RECENT PROGRESS IN THE CHEMISTRY OF FLUOROPHOSPHINES

John F. Nixon

School of Molecular Sciences, University of Sussex, Brighton, England

I. Introduction

Fluorophosphines are tervalent phosphorus compounds containing phosphorus–fluorine bonds and they often show markedly different chemical behavior compared with other halogenophosphines. This article is mainly concerned with recent advances in the chemistry of derivatives of PF_3 of the type $PF_{3-n}X_n$, with particular reference to (*a*) synthesis of new structural types, (*b*) the role of fluorophosphines as ligands, particularly in transition metal complexes, and (*c*) nuclear magnetic resonance (NMR) studies.

Since fluorophosphines form part of a general review of phosphorus fluorides (*282*), and there is an excellent account of transition metal–trifluorophosphine complexes (*152*), the present article is not intended to be comprehensive, but rather to highlight some of the more recent developments in this expanding area of inorganic chemistry.

II. Trifluorophosphine

The parent compound trifluorophosphine (b.p. −101.4°C) will only be discussed briefly since preparative methods, physical properties, and general reactions have been adequately discussed previously by Schmutzler (*282*) and will not be repeated here. Usually trifluorophosphine is obtained by fluorination of other phosphorus trihalides, but 50 gm quantities have also been obtained by reacting anhydrous hydrogen fluoride and orthophosphorous acid at −78°C in a polythene vessel (*27*).

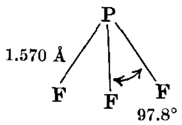
$$PCl_3 \xrightarrow{MF_x} PF_3 \quad (MF_x = KF, ZnF_2, SbF_3, AsF_3)$$

$$H_3PO_3 \xrightarrow[-78^\circ C]{HF} PF_3 + PF_4H$$

A. STRUCTURE

The molecular structure of trifluorophosphine has been the subject of several papers and considerable differences in bond length and bond angles have been reported. The very early work by Brockway *et al.* (*33*, *258*) gave r(P–F) = 1.52 Å, θ(FPF) = 104°, and more recently Hersh (*131*) found r(P–F) = 1.537 ± 0.04 Å, θ(FPF) = 98.2° ± 0.6°. In neither case, however, were these data consistent with microwave studies (*113*, *208*, *209*).

In a very recent electron diffraction study (*211*) r(P–F) is found to be 1.570 Å and θ(FPF) = 97.8° and these results are in accord with the microwave data.[1]



The new data means that the XMX bond angles in the Group V trihalides MX_3 (X = halogen, M = P, As, Sb) increase fairly systematically on going from the fluorides to the iodides, and likewise the FM′F bond angle (M′ = N, P, As, Sb) steadily decreases down the group (see Table I). This necessitates a modification of the ideas of Gillespie (*112*), who has previously invoked partial double-bond character in the P–F bonds to explain the apparent anomaly of a large FPF bond angle.

TABLE I

XMX BOND ANGLES IN GROUP V TRIHALIDES (MX_3)[a]

Halogen(X)	Nitrogen	Phosphorus	Arsenic	Antimony
F	102.17° ± 0.14°	97.8° ± 0.2° 98.2° ± 0.6°	96.1° ± 0.2° 95.8° ± 0.7°	~88°
Cl	—	100.27° ± 0.09° 100.1°	98.7° ± 0.3° 98.4°	99.5° ± 1.5°
Br	—	101.5°	99.6° ± 0.26°	~97°
I	—	102°	100.2° ± 0.4°	99.1° ± 2°

[a] For individual references see (*211*).

There is disagreement about the importance of *d*-orbital participation in trifluorophosphine. On the basis of dipole moment data and using a

---

[1] In (*212*) there is a reference to an unpublished microwave study of PF_3 by Hirota which gives r(P–F) = 1.565°A (FPF) = 96.3°.

C.N.D.O. procedure, it has been concluded that *d*-orbital participation in the bonding is important (*280*), but this has been disputed (*36*).

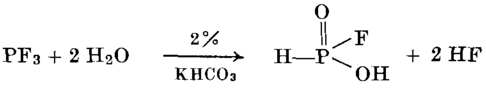
Hillier and Saunders (*131a*) have recently carried out an all electron *ab initio* SCF-MO calculation on PF_3 and find that there is a relatively large $3d$-population (0.7e). There is significant π-bonding between the phosphorus $3p$ and $3d$ and fluorine $2p\pi$ orbitals, the major contribution being of the $3d\pi$-$2p\pi$ type. Such π-bonding is absent in PMe_3. The highest occupied orbital is localized on the phosphorus atom (i.e., the lone pair orbital) and has approximately equal (ca. 35%) $3s$ and $3p$ components. The calculated first ionization potential (assuming Koopmans' theorem) is 12.69 eV which is in very good agreement with the experimental value (12.31 eV) obtained from photoelectron spectroscopy (*98a*).

B. HYDROLYSIS

The slow hydrolysis of trifluorophosphine compared with the other trihalogenophosphines has been long known (*282*) and the gas may be washed with water without any significant loss. This offers a convenient way of removing small amounts of HF and SiF_4 from trifluorophosphine during its preparation. The ultimate products of hydrolysis of trifluorophosphine are hydrogen fluoride and orthophosphorous acid (*282*).

$$PF_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HF$$

Aqueous base, on the other hand, rapidly hydrolyzes trifluorophosphine, but early workers (*215*) found no evidence for intermediate P–F compounds. A detailed study, however, now shows that whereas hydrolysis by aqueous potassium hydroxide affords fluoride and phosphite, dilute alkaline bicarbonate solutions produce salts of monofluorophosphorous acid (H_2PO_2F) (*28*). This acid is stable against iodine oxidation in alkaline bicarbonate, but bromine oxidizes it at a measurable rate. Orthophosphate and monofluorophosphorous acid rapidly form salts of the acid $HP(O)(OH)OP(O)(OH)_2$.



$$PF_3 + 2\,H_2O \xrightarrow[KHCO_3]{2\%} H\text{—}P(=O)(F)(OH) + 2\,HF$$

An equilibrium amount of H_2PO_2F is also found in solutions of H_3PO_3 in hydrofluoric acid (*28*).

$$H_3PO_3 + HF \rightleftharpoons HP(O)F(OH) + H_2O$$

OPF_2H can be isolated among the products from the vapor phase hydrolysis of PF_3, and is also obtained by treating halogenodifluorophosphines PF_2X with Me_3SnOH (*50*).

C. OTHER REACTIONS

The extensive coordination chemistry of PF_3 is discussed in detail in Sections VIII to X. Newer examples of the well-known oxidation of PF_3 to the pentavalent fluorophosphorane have appeared (*110, 99*), and

$$PF_3 + TeF_5Cl \rightarrow PF_3Cl_2, PF_4Cl, PF_5$$

$$PF_3 + (CF_3)_2NCl \rightarrow (CF_3)_2NPF_3Cl$$

there is an interesting report of the addition of the bis(trifluoromethyl)-nitroxide free radical (*303*).

$$PF_3 + 2\ (CF_3)_2NO^{\bullet} \rightarrow PF_3[(CF_3)_2NO]_2$$

III. Fluorophosphines Containing Phosphorus–Carbon Bonds. Alkyl- or Arylfluorophosphines, R_nPF_{3-n}

Although the parent compound trifluorophosphine has been known for at least 80 years, organic derivatives of tervalent phosphorus fluorides were first described only about 10 years ago (*183*). They are volatile liquids or gases which often exhibit strongly reducing properties and spontaneous inflammability in the atmosphere. Much of the synthetic work therefore necessitates the use of the high-vacuum manifold or rigorous exclusion of air and moisture from the system.

The main preparative methods are listed below. The suitability of the particular method is largely determined by the nature of the substituent group R; for example, the easy oxidation of RPF_2 or R_2PF to pentavalent phosphorus compounds, when R = alkyl or aryl, precludes the use of antimony (or arsenic) trifluoride as a fluorinating agent (see below), whereas when R contains an electronegative group, e.g., CH_2Cl, CCl_3, CF_3, or C_6F_5, this method is entirely suitable. The known alkyl- or arylfluorophosphines are listed in Table II together with the appropriate method of synthesis.

