Phosphorus–Fluorine Chemistry. Part XXIX.[1] Reaction of Aminosilanes and *N*-Alkyl(or aryl)hexamethyldisilazanes with Fluorophosphoranes: Chemical and Spectroscopic Studies on Dialkylaminofluorophosphoranes and Fluoro-1,3,2,4-diazadiphosphetidines

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The reaction of phosphorus pentafluoride and its organic derivatives, R_nPF_{5-n} (n = 1, 2) with *NN'*-disubstituted aminotrimethylsilanes, $R_2N{\cdot}SiMe_3$, provides a facile method of synthesis of fluorophosphoranes of types R_2NPF_4, $(R_2N)_2PF_3$, $RPF_3NR'_2$, and $R_2PF_2NR'_2$. When PF_5 and RPF_4 are allowed to react with *N*-substituted hexamethyldisilazanes, $RN(SiMe_3)_2$, the cyclic fluorophosphoranes, $[RNPF_3]_2$ and $[R'NPF_2R]_2$, are formed. Diphenyltrifluorophosphorane with $MeN(SiMe_3)_2$ gives only a monomeric fluorophosphine imide, $MeNPFPh_2$. All the compounds reported are of stereochemical interest, as derivatives of phosphorus pentafluoride. Their ^1H, ^{19}F, and ^{31}P n.m.r. spectra are presented and discussed.

It has been observed that fluorophosphoranes, R_nPF_{5-n} (n = 0—2) [2] react readily with a variety of element–trimethylsilyl compounds with cleavage of the element–trimethylsilyl bond and elimination of trimethylfluorosilane, *i.e.*

$$R_nPF_{5-n} + E\text{–}SiMe_3 \longrightarrow R_nPF_{4-n}E + Me_3SiF$$

The reaction provides a facile means of attaching atoms such as N, P, O, and S to five-co-ordinate phosphorus [2-6] and numerous stereochemically interesting substitution products derived from PF_5 could thus be obtained. As a result of the availability of many silicon–nitrogen precursors,[7] special attention was given

TABLE 1

Dialkylaminofluorophosphoranes, $(R_2N)_nPF_{5-n}$ (n = 1 or 2)

Compound	Reactants, moles		Reaction conditions [a]	Yield of fluorophosphorane %	Yield of Me_3SiF	B.p. °C (mmHg)	Analyses	C	H	F	N	P	*M*
$Me_2N{\cdot}PF_4$	$Me_2N{\cdot}SiMe_3$ [b]	1·25	Warmed up from −78° to room temp. over 2 h; 1 h at 50°	78	96	63	Calc.	15·9	4·0	50·3	9·3	20·5	151·06
	PF_5	1·35					Found	15·8	4·1	48·4	9·4	19·3	151 [c]
$(Me_2N)_2PF_3$	$Me_2N{\cdot}SiMe_3$ [b]	0·1	3 h at 175° [d]	56	70	43(19) [e]	Calc.	27·2	6·9	32·4	15·9	17·6	176·14
	$Me_2N{\cdot}PF_4$	0·1					Found	27·4	7·0	31·9	16·1	17·3	176 [c]
$Et_2N{\cdot}PF_4$	$Et_2N{\cdot}SiMe_3$ [f]	1·83	Warmed up from −78° to room temp. over 2 h; 2 h at 50—60°	50	100	99—100	Calc.	26·8	5·6	42·5	7·8	17·3	179·11
	PF_5	1·9					Found	27·0	5·5	41·6	7·9	17·5	180 ± 1 [c]
$(Et_2N)_2PF_3$	$Et_2N{\cdot}SiMe_3$	0·08	2·5 h at 150—170° [d]	82	61	79(14) [g]	Calc.	41·3	8·7	24·5	12·1	13·3	232·24
	$Et_2N{\cdot}PF_4$	0·1					Found	41·3	8·7	24·7	12·3	12·9	232 [c]
$Ph_2N{\cdot}PF_4$	$Ph_2N{\cdot}SiMe_3$ [i]	0·15	Warmed up from −78° to room temp. over 1·5 h; 1 h at 100°	52	*h*	*j*	Calc.	52·4	3·7	27·6	5·1	11·2	275·19
	PF_5	0·16					Found	52·7	3·9	26·7	5·1	10·7	275 [c]

[a] All reactions were conducted under autogenous pressure. [b] O. Mjörne, *Svensk kem. Tidskr.*, 1950, **62**, 120. [c] Molecular weights were obtained from mass spectra. [d] Reactor tube evacuated to 0·1 mmHg at −196° prior to heating period. [e] n_D^{23} = 1·3837. [f] R. O. Sauer and R. H. Hasek, *J. Amer. Chem. Soc.*, 1946, **68**, 241. [g] n_D^{25} = 1·4049. [h] No attempt was made to determine quanitatively the amount of Me_3SiF formed. [i] J. Hils, V. Hagen, H. Ludwig, and K. Rühlmann, *Chem. Ber.*, 1966, **99**, 776. [j] The product was a low-melting solid, which could readily be sublimed at 90° (bath temperature), 0·2 mmHg.

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[1] Part XXVIII: O. Stelzer and R. Schmutzler, *J. Chem. Soc.* (*A*), 1971, 2867.

[2] For a summary of chemistry and stereochemistry of fluorophosphoranes see: (*a*) R. Schmutzler, *Angew. Chem.*, 1965, **77**, 530; (*b*) R. Schmutzler, in 'Halogen Chemistry,' ed. V. Gutmann, vol. 2, p. 31; Academic Press, London and New York, 1967.

[3] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 410; *J. Chem. Soc.*, 1964, 4551; and unpublished observations.

[4] H. Koop and R. Schmutzler, unpublished work (1970).

[5] S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 665, 1662; *J. Chem. Soc.* (*A*), 1970, 1049.

[6] R. Schmutzler, (*a*) *Angew. Chem.*, 1964, **76**, 893; (*b*) *Z. Naturforsch.*, 1964, **19b**, 1101; (*c*) *Chem. Comm.*, 1965, 19; (*d*), U.S.P., 3,287,406/1966; (*e*) U.S.P., 3,300,503/1967; (*f*) *Inorg. Chem.*, 1968, **7**, 1327; (*g*) for a review of the chemistry of fluorine–phosphorus–nitrogen compounds see M. Murray and R. Schmutzler, *Z. Chem.*, 1968, **8**, 241.

[7] (*a*) R. Fessenden and D. J. Fessenden, *Chem. Rev.*, 1961, **61**, 363; (*b*) O. J. Scherer, *Organometallic Chem. Rev.*, 1968, **3**, 281; (*c*) U. Wannagat, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 225; (*d*) V. Bazant, V. Chvalovsky, and J. Rathousky, 'Organosilicon Compounds,' Academic Press, New York and London, 1965; (*e*) B. J. Aylett, in 'Preparative Inorganic Reactions,' ed. W. L. Jolly, Interscience, New York, London, and Sydney, 1965, vol. 2, p. 93.

to the study of phosphorus–nitrogen compounds. Usually, in these reactions of Si–N compounds with *fluorophosphoranes*, the co-ordination number five around phosphorus is preserved. The study of the chemistry and stereochemistry of the compounds of the types $(R_2N)_nPF_{5-n}$ ($n = 1, 2$), $R_nPF_{4-n}NR'_2$ ($n = 1, 2$), and $(F_{3-n}R_nPNR')_2$ ($n = 0, 1$) is the subject of this paper.

