1048. *Phosphorus–Fluorine Chemistry. Part XVI.*[1] *Chemistry of Alkyl- and Aryl-dialkylaminofluoro-phosphoranes and -phosphines*

By REINHARD SCHMUTZLER

Alkyl- and aryl-dialkylaminochlorophosphines, R(or Ar)$PClNR'_2$, react with Group V trifluorides such as AsF_3 or SbF_3 to give alkyl- and aryl-dialkylaminotrifluorophosphoranes, R(or Ar)$PF_3NR'_2$. The oxidation number of phosphorus remains unchanged upon interaction of alkyl- and aryl-dialkylaminochlorophosphines with sodium fluoride in a tetramethylene sulphone medium. Alkyl- and aryl-dialkylaminofluorophosphines thus obtained may serve as ligands in co-ordination compounds with nickel(0) and molybdenum(0). ^1H, ^{19}F, and ^{31}P n.m.r. data for alkyl- and aryl-dialkylaminofluoro-phosphoranes and -phosphines will be presented. The spontaneous rearrangement

$$2MePF_3{\cdot}NMe_2 \longrightarrow [MePF(NMe_2)_2]^+[MePF_5]^-$$

has been established by ^{19}F and ^{31}P n.m.r. studies.

IN a number of recent publications [2,3] the reaction of chlorophosphines with Group V trifluorides has been reported to provide a convenient route towards the preparation of fluorophosphoranes, R_nPF_{5-n} (R = hydrocarbon group, $n = 1$ or 2). It was observed that electronegative substituents on the tervalent phosphorus may prevent its oxidation to the quinquevalent state, and in perfluoroalkyl halogenophosphines, but also in dialkylaminodichlorophosphines, R_2NPCl_2, or chlorophosphites, $(RO)_nPCl_{3-n}$, for example, a simple halogen exchange took place with the Group V fluoride. The present study investigates the interaction of Group V trifluorides with dialkylaminochlorophosphines, R(or Ar)$PClNR'_2$, intermediate between dichlorophosphines, R(or Ar)PCl_2, and dialkylaminodichlorophosphines, R_2NPCl_2. Both types of products to be expected, R(or Ar)$PFNR'_2$, and R(or Ar)$PF_3NR'_2$, were unknown until recently, and their chemistry is virtually unexplored.

EXPERIMENTAL

The usual precautions required in handling air- and moisture-sensitive materials were observed.

Materials.—Hydrocarbon solvents such as light petroleum, benzene, hexane, ether, etc., were dried over sodium wire. Tetramethylene sulphone (TMS) was used as obtained from Shell Chemical Co., Ltd., Industrial Chemicals Division, Marlborough House, London W.1. Sodium fluoride (AnalaR) was dried for 10 hr. at 500°, and was allowed to cool in a desiccator. Methyl- and phenyl-dichlorophosphine were obtained from Dr. A. F. Childs, Research Department, Albright and Wilson (Mfg) Ltd., Oldbury, Birmingham, and Dr. E. N. Walsh, Stauffer Chemical Co., Victor Division, Chicago, Ill., U.S.A., respectively. Antimony and arsenic trifluorides were used as obtained from Ozark-Mahoning Co., Tulsa, Oklahoma, U.S.A. Tetracarbonylnickel and hexacarbonylmolybdenum were used as obtained from Mond Nickel Co., and Climax Molybdenum Co., respectively. Cycloheptatriene was obtained from Shell Chemical Co. Ltd.

Infrared Spectra.—They were obtained on a Perkin-Elmer model 21 (2—15 μ) and model 337 (2—25 μ) spectrometer.

Mass Spectra.—A Bendix time-of-flight mass spectrometer, model 12-101, was used, employing the following standard conditions: electron energy 70 ev, filament current 3 A, trap current 0·13 μA. Sample size 0·2—0·5 μl., inlet temperature 100—200°.

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[1] Part XV, Fluoro-1,2,3,4-diazadiphosphetidines, R. Schmutzler, *Chem. Comm.*, 1965, 19.

[2] I. P. Komkov, S. Z. Ivin, K. V. Karavanov, and L. Ye. Smirnov, *Zhur. obshchei Khim.*, 1962, **32**, 301.

[3] R. Schmutzler, *Chem. and Ind.*, 1962, 1868; *Inorg. Chem.*, 1964, **3**, 410.

N.m.r. Spectra.—^1H N.m.r. spectra were obtained at 60 Mc./sec. both on a Perkin-Elmer and a Varian Associates (A60) analytical spectrometer. ^{19}F and ^{31}P N.m.r. spectra were obtained on a Varian Associates spectrometer, model 4300 B, equipped with a 12-in. electromagnet with flux stabilisation. Non-spinning 10-mm. tubes were used for the ^{31}P spectra, and 5-mm. spinning tubes for the ^{19}F spectra. ^{19}F Spectra were obtained at 40 Mc./sec., and ^{31}P spectra at 16·2 Mc./sec., at a magnetic field of 9400 gauss. Sealed capillaries containing 85% H_3PO_4 were inserted into the phosphorus n.m.r. tubes as a reference, while trichlorofluoromethane was used as an internal standard for the ^{19}F spectra.

Molecular Weights.—They were determined in acetone solutions, using the osmometer of Mechrolab, Inc., Mountain View, California.

Preparation of Alkyl- and Aryl-dialkylaminofluorophosphines.—Pertinent data are summarised in Table 1. Alkyl- and aryl-dialkylaminochlorophosphines were prepared according to literature procedures referred to in Table 1. The new compound $ClCH_2PClNMe_2$ was obtained by the reaction of chloromethyldichlorophosphine (160 g., 1·06 moles) with a stoicheiometric amount (95·6 g., 2·12 moles) of dimethylamine in ether (2 l.) at −50° to 0°. Work-up in the usual manner gave 105 g. (62%) of the *compound*, b. p. 64°/12 mm. (Found: C, 22·3; H, 5·0; Cl, 44·5; N, 8·7. $C_3H_8Cl_2NP$ requires C, 22·5; H, 5·0; Cl, 44·3; N, 8·8%).