A. PREPARATIVE METHODS

1. *Fluorination of Halogenophosphines Using Antimony or Arsenic Trifluoride*

In 1959 Kulakova *et al.* (*183*) reported the successful isolation of several rather unstable alkyl- and aryldifluorophosphines RPF_2 (R = Me, Et, Ph, *n*-Bu) by reacting the corresponding dichlorophosphines $RPCl_2$ with antimony trifluoride in an inert solvent under mild conditions. The resulting difluorophosphines are inflammable liquids or gases which

TABLE II

FLUOROPHOSPHINES CONTAINING PHOSPHORUS–CARBON BONDS

Compound	Method of preparation[a] (section number)	Boiling point (°C/mm)	n_D	(°C)	d_4^{20}	Refs.	ϕ_F[b]	δ_P[c]	J_{PF}[d]	Refs.
$MePF_2$	(1), 2, 4–6	−28	—	—	—	(*183, 84, 298, 97*)	92.9	−250.7	1157	(*84, 298, 97*)
$EtPF_2$	(1), 2, 5	6–7	—	—	—	(*183, 84, 97*)	104.5	−234.1	1114	(*84, 301, 97*)
$CF_2{=}CFPF_2$	1	2–3	—	—	—	(*307, 308, 69c*)	103.6	—	1202	(*69c*)
$ClCH_2PF_2$	1	33.5–34.5	—	—	—	(*281*)	96.3	−201.8	1190	(*226*)
Cl_2CHPF_2	1	58	—	—	—	(*103*)	98.8	−164.2	1283	(*103*)
CCl_3PF_2	1	73.1 (m.p. 15.8–16.4)	—	—	—	(*229, 230*)	88.0	−130.9	1285	(*229, 230*)
n-$BuPF_2$	(1)	70–72	—	—	—	(*183*)	—	—	—	—
t-$BuPF_2$	1,3	54	—	—	—	(*103*)	111.5	−231.2	1215	(*103*)
CF_3PF_2	1	−43	—	—	—	(*183*)	104.1	−158.3	1245	(*226, 230*)
$C_3F_7PF_2$	1	15.8 (est.)	—	—	—	(*231*)	102.5	−167.8	1257	(*231, 226*)
$PhPF_2$	(1), 2, 3, 5, 7	30–31/20; 64/70	1.4903	20	1.2202	(*183, 82, 83, 84, 292*)	92.3	−208.3	1173	(*292*)

$C_6H_5CH_2PF_2$	2, 3	43–45/10	1.4974	20	—	(*83*, *84*)	97.6	−223.8	1190	(*84*)
$C_6F_5PF_2$	1, (3)	30–31/20	—	—	—	(*15*, *102*)	94.5	−193.4	1215	(*102*, *15*)
p-$ClC_6H_4PF_2$	2	33–35/5	1.4957	20	1.3209	(*83*, *84*)	—	−196.8	1118	(*84*)
p-$MeC_6H_4PF_2$	2, 5, 6	70–72/50	1.5040	20	1.2041	(*82*, *83*, *84*)	92.1	−205.3	1130	(*84*)
p-$FC_6H_4PF_2$	3	58/40	—	—	—	(*266*)	90.4	—	1074	(*266*)
m-$FC_6H_4PF_2$	3	47/22	1.4648	25	—	(*266*)	92.2	—	1182	(*266*)
ICH_2PF_2	—	—	—	—	—	(*29*)	—	—	—	—
$CH_2(PF_2)_2$	—	—	—	—	—	(*29*)	—	—	—	—
Me_2PF	4	26.3 (m.p. −109)	—	—	—	(*296*, *297*)	195.5	−187	823	(*296*, *297*)
$(CF_2{=}CF)_2PF$	1	63–65	—	—	—	(*307*, *308*)	—	—	—	—
$(CF_3)_2PF$	1, 7	−11	—	—	—	(*183*, *38*)	219.0	−123.9	1013	(*231*, *226*, *253*)
$(C_3F_7)_2PF$	1	92.2 (est.)	—	—	—	(*231*)	215.5	−138.8	1025	(*231*, *226*)
$(C_6F_5)_2PF$	(1), 3	104–106/0.02 (m.p. 49)	—	—	—	(*102*)	216·6	−136·0	1002	(*102*)
EtPFMe	—	—	—	—	—	—	—	−182	~820	(*301*)
(t-Bu)$_2$PF	3	67–70/48	—	—	—	(*103*)	223.5	−210.4	848	(*103*)

---

[a] Parentheses denote *not* best preparative method.

[b] In ppm relative to CCl_3F.

[c] In ppm relative to H_3PO_4.

[d] In Hz.

on standing rapidly disproportionate to the corresponding pentavalent fluorophosphorane and cyclic polymers.

$$n\mathrm{RPF_2} \rightarrow \mathrm{RPF_4} + [\mathrm{RP}]_n$$

Difluorotrifluoromethylphosphine, on the other hand, is stable (*183*) and was also isolated during the syntheses of the cyclic phosphines $[CF_3P]_{4,5}$ by treating CF_3PI_2 with mercury (*41*).

A report that $C_2H_5PF_2$ and C_2H_5PFCl are formed in the antimony trifluoride–ethyldichlorophosphine reaction (*134*) was later shown to be erroneous (*289*), and the products correctly identified as ethyltetrafluorophosphorane, $C_2H_5PF_4$, and its hydrolysis product ethylphosphonic difluoride, $C_2H_5POF_2$.

Indeed the reaction between alkyl- or arylchlorophosphines R_nPCl_{3-n} and either antimony (or arsenic) trifluoride in the absence of solvent offers a convenient route to the pentavalent fluorophosphoranes R_nPF_{5-n} (*151, 283, 286, 298*).

$$3\,\mathrm{RPCl_2} + 4\,\mathrm{MF_3} \rightarrow 3\,\mathrm{RPF_4} + 2\,\mathrm{M} + 2\,\mathrm{MCl_3}$$

$$3\,\mathrm{R_2PCl} + 3\,\mathrm{MF_3} \rightarrow 3\,\mathrm{R_2PF_3} + 2\,\mathrm{M} + \mathrm{MCl_3}$$

(M = As or Sb)

These reactions involve the oxidation of the phosphine and reduction of the Group V metal trifluoride to the metal.

On the other hand, when the group R contains an electron-withdrawing substituent, fluorination affords only the corresponding tervalent fluorophosphine (*229*),

$$3\,\mathrm{CCl_3PCl_2} + 2\,\mathrm{SbF_3} \rightarrow 3\,\mathrm{CCl_3PF_2} + 2\,\mathrm{SbCl_3} \qquad (229, 230)$$

$$3\,\mathrm{(CF_3)_2PI} + \mathrm{SbF_3} \rightarrow 3\,\mathrm{(CF_3)_2PF} + \mathrm{SbI_3} \qquad (38, 183)$$

$$3\,\mathrm{C_3F_7PI_2} + 2\,\mathrm{SbF_3} \rightarrow 3\,\mathrm{(C_3F_7)PF_2} + 2\,\mathrm{SbI_3} \qquad (321)$$

$$3\,\mathrm{C_6F_5PCl_2} + 2\,\mathrm{SbF_3} \rightarrow 3\,\mathrm{C_6F_5PF_2} + 2\,\mathrm{SbCl_3} \qquad (102)$$

$$3\,\mathrm{ClCH_2PCl_2} + 2\,\mathrm{SbF_3} \rightarrow 3\,\mathrm{ClCH_2PF_2} + 2\,\mathrm{SbCl_3} \qquad (281)$$

the redox reaction being suppressed. In the case of monochloromethyldichlorophosphine the presence of the single chlorine atom in the side chain is sufficient to stabilize the tervalent fluorophosphine, $ClCH_2PF_2$, relative to the pentavalent fluorophosphorane, $ClCH_2PF_4$, and the compound can be distilled unchanged, in contrast with the analogous methyl derivative. Only trace amounts of $C_6F_5PF_4$ are obtained in the $SbF_3/C_6F_5PCl_2$ reaction (*102*), whereas a considerable amount of $(C_6F_5)_2PF_3$ is formed, in addition to $(C_6F_5)_2PF$, when $(C_6F_5)_2PCl$ is fluorinated.

Antimony trifluoride fluorination of *m*- or *p*-fluorophenyldichlorophosphines affords only the pentavalent derivatives (*266*).

Although trifluoromethyldifluorophosphine, CF_3PF_2, is essentially unchanged after storage for 6 months at room temperature, the use of elevated temperatures (e.g., 115°/4 hours) produces small amounts of the tetrafluorophosphorane (*4*). The stability of the RPF_2 fluorophosphines is significantly greater than the corresponding R_2PF derivatives and decreases along the series $CF_3 \gg Ph > Me$ (see Section III,B,1).

Very recently it has been found that the tertiary butyl derivative $(t\text{-Bu})PF_2$ (b.p. 54°C) can be isolated from the chlorophosphine using antimony trifluoride as fluorinating agent (*103*), suggesting that steric effects may be important in the redox reactions.