EXPERIMENTAL

The appropriate precautions required in handling moisture-sensitive products were observed throughout this work.

Silicon–nitrogen compounds were synthesized by the literature procedures indicated. Phosphorus pentafluoride was purchased from Matheson. The synthesis of the fluorophosphoranes used has been reported.[8]

Organic solvents were dried by standard procedures.

N.m.r. spectra were recorded, using the previously described instruments and conditions.[1]

Preparation of Dialkylamino-tetra- and -tri-fluorophosphoranes.—Data pertinent to the preparation of these compounds, including analyses, are listed in Table 1 and n.m.r. data in Table 2. The following preparation is typical.

Dimethylaminotetrafluorophosphorane. Dimethylaminotrimethylsilane (146·5 g, 1·25 mol) and phosphorus pentafluoride (170 g, 1·35 mol) were combined in a stainless steel shaker tube at −78°. The mixture was allowed to warm up to room temperature over 2 h (exothermic reaction) and was then heated at 50° for 1 h. After the excess of PF_5 had been bled off, products volatile at 25° were pumped off at 150 mmHg into a dry-ice-cooled trap. Fractional distillation through a 12 in glass helix-packed column gave trimethylfluorosilane (110 g, 96%), followed by dimethylaminotetrafluorophosphorane (145 g, 78%), b.r. 60—73°; b.p. on redistillation 63°. Purity by v.p.c. (temperature of injection port 100°) >98%. Trimethylfluorosilane was identified from its ^1H and ^{19}F n.m.r. spectrum; in all other runs Me_3SiF was identified by its i.r. spectrum in the gas phase,[9] after its purity had been checked by v.p.c.

Preparation of Alkyl(or aryl)dialkylaminofluorophosphoranes.—Preparative data and analyses are listed in Table 3, and n.m.r. data in Table 4. A typical preparation follows.

Dimethylamino(ethyl)trifluorophosphorane. A three-necked flask was equipped with a thermometer, a dropping funnel with sidearm, and a reflux condenser, the latter was connected to a dry-ice-cooled trap which was protected towards atmospheric moisture with a drying tube. In a counter-current of nitrogen, diethylaminotrimethylsilane (16 g, 0·137 mol) was placed in the dropping funnel while $EtPF_4$ (20·4 g, 0·15 mol) was charged in the flask. An exothermic reaction, moderated by occasional cooling with ice, took place upon dropwise addition of the aminosilane to the magnetically stirred fluorophosphorane during 30 min. The mixture was then refluxed for 30 min. Trimethylfluorosilane was condensed in the trap. No attempt was made to determine its exact amount in this particular experiment, as there was some excess $EtPF_4$ whose volatility is very similar to that of Me_3SiF. Distillation of the crude reaction mixture gave $EtPF_3NEt_2$ (18·3 g, 83%); b.p. 45—47° (54 mmHg).

*Preparation of Fluoro-*1,3,2,4-*Diazadiphosphetidines.*—Experimental data, analyses, *etc.* pertinent to this class of compounds are listed in Table 5; for i.r. and n.m.r.

TABLE 2

^1H, ^{19}F, and ^{31}P N.m.r. data for dialkylamino-tetra-and -tri-fluorophosphoranes

	^1H			^{19}F					^{31}P
Compound	δ_H [a] (p.p.m.	J(HP) (Hz)	J(HF) (Hz)	δ_F [b] (p.p.m.)	$\delta_{F_e} - \delta_{F_a}$ [c] (p.p.m.)	$J(F_aF_e)$ [c] (Hz)	J(PH) [d] (Hz)	J(FP) [d] (Hz)	δ_P [e] (p.p.m.)
$Me_2N{\cdot}PF_4$	−2·85	11·6	2·05 [f]	+66·8			*g*	847	+69·7
(25°)	−2·87	11·5	2·01 [h]						
$Me_2N{\cdot}PF_4$	*i*	*i*	*i*	+75·9 (equat.)	16·9	72	*j*	915 (equat.)	*i*
(−90°)				+59·0 (axial)				778 (axial)	
$(Me_2N)_2PF_3$	−2·72 [f]	10·8	2·7 (H–F_a)	+73·0 (equat.)	19·0	44	2·7 (F_a–H)	862 (equat.)	+65·0
			1·55 (H–F_e)	+54·0 (axial)			1·1 (F_e–H)	744 (axial)	
$Et_2N{\cdot}PF_4$	−1·21 (CH_3) [f]	*ca.* 16—17 (CH_2–P)	1·7 (CH_2–F)	+66·5			*g*	851	+69·8
	−3·24 (CH_2)								
$(Et_2N)_2PF_3$	−1·14 (CH_3) [f]	*ca.* 16 (CH_2–P)	*k*	+67·5 (equat.)	8·0	44	*g*	875 (equat.)	+64·7
	−3·10 (CH_2)			+59·5 (axial)				751 (axial)	
$Ph_2N{\cdot}PF_4$ [l]	*i*	*i*	*i*	+60·0			*g*	864	+75·1

Spectra were obtained on neat samples, unless otherwise stated.

[a] $SiMe_4$ Internal reference. [b] CCl_3F Internal reference. [c] F_a,F_e: Fluorine atoms in axial and equatorial positions, respectively, of the trigonal bipyramid. [d] J(PF) Values are taken from the ^{19}F spectra, and are believed to be slightly more accurate than those obtained from ^{31}P spectra. [e] H_3PO_4 (85%) External reference. [f] ^1H Data obtained on neat sample. [g] Not measured. [h] ^1H Data obtained on 20% solution in CCl_4. [i] Not recorded. [j] Calc. J(PF) (average) at −90°: 847 Hz; *i.e.* identical to the value obtained at room temperature. [k] H–F Coupling is apparent, but not well resolved. [l] Spectra were obtained on a solution of the compound in benzene.

[8] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 410; *Inorg. Synth.*, 1967, **9**, 65.

[9] H. Kriegsmann, *Z. anorg. Chem.*, 1958, **294**, 113; *Ber. Bunsengesellschaft Phys. Chem.*, 1958, **62**, 1033.

data see Tables 6 and 7. Two typical preparations are as follows.

1,3-*Dimethyl*-2,2,2,4,4,4-*hexafluoro*-1,3,2,4-*diazadiphosphetidine*. A stainless steel autoclave (1 l) was flushed with nitrogen and charged with heptamethyldisilazane (280 g, 1·6 mol). The autoclave was cooled to −78° and evacuated to *ca.* 1 mmHg. Phosphorus pentafluoride (200 g, *ca.* 1·6 mol) was then added. The reaction mixture was allowed to warm up to room temperature over 1 h, when a mildly exothermic reaction took place, and was then kept for 2 h at 35°, 2 h at 80°, and 1 h at 130°.

The liquid reaction mixture was discharged into a distillation flask. Trimethylfluorosilane was distilled off through a 10 in glass helix-packed column, the higher boiling product was recovered by distillation *in vacuo*. After two fractionations, employing a 25 in. spinning band still, 155 g (62%) of product was obtained; b.p. 48° (150 mmHg), n_D^{24} 1·3340. Density d_{25}^{25} 1·536; d_4^{25} 1·532. The purity of the product was found to be 100% by v.p.c. (typical conditions: F & M program-temperature unit (10° min⁻¹); 4 ft. (20%) silicone rubber column on 60—80 super support; helium flow 50 ml/min⁻¹).

