View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1971. Downloaded by University of Florida Libraries on 28/12/2017 06:05:02.

Preparation and Characterisation of Some Nitrogen-bridged Phosphorus Fluorides

By **J. S. Harman, M. E. McCartney,** and **D. W. A. Sharp,*** Department of Chemistry, University of Glasgow, Glasgow W.2

Difluorophosphino(tetrafluorophosphoranyl)methylamine, $PF_2{\cdot}NMe{\cdot}PF_4$, and difluorophosphino(difluorophosphoryl)methylamine, $PF_2{\cdot}NMe{\cdot}POF_2$, result from the action of difluorophosphino(trimethylsilyl)methylamine on phosphorus pentafluoride and phosphoryl trifluoride respectively. Difluorophosphino(trimethylsilyl)methylamine can be prepared in good yield from chlorodifluorophosphine and heptamethyldisilazane. An alternative route to difluorophosphino(difluorophosphoryl)methylamine is the reaction between methylaminophosphoryl difluoride and chlorodifluorophosphine in the presence of base. Some other routes for these derivatives are described with the properties of these nitrogen-bridged derivatives. Comparable reactions with thionyl fluoride and sulphur dioxide do not yield products containing nitrogen bridges between phosphorus and sulphur atoms. Spectroscopic data are presented for all of these compounds.

THE cleavage of silicon–nitrogen bonds by fluorophosphoranes has proved a useful route to amino-derivatives of quinquevalent phosphorus.[1] By using difluorophosphino(trimethylsilyl)methylamine, $Me_3Si{\cdot}NMe{\cdot}PF_2$,[2] as a starting reagent we have extended this method to prepare some nitrogen-bridged phosphorus fluorides. The only previously known fluoro-substituted quinquevalent compounds of this type are bis(difluorophosphoryl)methylamine and its thiophosphoryl analogue, $(F_2PX)_2NMe$ (X = O, S),[3] and the 1,3,2,4-diazafluorodiphosphetidines, $(F_3P{\cdot}NR)_2$.[1] The only compounds containing two fluorinated phosphorus nuclei in different valence states linked by a bridge, which are known to us, are $PF_2(X){\cdot}X{\cdot}PF_2$ (X = O, S).[4]

$Me_3Si{\cdot}NMe{\cdot}PF_2$ has previously been produced in low yield by the fluorination of the corresponding chloride with SbF_3.[2] Schmutzler reported that no reaction takes place between phosphorus trifluoride and heptamethyldisilazane,[5] while that between phosphorus trichloride and heptamethyldisilazane takes place below room temperature.[2] At 90 °C the P–Cl bond in PF_2Cl is readily cleaved by heptamethyldisilazane to give $Me_3SiNMePF_2$ in good yield [reaction (1)]. $Me_3Si{\cdot}NMe{\cdot}PF_2$ could be prepared in the presence of excess of PF_2Cl without evidence for the cleavage of the second Si–N bond. It cannot be produced from the reaction between $MeNHPF_2$ and Me_3SiCl in the presence of a base.

$$(Me_3Si)_2NMe + PF_2Cl \longrightarrow Me_3Si{\cdot}NMe{\cdot}PF_2 + Me_3SiCl \quad (1)$$

$Me_3Si{\cdot}NMe{\cdot}PF_2$ reacts readily with PF_5 below room temperature to give difluorophosphino(tetrafluorophosphoranyl)methylamine, $PF_2{\cdot}NMe{\cdot}PF_4$ [reaction (2)].

$$Me_3Si{\cdot}NMe{\cdot}PF_2 + PF_5 \longrightarrow PF_2{\cdot}NMe{\cdot}PF_4 + Me_3SiF \quad (2)$$

The analogous reaction with POF_3 does not take place at room temperature, and only partial conversion into difluorophosphino(difluorophosphoryl)methylamine, $PF_2{\cdot}NMe{\cdot}POF_2$, takes place at 60 °C. At higher temperatures $(POF_2)_2NMe$ and a small amount of $PF_2{\cdot}NMe{\cdot}POF_2$ are identified among the volatile products. The relative ease of these reactions is suggested to depend on both the Lewis acidity of the phosphorus fluoride and the Lewis basicity of the silicon–nitrogen compound.