Following the establishment of the redox fluorination of alkyl- or aryldichlorophosphines, doubts were expressed regarding the reproducibility of the original results of Kulakova *et al.* (*183*), and a further complication resulted from a misprint in the last paper in which the boiling point of $PhPF_2$ was listed as 64°–70°C rather than 64°–65°C/70 mm. The situation has now been clarified by a detailed study (*83*, *84*) of the effect of solvents on the yields of alkyl- and aryldifluorophosphines by the $SbF_3/RPCl_2$ method.

2. *Fluorination in the Presence of Solvents, e.g., Pyridine or N,N-Dialkylaniline*

In the absence of solvent methyldichlorophosphine and antimony trifluoride afford only a 6% yield of methyldifluorophosphine (*84*), whereas use of an inert solvent increases the yield to 25–30%. Aryldichlorophosphines and antimony trifluoride in ether or benzene solution give inseparable mixtures of the tervalent and pentavalent phosphorus fluorides RPF_2 and RPF_4 (*84*).

The halogen exchange reaction can be accelerated in polar solvents and 85% yields of alkyldifluorophosphines are obtained when pyridine or *N*,*N*-dibutylaniline are used as reaction media. A pyridine complex $SbF_3 \cdot 2C_5H_5N$ has been identified.

$$RPCl_2 + SbF_3 \xrightarrow[\substack{N,N\text{-dibutylaniline} \\ \text{(solvent)}}]{\text{pyridine or}} RPF_2$$

Nitrobenzene is less useful as a solvent because of its pronounced tendency to oxidize the product to the corresponding phosphonic difluoride $RPOF_2$ (*84*).

3. *Fluorination with Sodium Fluoride in Tetramethylene Sulfone*

Phenyldifluorophosphine is obtained in high yield from phenyldichlorophosphine when sodium fluoride in tetramethylene sulfone (TMSO) is the fluorinating agent (*292*). Under these nonoxidizing conditions no phenyltetrafluorophosphorane is formed, although as in the case of the alkyldifluorophosphines on standing at room temperature the compound slowly disproportionates (*292*). Phenyldifluorophosphine is smoothly converted to phenyltetrafluorophosphorane on heating with antimony trifluoride (*292*).

$$\mathrm{PhPCl_2 + 2\ NaF \xrightarrow{TMSO} PhPF_2 + 2\ NaCl}$$

$$\mathrm{PhPF_2 \xrightarrow[\text{temperature}]{\text{room}} [PhP]_5 + PhPF_4}\ \text{(fairly slow)}$$

$$\mathrm{3\ PhPF_2 + 2\ SbF_3 \longrightarrow 3\ PhPF_4 + 2\ Sb}$$

Although both pentafluorophenylfluorophosphines $C_6F_5PF_2$ and $(C_6F_5)_2PF$ may as expected be isolated (*102*) from the $SbF_3/(C_6F_5)\text{-}PCl_{3-n}$ reactions on account of the electronegativity of the pentafluorophenyl group, there is still significant oxidation in the case of the monofluorophosphine and it is best prepared using sodium fluoride in acetonitrile solvent (*102*). A report that NaF/TMSO fluorination of $C_6F_5Br_2$ is a convenient route to $C_6F_5PF_2$ (*207*) could not be substantiated (*102*).

m- and *p*-fluorophenyldichlorophosphines are converted to the corresponding difluorophosphines by NaF/TMSO, although smaller amounts of the tetrafluorophosphoranes are also formed presumably via disproportionation reactions (*266*).

Interestingly, potassium bifluoride is not a suitable fluorinating agent for the synthesis of alkyldifluorophosphines since addition of hydrogen fluoride occurs affording the pentacoordinate trifluorophosphorane RPF_3H (*139*) (see also Section III, B).

$$\mathrm{RPCl_2}\ \cancel{\xrightarrow{\mathrm{KHF_2}}}\ \mathrm{RPF_2}$$

$$\mathrm{RPCl_2 + 2\ KHF_2 \longrightarrow RPF_3H + 2\ KCl + HF}$$

Potassium fluorosulfinate, KSO_2F, reacts with alkyl- or aryldichlorophosphines to form phosphonic acid fluorides $RPOF_2$ and phosphonothioic acid fluorides $RPSF_2$ rather than the desired difluorophosphine (*285*). Contrary to a previous report (*299*), KSO_2F fluorination of dimethylchlorophosphine affords dimethylphosphonic acid and dimethylphosphinothioic fluorides $(CH_3)_2POF$ and $(CH_3)_2PSF$ rather than dimethylfluorophosphine (*285*). Surprisingly only very small yields of chloromethyldifluorophosphine result from the reaction between KSO_2F and $ClCH_2PCl_2$ in spite of the presence of the chlorine atom in the side chain (*281*).

4. *Fluorination with "Active" Potassium Fluoride*

Seel and co-workers (*296–298*) have obtained methyldifluorophosphine and dimethylfluorophosphine by reacting the vapor of the corresponding chlorophosphine with "active" potassium fluoride formed by pyrolysis of potassium fluorosulfinate *in vacuo*.

$$\mathrm{MePCl_2} \xrightarrow{\text{“active” KF}} \mathrm{MePF_2}$$

$$\mathrm{Me_2PCl} \xrightarrow{\qquad} \mathrm{Me_2PF}$$

As expected dimethylfluorophosphine (b.p. 26.3°, m.p. −109°C) is spontaneously inflammable and undergoes a rapid disproportionation to dimethyltrifluorophosphorane and tetramethyldiphosphine (*296*, *297*) at room temperature.

$$3\,\mathrm{Me_2PF} \rightarrow \mathrm{Me_2PF_3} + \mathrm{Me_2P{-}PMe_2}$$

5. *Dehydrofluorination of Trifluorophosphoranes, RPF_3H*

Another more recent synthesis of aryl difluorophosphines involves dehydrofluorination of an aryltrifluorophosphorane with potassium fluoride at 100°–120°C (*84*).

$$\mathrm{RPF_3H} \xrightarrow{\mathrm{KF}} \mathrm{RPF_2} + \mathrm{KHF_2}$$
$$(\mathrm{R} = \mathrm{Ph},\ \mathrm{CH_3C_6H_4}\text{-})$$

On the other hand, it is impossible to remove hydrogen fluoride from methyltrifluorophosphorane under similar conditions (*82*).

When tertiary amines are used as dehydrofluorination reagents both alkyl- and aryldifluorophosphines are formed in 30–35% yield according to the following scheme:

$$\mathrm{RPF_3H} + \mathrm{R'_3N} \rightarrow [\mathrm{RPF_3H{\cdot}NR'_3}] \rightarrow \mathrm{RPF_2} + \mathrm{R'_3NHF}$$

$$\mathrm{RPF_3H} + \mathrm{R'_3NHF} \rightarrow [\mathrm{R'_3NH}]^+[\mathrm{RPF_4H}]^-$$

These dehydrofluorination reactions are particularly interesting in view of reports of the oxidation of certain fluorophosphines to derivatives of the hexafluorophosphate ion by bifluoride ion (*235*, *238*, *249*), namely,

$$\mathrm{R}_n\mathrm{PF}_{3-n} + \mathrm{HF_2}^{\ominus} \rightarrow [\mathrm{R}_n\mathrm{PF}_{5-n}\mathrm{H}]^{\ominus}$$
$$(\mathrm{R} = \mathrm{CF_3},\ \mathrm{F})$$

6. *Addition of Hydrogen Fluoride to Halogenophosphines Followed by Dehydrochlorination*

Although the direct reaction between alkyl- or aryldichlorophosphines and hydrogen fluoride only produces 10–15% yields of aryldifluorophosphines and no isolable alkyl derivatives (*84*), treatment of the intermediate products of the reaction with tertiary amines significantly increases the yields (30–35%, R = aryl; 15–20%, R = alkyl).

The following reaction scheme has been suggested:

$$RPCl_2 \xrightarrow{HF} [RPHF_2Cl] \xrightarrow{R_3'N} RPF_2 + R_3'N \cdot HCl$$

although no evidence for an intermediate of the type RPF_2HCl [R = CH_3, CCl_3] was found in two independent NMR studies of RPF_2–HCl mixtures (*82, 243*).