TABLE 3

Alkyl(or aryl)-dialkylaminofluorophosphoranes, $R_nPF_{4-n}NR'_2$ (n = 1 or 2)

Compound	Reactants,	moles	Reaction conditions	Yield of fluorophosphorane %	Yield of Me_3SiF %	B.p. °C (mmHg)		Analyses C	H	F	N	P	*M*
$EtPF_3NMe_2$	$Me_2N{\cdot}SiMe_3$ $EtPF_4$	0·137 0·15	$Me_2N{\cdot}SiMe_3$ added to $EtPF_4$ over 0·5 h at <50°, refluxed 0·5 h	83	*a*	45—47 (54)	Calc. Found	29·8 29·6	6·9 6·8	35·4 35·3	8·7 8·9	19·2 19·1	161·12 161 *b*
$EtPF_3NEt_2$	$Et_2N{\cdot}SiMe_3$ $EtPF_4$	0·06 0·085	$Et_2N{\cdot}SiMe_3$ added to $EtPF_4$ over 0·5 h *c*	79	100	67 *d* (31)	Calc. Found	38·1 38·1	7·0 8·2	30·1 30·7	7·4 7·6	16·4 16·5	189·15 189 *b*
$EtPF_3N$	$N{\cdot}SiMe_3$ $EtPF_4$	0·067 0·085	No evolution of heat upon addition of silazane to $EtPF_4$ at atm. pressure; heated 1 h at 70° and 1 h at 120° under autogeneous pressure	*e*	*e*	*ca.* 40—50 *e* (16)				*e*			
$PhPF_3NMe_2$	$Me_2N{\cdot}SiMe_3$ $PhPF_4$	0·076 0·07	$Me_2N{\cdot}SiMe_3$ added to $PhPF_4$ over 1 h at <50°; heated with stirring 1 h at 80°	85	88	48 (0·25)	Calc. Found	46·2 45·9	5·2 5·3	 *f*	6·3 6·7	14·4 14·8	209·16 *g*
$PhPF_3NEt_2$	$Et_2N{\cdot}SiMe_3$ $PhPF_4$	0·1 0·11	$Et_2N{\cdot}SiMe_3$ added to $PhPF_4$ over 0·3 h; *h* heated with stirring 1 h at 70—90°	86	98	70 *i* (0·5)				*j*			237·21 237 *b*
$PhPF_3NEt_2$	$(Et_2N)_2SiMe_2$ *k* $PhPF_4$	0·1 0·22	$(Et_2N)_2SiMe_3$ added to $PhPF_4$ over 40 min at <40° *l*	89	84 *m*	60 *n* (0·08)				*j*			
$PhPF_3N$	$N{\cdot}SiMe_3$ $PhPF_4$	0·1 0·1	No evolution of heat upon addition of silazane to $PhPF_4$ (0·3 h); heated 1 h at 90°	73	70	73—74 *o* (0·25)	Calc. Found	52·0 52·1	3·9 4·0	24·7 24·5	6·0 6·2	13·4 13·3	231·16 231 *b*
$Ph_2PF_2NMe_2$	$Me_2N{\cdot}SiMe_3$ Ph_2PF_3	0·14 0·13	$Me_2N{\cdot}SiMe_3$ added to Ph_2PF_3 over 0·5 h; stirred 7 h at 90°	82	67	128 (1)	Calc. Found	62·9 62·8	6·0 5·8	14·2 15·0	5·3 5·4	11·6 11·8	267·26 *p*

a Yield of Me_3SiF not determined quantitatively. *b* Molecular weights were obtained from mass spectra. *c* There was a slow rise in temperature from 24 to 38° during combination of the reactants. *d* n_D^{30} = 1·3848. *e* The product was contaminated with some $EtPOF_2$ which could not be separated by fractionation. A sample of pure product was collected by v.p.c. for mass spectroscopy which, together with the n.m.r. data (Table 5), serves to establish the identity of the product. *f* No fluorine analysis was conducted. *g* No mass spectrum was recorded. *h* Slow rise in temperature from 25 to 65°. *i* n_D^{25} = 1·4689 (reported: n_D^{25} = 1·4690). *j* The compound was identified by comparison of its refractive index, i.r. spectrum, and n.m.r. data with those of authentic $PhPF_3NEt_2$. *k* R. M. Pike, *J. Polymer Sci.*, 1961, **50**, 151. *l* There was a vigorous reaction which had to be moderated by cooling with ice. *m* Me_2SiF_2. *n* n_D^{26} = 1·4695. *o* n_D^{26} = 1·5134. *p* No molecular weight peak was observed in the mass spectrum. The strongest fragment (223 *m/e*) corresponds to loss of NMe_2 from the parent.

A vapour pressure determination on $(F_3PNMe)_2$ was carried out using a sickle cell.[10] The molar heat of vaporization was calculated as 9160 cal mol⁻¹ and the Trouton constant as 25·1 cal deg⁻¹ mol⁻¹.

[10] T. E. Phipps, M. L. Spealman, and T. G. Cooke, *J. Chem. Educ.*, 1935, **12**, 318. The author is indebted to Mr. C. G. Wortz of the Central Research Department for this measurement.

1,3-*Dimethyl*-2,4-*bis*(m-*trifluoromethylphenyl*)-2,2,4,4-*tetrafluoro*-1,3,2,4-*diazadiphosphetidine*. The intermediates, m-$CF_3C_6H_4PCl_2$ and m-$CF_3C_6H_4PF_4$ are new. Their preparation, as well as that of the corresponding phosphonic acid, is described below.

m-*Trifluoromethylphenyldichlorophosphine*. Prepared on a 1 mole scale, following the general procedure given by Erlenmeyer.[11,12] Yield 58·7%; b.p. 42° (0·07 mmHg); n_D^{26} 1·5214 (Found: C, 33·2; H, 1·7; Cl, 28·4. $C_7H_4Cl_2F_3P$ requires C, 34·0; H, 1·6; Cl, 28·7%). ^{19}F N.m.r. (CF_3), δ_F +63·5 p.p.m.; ^{31}P n.m.r. δ_P −155·8 p.p.m.

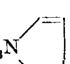
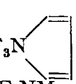
m-*Trifluoromethylphenylphosphonic acid*. This was obtained by repeatedly evaporating a small amount of the (26·3 g, 0·15 mol), using a set-up similar to the one described for dimethylamino(ethyl)trifluorophosphorane.

Reaction of Nonamethylcyclotrisilazane with Phenyltetrafluorophosphorane.—$PhPF_4$ (22 g; 0·12 mol) was allowed to react with $(Me_2SiNMe)_3$.[13] The diazadiphosphetidine $(PhF_2PNMe)_2$ was obtained in 76% yield; its identity was confirmed by mixed m.p. (161—162°) and analysis; i.r. and n.m.r. spectra were in agreement to those of the authentic compound.