While $PF_2{\cdot}NMe{\cdot}POF_2$ can also be prepared in low yield by the fluorination of $PCl_2{\cdot}NMe{\cdot}POCl_2$, the best route to this compound is through the reaction (3) between methylaminophosphoryl difluoride and chlorodifluorophosphine in the presence of *NN*-dimethylaniline. While both this reaction and that between $MeNH{\cdot}POF_2$ and POF_2Cl (ref. 3) only take place in the presence of a base, base is not required for reaction (4) between $MeNHPF_2$ and PF_5 from which $PF_2{\cdot}NMe{\cdot}PF_4$, $MeNH{\cdot}PF_4$[6] and $(PF_2)_2NMe$[7] can be isolated.

$$MeNH{\cdot}POF_2 + PF_2Cl \xrightarrow[-HCl]{PhNMe_2} PF_2{\cdot}NMe{\cdot}POF_2 \quad (3)$$

$$MeNH{\cdot}PF_2 + PF_5 \longrightarrow MeNH{\cdot}PF_4 + (PF_2)_2NMe + PF_2{\cdot}NMe{\cdot}PF_4 + \text{solids} \quad (4)$$

Difluorophosphino(tetrafluorophosphoranyl)methylamine is a volatile compound which is stable for short periods at room temperature. However, deposition of solids takes place at 50 °C; the volatile products of the decomposition (5) are identified as PF_3 and $(F_3PNMe)_2$;

$$PF_2{\cdot}NMe{\cdot}PF_4 \longrightarrow (F_3PNMe)_2 + PF_3 \quad (5)$$

$(F_3PNMe)_2$ has also been obtained from the reaction between $Me_3Si{\cdot}NMe{\cdot}POF_2$ and PF_5, which was postulated to proceed through the intermediate formation of $POF_2{\cdot}NMe{\cdot}PF_4$.[8] The thermal instability of $PF_2{\cdot}NMe{\cdot}PF_4$ and the higher reaction temperature required on account of this compound's poor Lewis acidity precluded the further substitution of a second fluorine

---

[1] M. Murray and R. Schmutzler, *Z. Chem.*, 1968, **8**, 241; R. Schmutzler, in 'Halogen Chemistry,' Academic Press, London and New York, 1967, vol. 2, p. 31.

[2] R. Keat and L. Stobbs, personal communication to be published.

[3] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1970, **9**, 379.

[4] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1969, **8**, 2436; D. D. DesMarteau, *J. Amer. Chem. Soc.*, 1969, **91**, 6211.

[5] R. Schmutzler, *Chem. Comm.*, 1965, 19.

[6] J. S. Harman and D. W. A. Sharp, to be published.

[7] J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2689.

[8] J. S. Harman and W. E. Hill, unpublished work.

View Article Online

Published on 01 January 1971. Downloaded by University of Florida Libraries on 28/12/2017 06:05:02.

atom by a difluorophosphino-group. I.r. spectroscopy shows that $PF_2{\cdot}NMe{\cdot}PF_4$ is readily hydrolysed by moist air to PF_3 and POF_3.[9] A mass spectrum of $PF_2{\cdot}NMe{\cdot}PF_4$ is mainly that of its hydrolysis products.

$PF_2{\cdot}NMe{\cdot}POF_2$ is thermally more stable than $PF_2{\cdot}NMe{\cdot}PF_4$ and remains intact at 100 °C. A *ca.* 1 : 1 molar ratio of $PF_2{\cdot}NMe{\cdot}POF_2$ and HCl react together at room temperature. An investigation of the volatile products shows that all the HCl is absorbed and that excess of $PF_2{\cdot}NMe{\cdot}POF_2$ is recovered along with POF_3, POF_2Cl, $MeNH{\cdot}POF_2$, PF_3, and PCl_3 (from the disproportionation of PF_2Cl). The reaction temperature is much lower than that required partially to cleave the P–N bonds in the quinquevalent PNP bridged compounds[3] and close to that required to cleave both P–N bonds in $(PF_2)_2NMe$[7] (which presumably involves the formation of $MeNH{\cdot}PF_2$ as an intermediate). The non-isolation of $MeNH{\cdot}PF_2$ probably indicates the enhanced basicity of the nitrogen atom in the latter compound compared with that in $MeNH{\cdot}POF_2$.