TABLE 1

Alkyl- and aryl-dialkylaminofluoro-phosphines and -phosphoranes

No.	Compound	Reactants (moles)	Reaction time (hr.) and temp.	Yield (%)	B. p./mm.
1	$MePF{\cdot}NMe_2$	$MePCl{\cdot}NMe_2$ [a] (0·43), NaF (1·5), TMS (150 ml.)	1 at 80°, then 1 at 120	90	85—86°/760
2	$PhPF{\cdot}NMe_2$	$PhPCl{\cdot}NMe_2$ [b] (0·305), NaF (0·6), TMS (100 ml.)	2·5 at 100—130	68	88—90/15
3	$PhPF{\cdot}NEt_2$	$PhPCl{\cdot}NEt_2$ [c] (0·25), NaF (0·5), TMS (120 ml.)	1 at 100, then 1 at 130, then 1 at 170	72	54—56/0·25
4	$MePF_3{\cdot}NMe_2$	$MePCl{\cdot}NMe_2$ [a] (0·19), SbF_3 (0·25)	0·7 at 20—50, then 1 at 80	48 [d]	85/760
5	$PhPF_3{\cdot}NMe_2$ [e]	$PhPClNMe_2$ [b] (0·1), AsF_3 (0·14)	1 at 25—45, then 0·5 at 40—50	52	42/0·3
6	$PhPF_3{\cdot}NEt_2$ [e]	$PhPCl{\cdot}NEt_2$ [c] (0·1), AsF_3 (0·15)	1 at 25—50, then 3 at 60	33	51/0·03

	Found (%)							Calc. (%)					
No.	C	H	F	N	P	*M* [f]	Formula	C	H	F	N	P	*M*
1	33·4	8·5	17·4	13·0	28·0	109	C_3H_9FNP	33·0	8·3	17·4	12·8	28·4	109
2	55·8	6·6	11·5	8·2	18·0	171	$C_8H_{11}FNP$	56·1	6·5	11·1	8·2	18·1	171
3	59·4	7·6	9·1	7·2	14·9	199	$C_{10}H_{15}FNP$	60·3	7·6	9·5	7·0	15·5	199
4	24·9	6·5	—	9·3	—	147	$C_3H_9F_3NP$	24·5	6·2	—	9·5	—	147
6	—	—	—	—	—	237	$C_{10}H_{15}F_3NP$	—	—	—	—	—	237

[a] E. M. Evleth, L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, 1962, **27**, 2192. [b] H. Nöth and H. J. Vetter, *Chem. Ber.*, 1963, **96**, 1109. [c] G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J.*, 1962, 3984. [d] Elemental antimony was recovered in 86% yield based on the $MePCl{\cdot}NMe_2$ used (Found: Sb, 99·9. Calc. Sb, 100%). [e] Identified by comparison of ^1H, ^{19}F, and ^{31}P n.m.r. and i.r. spectra with those of authentic samples. [f] Obtained by mass spectrometry.

The preparation of phenyldiethylaminofluorophosphine, $PhPF{\cdot}NEt_2$, is typical. The fluorination was conducted in a 4-necked flask, equipped with a mechanical stirrer, a reflux condenser with drying tube, a thermometer reaching to the bottom of the flask, and a dropping funnel with side-arm. Phenyldiethylaminochlorophosphine (53·8 g., 0·25 mole) was added dropwise with stirring to a suspension of sodium fluoride (21 g., 0·5 mole) in tetramethylene sulphone (120 ml.).[Cf. 18] The mixture was heated with stirringf or 1 hr. at 100°, 1 hr. at 130°, and 1 hr. at 170°. Material distilling at 60—100°/0·2 mm. was collected and was fractionated twice through a 6-in. Vigreux column. Phenyldiethylaminofluorophosphine (35·6 g., 72%), b. p. 54—56°/0·25 mm., was thus obtained.

The fluorophosphines were stored in glass containers, and, in the absence of air and moisture, were stable for long periods.

Reactions of Alkyl- and Aryldialkylaminochlorophosphines with Antimony (*or Arsenic*) *Trifluoride.*—The reactions were conducted essentially as described for the preparation of fluorophosphoranes, R_nPF_{5-n}, from chlorophosphines and Group V trifluorides.[3] The preparation of methyldimethylaminotrifluorophosphorane is typical. A mildly exothermic reaction commenced upon addition of antimony trifluoride (44·6 g., 0·25 mole) to magnetically stirred methyldimethylaminochlorophosphine (24·1 g., 0·19 mole). A black precipitate was formed almost immediately. The addition of antimony trifluoride being completed in 0·7 hr. (temperature below 50°), the mixture was heated for 1 hr. at 80° (internal temp.). Distillation gave a colourless liquid (13·5 g., 48%), b. p. 85—89°, which was once redistilled through a 4-in. Vigreux column, b. p. 85°. From the distillation residue a total of 13·2 g. (86%) of elemental antimony was recovered after treatment with 10% hydrochloric acid, and was washed with methanol and ether and dried *in vacuo.*

The reactions of the other alkyl- and aryl-dialkylaminochlorophosphines with antimony trifluoride or arsenic trifluoride were conducted analogously (Table 1).

Reactions of Dialkylaminofluorophosphines with Metal Carbonyls and Some of their Derivatives.—(*a*) *Tris(phenyldiethylaminofluorophosphine)nickel*(0). The reaction was conducted in a 3-necked flask fittted with a reflux condenser, a thermometer, and a dropping funnel. The system was repeatedly flushed with nitrogen. Then phenyldiethylaminofluorophosphine (15·9 g., 0·08 mole) was placed in the flask in a countercurrent of nitrogen. Vigorous evolution of carbon monoxide commenced upon dropwise addition of tetracarbonylnickel (2·56 g., 0·015 mole) to the fluorophosphine over 30 min. The mixture was stirred for 20 hr. at room temperature, and 3 hr. at 70° (internal temp.). A strong CO doublet (2030, 1965 cm.$^{-1}$) was observed in the infrared (i.r.) spectrum, which remained essentially unchanged after two further heating periods (4 hr. at 140—150° and 8 hr. at 200°). There was slight decomposition under these vigorous conditions but no indications were found for tetrasubstitution of CO in tetracarbonylnickel. Still, two CO absorptions were observed in the i.r. spectrum at 1965 and 2035 cm.$^{-1}$, the latter being about half as intense as the former.

After addition of hexane (20 ml.) the mixture was kept for 2 days at 0°. Colourless crystals were thus obtained which were filtered and recrystallised from benzene–hexane (1 : 1). Hard crystals (2·1 g.), up to 10 mm. long, were obtained, and were filtered, washed with hexane, and dried *in vacuo.* Chemical analysis and the i.r. spectrum indicated formation of a trisubstituted derivative of tetracarbonylnickel (cf. Table 2).

