ($^2J_{PF} = 86$ Hz, $^3J_{FF} = 16$ Hz), was observed.

The low-temperature ^{19}F nmr spectrum of the monofluorophosphorane gave rise to four chemically shifted regions at −90°. This spectrum is unchanged at −105° suggesting that a limiting spectrum has been obtained. Three of these signals, which integrated in the approximate ratio of 1:2:3, can be assigned to CF_3 groups (Figure 2) which suggests that the two CF_3 groups are divided into axial and equatorial environments at this temperature. Further, the splitting patterns suggest that a secondary averaging process (such as rotation of the $N(CH_3)_2$ groups about the PN bond) has been slowed down such that the F atoms in one CF_3 group have become nonequivalent giving rise to second-order nmr spectral behavior. Thus the highest field area of intensity 3 is due to the CF_3 group which is unaffected by this secondary process (the equatorial CF_3 group) and this area of the spectrum appears as a doublet of quartets of doublets ($^2J_{FP} = 125.5$ Hz, $^4J_{FF} = 21.5$ Hz, $^3J_{FF} = 6.0$ Hz) with the $^4J_{FF}$ coupling constant being caused by equal coupling to the three fluorine atoms of the axial CF_3 group. The other two signals (intensity 1:2) showed much more complex fine structure and both appeared to be coupled to each other as well as to the P atom, the fluorine atom attached to phosphorus, and the equatorial CF_3 group. Furthermore the proximity of coupling constant and chemical shift difference between the axial CF_3 and the single F directly bound to P is probably partly responsible for the complexity of the spectrum at the low-field end. The signal from the directly bound fluorine was not explicitly observed at low temperature (this signal was difficult to observe even at room temperatures because of its low relative intensity and the extensive splitting of the signal due to spin-coupling interactions with the different CF_3 groups and with the 12 amino protons). It is possible that at the lowest temperatures a portion of the directly bound fluorine signal is incorporated in the signals observed at the lowest field end of the so-called CF_3 region of the spectrum. Exchange processes could also lead to collapse of the signal with consequent nonobservance of this signal bound fluorine but this is unlikely. These features are similar to those observed in the low-temperature spectra of $(CF_3)_3P[N(CH_3)_2]_2$[3] and $(CF_3)_3P[OSi(CH_3)_3]_2$.[2] From the average value of 86 Hz for $^2J_{PF}$ at room temperature and $^2J_{PF}(eq)$ value of 125 Hz observed above we may deduce that $^2J_{FP}(ax)$ is about 50 Hz, similar to that observed for equatorial $^2J_{PF}$ in $(CF_3)_3P[N(CH_3)_2]_2$.[3]

It is also worth noting that we have apparently obtained the essential features (chemical shift and P–F coupling constant) of the equatorial CF_3 group at −30° and further cooling adds fine structure due to other couplings and the onset of second-order effects but does not appear to change the parameters associated with the equatorial group.

The behavior of these fluorophosphoranes provides further support for the suggestion[3,20] that CF_3PF_4, $(CF_3)_2PF_3$, and $(CF_3)_3PF_2$ with $^2J_{PF}$ values of 172,[21] 175,[16,21] and 167[21] Hz, respectively, should be consistently interpreted in terms of equatorial CF_3 groups since the presence of axial CF_3 groups appears to be betrayed by characteristically low $^2J_{PF}$ values.[20] In addition these and other[2,3,11,20] results suggest that CF_3 is capable of existing in more than one environment although it appears to prefer an equatorial location when halogens are also present. The process by which axial and equatorial environments are interconverted has a relatively large barrier since axial and equatorial environments appear to be distinguishable at relatively high temperatures (approximately −30 to −50° in $(CF_3)_2PF[N(CH_3)_2]_2$, −40° in $(CF_3)_3P[N(CH_3)_2]_2$[3]). It seems therefore reasonable to suggest that those CF_3 compounds which exhibit large coupling constants and no change of the CF_3 portion of the spectrum with temperature, such as CF_3PF_4,[11,21] $(CF_3)_2PF_3$,[11,16] $(CF_3)_3PF_2$,[11,21] $(CF_3)_2PCl_3$,[3,11] $(CF_3)_3PCl_2$,[6,11] $(CF_3)_2PCl_2N(CH_3)_2$,[3,21] and $CF_3PF_2[N(CH_3)_2]_2$ in the present case are examples of equatorial CF_3 groups on five-coordinate phosphorus. Since it seems to be relatively easy to resolve CF_3 in different environments, the lack of resolution in the fluorophosphoranes provides stronger support for equivalent CF_3 location than chemical shift arguments.[3,16] Our studies have shown that the chemical shift of both CF_3 and F on phosphorus is subject to relatively wide variations with substituents[22] and is therefore not reliably treated as an invariant parameter for structural interpretations.

Observation of directly bound $^1J_{PF}$ coupling constants and spin-spin splitting patterns consistent with the formulas given for each of the fluorophosphoranes provides the best direct evidence that both new compounds are truly five-coordinate phosphoranes and not phosphonium salts. There is evidence that the phosphonium salt $(CF_3)_2P[N(CH_3)_2]_2^+F^-$ is also formed as an involatile product of the 100° pyrolysis and its nmr parameters are markedly different from those due to either of the two fluorophosphoranes. This difference of nmr parameters, plus the expected involatility and the insolubility of the phosphonium salt in CCl_3F, indicates that phosphonium salts are not likely to be confused with phosphoranes in this system and we can be confident of our identification of these compounds as phosphoranes.

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Registry No. $(CF_3)F_2P[N(CH_3)_2]_2$, 52500-14-8; $(CF_3)_2FP[N(CH_3)_2]_2$, 51874-43-2; $(CF_3)_3P[N(CH_3)_2]_2$, 52553-43-2.

(21) R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 4, 496 (1965).
(22) R. G. Cavell, A. A. Pinkerton, and A. J. Tomlinson, unpublished data.