TABLE 1

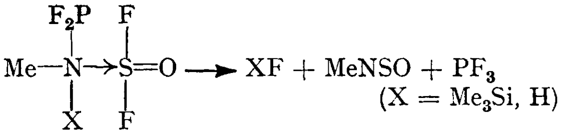
N.m.r. spectra of $PF_2{\cdot}NMe{\cdot}PF_2X$ ($X = O, F_2$) and $MeNH{\cdot}PXF_2$ (X = lone pair, O, F_2)[a,b]

	$\delta_{F(A)}$	$\delta_{F(B)}$	$J(P_AF_A)$	$J(P_BF_B)$
$PF_2{\cdot}NMe{\cdot}PF_4$	70	61	1280	896
$PF_2{\cdot}NMe{\cdot}POF_2$	71	78	1272	1039
$MeNH{\cdot}PF_2$[c]	71		1193	
$MeNH{\cdot}POF_2$		79		1000
$MeNH{\cdot}PF_4$[d]		74		847

	$J(P_BF_A)$	$J(P_AF_B)$	$J(F_AF_B)$	δ_{Me}	$J(P_AH)$	$J(P_BH)$	$J(F_AH)$	$J(F_BH)$
$PF_2{\cdot}NMe{\cdot}PF_4$	3·7	87·0	9·8	−2·9	2·2	15·2	2·7[f]	2·0[f]
$PF_2{\cdot}NMe{\cdot}POF_2$	8·2	<1[e]	4·5	−2·9	1·7	12·0	1·7[f,h]	0·5[h]

[a] δ_F and δ_H given with respect to internal CCl_3F and Me_4Si. [b] 'A' represents PF_2 and 'B' represents POF_2 or PF_4. [c] Ref. 28. Recorded +70 °C; ref. 6. [e] Not resolvable in ^{19}F n.m.r. spectrum. [f] Obtained from ^{19}F n.m.r. spectrum. [h] Obtained from ^1H n.m.r. spectrum.

While thionyl fluoride reacts with either a secondary amine[10] or a dialkylaminotrimethylsilane[11] to produce *NN*-dialkylfluorosulphinamides, R_2NSOF, the reactions between SOF_2 and $MeNH{\cdot}PF_2$ or $Me_3Si{\cdot}NMe{\cdot}PF_2$ do not produce the expected $PF_2{\cdot}NMe{\cdot}SOF$. The volatile products from the reaction of SOF_2 or SO_2 with $MeNH{\cdot}PF_2$ were identified as PF_3, MeNSO, $MeNH{\cdot}POF_2$, and $MeNH{\cdot}PSF_2$. Previous work has shown that SO_2 is capable of oxidising P^{III} to P^V through initial nucleophilic attack by either the phosphorus or the oxygen atom on the sulphur or phosphorus atom respectively.[12,13] It is suggested that in these reactions an additional mechanism involves nucleophilic attack by a nitrogen atom in either $MeNH{\cdot}PF_2$ or $Me_3Si{\cdot}NMe{\cdot}PF_2$ on the sulphur atom in SOF_2. The intermediate adduct formed can then eliminate not only a molecule of HF (which is then removed by attacking the starting reagents) or Me_3SiF but also a molecule of PF_3 [reaction (6)].



$$Me{-}\underset{X}{\overset{F_2P}{N}}{\rightarrow}\underset{F}{\overset{F}{S}}{=}O \longrightarrow XF + MeNSO + PF_3 \quad (X = Me_3Si, H) \qquad (6)$$