Reaction of 1,1,3,3,5,5-*Hexamethyl*-2,4,6-*triethylcyclotrisilazane with Phenyltetrafluorophosphorane*.—A 51% yield of $(PhF_2PNEt)_2$, m.p. 110°, was obtained; identification was by analysis, ^1H, and ^{31}P n.m.r.

TABLE 4

^1H, ^{19}F, and ^{31}P N.m.r. data for alkyl(or aryl)dialkylaminofluorophosphoranes, $R_nPF_{4-n}NR'_2$

	^1H			^{19}F					^{31}P
Compound	δ_H [a] (p.p.m.)	J(HP) (Hz)	J(HF) (Hz)	δ_F [b] (p.p.m.)	$\delta_{F_e} - \delta_{F_a}$ [c] (p.p.m.)	$J(F_aF_e)$ (Hz)	J(FH) (Hz)	J(PF) [d] (Hz)	δ_P [e] (p.p.m.)
$EtPF_3NMe_2$	−2·80 (NCH_3) [f]	10·4 (NCH_3-P)	2·6 (NCH_3-F)	+72·5 (equat.) +38·4 (axial)	34·1	54	11 (F_a–CH_2)	982 (equat.) 830 (axial)	+36·1
$EtPF_3NEt_2$	*g*	*g*	*g*	+70·0 (equat.) +41·4 (axial)	28·6	56	11·3 (F_a–CH_2 of P–C_2H_5 group)	982 (equat.) 831 (axial)	+35·7
$EtPF_3N$ 	*h*	*h*	*h*	+73·1 (equat.) +33·2 (axial)	39·9	57	10 (F_a–CH_2)	996 (equat.) 872 (axial)	+38·5
$PhPF_3NMe_2$	−2·72 [i]	11·0	2·7 (average)	+68·3 (equat.) +40·0 (axial)	28·3	55	*j*	954 (equat.) 817(axial)	+53·4
$PhPF_3NEt_2$	−1·15 (CH_3) [k,l] −3·12 (CH_2)	14—15 (CH_2–P)	*m*	+66·5 (equat.) +43·5 (axial)	23·0	56	*i*	966 (equat.) 823 (axial)	+52·3
$PhPF_3N$ 	−6·35 (C_4H_4N [n] group)	*j*	*j*	+69·1 (equat.) +39·2 (axial)	29·9	58	*j*	979 (equat.) 860 (axial)	+59·5
$Ph_2PF_2NMe_2$	−2·80 (NCH_3) [o]	10·0 (NCH_3–P) [o]	2·5 (NCH_3–F_a) [o]	+35·8			2·5 (F_a–NCH_3)	709	+54·0

Spectra were obtained on neat samples, unless otherwise stated. Aromatic ^1H resonances have not been listed in the Table.

[a] $SiMe_4$ Internal reference. [b] $CFCl_3$ Internal reference. [c] F_e,F_a: Fluorine atoms in equatorial and axial positions, respectively, of the trigonal bipyramid. [d] J(PF) Values are taken from the ^{19}F spectra and are believed to be slightly more accurate than those obtained from ^{31}P spectra. [e] H_3PO_4 (85%) External reference. [f] ^1H Spectra resonance due to Et group poorly resolved and spread out over *ca.* −0·8 to −2·4 p.p.m. [g] The ^1H spectrum of $EtPF_3NEt_2$ was not assigned because of overlap of resonances and poor resolution. [h] ^1H Spectrum not recorded. [i] Integration gave the correct ratio, H aromatic : H aliphatic = 5 : 6. [j] Not measured. [k] 20% Solution in CCl_4. [l] Integration gave H aromatic : H aliphatic = 5 : 10. [m] No accurate value obtained. [n] Centre of multiplet. [o] ^1H Spectrum recorded on 20% solution in CCl_4.

dichlorophosphine, after adding water–hydrogen peroxide (30%). Recrystallization from water afforded white plates, m.p. 116—117° (Found: C, 37·3; H, 2·7; P, 14·0. $C_7H_6F_3PO_3$ requires: C, 37·2; H, 2·7; P, 13·7%). ^{19}F N.m.r. (CF_3) δ_F +62·5 p.p.m.; ^{31}P n.m.r.: δ_P −13·0 p.p.m. (both measurements in acetone solution).

m-*Trifluoromethylphenyltetrafluorophosphorane*. From the dichlorophosphine (0·3 mol) and SbF_3 (0·5 mol).[8] Yield 88%; b.p. 64° (40 mmHg) (Found: C, 33·6; H, 1·6; F, 50·8; P, 12·5. $C_7H_4F_7P$ requires: C, 33·4; H, 1·6; F, 52·7; P, 12·3%). ^{19}F N.m.r.: P–F, 1 : 1 doublet, J(PF) 955 Hz, δ_F +54·1 p.p.m.; CF_3: δ_F +63·8 p.p.m. ^{31}P N.m.r.: quintet, δ_P +52·9 p.p.m.

The phosphetidine was prepared by combining the fluorophosphorane (37·8 g; 0·15 mol) with $MeN(SiMe_3)_2$

Preparation of N-*Methyldiphenylfluorophosphine Imide*.—A mixture of Ph_2PF_3 (24·2 g, 0·1 mol) and $MeN(SiMe_3)_2$ (20·0 g, 0·115 mol) was heated for 7 h at 150°. The solid product obtained on cooling was recrystallized from toluene; yield 11·7 g (50%) of white crystals; m.p. 144—146·5°. The product could be sublimed *in vacuo*. Yield of Me_3SiF 11·5 g (63%) [Found: C, 66·7; H, 5·5; F, 7·9; N, 6·2; P, 13·1%; *M* (cryoscopic in benzene) 210. $C_{13}H_{13}FPN$ requires: C, 67·0; H, 5·6; F, 8·1; N, 6·0; P, 13·3%; *M* (monomer) 233·22]. Principal i.r. absorptions (KBr pellet): *ca.* 3050, 2933vw; 2807w; 1480m; 1436s; 1181, 1170vs; 1106, 1094s; 865vs; 760, 753m; 726, 714vs; 703m; 693w; 664s; 618s; 565vs; 506, 495m; 470m;

[11] T. Weil, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, 1952, **35**, 1412.

[12] T. Weil, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, 1953, **36**, 1314.

[13] E. W. Abel and R. P. Bush, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1685.