TABLE 2

Co-ordination compounds containing dialkylaminofluorophosphine ligands

No.	Compound	Reactants (moles)	Reaction conditions	Yield (%)	Colour	M. p.
1	$Ni(CO)_2[MePFNMe_2]_2$	$Ni(CO)_4$ (0·0325), $MePF{\cdot}NMe_2$ (0·0645)	Stirred at 25° for 20 hr., 50—60° for 9 hr., and 70° for 3 hr.	92·5 [a]	Pale yellow	Liquid
2	$Ni(CO)_2[(Me_2N)_2PF]_2$	$Ni(CO)_4$ (0·0325), $(Me_2N)_2PF$ (0·065)	As for no. 1	83 [a]	Pale orange	Liquid
3	$Ni(CO)[PhPF{\cdot}NEt_2]_3$	$Ni(CO)_4$ (0·015), $PhPF{\cdot}NEt_2$ (0·08)	Cf. text	Cf. text	Colourless	97°
4	$Mo(CO)_3[MePF{\cdot}NMe_2]_3$	$C_7H_8Mo(CO)_3$ (0·011) [b] $MePF{\cdot}NMe_2$ (0·11)	Heated at 40° for 10 min.	54	Colourless	127—128 [c]
5	$Mo(CO)_3[PhPF{\cdot}NEt_2]_3$	$C_7H_8Mo(CO)_3$ (0·008) [b] $PhPF{\cdot}NEt_2$ (0·04)	As for no. 4	51	Colourless	138—139 [d]
6	$Mo(CO)_3[(Me_2N)_2PF]_3$	$C_7H_8Mo(CO)_3$ (0·014) [e] $(Me_2N)_2PF$ (0·095)	As for no. 4	24	Colourless	108—110

	Found (%)						Calc. (%)				
No.	C	H	F	N	*M*	Formula	C	H	F	N	*M*
1	28·6	5·5	—	8·6	301	$C_8H_{18}F_2N_2NiO_2P_2$	28·8	5·5	—	8·4	333
2	31·0	6·5	—	14·8	—	$C_{10}H_{24}F_2N_4NiO_2P_2$	30·7	6·2	—	14·3	—
3	54·8	6·8	—	6·1	—	$C_{31}H_{45}F_3N_3NiOP_3$ [f]	54·5	6·6	—	6·1	—
4	28·1	5·4	11·2	8·2	491	$C_{12}H_{27}F_3MoN_3O_3P_3$	28·4	5·4	11·2	8·3	507
5	51·0	6·3	6·8	5·3	752	$C_{33}H_{45}F_3MoN_3O_3P_3$	51·6	5·8	7·3	5·4	778
6	29·8	5·9	9·7	8·6	595	$C_{15}H_{36}F_3MoN_6O_3P_3$	30·4	6·1	9·6	8·4	594

[a] Yield after removal of volatile material by pumping at 25°/1·5 mm. for 16 hr. [b] In ether (20 ml.). [c] With darkening. [d] With darkening from 130°. [e] In ether (25 ml.). [f] Found: Ni (by EDTA), 8·3; P, 14·0. Calc. Ni, 8·6; P, 13·6%.

The dicarbonylnickel(0) derivatives were prepared by the reaction of tetracarbonylnickel and the appropriate ligand in a molar ratio of 1 : 2 (cf. Table 2).

(*b*) *Tricarbonylmolybdenum*(0) *derivatives.* The general procedure, involving the reaction of cycloheptatrienetricarbonylmolybdenum(0) [4] with excess of the ligand, has been described repeatedly.[5-7] The preparation of tris(methyldimethylaminofluorophosphine)tricarbonylmolybdenum(0) is typical.

With exclusion of air and moisture a solution of cycloheptatrienetricarbonylmolybdenum(0) [4] (3·0 g., 0·011 mole) in ether (30 ml.) was added dropwise with stirring to methyldimethylaminofluorophosphine (12·0 g., 0·11 mole). The mildly exothermic reaction was accompanied by an immediate colour discharge of the deep red solution of the π-complex. After 10 min. under reflux, the mixture was cooled and evaporated to dryness at room temperature and 100, 10, and 1 mm., successively. The residue was dissolved in ether (10 ml.), boiled briefly with activated carbon, filtered, and allowed to crystallise at 0° after addition of light petroleum (10 ml.; b. p. 36—53°). Colourless crystals (3·0 g., 54%) thus obtained were recrystallised once more from ether–light petroleum, m. p. 127—128° (with darkening). Analytical data for this and the other compounds are presented in Table 2.

It is interesting to note that a sample of bisdimethylaminofluorophosphine used in this work, after several months storage at room temperature, had apparently undergone the following disproportionation:

$$2(\mathrm{Me_2N})_2\mathrm{PF} \longrightarrow \mathrm{Me_2NPF_2} + (\mathrm{Me_2N})_3\mathrm{P}$$

The presence of the difluoro-compound was shown by the ^{19}F ($J_{\mathrm{P-F}} = 1190$ c./sec.; δ_{F} $+64{\cdot}3$ p.p.m.; $J_{\mathrm{F-H}} \sim 3{\cdot}7$ c./sec.) and ^{31}P n.m.r. spectrum ($J_{\mathrm{P-F}} = 1190$ c./sec.; $\delta_{\mathrm{P}} = -142{\cdot}0$ p.p.m.). The trisdimethylamino-derivative was identified by ^{31}P and ^{1}H n.m.r. as the high-boiling residue left after the fractionation of $(\mathrm{Me_2N})_2\mathrm{PF}$: $\delta_{\mathrm{P}} = -122{\cdot}5$ p.p.m.; $\delta_{\mathrm{H}} = -2{\cdot}42$ p.p.m.; $J_{\mathrm{H-P}} = 9$ c./sec. These data are in agreement with those for the authentic compounds.[8]

Infrared Spectra of Co-ordination Compounds containing Dialkylaminofluorophosphine Ligands.—The following principal absorptions (cm.$^{-1}$) were observed:

$\mathrm{Ni(CO)_2(MePF{\cdot}NMe_2)_2}$ (in $\mathrm{CCl_4}$): 2988m, 2900s, 2858sh, 2800m ($\mathrm{N{-}CH_3}$); 2020, 1961vs (CO); 1467s; 1419, 1409m; 1309m; 1290s; 1278m; 1181s; 1092w; 1060m; 980vs; 882vs,b; (cf. $\mathrm{N{-}CH_3}$ absorption in unco-ordinated ligand: 2800vs).

$\mathrm{Ni(CO)_2[(Me_2N)_2PF]_2}$ (in $\mathrm{CCl_4}$): 2990sh; 2930s; 2800s ($\mathrm{N{-}CH_3}$); 2460m; 2019, 1961vs; 1469s; 1410vw; 1299, 1255m; 1190, 1143m; 1092m; 1062s; 1022m; 980, 959vs; 889w; 848m; 727, 705s; (cf. $\mathrm{N{-}CH_3}$ absorption in unco-ordinated ligand: 2792s).

$\mathrm{Ni(CO)(PhPF{\cdot}NEt_2)_3}$ (in KBr): ~3050m; 2980, 2940, 2880m; ~1960vs,b; 1592w; 1576m; 1490, 1466, 1441s; 1380vs; 1345s; 1310w; 1291m; 1207vs; 1177vs,b; 1107vs; 1063m; 1023vs,b; 938, 920vs; 792vs; ~750vs,b; ~700vs,b; ~670vs,b.