The inability to isolate $PF_2{\cdot}NMe{\cdot}SOF$ presumably has its origin in the much higher strength of the P–F than the S–F bond [117 kcal/mol in PF_3[14] as compared with 76 in SF_4[15]]. A similar migration of a fluorine atom to that postulated in this reaction takes place in $POF_2{-}N{=}SF_2$, which decomposes at room temperature to form POF_3 and NSF.[16]

Alkylamino-phosphoryl and -thiophosphoryl difluorides are well established.[17] Both $MeNH{\cdot}POF_2$ and $MeNH{\cdot}PSF_2$ which are products of the above reactions have been prepared in good yield by the fluorination of the corresponding chlorides,[18] and Roesky and Klocker have recently characterised $MeNH{\cdot}POF_2$ by n.m.r. and i.r. spectroscopy.[19] The additional spectroscopic properties of $MeNH{\cdot}POF_2$ are described below and the properties of $MeNH{\cdot}PSF_2$ will be detailed elsewhere.[8]

N.m.r. Spectra.—Both $PF_2{\cdot}NMe{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}PF_4$ give apparently complicated n.m.r. spectra, but these are readily interpreted on the basis of a first-order analysis (Table 1). A variable-temperature n.m.r. study shows only one resonance for the tetrafluorophosphoranyl group in the ^{19}F n.m.r. spectrum of $PF_2{\cdot}NMe{\cdot}PF_4$, which indicates that pseudorotational processes operate down to −80 °C and render the fluorine atoms equivalent. While the ^{19}F chemical shifts are altered to a different extent, the values of $^1J(PF)$ are appreciably larger in both $PF_2{\cdot}NMe{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}PF_4$ than in the corresponding parent methylamino-derivatives.

---

[9] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, 1952, **20**, 1652.

[10] M. Goehring and G. Voigt, *Chem. Ber.*, 1956, **89**, 1050.

[11] D. H. Brown, K. D. Crosbie, J. I. Darragh, D. S. Ross, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1970, 914.

[12] B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 1965, 5516.

[13] E. Fluck and H. Binder, *Z. anorg. Chem.*, 1967, **354**, 139.

[14] S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.*, 1963, **17**, 204.

[15] P. A. G. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, *J. Chem. Thermodynamics*, 1970, **2**, 71.

[16] O. Glemser, H. W. Roesky, and P. R. Heinze, *Angew. Chem. Internat. Edn.*, 1967, **6**, 710.

[17] R. Schmutzler, *Adv. Fluorine Chem.*, 1965, **5**, 31.

[18] G. Schrader, unpublished results; Houben-Weyl, 'Methoden der Organischen Chemie,' Georg Thieme Verlag, Stuttgart, 4th edn., 1965.

[19] H. W. Roesky and W. Klocker, *Z. anorg. Chem.*, 1970, **375**, 140.

View Article Online

Published on 01 January 1971. Downloaded by University of Florida Libraries on 28/12/2017 06:05:02.

In both its preparation and its cleavage reaction with HCl, $PF_2{\cdot}NMe{\cdot}POF_2$ is present with $MeNH{\cdot}POF_2$. While $PF_2{\cdot}NMe{\cdot}POF_2$ is appreciably more volatile than $MeNH{\cdot}POF_2$, a mixture of these compounds is difficult to separate. Both this observation and an n.m.r. analysis of the mixture are in agreement with the formation of a weak adduct between these two compounds with interaction taking place at the difluorophosphino- end of the $PF_2{\cdot}NMe{\cdot}POF_2$ molecule. It is tentatively suggested that hydrogen bonding takes place between the fluorine atoms in the PF_2 group and the relatively acidic amino-proton in $MeNH{\cdot}POF_2$ or that there is interaction between the lone pair on the nitrogen of $MeNH{\cdot}POF_2$ and the phosphorus(III) of $PF_2{\cdot}NMe{\cdot}POF_2$. The difluorophosphoryl resonances of both $MeNH{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}POF_2$ are essentially unaffected, but the difluorophosphino- resonance in the ^{31}P n.m.r. spectrum at −171 p.p.m. (with reference to external 85% H_3PO_4) is shifted downfield of the uncomplexed resonance (−135 p.p.m.) and is absent from the ^{19}F n.m.r. spectrum indicating complete decoupling of the P^{III} and fluorine nuclei on the n.m.r. time-scale.