7. *Other Methods*

Very recently phenyldifluorophosphine has been synthesized in an interesting reaction in which phenyltetrafluorophosphorane is reduced by (diphenyl)trimethylsilylphosphine (*220*).

$$PhPF_4 + 2\ Ph_2PSiMe_3 \xrightarrow[\text{temperature}]{\text{room}} PhPF_2 + Ph_2PPPh_2 + 2\ Me_3SiF$$

Diphenyltrifluorophosphorane, on the other hand, gives only tetraphenyldiphosphine and trimethylfluorosilane

$$Ph_2PF_3 + 3\ Ph_2PSiMe_3 \xrightarrow[\text{4 hours}]{150°\text{C}} 2\ Ph_2PPPh_2 + 3\ Me_3SiF$$

the reaction presumably involving the intermediate diphenylfluorophosphine which could not be isolated, namely,

$$3\ Ph_2PF \rightarrow Ph_4P_2 + Ph_2PF_3$$

Diphenylfluorophosphine is also suggested as the intermediate in the reaction between diphenylphosphine and perfluorocyclobutene (*71*). Similarly, initial formation of dimethylfluorophosphine would account for the isolation of dimethyltrifluorophosphorane from the products of the reaction between dimethylphosphine and difluorotrichloromethylphosphine (*14*), e.g.,

$$CCl_3PF_2 + Me_2PH \rightarrow CCl_3H + [Me_2PPF_2] \rightarrow [Me_2PF] \rightarrow Me_2PF_3$$

There is also a report of fluorophosphine formation via fluorine migration from carbon to phosphorus in the thermal decomposition of bistrifluoromethyldiphosphoxane (*119*).

$$(CF_3)_2POP(CF_3)_2 \rightarrow (CF_3)_2PF + CO + (CF_3)_3P + PF_3$$

Formation of phosphorus–fluorine bonds is known to be an important process from electron impact studies of many trifluoromethylphosphines (*45*, *46*).

B. REACTIONS

Oxidation of trifluorophosphine by halogens is well known (*282*) and although corresponding reactions with alkyl or aryl fluorophosphines have received only little attention, it has become apparent that oxidation to the pentavalent phosphorus fluorides can be brought about by a wide variety of reagents. In certain cases the reducing property of the fluorophosphine has been utilized in the synthesis of zero-valent transition metal fluorophosphine complexes (Section IX).

Oxidation to the Pentavalent Fluorophosphorane

a. Spontaneously. The strongly reducing property of the alkyl- or arylfluorophosphines is reflected by their spontaneous inflammability in the air, and as already mentioned in Section III,A they show a varying tendency to disproportionate to the corresponding fluorophosphorane and diphosphine or cyclic polyphosphine. The behavior of several fluorophosphines at room temperature is shown below:

$3\,Me_2PF \rightarrow Me_2PPMe_2 + Me_2PF_3$ very rapid (*296, 297*)

$10\,MePF_2 \rightarrow [MeP]_5 + 5\,MePF_4$ rapid (*183*)

$10\,PhPF_2 \rightarrow [PhP]_5 + 5\,PhPF_4$ fairly slow (*4*, *292*)

$C_6F_5PF_2 \rightarrow [C_6F_5P]_x + C_6F_5PF_4$ very slow (*102*)

$ClCH_2PF_2 \rightarrow [ClCH_2P]_x + ClCH_2PF_4$ very slow (*228*)

$CF_3PF_2 \rightarrow (CF_3P)_{4,5} + CF_3PF_4$ very, very slow (*4*)

b. By Halogens. Like the parent trifluorophosphine, controlled addition of halogen to fluorophosphines R_nPF_{3-n} affords the corresponding pentacoordinate halogenofluorophosphorane, e.g.,

$CCl_3PF_2 + X_2 \rightarrow CCl_3PF_2X_2$

$(X = Cl, Br)$ (*229, 230*)

$R_nPF_{3-n} + Cl_2 \rightarrow R_nPF_{3-n}Cl_2$

$(R = CF_3, n = 1, 2; C_3F_7, n = 1)$ (*244*)

Attempts to prepare the corresponding alkyl or aryl difluorodihalogenophosphorane, RPF_2X_2 (R = alkyl, aryl; $X = Cl$, Br) were unsuccessful because of a rapid intermolecular exchange process (*86*, *102*).

c. By Transition Metal Halides. The reaction between platinous chloride or potassium chloroplatinite and trifluoromethyldifluorophosphine or bistrifluoromethylfluorophosphine affords the tetrakisfluorophosphine platinum(0) complex and the corresponding dichlorofluorophosphorane (see also Section IX) (*234, 247*).

$$5\,CF_{3-n}PF_{3-n} + PtCl_2 \rightarrow Pt[(CF_3)_nPF_{3-n}]_4 + (CF_3)_nPF_{3-n}Cl_2 \qquad (n = 1, 2)$$

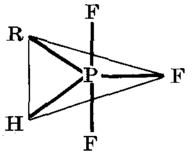
$$K_2PtCl_4 + 5\,(CF_3)_2PF \rightarrow Pt[(CF_3)_2PF]_4 + 2\,KCl + (CF_3)_2PFCl_2$$

d. By Antimony Trifluoride. Phenyldifluorophosphine is smoothly converted to the pentavalent derivative by heating with SbF_3.

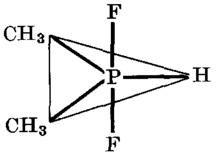
$$3\,PhPF_2 + 2\,SbF_3 \rightarrow 3\,PhPF_4 + 2\,Sb \qquad (292)$$

e. By Hydrogen Fluoride. Several alkyl- and aryldifluorophosphines RPF_2 have been found to form 1 : 1 adducts (I) with hydrogen fluoride (*82*). ^{19}F and ^{31}P nuclear magnetic resonance studies show clearly that the compound formed is a trifluorophosphorane RPF_3H, containing a phosphorus–hydrogen bond.

$$RPF_2 + HF \rightarrow RPF_3H$$



(I)



(II)

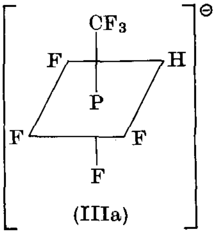
Similarly dimethylfluorophosphine and hydrogen fluoride produce dimethyldifluorophosphorane, Me_2PF_2H (II) (*296*), the latter also being formed as a by-product when dimethylfluorophosphine and dimethylphosphine are condensed together (*296*), or by reacting Me_4P_2 with HF.

$$Me_2PF + HF \rightarrow Me_2PF_2H$$

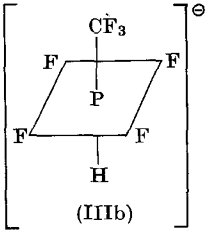
$$2\,Me_2PF + Me_2PH \rightarrow Me_2PPMe_2 + Me_2PF_2H$$

f. By Bifluoride Ion. Trifluoromethyldifluorophosphine and bistrifluoromethyl fluorophosphine are oxidized to hexacoordinate phosphorus anions $[(CF_3)_nPF_{5-n}H]^-$ when heated with potassium bifluoride (*235*). The reactions occur even more readily in the presence of acetonitrile at room temperature.

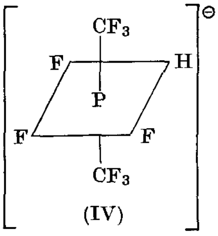
$$CF_3PF_2 + HF_2^{\ominus} \rightarrow [CF_3PF_4H]^{\ominus} \text{ cis (IIIa) and trans (IIIb)}$$
$$(CF_3)_2PF + HF_2^{\ominus} \rightarrow [(CF_3)_2PF_3H]^{\ominus} \text{ (IV)}$$



(IIIa)



(IIIb)



(IV)

^{19}F and ^{1}H NMR studies have shown that of the three possible isomers, the structure of $(CF_3)_2PF_3H^{\ominus}$ is as shown in (IV).

Similar behavior has been observed for the parent PF_3 which gives the $[PF_5H]^{\ominus}$ ion (*238*).

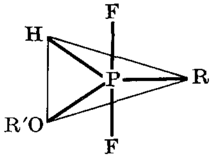
The mechanism probably involves the following steps

$$HF_2^{\ominus} \rightleftharpoons HF + F^{\ominus}$$

$$RPF_2 + HF \rightarrow RPF_3H$$

$$RPF_3H + F^{\ominus} \rightarrow [RPF_4H]^{\ominus}$$

g. By Alcohols. Primary alcohols R′OH add to alkyldifluorophosphines at low temperatures (*94*, *96*, *140*) to give the pentacoordinate $RPF_2H(OR')$, which have a trigonal–bipyramid structure (V) with fluorine atoms occupying axial positions. When the reaction is carried out in the presence of triethylamine, a crystalline salt is also formed for which the structure $Et_3NH^+[RPF_3H(OR)]^-$ has been suggested (*96*).