$\mathrm{Mo(CO)_3(MePF{\cdot}NMe_2)_3}$ (in KBr): 2925, 2860m; 2794w ($\mathrm{N{-}CH_3}$); 1959, 1858vs; 1460, 1421, 1321m; 1293, 1278, 1175, 1115s; 1060m; 980vs; 895, 880vs; 738, 712, 670vs. (CO region in $\mathrm{CCl_4}$: 1970, 1882vs, sharp; $\mathrm{N{-}CH_3}$ absorption in free ligand: 2800).

$\mathrm{Mo(CO)_3(PhPF{\cdot}NEt_2)_3}$ (in KBr): 3040w; 2960, 2920, 2864s; *ca.* 1950, 1850vs,b; 1480m; 1458, 1433, 1377, 1361, 1340s; 1309w; 1286m; 1200, 1165, 1103s; 1070vw; 1060m; 1023vs; 940, 917vs; 852w; 789, 765, 751vs,b; 698, 669vs,b; (CO region in $\mathrm{CCl_4}$: 1960, 1873vs, sharp).

$\mathrm{Mo(CO)_3[(Me_2N)_2PF]_3}$ (in KBr): 3018vs; 2900s,b; 2848sh; 2802s ($\mathrm{N{-}CH_3}$); 1950, 1860vs; 1481, 1452, 1405m; 1381w; 1286s; 1190, 1171s; 1141w; 1063s; 988, 977, 965vs; 753, 735, 707, 697, 670vs; (CO region in $\mathrm{CCl_4}$: 1969, 1878vs, sharp).

RESULTS AND DISCUSSION

The reaction of Group V trifluorides, such as $\mathrm{AsF_3}$ or $\mathrm{SbF_3}$, with several alkyl- and aryldialkylaminochlorophosphines proceeded essentially analogously to the reaction of the same fluorinating agents with chlorophosphines, $\mathrm{R}_n\mathrm{PCl}_{3-n}$ ($n = 1,2$),[2,3] *viz.*,

$$3\mathrm{R(or\ Ar)PCl{\cdot}NR'_2} + 3\mathrm{MF_3} \longrightarrow 3\mathrm{R(or\ Ar)PF_3{\cdot}NR'_2} + 2\mathrm{M} + \mathrm{MCl_3}\ (\mathrm{M} = \mathrm{As,\ Sb})$$

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[4] E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J.*, 1958, 4559.

[5] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J.*, 1959, 2323.

[6] R. Schmutzler, *Chem. Ber.*, 1963, **96**, 2435.

[7] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 415.

[8] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, 1965, **20*b***, 104.

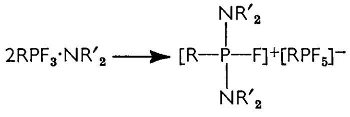
The redox reaction does not proceed as readily as with the dichlorophosphines, however, and furthermore, oxidation of the tervalent phosphorus to the quinquevalent state is sometimes incomplete. In the reaction of dialkylaminodichlorophosphines, R_2NPCl_2, with antimony trifluoride [7] only dialkylaminodifluorophosphines, R_2NPF_2, were detected. Thus, the behaviour of R(or Ar)$PCl{\cdot}NR_2'$ towards AsF_3 or SbF_3 is indeed intermediate between $RPCl_2$,[2,3] and R_2NPCl_2.[7]

Preparative details for the three compounds of the type $RPF_3{\cdot}NR'_2$ thus obtained are given in Table 1. $MePF_3{\cdot}NMe_2$ is a new compound, $PhPF_3{\cdot}NMe_2$ and $PhPF_3{\cdot}NEt_2$ have been made previously by different routes.[9–11] Surprisingly, $ClCH_2PCl{\cdot}NMe_2$ reacted with SbF_3 to give a complex mixture of products, not containing the expected $ClCH_2PF_3{\cdot}NMe_2$. The identity of our trifluorophosphoranes was established especially by their n.m.r. spectra (Table 3).

The ^{19}F and ^{31}P n.m.r. data may be interpreted in terms of a trigonal bipyramidal model, in which the two axial (F_a) and one equatorial (F_e) positions are occupied by fluorine atoms.[9,11–13] Accordingly, a doublet (J_{P-Fa}) of doublets (J_{Fa-Fe}) and a doublet (J_{P-Fe}) of triplets (J_{Fe-Fa}) are observed in the ^{19}F spectra, whilst the ^{31}P spectra consist of a doublet (J_{P-Fe}) of triplets (J_{P-Fa}). The positive values of the ^{31}P chemical shifts, ranging between $+37{\cdot}2$ and $+53{\cdot}6$ p.p.m., are indicative of pentaco-ordinate phosphorus,[13] and are similar in magnitude to δ_P of $(C_2H_5O)_5P$ ($+70{\cdot}9$) [14] or of the adducts of trialkyl phosphites with *o*-quinones and α-diketones,[15] which also contain pentaco-ordinate phosphorus.

The ^1H n.m.r. spectra of alkyl- and aryl-dialkylaminotrifluorophosphoranes (cf. Table 3) are also consistent with the assigned structures. Thus, the ^1H spectrum of $MePF_3{\cdot}NMe_2$ shows a basic doublet both in the Me and the NMe_2 region. The two components of the methyl resonance are further split into triplets (J_{CH_3-Fa}), each component finally being split into another doublet (J_{CH_3-Fe}). The observation of much stronger coupling between CH_3 and axial than between CH_3 and equatorial fluorine is quite reasonable for the proposed configuration, the strongest interaction being expected between groups at close to 90° angles (F_a and CH_3). The protons of the Me_2N group in $MePF_3NMe_2$ (and also in $PhPF_3NMe_2$) are coupling equally with the three fluorine atoms, however, and a 2·6—2·7 c./sec. coupling constant is observed. Each component of the basic doublet (J_{NMe_2-P}) is therefore split into a quartet.

A very interesting feature of certain compounds of the type $RPF_3NR'_2$ is a rearrangement to an ionic structure, the overall reaction being



$$2RPF_3{\cdot}NR'_2 \longrightarrow [R{-}\overset{\displaystyle NR'_2}{\underset{\displaystyle NR'_2}{P}}{-}F]^+[RPF_5]^-$$

This rearrangement has been established, thus far, for the compound $PhPF_3{\cdot}NMe_2$, which, after being isolated as a typically covalent, distillable liquid, on standing at room temperature changes to a salt-like product, containing the two novel ionic species, $[PhPF(NMe_2)_2]^+$ and $[PhPF_5]^-$.[16] It has now been found that the methyl analogue undergoes the same type of rearrangement,

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[12] (*a*) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613; (*b*) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

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[14] D. B. Denney and H. M. Relles, *J. Amer. Chem. Soc.*, 1964, **86**, 3897.