I.r. Spectra.—The assignments given in Table 2 for $PF_2{\cdot}NMe{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}PF_4$ are made by comparison with the i.r. spectra of $Me_2N{\cdot}PF_2$,[20] $MeNH{\cdot}POF_2$,[19] $MeNH{\cdot}PF_4$,[6] $(PF_2)_2NMe$,[7] and $(POF_2)_2NMe$.[3] Charlton and Cavell have suggested that a large increase in the value of $\nu_{as.PNP}$ takes place on replacing both the PF_2 groups in $(PF_2)_2NMe$ by POF_2 groups.[3] Since a less drastic change is observed for this mode in the chloro-compounds $(PCl_2)_2NMe$,[7] $PCl_2{\cdot}NMe{\cdot}POCl_2$, and $(POCl_2)_2NMe$,[21] $\nu_{as.PNP}$ is assigned to a peak at a lower frequency in $PF_2{\cdot}NMe{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}PF_4$ than that previously assigned for $(POF_2)_2NMe$. The value of $\nu_{sym.PNP}$ is less dependent on the oxidation state of the phosphorus atoms.

TABLE 2

Gas-phase i.r. spectra of $PF_2{\cdot}NMe{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}PF_4$

$PF_2{\cdot}NMe{\cdot}POF_2$	$PF_2{\cdot}NMe{\cdot}PF_4$	Assignments
2970w	3035w	ν(CH)
2910vw	2988w	
2842vw	2925vw,sh	
	2862vw	
1436vw	1477w	δ(CH)
1370s		ν(P=O)
1226w	1208m	ρ(Me)
1215w,sh		
1096m,br	1121ms	ν(CN)
	973s	ν[as. PF_2(e)]
937vs		ν[PF_2(O)]
927vs,sh	954vs	ν(as. PNP)
	888s	ν[sym. PF_2(e)] and ν[as. PF_2(a)]
888w		Combination
840 837 vs PQR 832	838 833 vs PQR 828	ν(as. $P^{III}F_2$)
811ms	817s	ν(sym. $P^{III}F_2$)
664w	663w	ν(sym. PNP)
	613w	ν[sym. PF_2(a)]
517	570w	δ(PNP) and δ(PF)
514 ms PQR	538ms	
508	429w	
480w	399m	
400m		

Bands at 1100 cm^{-1} and 1200 cm^{-1} are present in all the compounds containing a PNP skeleton and in $Me_3Si{\cdot}NMe{\cdot}PXF_2$ (X = lone pair, O, or S), where these were assigned to ν_{CN} and ρ_{Me} respectively.[8] The PF stretching modes for $PF_2{\cdot}NMe{\cdot}PF_4$ and $PF_2{\cdot}NMe{\cdot}POF_2$ are at slightly greater frequencies than in $MeNH{\cdot}PF_2$,[22] $MeNH{\cdot}POF_2$ (gas phase 935 and 919 $cm.^{-1}$), and $MeNH{\cdot}PF_4$.

Mass Spectra.—The mass spectrum of $PF_2{\cdot}NMe{\cdot}PF_4$ is that of its volatile hydrolysis products PF_3, POF_3, and $PF_2{\cdot}NMe{\cdot}POF_2$. The mass spectrum of $PF_2{\cdot}NMe{\cdot}POF_2$ shows similar species to those observed for $(POF_2)_2NMe$[3] and has a relatively weak molecular ion and a strong $[M - H]^+$ ion.

EXPERIMENTAL

The practical details are those previously described.[13] Products were identified by i.r., n.m.r., or mass spectroscopy.