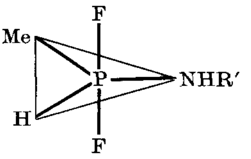
(V)

$$RPF_2 + ROH \rightarrow RPF_2H(OR) \xrightarrow{F^-} RPF_3H(OR)^-$$

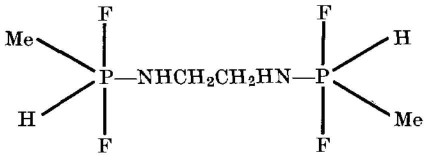
h. By Amines. (*i.*) *Primary amines.* Methyldifluorophosphine reacts with primary amines $R'NH_2$, in ether at –40° to –60°C to give distillable 1:1 adducts (VI), whose identity as trigonal–bipyrimidal alkylaminodifluorophosphoranes $MePHF_2(NHR')$ (*87*, *88*) was confirmed by NMR studies. Similarly ethylenediamine affords a 1:2 adduct formulated as (VII) on the basis of its phosphorus and fluorine NMR spectra.

$$MePF_2 + R'NH_2 \rightarrow MePHF_2(NHR') \qquad (87, 88)$$

$$2\,MePF_2 + H_2NCH_2CH_2NH_2 \rightarrow (MePF_2H)_2(NHCH_2CH_2NH) \qquad (81)$$



(VI)



(VII)

(*ii.*) *Secondary amines.* Both trifluoromethyldifluorophosphine and fluorobistrifluoromethylphosphine have been shown to form hexacoordinate phosphorus anions $[(CF_3)_nPF_{4-n}H]^{\ominus}$ when treated with dimethylamine under mild conditions (*49, 249*).

$$3\ CF_3PF_2 + 3\ Me_2NH \rightarrow 2\ CF_3PF(NMe_2) + (Me_2NH_2)^{\oplus}[(CF_3PF_4H]^{\ominus}$$

$$(CF_3)_2PF \xrightarrow{Me_2NH} (CF_3)_2PNMe_2 + [Me_2NH_2]^{\oplus}[(CF_3)_2PF_3H]^{\ominus}$$

and the reaction has been shown to involve the intermediate bifluoride salt (see also Section V). The $[(CF_3)_2PF_4]^{\ominus}$ ion has also been obtained as a reaction product from the aminolysis of fluorobistrifluoromethylphosphine and shown to have the trans structure (*26, 249*).

i. Substitution reactions not involving oxidation. Secondary aminolysis of alkyldifluorophosphines affords 35–45% yields of the $RFP(NR_2')$ compounds (*87*) and a recent report describes the synthesis of the related

$$RPF_2 \xrightarrow{R_2'NH} RPF(NR_2')$$

$$R = Me,\ R' = n\text{-Bu},\ i\text{-Bu}$$

$$R = Et,\ R' = n\text{-Bu}$$

methylphosphonofluoridous esters MePF(OR′) by the low-temperature reaction between methyldifluorophosphine and sodium alkoxides (*185*).

$$MePF_2 \xrightarrow[-50°C]{R'ONa} MePF(OR') + NaF$$

IV. Halogeno- and Pseudohalogenofluorophosphines

A. CHLORO- AND BROMOFLUOROPHOSPHINES

Chloro- and bromofluorophosphines of the type PF_2X and PFX_2 ($X = Cl$, Br) have been known for a long time and originally were obtained by incomplete fluorination of the appropriate PX_3 compound with a variety of fluorinating agents, e.g., antimony trifluoride (*282, 133, 149*), calcium fluoride (*32*), or ammonium fluoride (*324*), sometimes with the addition of $SbCl_5$ or PX_5 as a catalyst (*133, 149*). Separation of the mixtures of products may be effected by fractional distillation or facilitated by selectively removing the desired product as rapidly as possible from the reaction site.

Equilibration of PCl_3 and PF_3 at high temperature affords either PF_2Cl or $PFCl_2$, and likewise warming mixtures of PCl_3 and PF_2NMe_2 produces chlorodifluorophosphine (*138*). More recently PF_2Cl and PF_2Br have been obtained by the facile cleavage of the phosphorus–nitrogen bond in dialkylaminodifluorophosphines (*47, 107, 213*) or alkylaminobisdifluorophosphines (*236, 237*). The ready availability of these aminodifluorophosphines makes this an attractive route.

Bromodifluorophosphine is also obtained by HBr cleavage of the phosphorus–oxygen bond of μ-oxobisdifluorophosphine (*50*), and there is one report of HCl cleavage of a phosphorus–sulfur bond (*48*)

$$R_2NPF_2 + 2\,HCl \rightarrow PF_2Cl + R_2NH_2Cl$$

$$EtN(PF_2)_2 + 3HCl \rightarrow 2\,PF_2Cl + EtNH_2HCl$$

$$PF_2OPF_2 + HBr \rightarrow PF_2Br + OPF_2H$$

TABLE III

HALOGENO- AND PSEUDOHALOGENOFLUOROPHOSPHINES

Compound	Boiling point (°C/mm)	Melting point (°C)	Refs.	ϕ_F[a]	δ_P[b]	J_{PF}[c]	Refs.
PF_2Cl	−47.3	−164.8	(*217*, *219*, *213*)	38.1	−176	1390	(*217*, *133*)
PF_2Br	−16.1	−133.8	(*217*, *213*)	40.1	−218	1388	(*217*)
PF_2I	26.7	−93.8	(*277*, *213*, *47*)	46.0	−242.2	1340	(*277*)
$PFCl_2$[d]	13.8	−144.4	(*217*, *219*)	55.9	−224	1320	(*217*, *133*)
$PFBr_2$	78.4	−115	(*217*, *219*)	70.4	−255	1301	(*217*)
PFClBr	—	—	(*78*)	—	—	—	—
CF_3PFCl	—	—	(*227*)	144	—	1178	(*227*)
C_6H_5PFCl	—	—	(*87*, *89*)	72	—	1050	(*87*, *89*)
$(Me_2N)PFBr$	37/20	~−73	(*64*)	76.1	—	1172	(*64*)
$(Me_2N)PFCl$	44/85	—	(*273a*)	70.0	—	1170	(*273a*)
$(Et_2N)PFCl$	35/12	—	(*273a*)	67.3	—	1164	(*273a*)
(MeO)PFCl	38.9	—	(*202*)	—	—	—	—
PF_2CN	—	—	(*105*, *274*)	89.7	−140.8	1273	(*274*)
PF_2NCO	12.3 (dec.)	~−108	(*105*, *3*)	39.2	−130.6	1361	(*105*, *109*)
PF_2NCS	54.5	—	(*273*)	54.2	−132.0	1336	(*273*)
$PF(NCO)_2$	98.7	−55.0	(*109*, *3*)	—	−127.9	1226	(*109*)
$PF(NCS)_2$	51/1.5	—	(*273*)	80.3	−126.5	1252	(*273*)
MePFCl	—	—	(*301*)	—	−240	1040	(*301*)

[a] In ppm relative to CCl_3F.
[b] In ppm relative to H_3PO_4.
[c] In Hz.
[d] P–F = 1.55 ± 0.05°A; P–Cl = 2.02 ± 0.03°A; FPCl = 102 ± 3° (*282*).

There is Raman spectroscopic evidence for the presence of bromochlorofluorophosphine PFClBr in the equilibrium mixture of $PFBr_2$ and $PFCl_2$, and also for other mixed halogenofluorophosphines obtained in PF_3/PX_3 mixtures (X = Cl, Br) (*77*, *78*, *217–219*, *222*).

$$PFBr_2 + PFCl_2 \rightarrow 2\,PFClBr$$

Revised Raman and infrared data for several mixed halogenofluoro phosphines have been published (*219*, *222*) and thermodynamic functions in the 200°–2000°K range have been calculated.

Although PBrClF cannot be isolated in the pure state from the above reactions, Clune and Cohn (*64*) have very recently obtained the unsymmetrical fluorophosphine Me_2NPFBr by reacting cyanogen bromide with dimethylaminodifluorophosphine. The formula of the compound

$$2\ Me_2NPF_2 + BrCN \rightarrow Me_2NPFBr + Me_2NPF_3CN$$

(b.p. 37°C/20 mm, m.p. −73° ± 5°C) is established by its mass spectrum and its proton and fluorine NMR spectrum. It will be of interest to see if PFClBr can be synthesized by cleavage of the phosphorus–nitrogen bond in Me_2NPFBr with hydrogen chloride. Roesky (*273a*) has very recently obtained compounds of the type R_2NPFCl (R = Me, Et) in low yield by partial fluorination of the corresponding R_2NPCl_2 with antimony trifluoride.

Hydrogen chloride reacts with $CF_3PF(NMe_2)$ to afford CF_3PCl_2, CF_3PFCl and CF_3PF_2 (*227*). NMR and infrared studies show that CF_3PFCl is also formed when CF_3PF_2/CF_3PCl_2 mixtures are heated to 60°C (*227*). C_6H_5PFCl is a likely product from the reaction between HF and $C_6H_5PCl_2$ (*87*).