[15] F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Amer. Chem. Soc.*, 1963, **85**, 3465.

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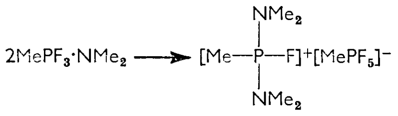

$$2\,MePF_3{\cdot}NMe_2 \longrightarrow [Me{-}\overset{NMe_2}{\underset{NMe_2}{P}}{-}F]^+[MePF_5]^-$$

A sample of the methyl analogue, dissolved in acetonitrile, for instance, according to its ^{19}F n.m.r. spectrum, recorded 3 months after the preparation, was completely rearranged

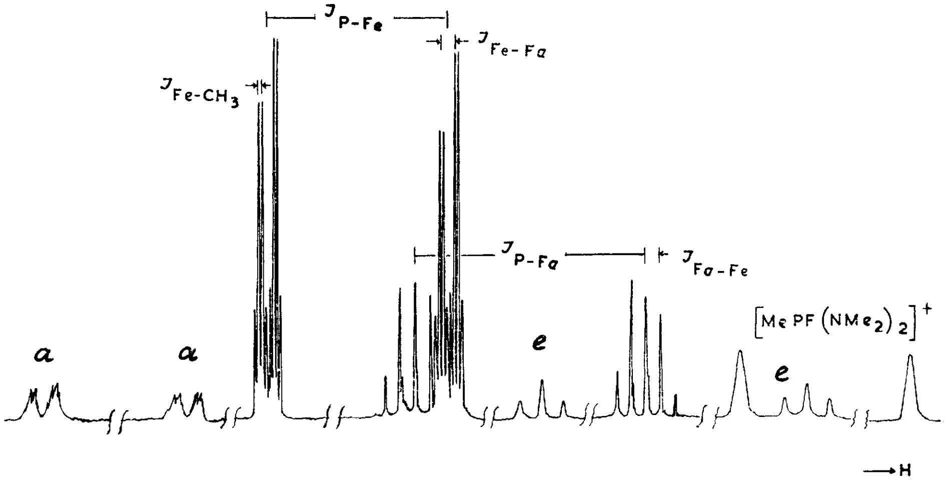

FIGURE 1. ^{19}F N.m.r. spectrum at 56·4 Mc/sec. of $[MePF(NMe_2)_2]^+[MePF_5]^-$, observed on a neat sample of $MePF_3{\cdot}NMe_2$, kept 10 days at room temperature after its distillation. Resonances due to traces of $MeP(\dot{:}O)F_2$, $MeP(\dot{:}O)F{\cdot}NMe_2$, and $MePF{\cdot}NMe_2$, are omitted. A small amount of unrearranged $MePF_3{\cdot}NMe_2$ is shown (*a*, *e*: resonances due to axial and equatorial fluorine in $MePF_3{\cdot}NMe_2$, cf. text)

TABLE 4

N.m.r. data (*J* values in c./sec., δ values in p.p.m.) for the rearrangement product of $MePF_3{\cdot}NMe_2$ ($\longrightarrow [MePF(NMe_2)_2]^+[MePF_5]$)

Species	^{19}F	^{31}P
$[MePF_5]^-$	$J_{P-Fe} = 829$; $J_{P-Fa} = 680$; $J_{Fe-Fa} = 35$; $J_{Fe-CH_3} = 8{\cdot}9$; $\delta_{Fe} = +45{\cdot}8$; $\delta_{Fa} = +57{\cdot}6$; $\delta_{Fa} - \delta_{Fe} = 11{\cdot}8$	$J_{P-Fe} = 833$; $J_{P-Fa} = 685$; $J_{P-CH_3} = 20$; $\delta_P = +126{\cdot}4$
$[MePF{\cdot}(NMe_2)_2]^+$	$J_{P-F} = 1028$; $\delta_F = +82{\cdot}3$	$J_{P-F} = 1030$; $\delta_P = -71{\cdot}4$
$MeP(\dot{:}O)F_2$ *	$J_{P-F} = 1103$; $\delta_F = +59{\cdot}5$	$J_{P-F} = 1090$; $\delta_P = -26{\cdot}8$
$MeP(\dot{:}O)(F)NMe_2$ *	$J_{P-F} = 1020$; $\delta_F = +60{\cdot}0$	$J_{F-F} = 1015$; $\delta_P = -38{\cdot}4$
$MePFNMe_2$ *	$J_{P-F} = 918$; $\delta_F = +115{\cdot}0$	$J_{P-F} = 925$; $\delta_P = -170{\cdot}4$
$MePF_3NMe_2$ *	$J_{P-Fe} = 957$; $J_{P-Fa} = 804$; $J_{Fe-Fa} = 51$ $\delta_{Fe} = +67{\cdot}6$; $\delta_{Fa} = +27{\cdot}5$	cf. footnote
Compare:		
$[PhPF_5]^-$[16]	$J_{P-Fe} = 818$; $J_{P-Fa} = 690$; $J_{Fe-Fa} = 41$	$J_{P-Fe} = 816$; $J_{P-Fa} = 697$; $\delta_P = +136{\cdot}0$
$[PhPF{\cdot}(NMe_2)_2]^+$[16]	$J_{P-F} = 1046$; $\delta_F = +86{\cdot}7$	$J_{P-F} = 1037$; $\delta_P = -56{\cdot}0$

Spectra were recorded on a neat sample of $MePF_3NMe_2$, stored for 10 days at room temperature after its distillation. The sample had rearranged to a large extent, but a small amount of unchanged $MePF_3NMe_2$ was still detected in the ^{19}F, but not in the less sensitive ^{31}P n.m.r. spectrum. F_a, F_e refer to fluorine atoms in axial and equatorial position, respectively, of the octahedron ($[MePF_5]^-$, $[PhPF_5]^-$) or of the trigonal bipyramid ($MePF_3NMe_2$).

* Present in trace amount.