TABLE 5

Fluorinated 1,3,2,4-diazadiphosphetidines

Compound	Reactants, moles		Reaction conditions	Yield of fluoro-phosphetidine %	Yield of Me_3SiF %	Physical properties		Analyses C	H	F	N	P	M
F_3P–N–Me Me–N–PF_3	$(Me_3Si)_2NMe$ [a] PF_5	0·165 0·18	Silazane cooled to −78°; PF_5 added after evacuation to 1 mmHg, heated with shaking 2 h at 40°, 2 h at 70°, and 1 h at 120°	49 [b]	79	M.p. −8·3° b.p. 89° [c,d]	Calc. Found	10·3 10·5	2·6 2·4	48·7 48·2	12·0 11·7	26·4 26·4	234·04 234 [d]
F_2P–N–Ph Ph–N–PF_3	$(Me_3Si)_2NPh$ [e] PF_5	0·142 0·155	Reactants combined at −78°; heated with shaking 1 h at 80°, 2 h at 150°	86	92	Crystals, m.p. 188—190° [g]	Calc. Found	40·2 40·1	2·9 3·2	31·8 31·1	7·8 7·8	17·3 16·8	358·18 358 [h]
MeF_2P–N–Me Me–N–PF_2Me	$(Me_3Si)_2NMe$ [a] $MePF_4$	0·3 0·35	Reactants combined at −50°; heated 3 h at 150°	81	94	Crystals [i], m.p. 42°, b.p. 60° (14 mmHg)	Calc. Found	21·3 21·2	5·4 5·6	33·6 34·5	12·4 12·3	27·4 27·6	226·12 227 ± 1 [h]
MeF_2P–N–Ph Ph–N–PF_2Me	$(Me_3Si)_2NPh$ [e] $MePF_4$	0·04 0·04	3 h at 150° (sealed tube)	30	92	Crystals, [j] m.p. 138°	Calc. Found	48·0 48·3	4·6 4·8	21·7 20·7	8·0 7·9	17·7 17·7	350·24 330 [k]
$ClCH_2F_2P$–N–Me Me–N–PF_2CH_2Cl	$(Me_3Si)_2NMe$ [a] $ClCH_2PF_4$	0·16 0·17	Reactants combined in tube at room temp., evacuated to 0·1 mmHg at −190°; heated 3 h at 150°	25	[m]	Crystals, m.p. 47—48°, b.p. 68° (0·05 mmHg)	Calc. Found	16·3 16·4	3·4 3·5	25·8 25·2	9·5 9·2	21·0 20·7	295·02 294—298 [h,n]
EtF_2P–N–Me Me–N–PF_2Et	$(Me_3Si)_2NMe$ [a] $EtPF_4$	1·2 1·3	4 h at 120° (autoclave)	78 [o]	82	77° (9 mmHg), n_D^{21} 1·4185	Calc. Found	28·4 28·5	6·3 6·3	29·9 29·8	11·0 11·0	24·4 24·9	254·16 254·16 [p]
PhF_2P–N–Me Me–N–PF_2Ph	$(Me_3Si)_2NMe$ [a] $PhPF_4$ in toluene (200 ml)	1·51 1·55	$PhPF_4$ added dropwise with stirring to silazane (1 h); heated 2 h at 80°; cooled to −30° overnight	93	95	Crystals, m.p. 162°	Calc. Found	48·0 47·9	4·6 5·2	21·7 21·6	8·0 8·2	17·9 17·7	350·24 350·34 [q]
$2,5Me_2C_6H_3F_2P$–N–Me Me–N–$PF_2C_6H_3$–2,5Me_2	$(Me_3Si)_2NMe$ [a] $2,5Me_2C_6H_3PF_4$ in benzene (25 ml)	0·1 0·1	Silazane added dropwise with stirring to fluorophosphorane over 1 h (temp. kept by cooling at 25°); 1 h at 70; cooled to 0° overnight	84	[m]	Crystals, [r] m.p. 173—174°	Calc. Found	53·3 53·2	6·0 6·0	18·7 19·3	6·7 6·8	15·3 15·2	406·36 406 [h]
m-$CF_3C_6H_4F_2P$–N–Me Me–N–$PF_2C_6H_4$–m-CF_3	$(Me_3Si)_2NMe$ [a] m-$CF_3C_6H_4PF_4$	0·15 0·15	Fluorophosphorane added dropwise with stirring to silazane (1·5 h at <50°); heated 1 h at 100° and 1 h at 50°/0·05 mmHg	96	98	Crystals, [r,s] m.p. 164—166° (sealed capillary)	Calc. Found	39·5 39·5	2·9 2·9	39·1 39·1	5·8 5·7	12·7 12·8	436·26 422 [t]
PhF_2P–N–Et Et–N–PF_2Ph	$(Me_3Si)_2NEt$ [u] $PhPF_4$	0·008 0·011	$PhPF_4$ added dropwise with stirring to silazane (exothermic reaction); heated 1 h at 80°, 1 h at 130°	84	[m]	Crystals, m.p. 108°	Calc. Found	50·7 50·7	5·3 4·9	20·1 19·5	7·4 6·7	16·4 15·1	378·30 395 [t]
PhF_2P–N–Ph Ph–N–PF_2Ph	$(Me_3Si)_2NPh$ [e] $PhPF_4$	0·143 0·16	As above; reaction mixture heated 2 h at 40° 0·5 h at 100°	56 [v]	88	Crystals, m.p. 134—136° (softening from 129°)	Calc. Found	60·8 60·7	4·2 4·5	16·0 15·5	5·9 5·9	13·1 12·8	474·38 428 [t]

[a] R. C. Osthoff and S. W. Kantor, *Inorg. Synth.*, 1957, **5**, 58. [b] There was considerable handling loss in this experiment, and the actual yield is undoubtedly higher. In another run, employing a ten-fold excess of reactants, a 62% yield of $(F_3PNMe)_2$ was realised. [c] Vapour pressure measurements over the range 25·0 to 91·6° were conducted using a sickle cell, as described by T. E. Phipps, M. L. Spealman, and T. G. Cooke, *J. Chem. Educ.*, 1935, **12**, 1318. See Experimental section. Purity by v.p.c. >99%. [d] Determination by mass spectroscopy. A value 260 (calc. 234·04) was found on cryoscopic determination in benzene. [e] E. W. Abel and C. R. Willey, *J. Chem. Soc.*, 1964, 1528. [f] Yield of purified product, recovered by sublimation at 120° (oil bath), 0·3 mmHg from the crude reaction mixture. [g] Determination of m.p. in sealed capillary. M.p.s taken on a block were rather erratic. [h] Determination by mass spectroscopy. [i] The product has a characteristic, camphor-like odour. Its unusual tendency to crystallize, despite its low m.p. and good solubility in all common organic solvents, is particularly noteworthy. Purity by v.p.c. >99%. [j] Crude product recrystallized from toluene. [k] Cryoscopic determination in benzene. [l] Due to an unexpectedly vigorous reaction upon first combination of reactants, much product was lost, and the actual yield is much higher. [m] Yield of Me_3SiF not determined. [n] M values found: 294, 296, 298, due to different isotopes of Cl. [o] Purity by v.p.c. >99%. [p] A value 272 (calc. 254·16) was found on cryoscopic determination in benzene. [q] Determination by osmometer in acetonitrile. [r] Recrystallization from benzene. [s] An analytical sample was readily obtained by sublimation (*ca.* 150°, 0·5 mmHg; water-cooled probe). [t] Cryoscopic determination in benzene. [u] K. Rühlmann, *Chem. Ber.*, 1961, **94**, 2311. [v] Yield of product recrystallized from benzene. The crude product was recovered after pumping off volatile products at 40°, 1 mmHg.

416, 404s,b cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): doublet of doublets, $J(CH_3-P)$ 17·4 Hz; $J(CH_3-F)$ 6·3 Hz; δ_H −2·32 p.p.*m*. (NCH_3). An aromatic multiplet is spread over the range *ca.* −7·3 to −8 p.p.m. Integration (H aliphatic : H aromatic = 3 : 10) confirms the composition Ph_2FPNMe. The poor solubility of the compound in all common organic solvents precluded the observation of ^{19}F and ^{31}P n.m.r. spectra.