B. DIFLUOROIODOPHOSPHINE, PF_2I

The only known iodofluorophosphine, difluoroiodophosphine, PF_2I, first synthesized in 1966 by Rudolph, Morse, and Parry (*277*), plays a key role for the introduction of the PF_2 group into other compounds. It can be readily obtained (in 94% yield) via hydrogen iodide cleavage of the phosphorus–nitrogen bond of dimethylaminodifluorophosphine (*47*, *213*, *277*) (Section V).

$$F_2PNMe_2 + 2\ HI \rightarrow PF_2I + Me_2NH{\cdot}HI$$

The compound (b.p. 26.7°C, m.p. −93.8° to −93.3°C) is reasonably stable in the vapor phase at room temperature, but the rate of disproportionation to trifluorophosphine and phosphorus triodide (*277*, *47*) i.e.,

$$3\ PF_2I \rightarrow 2\ PF_3 + PI_3$$

is greatly enhanced at high vapor pressures.

1. *Reactions*

The synthetic utility of difluoroiodophosphine may be seen from Fig. 1, which summarizes some of its main reactions.

The weak phosphorus–iodine bond is readily cleaved by a variety of reagents, for example, mercury readily affords tetrafluorodiphosphine (*274*), and cuprous oxide gives the μ-oxobisdifluorophosphine in good yield (*274*).

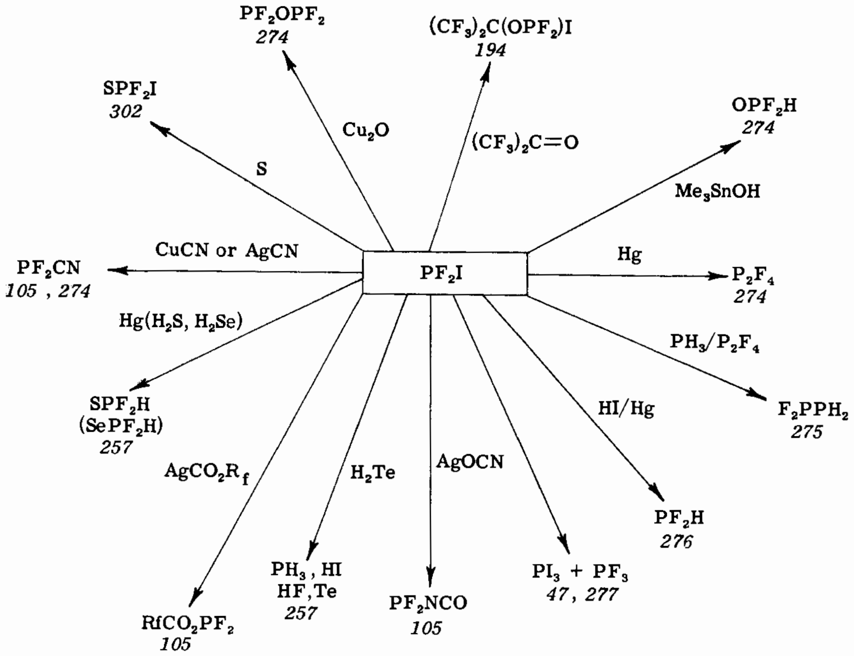


FIG. 1. Some reactions of difluoroiodophosphine, PF_2I.

Hydrogen chalcogenides H_2X ($X = S$, Se, Te) react differently with difluoroiodophosphine in the presence of mercury. The sulfur and selenium derivatives give the pentavalent compound XPF_2H ($X = S$, Se), whereas hydrogen telluride produces a mixture of phosphine, hydrogen halides, and elementary tellurium (*257*).

$$PF_2I + H_2X \rightarrow XPF_2H + HI$$
$$(X = S, Se)$$

$$PF_2I + 3\,H_2Te \rightarrow PH_3 + HI + 2\,HF + 3\,Te$$

2. *Reactions of other halogenofluorophosphines*

Me_3SnOH reacts with all the halogenodifluorophosphines PF_2X ($X = Cl$, Br, I) to give the pentavalent compound OPF_2H rather than the trivalent F_2POH (*274*) (see Section VI,A.).

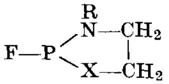
The greater reactivity of the P–X bond compared with the P–F bond is also evident from metathetical reactions with silver pseudohalides (*105, 274*) and silver salts of perfluorinated carboxylic acids (*105*), e.g.,

$$PF_2X + AgY \rightarrow PF_2Y + AgX$$
$$(Y = CN, CNO)$$

$$PF_2X + AgCO_2Rf \rightarrow PF_2CO_2Rf + AgX$$
$$(Rf = CF_3, C_2F_5, n\text{-}C_3F_7, Me\text{-})$$

Similarly alcohols readily react with $PFCl_2$ to produce monofluorophosphites (*55, 67, 205*), while amino alcohols and amino thiols afford cyclic compounds (*179, 203*).

$$PFCl_2 + 2\,ROH \longrightarrow (RO)_2PF + 2\,HCl$$

$PFCl_2 + NHRCH_2CH_2XH \longrightarrow$  $+ \quad 2\,HCl$

(X = O or S)

Mixed halogenofluorophosphoranes $PF_{5-n}X_n$ may be obtained by controlled reactions between the appropriate fluorophosphines with a halogen.

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2$$

$$PF_2Cl + Cl_2 \rightarrow PF_2Cl_3$$

$$PFBr_2 + Br_2 \rightarrow PFBr_4$$

These reactions have been discussed in more detail elsewhere (*133, 282*). A closely related reaction is the addition of bis(trifluoromethyl)-chloroamine to chlorodifluorophosphine (*99*).

$$(CF_3)_2NCl + PF_2Cl \rightarrow (CF_3)_2NPF_2Cl_2$$

In the presence of antimony pentachloride $PFCl_2$ and chlorine afford a salt $[PFCl_3][SbCl_6]$, which is also formed more slowly from $SbCl_5$ and $PFCl_2$ directly. NMR and IR studies indicate the presence of the $PFCl_3{}^+$ cation (*278*).

$$PCl_2F + SbCl_5 + Cl_2 \rightarrow [PFCl_3][SbCl_6]$$

Phosphorus–oxygen bonds are formed when either bromo- or iododifluorophosphine react with hexafluoroacetone (*194*) (see also Section VI,B.).

Sulfur adds to difluoroiodophosphine at 80°–90°C to give 50% yields of SPF_2I (*302*).

C. Cyanodifluorophosphine, PF_2CN

This rather unstable volatile liquid is obtained in 32% yield on warming a mixture of iododifluorophosphine and cuprous cyanide from the temperature of liquid nitrogen to room temperature (*274*). Even at −20°C there is significant disproportionation to trifluorophosphine and a white solid, presumably $P(CN)_3$. The formulation of PF_2CN as a

$$PF_2I + CuCN \rightarrow PF_2CN + CuI$$

$$3\,PF_2CN \xrightarrow{-20°C} 2\,PF_3 + P(CN)_3$$

cyanide rather than an isocyanide is based on the breakdown pattern in the mass spectrum.

There is also a report that PF_2CN, formed from PF_2I and AgCN, is stable when dry, but decomposes slowly in the presence of moisture affording μ-oxobisdifluorophosphine (*105*, *106*).

$$2\,PF_2CN + H_2O \rightarrow F_2POPF_2 + 2\,HCN$$

D. ISOCYANATES AND ISOTHIOCYANATES

The isocyanate compounds F_2PNCO and $FP(NCO)_2$ were first obtained by Anderson (*3*) via fluorination of $P(NCO)_3$ with antimony trifluoride. Similarly $PF_2(NCS)$ was said to be formed from $P(NCS)_3$. More recent work (*273*), however, has indicated that Anderson's product is identical with the pentavalent phosphorus compound $SPF_2(NCS)$ formed by fluorination of $SP(NCS)_3$.

Both PF_2NCS and $PF(NCS)_2$ can be formed in about 15% yield by fluorination of $P(NCS)_3$ with antimony trifluoride, but some $SPF_2(NCS)$ is also formed. The concentration of the latter may be reduced by using freshly prepared $P(NCS)_3$ (*273*).

A convenient route to PF_2NCO using difluoroiodophosphine and

$$PF_2I + AgOCN \rightarrow PF_2NCO + AgI$$

silver cyanate has recently been described (*105*). The mass spectrum confirms that the compound is an isocyanate rather than a cyanate.

Structures

Rankin (*266a*) has recently determined the structures of three pseudohalofluorophosphines PF_2X ($X = CN$; NCO; NCS) by electron diffraction. The relatively short P–N bond lengths in PF_2NCO (1.68 ± 0.02°A) and PF_2NCS ($1.70 \pm 0{\cdot}02$°A) and the very wide PNC bond angles (ca. 150°) suggest π-contributions to the P–N bonds are important.