Heptamethyldisilazane–Chlorodifluorophosphine.— Chlorodifluorophosphine[23] (2·19 g, 21 mmol) and heptamethyldisilazane[24] (2·7 g, 15·5 mmol) were condensed together into an ampoule and slowly warmed to 90 °C and then left overnight. The products were purified by fractional distillation and identified by i.r. spectroscopy. Difluorophosphino(trimethylsilyl)methylamine[8] (2·19 g, indicating 85% yield), passed a −23 °C bath but was trapped out at −45 °C, thus removing $(Me_3Si)_2O$[25] (trapped at −65 °C), MeSiF[26] (trapped at −126 °C), excess of PF_2Cl[27] (trapped at −110 °C), and a trace of PF_3[9] (trapped at −196 °C). Slight decomposition occurred if the reaction mixture was heated beyond 90 °C.

Trimethylchlorosilane–Methylaminodifluorophosphine.— Methylaminodifluorophosphine[28] (1·44 g, 14·4 mmol), trimethylchlorosilane (3·078 g, 28·5 mmol) (Midland Silicones Ltd.), and trimethylamine (1·268 g, 21·4 mmol) (Matheson Co.) were condensed together into an ampoule and warmed to room temperature. The mixture was shaken to complete the reaction. A white solid was formed together with Me_3SiF.[26,29] There was no n.m.r. evidence[2] for the production of any $Me_3Si{\cdot}NMe{\cdot}PF_2$.

Difluorophosphino(trimethylsilyl)methylamine–Phosphorus

---

[20] Sr. M. A. Fleming, R. J. Wyma, and R. C. Taylor, *Spectrochim. Acta*, 1965, **21**, 1189.

[21] R. Keat, *J. Chem. Soc.* (*A*), **1970**, **2732**.

[22] C. G. Barlow, R. Jefferson, and J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2692.

[23] R. G. Cavell, *J. Chem. Soc.*, 1964, 1992.

[24] R. C. Osthoff and S. W. Kantor, *Inorg. Synth.*, 1957, **5**, 55.

[25] H. Bürger, *Organometallic Chem. Rev.* (*A*), 1968, **3**, 425.

[26] H. Kriegsmann, *Z. anorg. Chem.*, 1958, **294**, 113.

[27] A. Müller, E. Niecke, B. Krebs, and O. Glemser, *Z. Naturforsch.*, 1968, **23**b, 588.

[28] J. S. Harman and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1970, 1935.

[29] H. Vahrenkamp and H. Nöth, *J. Organometallic Chem.*, 1968, **12**, 281; S. S. Danyla, *J. Amer. Chem. Soc.*, 1964, **86**, 4504; H. Schmidbauer, *J. Amer. Chem. Soc.*, 1963, **85**, 2336.

View Article Online

Published on 01 January 1971. Downloaded by University of Florida Libraries on 28/12/2017 06:05:02.

Pentafluoride.— Difluorophosphino(trimethylsilyl)methylamine (0·585 g, 3·4 mmol) and phosphorus pentafluoride (0·45 g, 4·2 mmol) (Matheson Co., purified by low-temperature distillation) were condensed into a reaction vessel at −196 °C and allowed to warm slowly to room temperature. The volatile components were removed to leave a very small amount of solid product. Me_3SiF and excess of PF_5 were both removed by passing the mixture through a trap held at −90 °C to leave a volatile liquid, *difluorophosphino(tetrafluorophosphoranyl)methylamine* [Found: C, 5·8; H, 1·5; F, 55·6; N, 6·8; P, 30·3%; *M*, 206 (vapour density; average of three readings). $CH_3F_6NP_2$ requires: C, 5·7; H, 1·6; F, 55·3; N, 6·6; P, 29·9%; *M*, 205].