RESULTS AND DISCUSSION

Dialkylaminofluorophosphoranes, $(R_2N)_nPF_{5-n}$ (n = 1, 2) *and Alkyl* (*or Aryl*)*dialkylaminofluorophosphoranes*, $R_nPF_{4-n}NR'_2$ (n = 1, 2).—The reaction of the Lewis acid fluorides, R_nPF_{5-n} (n = 0, 1; n = 2 only for R = Ph) with dialkylaminotrimethylsilanes was found to provide a convenient method of preparation for a variety of substitution products of phosphorus pentafluoride. Bis(dialkylamino)dimethylsilanes were also employed as Si–N precursors.

The reactions were carried out by gradually adding one reactant to the other under anhydrous conditions. The course of the reaction was independent of the order of combination of the reactants. Reactions involving phosphorus pentafluoride, a gas of low b.p., were conducted in an autoclave. All other reactions were carried out at atmospheric pressure. The fluorosilanes, Me_3SiF or Me_2SiF_2, formed besides the phosphorus–nitrogen compound could readily be separated, due to their volatility. The quantitative determination of the amount of fluorosilane formed gave further evidence as to the extent of the reaction. Usually, the yields of both P–N compounds and fluorosilane were high.

Dialkylaminofluorophosphoranes are a new class of derivatives of phosphorus pentafluoride, some representatives of which were first reported simultaneously by three research groups.[6a,6c,14] Sharp and his co-workers[14a] have prepared R_2NPF_4 and $(R_2N)_2PF_3$ by thermal decomposition of the dialkylamine adducts of PF_5 and R_2NPF_4, respectively. Demitras and MacDiarmid[14b,c] have employed the Me_2NSiMe_3/PF_5 cleavage reaction as reported in this paper to prepare Me_2NPF_4. We have also used this route to prepare compounds of the type R_2NPF_4 (R = Me, Et, Ph), and have extended it to the preparation of $(R_2N)_2PF_3$ (R = Me, Et). An attempt was made during the present work to obtain a mixed species, $(Me_2N)(Et_2N)PF_3$, as follows.

$$Et_2NPF_4 + Me_2N{\cdot}SiMe_3 \xrightarrow[170^\circ]{3\text{ h}} (Me_2N)(Et_2N)PF_3 + Me_3SiF$$

^{19}F N.m.r, spectroscopy revealed that not only the expected compound, $(Me_2N)(Et_2N)PF_3$ (*ca.* 40%) but also the two possible reorganization products, $(Me_2N)_2PF_3$ (*ca.* 20%) and $(Et_2N)_2PF_3$ (*ca.* 40%) were formed under the reaction conditions employed. $(Me_2N)(Et_2N)PF_3$ was readily identified from its ^{19}F n.m.r. spectrum: J[P–F(axial)] 745 Hz (doublet of doublets); J[F(axial)–F(equat.)] 43 Hz; δF(axial) + 56·9 p.p.m.; J[P–F(equat.)] 870 Hz; δF(equat.) +69·7 p.p.m. (doublet of triplets).

Some compounds of type $ArNHPF_4$, related to our disubstituted tetrafluorophosphoranes, have been obtained in the reaction of phosphorus pentafluoride with aniline and its derivatives.[15]

TABLE 6

^{1}H N.m.r. and i.r. data for *NN'*-dimethylfluorodiazadiphosphetidines

	^{1}H N.m.r. (N–CH_3 group)			I.r.	
Compound	Solvent	J(HP) (Hz)	δ_H (p.p.m.)	Medium	N–CH_3 (cm^{-1})
$(F_3PNMe)_2$	CCl_4	14·5	−2·65	Gas [a]	2850
$(MeF_2PNMe)_2$	CCl_4	12·5	−2·50	CCl_4 Solution	2830
$(ClCH_2F_2PNMe)_2$	CCl_4	12·7	−2·60 [b]	Neat (super-cooled)	2815
$(EtF_2PNMe)_2$	CCl_4	12·5	−2·53	CCl_4 Solution [c]	2830
$(PhF_2PNMe)_2$	$CDCl_3$	12·5	−2·38	KBr Pellet [d]	2820
$(m\text{-}CF_3C_6H_4F_2PNMe)_2$	$CDCl_3$	13·0	−2·40	KBr Pellet	2822
$(2,5Me_2C_6H_3F_2PNMe)_2$	$CDCl_3$	12—13	−2·37	KBr Pellet	2830

[a] The position of the band was found unchanged on the neat liquid. [b] $J(NCH_3-F)$ *ca.* 0·7 Hz. A doublet of partially overlapping triplets [$J(ClCH_2-P)$ *ca.* 9·5 Hz; $J(ClCH_2-F)$ *ca.* 4·7 Hz] was observed for the $ClCH_2$ group; $\delta(ClCH_2)$ = −3·76 p.p.m. [c] No shift of this band was observed in the spectrum of the neat liquid. [d] There was no change when the spectrum was recorded in $CHCl_3$, $CDCl_3$, or CCl_4.

TABLE 7

^{31}P and ^{19}F Chemical shift values for fluoro-1,3,2,4-diazaphosphetidines

Compound	Solvent	δ_P (p.p.m.)	δ_F (p.p.m.)
$(F_3PNMe)_2$	Neat	+71·3	+79·5
$(F_3PNPh)_2$	Benzene	*a*	+73·5
$(ClCH_2F_2PNMe)_2$	Benzene	+56·3	+62·9
$(PhF_2PNMe)_2$	Benzene	+55·1	+63·6
$(m\text{-}CF_3C_6H_4F_2PNMe)_2$	$CFCl_3$–$CDCl_3$	*a*	+62·6 [b]
$(2,5Me_2C_6H_3F_2PNMe)_2$	$CDCl_3$	*a*	+61·8
$(PhF_2PNEt)_2$	Benzene	+53·6	+60·3
$(MeF_2PNMe)_2$	Benzene	+50·7	+57·0
$(EtF_2PNMe)_2$	Neat	+45·5	+65·4
$(PhF_2PNPh)_2$	Benzene	*a*	+54·0
$(MeF_2PNPh)_2$	Benzene	*a*	+50·4

[a] Compound not sufficiently soluble in any common organic solvent to allow observation of ^{31}P n.m.r. spectrum. [b] δ_F (CF_3) +63·2 p.p.m.

[14] (*a*) D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *Chem. and Ind.*, 1964, 367; *J. Chem. Soc.* (*A*), 1966, 171; (*b*) G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. and Ind.*, 1964, 1712; (*c*) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903.

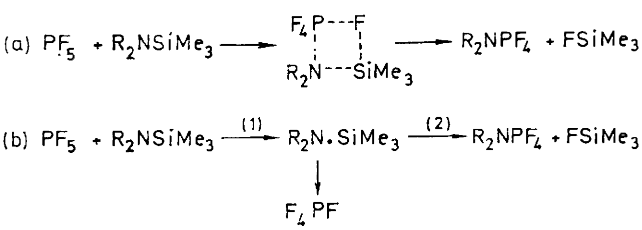
[15] J. J. Harris and B. Rudner, *J. Org. Chem.*, 1968, **33**, 1392.