TABLE 3

H^1, F^{19}, and P^{31} n.m.r. data (J values in c./sec., δ values in p.p.m.) for alkyl- and aryl-dialkylaminotrifluorophosphoranes

	^1H			^{19}F			^{31}P		
Compound	J_{H-P}	J_{H-F}	δ_H	$J_{F_a-F_e}$ [a]	δ_F	$\delta_{F_e} - \delta_{F_a}$	J_{P-F}	δ_P	Remarks
$MePF_3{\cdot}NMe_2$ [b]	20·4 (CH_3–P) 10·4 (Me_2N–P)	12·3 (CH_3–F_a) [a] 1·7 (CH_3–F_e) 2·6 (Me_2N–F, av.)	−1·55 (CH_3) −2·77 (Me_2N)	53	+27·6 (*ax*) +69·0 (*eq*)	41·4	806 (*ax*) 965 (*eq*)	+37·2	$J_{F_a-CH_3} = 12{\cdot}3$; J_{F-Me_2N} (av.) = 2·7 (from ^{19}F n.m.r.)
$PhPF_3{\cdot}NMe_2$ [c]	—	—	—	55	+40·1 (*ax*) +68·1 (*eq*)	28·0	817 (*ax*) 958 (*eq*)	—	Trace impurity of $PhPOF_2$ ($J_{P-F} = 1100$; $\delta_F = +65{\cdot}3$)
$PhPF_3{\cdot}NMe_2$ [d]	11·0 (Me_2N–P)	2·7 (Me_2N–F, av.)	−2·72 (Me_2N)	55—56	+39·8 +68·0	28·2	821 (*ax*) 963 (*eq*)	+53·6	*e*
$PhPF_3{\cdot}NEt_2$		*f*	−1·15 (CH_3) −3·12 (CH_2)	55—56	+43·5 +66·5	23·0	823 (*ax*) 966 (*eq*)	+52·5	*g*

All measurements were on neat samples, unless stated otherwise. Integration of the areas due to different kinds of protons in the ^1H spectra was consistent with the assigned structures. δ_H values are given relative to an internal $SiMe_4$, δ_F values to an internal CCl_3F, and δ_P values to an external 85% H_3PO_4 reference.

[a] The indices *a* and *e* (F_a, F_e) refer to fluorine atoms in axial and equatorial positions of the trigonal bipyramid. [b] Small impurities of $MePOF_2$ (J_{P-F} = 1107 c./sec.; $\delta_P = -26{\cdot}2$ p.p.m.; $\delta_F = +60{\cdot}3$ p.p.m.) and of $MePF{\cdot}NMe_2$ (J_{P-F} = 919 c./sec.; $\delta_P = -168{\cdot}3$ p.p.m.; $\delta_F = +117{\cdot}5$ p.p.m.) were detected in the ^{19}F and ^{31}P n.m.r. spectra of $MePF_3{\cdot}NMe_2$. [c] Obtained in the reaction of $PhPCl{\cdot}NMe_2$ with SbF_3. [d] Obtained in the reaction of $PhPCl{\cdot}NMe_2$ with AsF_3. [e] Contained a trace amount of $PhPF{\cdot}NMe_2$ (J_{P-F} = 975 c./sec.; $\delta_P = -156{\cdot}5$ p.p.m.). [f] The ^1H spectrum showed a sharp 1–2–1 triplet due to the CH_3 part of the ethyl groups, $J_{CH_3-CH_2}$ = 6·9 c./sec. The CH_2 region appeared as a symmetrical multiplet which was broad and poorly resolved. [g] The ^1H spectrum was recorded in 25% CCl_4 solution.

TABLE 5

^1H, ^{31}P, and ^{19}F n.m.r. data (J values in c./sec., δ values in p.p.m.) for dialkylamino-chloro- and -fluoro-phosphines

	^1H			^{19}F			^{31}P		
Compound	J_{H-P}	J_{H-F}	δ_H	J_{P-F}	J_{F-H}	δ_F	J_{P-F}	δ_P	Remarks
$CH_3PClN(CH_3)_2$	11·4 (CH_3–P) 13·3 [$(CH_3)_2N$–P]	—	−1·65 (CH_3) −2·66 [$(CH_3)_2N$]	—	—	—	—	−150·2 [a]	—
$CH_3PFN(CH_3)_2$	15·5 (CH_3–P) 9·6 [$(CH_3)_2N$–P]	8·3 (CH_3–F) 5·1 [$(CH_3)_2N$–F]	−1·22 (CH_3) −2·75 [$(CH_3)_2N$]	921	Not resolved	+117·5	917	−168·9	—
$ClCH_2PClN(CH_3)_2$ (neat)	10·9 ($ClCH_2$–P) 12·2 [$(CH_3)_2N$–P]	—	−3·82 ($ClCH_2$) −2·73 [$(CH_3)_2N$]	—	—	—	—	−123·0	High-field peak of $ClCH_2$ broadened, low-field peak sharp in ^2H spectrum
$ClCH_2PClN(CH_3)_2$ (1 : 1 in CCl_4)	11·0 ($ClCH_2$–P) 12·0 [$(CH_3)_2N$–P]	—	−3·79 ($ClCH_2$) −2·76 [$(CH_3)_2N$]	—	—	—	—	—	
$C_6H_5PClN(CH_3)_2$	13·0 [$(CH_3)_2N$–P]	—	−2·50 [$(CH_3)_2N$]	—	—	—	—	−141·0	—
$C_6H_5PFN(CH_3)_2$	9·1 [$(CH_3)_2N$–P]	5·4 [$(CH_3)_2N$–F	−2·60 [$(CH_3)_2N$]	989	5·6 (septet)	+128·5	985	−159·8	—
$C_6H_5PClN\begin{array}{l}\diagup CH_2{-}CH_3\\ \diagdown CH_2{-}CH_3\end{array}$	12·0 (CH_2–P)	—	−3·01 (CH_2) −0·98 (CH_3)	—	—	—	—	−140·4 [b]	$J_{CH_2CH_3}$ = 7·1 c.p.s.
$C_6H_5PFN\begin{array}{l}\diagup CH_2{-}CH_3\\ \diagdown CH_2{-}CH_3\end{array}$	—	—	−2·97 (CH_2) −0·97 (CH_3)	990	4·4 (F–CH_2)	+125·7	987	−156·0	$J_{CH_2CH_3}$ = 7·1 cp..s.
$[(CH_3)_2N]_2PCl$	12·0	—	−2·66 [c]	—	—	—	—	−158·7 [d]	—
$[(CH_3)_2N]_2PF$	8·9	3·2	−2·55	1042	~3	+99·6	1042	−150·8	—
$[(CH_3)_2N]_3P$	8·9	—	−2·43 [c]	—	—	—	—	−121·5 [d]	

The general remarks of Table 3 apply.

[a] Reported value: −151 p.p.m. (J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, 1964, **86**, 811). [b] This value differs significantly from a literature report: −118 p.p.m. (W. A. Hart and H. H. Sisler, *Inorg. Chem.*, 1964, **3**, 617). The reason for this discrepancy is not known, as yet (H. H. Sisler, personal communication). [c] Previously reported values for J_{H-P} and δ_H of $[(CH_3)_2N]_2PCl$ and $[(CH_3)_2N]_3P$: 12·1 c./sec., −2·65 p.p.m., and 8·8 c./sec., −2·43 p.p.m., respectively (H. J. Vetter, *Naturwiss.*, 1964, **51**, 240). [d] Reported values for δ_P of $[(CH_3)_2N]_2PCl$ and $[(CH_3)_2N]_3P$: −160 and −123 p.p.m., respectively (J. R. Van Wazer and L. Maier, *loc. cit.*).