After heating $PF_2{\cdot}NMe{\cdot}PF_4$ for 4 h in an n.m.r. tube at 50 °C, slight solid deposition and the formation of a small quantity of PF_3 [17] were noted. On increasing the temperature to 80 °C, PF_3 formation took place at a faster rate, but in addition a doublet of peaks appeared in the ^{19}F spectrum owing to the formation of $(F_3PNMe)_2$ [30] (confirmed by i.r.).[31]

Phosphorus Pentafluoride–Methylaminodifluorophosphine.—Excess of phosphorus pentafluoride and methylaminodifluorophosphine (0·51 g, 5·2 mmol) were slowly warmed from −196 °C. After being left at room temperature for a short time, the mixture was held at −90 °C and the excess of PF_5 together with POF_3 and PF_3 (identified by i.r.) were pumped off to show that less than 5·2 mmol of PF_5 had reacted. A white solid (0·33 g) was left after pumping off the remaining volatile material. The latter contained a mixture of PF_3,[9] PF_5,[9] POF_3,[9] $(PF_2)_2NMe$,[7] and $PF_2{\cdot}NMe{\cdot}PF_4$. The solid residue was heated to 100 °C and the volatile components POF_3,[9] $(PF_2)_2NMe$,[7] $PF_2{\cdot}NMe{\cdot}PF_4$, and $MeNH{\cdot}PF_4$ [6] trapped at −196 °C.

Chlorodifluorophosphine–Methylaminophosphoryl Difluoride.—Methylaminophosphoryl difluoride [18] (7·35 g, 63·5 mmol) and chlorodifluorophosphine (7·078 g, 67·8 mmol) were condensed together with an isopentane solution of *NN*-dimethylaniline (7·088 g, 61·5 mmol) (B.D.H.) into a reaction vessel and the mixture was shaken. The volatile material was freed from isopentane and a considerable quantity of PF_3 (identified by its i.r. spectrum [9]) by passage through a −60 °C trap. The mixture remaining was shown by its n.m.r. spectrum to consist of a mixture of unchanged $MeNH{\cdot}POF_2$ and $PF_2{\cdot}NMe{\cdot}POF_2$. While pure $MeNH{\cdot}POF_2$ only passed a −23 °C trap with difficulty and pure $PF_2{\cdot}NMe{\cdot}POF_2$ was only partially stopped at −44 °C, complete separation using these traps was a lengthy process and was not attempted for the whole mixture. A pure sample of *difluorophosphino(difluorophosphoryl)methylamine* [Found: C, 6·7; H, 1·8; F, 41·7; N, 7·5; O, 8·6; P, 33·7%; *M* (vapour density), 186. $CH_3F_4NOP_2$ requires C, 6·6; H, 1·6; F, 41·5; N, 7·7; O, 8·7; P, 33·9%; *M*, 183; v.p. 24 mmHg at 25 °C] (0·2 g, 1·2 mmol) was recovered and finally trapped at −60 °C.

Difluorophosphino(trimethylsilyl)methylamine–Phosphoryl Fluoride.— Difluorophosphino(trimethylsilyl)methylamine and excess of phosphoryl fluoride (Ozark-Mahoning) did not react in a closed vessel at room temperature. The temperature was slowly raised to 60 °C and the system kept at this temperature for several hours. Fractionation of the products gave some PF_3, POF_3, and Me_3SiF (which passed through a −65 °C trap) and a mixture of $PF_2{\cdot}NMe{\cdot}POF_2$ and $Me_3Si{\cdot}NMe{\cdot}PF_2$ which was retained in the −65 °C trap. On performing the reaction at 110 °C the products were traces of $PF_2{\cdot}NMe{\cdot}POF_2$ along with $(POF_2)_2NMe$ (n.m.r.).[32] A viscous oil was left in the reaction vessel.

Fluorination of Dichlorophosphino(dichlorophosphoryl)-methylamine.— Dichlorophosphino(dichlorophosphoryl)-methylamine [21] was heated at 60 °C in a closed vessel with a slurry of excess of sodium fluoride in sulpholan. A large quantity of PF_3 and a small trace of POF_3 [9] could be separated from $PF_2{\cdot}NMe{\cdot}POF_2$ which was formed in low yield.

Difluorophosphino(trimethylsilyl)methylamine–Difluorophosphino(tetrafluorophosphoranyl)methylamine.— Approximately equivalent quantities of difluorophosphino(trimethylsilyl)methylamine and difluorophosphino(tetrafluorophosphoranyl)methylamine were condensed together into an n.m.r. tube. No reaction was observed at room temperature but on raising the temperature to 50 °C deposition of solids was noted and PF_3,[17] $(F_3PNMe)_2$,[30] and Me_3SiF [29] were formed.