(Aryl)dialkylaminofluorophosphoranes, $ArPF_3NR_2$, were first reported by Ivanova and Kirsanov,[16] who allowed the difficultly accessible aryltrifluorochlorophosphoranes to react with secondary amines. We have reported more convenient preparations of RPF_3-NR'_2 (R = alkyl or aryl, R′ = alkyl) by the dialkylaminolysis of tetrafluorophosphoranes[17] or through the reaction of dialkylaminochlorophosphines with AsF_3 or SbF_3.[18]

The preparation of difluorophosphoranes, R_2PF_2-NR'_2, by the dialkylaminolysis of R_2PF_3 has recently been described.[19] It has been found in the present study that a Si–N cleavage reaction will also take place between Ph_2PF_3 and R'_2NSiMe_3.

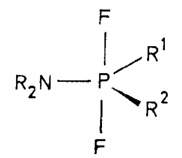
Generally, the ease of reaction between the Lewis acid phosphorus fluoride and the Si–N compound decreases in the order, $PF_5 > ArPF_4 > RPF_4 > R_2PF_3 > R_3PF_2$, and it seems reasonable to ascribe this to the decrease in acceptor strength of R_nPF_{5-n} (n = 0—2) which has been classified in the above order.[20]

The mechanism of the Si–N cleavage reactions successfully employed in our work has not yet been investigated in detail.[7b] Possible alternatives are illustrated for the reaction of PF_5 with R_2NSiMe_3. While



(a) involves a four-centre mechanism, the reaction of type (b) consists of the formation of an adduct, *i,e.* nucleophilic attack of nitrogen at phosphorus (1), followed by electrophilic attack of fluorine on silicon with elimination of Me_3SiF and formation of the P–N bond (2). In the specific case of the reaction of Me_2-$NSiMe_3$ with PF_5, a 1 : 1 adduct stable at $-78°$ which decomposes upon warming to room temperature has been observed.[14c] If the reactions proceed preferably *via* mechanism (b) the apparent dependence of the ease of the reaction and the Lewis acid strength of the fluorophosphorane is readily understandable.

Stereochemistry of Dialkylamino-substituted Fluorophosphoranes.—^{1}H, ^{19}F, and ^{31}P N.m.r. spectroscopy was employed in the study of the stereochemistry of our fluorophosphoranes (Tables 2 and 4). Data on some of our compounds have already been discussed in earlier publications by Muetterties and his co-workers.[21,22] The stereochemistry of all compounds follows the previously established pattern,[23] *i.e.* the basic configuration in the liquid or solution state is trigonal-bipyramidal, with the axial positions of the trigonal bipyramid invariably occupied by the most electronegative ligand, fluorine. The observed n.m.r. parameters are consistent with formulation (I), (R^1 =



(I)

R^2 = F for R_2NPF_4; R^1 = F, R^2 = R_2N for $(R_2N)_2$-PF_3; R^1 = hydrocarbon group, R^2 = F for RPF_3NR_2, or R^1 = R^2 = hydrocarbon group for $R_2PF_2NR_2$).

Room temperature n.m.r. spectra for all compounds R_2NPF_4[21,22] indicate that the positional exchange process of ligands characteristic of five-co-ordinate phosphorus compounds ('Berry process') is operative;[24] in contrast to other tetrafluorophosphoranes, the exchange can be brought within the time scale of the n.m.r. experiment by cooling; low temperature ^{19}F parameters which show non-equivalence of fluorine atoms, are included in Table 2. This has been demonstrated in earlier ^{19}F work for R_2NPF_4 (with R = Et, Ph)[21,22] and, more recently, by the variable temperature ^{31}P n.m.r. spectrum of Me_2NPF_4.[25]

^{1}H N.m.r. spectra, where appropriate with integration, were recorded for all compounds (Tables 2 and 4), and were consistent with the structures. The observed ^{31}P chemical shift values (Tables 2 and 4) were all positive, as is typical of five-co-ordinate phosphorus in fluorophosphoranes.[2,26]

Substituted 1,3,2,4-*Diazadiphosphetidines*, $(R_nPF_{3-n}$-$NR')_2$ (n = 0, 1).—These compounds, which may be viewed as dimers of the respective fluorophosphine imides, were formed with ease in the reaction of PF_5 or RPF_4 with *N*-substituted hexamethyldisilazanes, $R'N(SiMe_3)_2$. Again, a decrease in reactivity from PF_5 to RPF_4 was noted. Trifluorophosphoranes proved even less reactive and only in the case of Ph_2PF_3 was it possible, during a comparatively long reaction period, to obtain a defined product which was identified as the monomeric fluorophosphine imide, Ph_2FPNMe. The compound was too insoluble to permit the observation of ^{19}F and ^{31}P n.m.r. spectra but its structure has been fully established by an *X*-ray crystal structure determination.[27]

[16] Zh. M. Ivanova and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1962, **32**, 1592

[17] R. Schmutzler and G. S. Reddy, *Inorg. Chem.*, 1965, **4**, 191; 1966, **5**, 164.

[18] R. Schmutzler, *Angew. Chem.*, 1964, **76**, 570; *J. Chem. Soc.*, 1965, 5630

[19] S. C. Peake, M. J. C. Hewson, and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 2364.

[20] E. L. Muetterties and W. Mahler, *Inorg. Chem.*, 1965, **4**, 119.

[21] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

[22] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 172.

[23] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

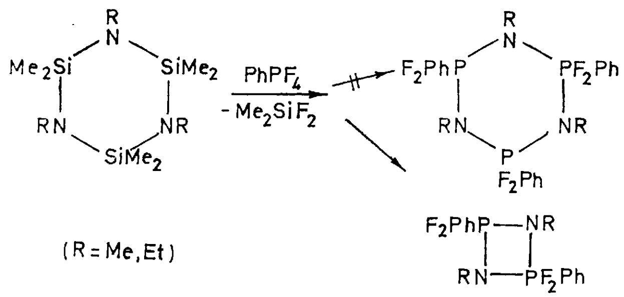
[24] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 960.

[25] G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, 1969, **91**, 5384.

[26] R. Schmutzler, *J. Chem. Soc.*, 1964, 4551.

[27] G. W. Adamson and J. C. J. Bart, *Chem. Comm.*, 1969, 1036; *J. Chem. Soc.* (*A*), 1970, 1452.

The $R_nPF_{5-n}/RN(SiMe_3)_2$ reaction may be rationalized as in the case of the synthesis of dialkylamino-substituted fluorophosphoranes (see above). The selectivity of the formation of the four-membered P–N ring system is evident from the reactions of the cyclic silazanes, $(RNSiMe_2)_3$ (R = Me, Et) with $PhPF_4$. Although formation of a six-membered ring system might be expected, the phosphetidines are the exclusive products (see Table 5).