Table III lists the known halogeno- and pseudohalogenofluorophosphines.

V. Fluorophosphines Containing Phosphorus–Nitrogen Bonds

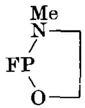
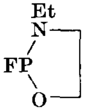
A. DIALKYLAMINOFLUOROPHOSPHINES (PHOSPHORAMIDOUS FLUORIDES), $(R_2N)_nPF_{3-n}$

1. *Synthesis*

The first report of this type of compound in the patent literature erroneously describes Et_2NPF_2 as a gas which condenses at −78°C (*294*); however, this could not be subsequently confirmed and later work showed that the compound in fact boils at 96°C (*287*).

TABLE IV

FLUOROPHOSPHINES CONTAINING PHOSPHORUS–NITROGEN BONDS

Compound	Boiling point (°C/mm)	n_D	(°C)	d_4^{20}	Refs.	$\phi_F{}^a$	$\delta_P{}^b$	$J_{PF}{}^c$	Refs.
Me_2NPF_2	48, 50.3	1.3580	20	—	(*225, 287, 47, 107*)	65.3	−143.0	1197	(*270*)
Et_2NPF_2	96–97, 47/100	1.3840	20	1.0495	(*138, 287, 13*)	64.8	−144.0	1194	(*270*)
$(allyl)_2NPF_2$	33/20	—	—	—	(*291*)	63.7	−142.2	1202	(*291*)
i-Pr_2NPF_2	129–130	1.3985	20	0.9873	(*138*)	—	—	—	—
i-Bu_2NPF_2	165–167	1.4160	20	0.9809	(*138*)	—	—	—	
$C_4H_8NPF_2$	32–33/27	—	—	—	(*13*)	67.9	−146.2	1198	(*13*)
$C_5H_{10}NPF_2$	134–135	1.4252	26	1.1434	(*138, 287, 13*)	65.2	−139.1	1193	(*270, 13*)
		1.4276	20	—					
$O(CH_2CH_2)_2NPF_2$	138–139	1.4300	20	1.2787	(*155*)	—	—	—	
$(Et)PhNPF_2$	97–98/40	1.4906	20	1.1625	(*138*)	—	—	—	
$MeNHPF_2$	52–53 (dec.)	—	—	—	(*11*)	70.6	−140.5	1191	(*11*)
$(Me_2N)_2PF$	125.9, 50–51/50 (m.p. −90)	—	—	—	(*270, 47, 107*)	100.6	−151.0	1046	(*270*)
$(Et_2N)_2PF$	46.5–47.5/1.3	—	—	—	(*273a*)	98.1	—	1037	(*273a*)
	52–53/50	1.4275	20	1.1750	(*203*)	—	—	—	
	70–71/50	1.4330	20	1.1400	(*203*)	—	—	—	

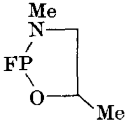
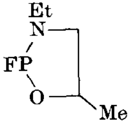
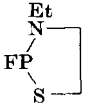
	57–58/50	1.4240	20	1.1099	(*203*)	—	—	—	
	89–91/50	1.4305	20	1.0742	(*203*)	—	—	—	
	60/1	1.5148	20	1.2045	(*179*)	—	—	—	
$(Me_2N)PF(OMe)$	28–31/100	1.3895	20	1.0215	(*91*)	—	−153	1136	(*91*)
$(Me_2N)PF(OEt)$	44–46/100	1.3947	20	—	(*91*)	—	−151	1130	(*91*)
$(Et_2N)PF(OMe)$	66–68/140	1.4120	20	0.9897	(*91*)	72.2	−151.9	1126	(*91, 291*)
$(Et_2N)PF(OC_5H_{11}\text{-}i)$	85–87/10	1.4250	20	0.9334	(*91*)	70	−152	1123	(*91*)
$(Me_2NNMe)PF_2$	154 (est.)	—	—	—	(*115*)	—	—	—	
$(Me_2NNMe)_2PF$	$30/10^{-4}$	—	—	—	(*115*)	—	—	—	
$(MeNOMe)PF_2$	198 (est.)	—	—	—	(*115*)	—	—	—	
$(MeNOMe)_2PF$	—	—	—	—	(*115*)	—	—	—	
$MePF(NMe_2)$	85–86	—	—	—	(*87, 290*)	—	−165.9	915	(*87*)
	29–30/100	1.4200	20	0.9473	(*89*)				
$MePF(NEt_2)$	52–54/80	1.4135	20	0.9460	(*87–89*)	110.2	−165.2	914	(*87, 89*)
$MePF(NBu_2)$	56–57/4	1.4069	20	0.8929	(*87–89*)	—	−166.9	924	(*87, 89*)
$MePF[N(i\text{-}Bu)_2]$	49–50/3	1.4075	20	0.8876	(*87, 89*)	—	—	—	
$MePF(NC_4H_8)$	67–69/6	1.4765	20	1.1316	(*87*)	—	—	—	
$MePF(NC_5H_{10})$	50–52/20	1.4450	20	1.0340	(*87*)	113.4	−165.1	927	(*87*)
$MePF[NH(i\text{-}Pr)]$	31–32/90	1.4254	20	0.9776	(*90*)	105.0	−169.0	1065	(*90*)

TABLE IV—*cont.*

FLUOROPHOSPHINES CONTAINING PHOSPHORUS–NITROGEN BONDS

Compound	Method of preparation[a] (section number)	Boiling point (°C/mm)	n_D	(°C)	d_4^{20}	Refs.	ϕ_F[b]	δ_P[c]	J_{PF}[d]	Refs.
$MePF[NH(i\text{-}Bu)]$	36–38/60	1.4214	20	0.9650	(*90*)		104.0	—	1040	(*90*)
$PhPF(NMe_2)$	88–90/15	—	—	—	(*88, 290*)		128.5	−159.8	989	(*290*)
$PhPF(NEt_2)$	83–84/2 -	1.4980	20	1.0375	(*87, 288, 290*)		123.5	−154.9	964	(*87, 290*)
$CF_3PF(NMe_2)$	54–56/0.25- 75	—	—	—	(*227*)		134.3	—	1010	(*227*)
$CF_2HCH_2PF(NMe_2)$	—	—	—	—	(*118*)		119.5	—	886	(*118*)
$EtPF(NBu_2)$	52–54/1.5	1.4167	20	—	(*89*)		—	—	—	—
$PhPF[NH(i\text{-}Bu)]$	—	—	—	—	(*87*)		—	−135.8	920	(*87*)
$MePF(NHC_3H_6)$	—	—	—	—	—		—	−151	873	(*87*)
$(FPNt\text{-}Bu)_2$	23.5/4 (m.p. 17–18)	—	—	—	(*250a*)		22.2	−164	1190	(*250a*)

[a] In ppm relative to CCl_3F.
[b] In ppm relative to H_3PO_4.
[c] In Hz.

Dialkylamino- and alkylarylaminodifluorophosphines which are listed in Table IV are colorless, mobile liquids with an unpleasant smell. They are hydrolyzed only fairly slowly by cold water and fume slightly in air.

Several synthetic approaches to this class of compounds have been developed, the most convenient being fluorination of the corresponding dialkylaminochlorophosphine with either antimony trifluoride (*287*, *13*, *138*), zinc fluoride (*138*, *252*), or sodium fluoride in tetramethylene sulfone (*287*, *291*, *270*, *213*). No redox reactions of the type discussed in Section III are observed.

$$3\ \mathrm{Me_2NPCl_2} + 2\ \mathrm{SbF_3} \rightarrow 3\ \mathrm{Me_2NPF_2} + 2\ \mathrm{SbCl_3}$$

$$\mathrm{Me_2NPCl_2} + 2\ \mathrm{NaF} \rightarrow \mathrm{Me_2NPF_2} + 2\ \mathrm{NaCl}$$

Several dialkylaminodifluorophosphines can also be prepared by treating difluorotrichloromethylphosphine with the appropriate secondary amine at room temperature (*13*, *225*), the reaction involving an

$$\mathrm{CCl_3PF_2} + \mathrm{R_2NH} \rightarrow \mathrm{R_2NPF_2} + \mathrm{CHCl_3}$$
$$(\mathrm{R} = \mathrm{Me, Et};\ \mathrm{R_2} = \mathrm{C_4H_8, C_5H_{10}})$$

unusual preferential cleavage of the phosphorus–carbon rather than the phosphorus–halogen bond. The corresponding trifluoromethyl derivative $\mathrm{CF_3PF_2}$ reacts differently affording dimethylaminofluorotrifluoromethylphosphine, $\mathrm{CF_3PFNMe_2}$ (*227*), and this may be related to the relative stabilities of the $\mathrm{CX_3}^-$ carbanions (*225*).