Difluorophosphino(difluorophosphoryl)methylamine–Hydrogen Chloride.—Difluorophosphino(difluorophosphoryl)methylamine (0·899 g, 4·91 mmol) was condensed together with hydrogen chloride (0·174 g, 4·76 mmol) and left to warm to room temperature; 0·088 g of solid product was formed. PF_3 (0·257 g, 2·92 mmol) passed a −126 °C trap and a mixture of POF_2Cl and POF_3 (0·108 g, shown by its n.m.r. spectrum to contain *ca.* 0·34 mmol POF_2Cl [17] and 0·65 mmol POF_3 [17]) passed a −65 °C trap to leave 0·611 g of a mixture of $MeNH{\cdot}POF_2$, PCl_3 (identified by its i.r. spectrum [28]) and unchanged $PF_2{\cdot}NMe{\cdot}POF_2$.

Thionyl Fluoride–Methylaminodifluorophosphine.—Methylaminodifluorophosphine (1·739 g, 17·0 mmol) was condensed with thionyl fluoride (0·786 g, 9·2 mmol) [33] in an ampoule and left to warm to room temperature. The volatile products were small quantities of PF_3 [9] and SO_2 [34] together with a larger quantity of MeNSO,[35] which all passed a −75 °C trap. The major part of the less volatile components was $MeNH{\cdot}PSF_2$ [18] (3·0 mmol) together with a small amount of $MeNH{\cdot}POF_2$ (2·0 mmol); these can be separated by trapping the latter in a −23 °C bath. Unidentified solid (0·689 g) was recovered. In the presence of an excess of SOF_2, less $MeNH{\cdot}POF_2$ and more PF_3 was produced.

Sulphur Dioxide–Methylaminodifluorophosphine.—Methylaminodifluorophosphine (0·349 g, 3·53 mmol) was condensed with an excess of SO_2 (B.D.H.) and left to warm to room temperature. After removal of PF_3 (0·025 g, 0·28 mmol) and excess of SO_2, 0·175 g of an approximately 1 : 1 mixture of $MeNH{\cdot}POF_2$ and $MeNH{\cdot}PSF_2$, was recovered. An unidentified viscous liquid (0·167 g) remained.

Difluorophosphino(trimethylsilyl)methylamine–Thionyl Fluoride.—Thionyl fluoride (1·024 g, 11·9 mmol) and di-

---

[30] R. K. Harris and C. M. Woodman, *Mol. Phys.*, 1966, **10**, 437.

[31] G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903; M. P. Yagupsky, *Inorg. Chem.*, 1967, **6**, 1770 A. J. Downs, *Chem. Comm.*, 1967, 628.

[32] R. Keat and L. Stobbs, unpublished observations.

[33] C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, 1960, **25**, 2016.

[34] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York and London, 1963.

[35] W. K. Glass and A. D. E. Pullin, *Trans. Faraday Soc.*, 1961, **57**, 546.

View Article Online

Published on 01 January 1971. Downloaded by University of Florida Libraries on 28/12/2017 06:05:02.

fluorophosphino(trimethylsilyl)methylamine (0·616 g, 3·6 mmol) were heated in a closed vessel for 24 h at 100 °C (no reaction took place at room temperature). After the volatile material had been pumped off, a viscous yellow liquid (0·047 g) was left in the reaction flask. The volatile fraction contained PF_3,[9] SOF_2,[34] Me_3SiF,[27] MeNSO,[35] and a mixture of compounds which were trapped at −65 °C. Most of the SOF_2 was recovered. The less volatile fraction contained $Me_3Si{\cdot}NMe{\cdot}PF_2$, MeNSO ($<1$ mmol) and a trace of $PF_2{\cdot}NMe{\cdot}POF_2$ (n.m.r.).

We thank the Ministry of Defence for financial support, and R. Keat and Midland Silicones Ltd. for the gift of some starting reagents.

[0/1694 *Received, October 5th*, 1970]