(for n.m.r. parameters see Table 4). The rearrangement is also observed on neat samples, and the presence of acetonitrile is not essential. Figures 1 and 2 show the ^{19}F and ^{31}P n.m.r. spectra, respectively, of a neat sample, stored at room temperature for 10 days after its preparation.

The identity of $[MePF_5]^-$ is established from the observed pattern both of the ^{19}F and ^{31}P n.m.r. spectrum (Figures 1 and 2). In the former, a doublet (J_{P-F_e}) of doublets ($J_{F_e-F_a}$) is due to equatorial fluorine atoms, while a doublet (J_{P-F_a}) of quintets ($J_{F_a-F_e}$) is observed for the axial fluorine atom (Figure 3). Each component of the doublets due to equatorial fluorine atoms is split into a quartet ($J_{F_e-CH_3}$) as a result of coupling between F_e and the protons of the methyl group.

A doublet (J_{P-F_a}) of quintets (J_{P-F_e}) is observed in the ^{31}P spectrum (Figure 2), each component having quartet fine structure (J_{P-CH_3}). The high positive value (126·4 p.p.m.) of the ^{31}P chemical shift is indicative of a highly shielded phosphorus atom, as expected for $[MePF_5]^-$. The ^{19}F n.m.r. parameters for $[MePF_5]^-$ found during this study are in agreement with those of the same species observed in solutions of $MePF_4$ in dimethyl sulphoxide.[17]

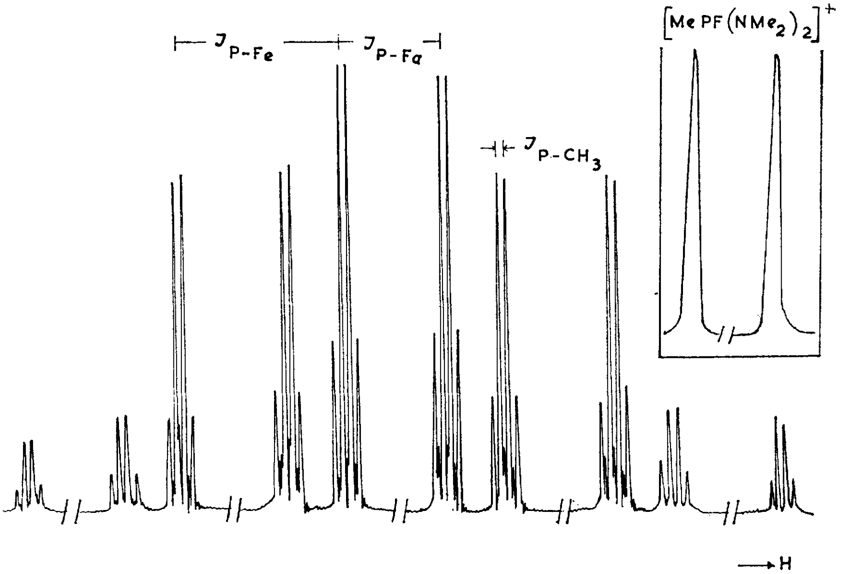

FIGURE 2. ^{31}P N.m.r. spectrum at 56·4 Mc./sec. of $[MePF(NMe_2)_2]^+[MePF_5]^-$, observed on a neat sample of $MePF_3{\cdot}NMe_2$, kept 10 days at room temperature after its distillation. Resonances due to traces of $MeP(:O)F_2$, $MeP(:O)F{\cdot}NMe_2$, and $MePF{\cdot}NMe_2$, are omitted

For the $[MePF(NMe_2)_2]^+$ cation, a 1–1 doublet is observed in both the ^{19}F and ^{31}P spectra, $J_{P-F} = 1030$ c./sec. (cf. 1042 c./sec. for the related $[PhPF(NMe_2)_2]^+$).[16]

It has been confirmed that the compound $PhPF_3NEt_2$,[9] closely related to $MePF_3NMe$ and $PhPF_3NMe_2$,[16] does not undergo the same rearrangement with formation of an ionic species. A ^{19}F n.m.r. check on a 2-year-old sample of $PhPF_3NEt_2$ showed it to be completely unchanged.

Co-ordination Chemistry of Alkyl(aryl)dialkylaminofluorophosphines.—The reaction of alkyl(aryl)dialkylaminochlorophosphines with the non-oxidising fluorinating agent,

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[17] E. L. Muetterties and W. Mahler, *Inorg. Chem.*, 1965, **4**, 119.
[18] C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, 1960, **25**, 2016.

sodium fluoride in tetramethylene sulphone, was used in the preparation of some representative alkyl(aryl)dialkylaminofluorophosphines (Table 1), a class of compounds unknown until recently, except for the perfluoroalkyl derivative, CF_3PFNMe_2.[19] The new compounds were characterised by chemical analysis, mass spectroscopy (Table 1), and by their ^1H, ^{19}F, and ^{31}P n.m.r. spectra. N.m.r. data, together with those for the corresponding chlorophosphines, are listed in Table 5.

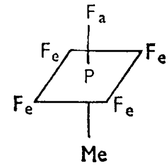

FIGURE 3. Proposed configuration of $[CH_3PF_5]^-$ (F_a, F_e = fluorine atoms in axial and equatorial position of the octahedron)

We have studied a few exchange reactions of these potentially interesting ligands with tetracarbonylnickel and cycloheptatrienetricarbonylmolybdenum.[4–7] The related bisdimethylaminofluorophosphine, $(Me_2N)_2PF$,[8] has also been included in the present work. A smooth reaction, commencing readily at room temperature, was observed in every case, both with tetracarbonylnickel and with cycloheptatrienetricarbonylmolybdenum. The dicarbonylnickel(0) derivatives were obtained upon reaction of the tetracarbonyl and the respective ligands, $MePF{\cdot}NMe_2$ and $(Me_2N)_2PF$, in a molar ratio of 1 : 2. An attempt to substitute all four CO groups by $PhPF{\cdot}NEt_2$ was unsuccessful: even under severe conditions (cf. Experimental) only three CO groups were substituted by this ligand, which may be too bulky to allow complete substitution. The reactions of cycloheptatrienetricarbonylmolybdenum with three of the new ligands proceeded as expected with exchange of the cycloheptatriene ligand,

$$C_7H_8Mo(CO)_3 + 3L \longrightarrow L_3Mo(CO)_3 + C_7H_8.$$
$$[L = MePF{\cdot}NMe_2,\ PhPF{\cdot}NEt_2,\ \text{or}\ (Me_2N)_2PF]$$

It is noteworthy that no trisubstituted product could be obtained upon reaction of $(Me_2N)_3P$, closely related to $(Me_2N)_2PF$, with $C_7H_8M(CO)_3$ (M = Cr or Mo).[20] It was suggested that three $(Me_2N)_3P$ ligands bonded to a single metal atom may promote too high an accumulation of negative charge on the metal atom which cannot be sufficiently back-donated into empty *d*-orbitals of phosphorus.[20] The present work seems to confirm this suggestion. The presence of only one strongly electron-withdrawing fluorine atom on the tervalent phosphorus apparently sufficiently affects the electronic situation, so as to permit formation of stable tricarbonylmolybdenum(0) derivatives.