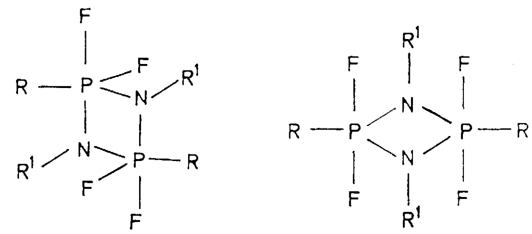


The general area of the chemistry of phosphorus–nitrogen compounds containing a four-membered P–N ring with phosphorus of co-ordination number 3, 4, or 5 has recently been reviewed.[28-31] Fluorophosphetidines, in particular, were first prepared by the present route, as in the case of $(F_3PNMe)_2$,[6c,d,14b,c] $(F_3PNPh)_2$, and $(RF_2PNR')_2$.[6c,d] More recently, it was found that the trichlorides, $(RNPCl_3)_2$ (R = alkyl) can be fluorinated with SbF_3, AsF_3, or Na_2SiF_6, in some cases, to give $(RNPF_3)_2$.[32,33,33a] Phosphorus pentafluoride was shown to react with primary amines under certain conditions, to give a range of compounds of type $(RNPF_3)_2$.[15,34]

Structure and Stereochemistry of Fluoro-1,3,2,4-*diazadiphosphetidines*.—Compounds of the types $(RNPF_3)_2$ and $(R'NPF_2R)_2$ have been investigated by a number of physical methods. Thus, the composition is clearly evident from molecular weight determinations by osmometry and mass spectrometry. In the latter case, a parent peak was invariably observed, the strongest peak corresponding to m/e equal to $(M/2 + 1)$ of the dimer. Strong evidence for the dimeric formulation comes from the ^1H n.m.r. spectra of a series of compounds with R' = Me. For all these compounds a 1 : 2 : 1 triplet (δ_H between −2·4 to −2·6 p.p.m.) is observed for the MeN group which indicates equal coupling between ^1H and two adjacent ^{31}P nuclei.[35] The observed values of ^3J(HP) (12—14·5 Hz) are indicative of HP-coupling through three bonds[36] (*cf*. Table 6), while H–F coupling is not normally resolved.

The observation of a characteristic C–H stretching frequency in the region 2760—2840 cm^{-1} has been taken as evidence for a $>$N–CH_3 group[37] whose lone electron pair is not tied up in bond formation. This absorption is affected by structural modifications involving the lone electron pair. We have observed this absorption in all compounds $(RF_2PNMe)_2$ (*cf* Table 6) and it may be concluded that the lone pair of electrons in *NN'*-dimethylfluorodiazadiphosphetidines is essentially retained.

Based on the reasonable assumption that fluorophosphetidines, like other fluorophosphoranes, involve trigonal bipyramidal phosphorus, the structural alternatives, (I) and (II), may be considered. Structure (II)



(I) (II)

(R = F, or R = alkyl, aryl; R' = alkyl, aryl).

appears unlikely since a N–P–N bond angle of *ca*. 120° (for diequatorial attachment of nitrogen to phosphorus) would require an improbably small P–N–P angle of *ca*. 60°.

A structure of type (I), involving a planar P–N ring, has been established[38] for the related trichloride, $(Cl_3PNMe)_2$ from *X*-ray diffraction data. The sp^2-hybridized nitrogen atoms are attached to trigonal-bipyramidal phosphorus in one axial and one equatorial position. As for other compounds of five-co-ordinate phosphorus,[39] equatorial bonds (both P–N and P–Cl) are shorter than axial bonds, and a correlation between bond length and bond strength for axial and equatorial P–N bonds has been found by calorimetry for $(Cl_3PNMe)_2$.[40] Likewise, it has invariably been observed that axial P–F coupling constants in fluorophosphoranes are smaller than equatorial J(P–F) values,[21,23] and this may again be correlated with bond lengths which are available for Me_2PF_3.[39b]

Structure (I) has been proved for several of our

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fluorophosphetidines, in various states of aggregation. Thus, the *X*-ray crystal structure of $(F_2PhPNMe)_2$ [*i.e.* R = Ph, R' = Me in (I)] has been determined,[41] and the same features as mentioned above for $(Cl_3PNMe)_2$ have been observed. An electron diffraction study has been conducted on $(F_3PNMe)_2$, as a representative fluorophosphetidine [*i.e.* R = F, R' = Me in (I)].[42] The structure is quite comparable to that of $(F_2PhPNMe)_2$, determined in the solid state.

Mention has already been made of the use of i.r. spectroscopy in the study of fluorophosphetidines. No attempt has been made completely to assign i.r. spectra, except for $(F_3PNMe)_2$. Both i.r. (liquid and vapour) and Raman spectra of this compound have been studied.[43,44] In the first study only the vibrational frequencies of the $(F_3PNC)_2$ skeleton were considered, and the data could best be accommodated in terms of a C_{2h} model [(I), R = F, R' = Me], rather than D_{2h} [(II), R = F, R' = Me]. The above mentioned characteristic difference in axial and equatorial bond lengths in trigonal-bipyramidal molecules (*cf.* also ref. 45) is also borne out in the observation of equatorial P–F and P–N stretching frequencies occurring at higher wavenumbers than axial stretching frequencies, which is another indication of the relative weakness of axial, compared to equatorial bonds.

^{31}P *and* ^{19}F *N.M.R. Spectra of Fluorophosphetidines*.—^{19}F and ^{31}P N.m.r. spectra were recorded for all compounds (see Table 7); in some cases considerable difficulty in obtaining spectra was experienced, on account of the low solubility of the compounds in all common organic solvents. This is especially true for ^{31}P spectra. The ^{31}P shift values which could be obtained are in the range +45·5 to +71·3 p.p.m.; they are thus typical of highly shielded phosphorus, as in other fluorophosphoranes.[26] The multiplicity of the ^{31}P spectra is in accord with the expectation, and no effect of P–P or P–F long range interaction is readily apparent.

A basic doublet is seen in the ^{19}F spectra of all compounds (Table 7) but the doublet components have considerable fine structure, and it is not possible to obtain accurate P–F coupling constants directly. The separation of the strongest peaks of the spectra is of the order of 900 Hz. The apparent observation of only one fluorine environment in fluorodiazadiphosphetidines, at a first glance, seems to contradict the otherwise well supported formulation (I) for both $(F_3PNR)_2$ and $(F_2RPNR')_2$ which would both require non-equivalent fluorine atoms. The spectrum for $(RF_2PNR')_2$ would be compatible with a structure (I) in which R is axial but this is against previous evidence, according to which the axial positions in fluorophosphoranes are virtually always occupied by the most electronegative groups.[20,21,46]

It seems reasonable to rationalize the observed 'simplified' ^{19}F n.m.r. spectra in terms of the well established 'pseudorotation' concept of Berry,[21–24] *i.e.* they are the result of a positional exchange process taking place within the trigonal-bipyramidal structure. The observed δ_F values [+73·5 to +79·5 p.p.m. for $(F_3PNR)_2$; +50·4 to +65·4 p.p.m. for $(RF_2PNR')_2$] thus represent average shift values (*cf.* Table 7). The ^{19}F n.m.r. spectrum of $(F_3PNMe)_2$ has been interpreted on that assumption, and accurate n.m.r. parameters (including the P–P coupling constant) have been obtained from the analysis of the spectrum which was treated as an $X_3AA'X'_3$ system.[47] Besides the Berry mechanism (which would require a transition state with a N–P–N angle $<90°$) the possibility has been suggested that equivalence of the fluorine atoms may also be the result of quasirotation of the F_3 group if the N–P–N angle remains fixed at 90°.[47] It is impossible for $(F_3PNMe)_2$ to exist in the normally favoured trigonal-bipyramidal configuration with two axial fluorine atoms, unless the P–N ring is considerably distorted. Presumably, the true interconversion process is intermediate between the two alternatives.[47,48]

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