The new co-ordination compounds involving dialkylaminofluorophosphine ligands are listed in Table 2. All compounds are sufficiently stable to be handled in air for short periods. The dicarbonylnickel(0) derivatives are non-crystallising liquids, the other complexes are crystalline solids.

Infrared spectra were recorded for all the new carbonyl derivatives. Two features in the i.r. spectra are of special interest: the synthesis of $Ni(CO)_2[(Me_2N)_2PF]_2$ completes the series $Ni(CO)_2[(Me_2N)_{3-n}PF_n]_2$ ($n = 0, 1, 2,$ or 3). The series $Mo(CO)_3[(Me_2N)_{3-n}PF_n]_3$ is nearly complete now with the new compound $Mo(CO)_3[(Me_2N)_2PF]_3$, only $Mo(CO)_3[(Me_2N)_3P]_3$ still missing (cf. ref. 20). A comparison of the CO stretching region of the various compounds provides a possibility of assessing the relative donor and acceptor properties in the ligand series $(Me_2N)_{3-n}PF_n$.

Table 6 lists CO stretching frequencies in the i.r. spectra of the series $Ni(CO)_2[(Me_2N)_{3-n}PF_n]_2$ ($n = 0, 1, 2,$ or 3), and $Mo(CO)_3[(Me_2N)_{3-n}PF_n]_3$ ($n = 0, 1,$ or 2). It is readily seen that a nearly linear relationship exists between ν_{CO} and n, *i.e.*, with the number of fluorine atoms per tervalent phosphorus atom. Since the CO stretching frequencies are found to increase with increasing n, they give a direct measure of the Lewis basicity of the ligand, $(Me_2N)_{3-n}PF_n$ (cf. ref. 21 for a discussion of factors affecting the position of CO and CN stretching frequencies). The positions of the CO stretching frequencies thus reflect the balance both of the donor and acceptor properties of the ligand, and it is quite

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[19] J. F. Nixon, personal communication.

[20] R. B. King, *Inorg. Chem.*, 1963, **2**, 936.

[21] D. K. Huggins and H. D. Kaesz, *Progr. Solid-State Chem.*, 1964, **1**, 446.

reasonable that the presence of three fluorine atoms makes PF_3 the strongest π-acceptor, both in the dicarbonylnickel and in the tricarbonylmolybdenum series, whereas $(Me_2N)_3P$ [in the former series] gives rise to the lowest CO stretching frequency, owing to the absence of strongly electron-withdrawing groups on the ligand (cf. refs. 6, 7, and 22).

TABLE 6

CO Stretching frequencies of some $Ni(CO)_2$ and $Mo(CO)_3$ derivatives

Compound	Medium	ν_{CO} (cm.$^{-1}$)	Ref.
$Ni(CO)_2[(Me_2N)_3P]_2$	Halocarbon oil mull	1992, 1929	20
$Ni(CO)_2[(Me_2N)_2PF]_2$	CCl_4 solution	2019, 1961	This work
$Ni(CO)_2[Me_2NPF_2]_2$	Neat	2040, 1993	7
	$CHCl_3$ solution	2049, 1997	
Cf. $Ni(CO)_2(C_5H_{10}N{\cdot}PF_2)_2$	Nujol mull	2041, 1993	7
	$CHCl_3$ solution	2049, 1996	
$Ni(CO)_2[PF_3]_2$............................	In cetane	2094, 2052	*a*, *b*
$Mo(CO)_3[(Me_2N)_3P]_3$	Unknown		Cf. ref. 20
$Mo(CO)_3[(Me_2N)_2PF]_3$	CCl_4 solution	1969, 1878	This work
$Mo(CO)_3[Me_2NPF_2]_3$	KBr	2000, 1923	7
$Mo(CO)_3[PF_3]_3$	KBr	2085, 2055	*c*
	Gas	2074, 2026	*d*

[a] M. Bigorgne and A. Zelwer, *Bull. Soc. chim. France*, 1960, 1986. [b] M. Bigorgne, *J. Inorg. Nuclear Chem.*, 1964, **26**, 107. [c] R. Schmutzler, *Adv. Chem. Series*, 1963, **37**, 150. [d] Th. Kruck and A. Prasch, *Z. Naturforsch*, 1964, **19***b*, 669.

The observation of only two infrared-active vibrations in the CO stretching region of our tricarbonylmolybdenum derivatives suggests a C_{3v} (*cis,cis,cis*) structure. Three infrared absorptions would be expected for a C_{2v} (*cis,cis,trans*) arrangement.[23] Two CO absorptions are observed for the dicarbonylnickel derivatives, and one for the trisubstituted compound, $Ni(CO)(PhPFNEt_2)_3$.

Further information on the nature of the metal–ligand bond in the present series of compounds and in numerous further co-ordination compounds involving fluorine-containing phosphine ligands [6,7] is to be expected from a current ^{31}P n.m.r. study which will be reported in due course.[24]

An inspection of the CH stretching region in the i.r. spectra of the co-ordinated ligands containing Me_2N groups bonded to phosphorus permits the determination of the bonding site in the ligand. As discussed previously for dimethylaminodifluorophosphine and its co-ordination compounds with nickel(0) and molybdenum(0),[7] compounds containing $>\bar{N}{-}CH_3$ groups in which the lone pair of electrons on the nitrogen is retained show a characteristic absorption in the 2800-cm.$^{-1}$ region. This absorption will disappear if the lone electron pair on the nitrogen becomes involved in bonding.[25] Thus, if in co-ordination compounds involving the present dimethylaminofluorophosphine ligands co-ordination through nitrogen would occur, this absorption would be expected to be affected. Actually, for all the compounds the characteristic i.r. absorption due to $>\bar{N}{-}CH_3$ is clearly observable. There is very little change, both in position and intensity of this absorption in the complexes, as compared to the unco-ordinated ligands. Co-ordination through phosphorus, rather than through nitrogen, is therefore strongly indicated. It is equally likely that co-ordination through phosphorus also occurs in the complexes involving $PhPF{\cdot}NEt_2$.

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[22] F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.
[23] R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301.
[24] G. S. Reddy and R. Schmutzler, unpublished results.
[25] J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J.*, 1958, 2780.

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