Trifluorophosphine and dimethylamine readily afford either dimethylaminodifluorophosphine or bis(dimethylamino)fluorophosphine (*47*, *107*). The latter until recently was the only well-characterized member of this particular class of compounds; however, coordination compounds of other $(\mathrm{R_2N})_2\mathrm{PF}$ ligands are known (*245*).[2] The $\mathrm{PF_3}$–$\mathrm{Me_2NH}$ reaction was originally believed to afford the dimethylammonium bifluoride salt (*47*), but more recently the novel anion $[\mathrm{PF_5H}]^-$ has also been identified in the reaction products (*238*) (see also Section III).

$$\mathrm{PF_3} \xrightarrow{\mathrm{Me_2NH}} \mathrm{PF_2NMe_2} \xrightarrow{\mathrm{Me_2NH}} \mathrm{PF(NMe_2)_2}$$

Almost quantitative yields of dimethylaminodifluorophosphine are obtained when trifluorophosphine and dimethylaminotrimethylstannane react at room temperature (*246*).

$$\mathrm{PF_3} + \mathrm{Me_3SnNMe_2} \rightarrow \mathrm{Me_2NPF_2} + \mathrm{Me_3SnF}$$

---

[2] Very recently the ethyl analog has been obtained by fluorinating $(\mathrm{Et_2N})_2\mathrm{PCl}$ with sodium fluoride in sulfolane (*273a*).

Exchange of groups attached to phosphorus occurs when trifluorophosphine or phosphorus pentafluoride and dimethylaminophosphines $R_nP(NMe_2)_{3-n}$, (R = Me; $n = 0, 1, 2$), are heated together forming mixtures of Me_2NPF_2 and $(Me_2N)_2PF$ (*34*). Similarly boron trifluoride and tris(dimethylaminophosphine) produce dimethylaminodifluorophosphine when BF_3 is not present in excess, otherwise trifluorophosphine is formed in high yield (*252*, *132*).

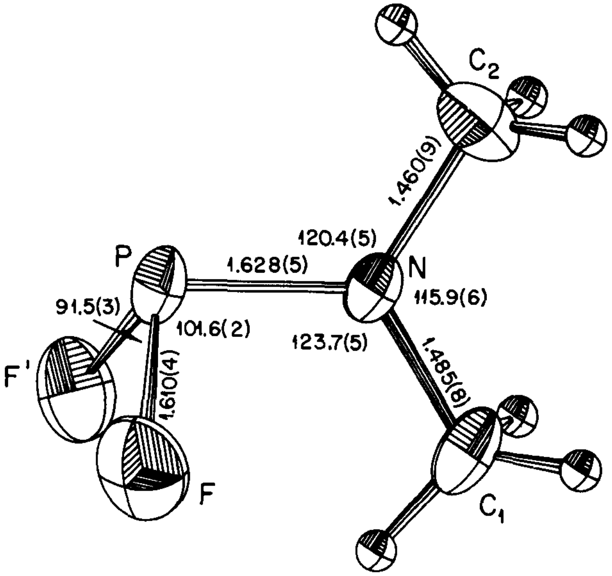


FIG. 2. ORTEP drawing of the $(CH_3)_2NPF_2$ molecule with 50% thermal motion ellipsoids for the nonhydrogen atoms. Bond lengths (in Ångstroms) and angles (in degrees) are given with standard deviations expressed in units of the last significant figure (*212*).

$$P(NMe_2)_3 + PF_3 \rightarrow Me_2NPF_2 + (Me_2N)_2PF$$

$$P(NMe_2)_3 + BF_3 \rightarrow Me_2NPF_2 + (Me_2N)_2BF$$

Very recently diethylaminodifluorophosphine has been obtained by an interesting route which involves the reduction of the pentavalent diethylaminotetrafluorophosphorane with Me_3SiPPh_2 (*220*).

$$EtNPF_4 + 2\ Ph_2PSiMe_3 \rightarrow Et_2NPF_2 + Ph_2PPPh_2 + 2\ Me_3SiF$$

2. *Structure*

The infrared and Raman spectra of Me_2NPF_2 were interpreted in terms of a pyrimidal arrangement of bonds around both nitrogen and phosphorus (*108*), but a recent X-ray study (*212*) shows that the two carbon atoms and the phosphorus and nitrogen atoms are all coplanar

(Fig. 2), which suggests that the lone-pair on nitrogen is involved in $p\pi$–$d\pi$ bonding with the phosphorus atom. It is interesting to compare the phosphorus–nitrogen bond length in Me_2NPF_2 (1.628 ± 0.005 Å) with the reported value (*323*) for Me_2NPCl_2 (1.694 ± 0.03 Å). This significant shortening can be understood in terms of a further enhancement of the partial double-bond character by the more electronegative fluorine atoms. Both values are substantially less than the sum of the covalent radii (1.84 Å) or that calculated from the Stevenson–Schomaker equation (1.75 Å). In dialkylaminodifluorophosphines π bonding between nitrogen and phosphorus should increase the donor property of the phosphorus atom and this aspect is discussed in Section IX and X on coordination complexes.

B. ALKYLAMINODIFLUOROPHOSPHINES, $RHNPF_2$, AND ALKYL(ALKYLAMINO)FLUOROPHOSPHINES, R(R′NH)PF

Only one example of the first class of compounds has so far been synthesized (*11*), namely, for R = methyl, although it was previously known as its borane adduct $MeNHPF_2$–BH_3, which was synthesized by partial aminolysis of the PF_3BH_3 complex (*148*). The free aminofluorophosphine [b.p. 52°–53°C (dec.)] can be obtained from methylamine and difluorotrichloromethylphosphine in an analogous way to the syntheses

$$CCl_3PF_2 + MeNH_2 \rightarrow MeNHPF_2 + CHCl_3$$

of R_2NPF_2 using secondary amines (Section V,A). An alternative method involving equilibration of methylamine and methylaminobisdifluorophosphine (*11*) (see Section V,C) avoids difficulties in isolation of the product. Although the compound is rather unstable, it was fully characterized by NMR spectroscopy. On standing at room temperature, it readily forms $MeN(PF_2)_2$ and other unidentified products.

$$MeN(PF_2)_2 + MeNH_2 \rightleftharpoons 2\ MeNHPF_2$$

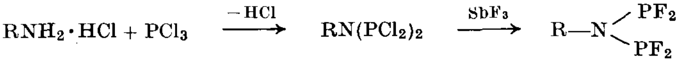
Direct primary aminolysis of trifluorophosphine apparently gives 1:1 adducts of the type $RNHPF_2 \cdot RNH_2$ under varying reaction conditions, the main evidence for the presence of the $RNHPF_2$ species coming from ^{19}F nmr studies (*90*).

First reports of methyl(monoalkylamino)fluorophosphines MePF(NHR′) have appeared only recently. Drozd *et al.* (*90*) have obtained these compounds in fairly low yield using a two-step process involving addition of the primary amine $R'NH_2$ to methyldifluorophosphine to afford the pentavalent fluorophosphorane $MePF_2H(NHR')$ (see also Section III), followed by dehydrofluorination with tertiary *n*-butylamine at 60°–70°C.

$$MePF_2 \xrightarrow{R'NH_2} MePF_2H(NHR') \xrightarrow{-HF} MePF(NHR')$$
$$(R' = i\text{-}C_3H_7,\ i\text{-}C_4H_9)$$

C. ALKYL- OR ARYLAMINOBISDIFLUOROPHOSPHINES, $RN(PF_2)_2$

Representatives of the class of compounds listed in Table V were first obtained in 1967 by fluorination of the corresponding bisdichloro derivatives with antimony trifluoride (*236, 237*).



$$RNH_2 \cdot HCl + PCl_3 \xrightarrow{-HCl} RN(PCl_2)_2 \xrightarrow{SbF_3} R{-}N\begin{matrix} PF_2 \\ PF_2 \end{matrix}$$

($R = Me$, Et, Ph, $m\text{-}ClC_6H_4$)

TABLE V

ALKYL- OR ARYLAMINOBISDIFLUOROPHOSPHINES, $RN(PF_2)_2$

Compound	Boiling point (°C/mm)	Refs.
$MeN(PF_2)_2$	40–2	(*236, 237*)
$EtN(PF_2)_2$	62–3	(*236, 237*)
$PhN(PF_2)_2$	41/10 [m.p. 26°]	(*239, 224*)
$m\text{-}ClC_6H_4N(PF_2)_2$	50/10	(*239, 224*)

An alternative route involves fluorination of the products from the reaction between phosphorus trichloride and heptamethyldisilazane (*141*) or ethylhexamethyldisilazane (*224*). In the former case the intermediate $Me_3SiNMePF_2$ (b.p. 20/6 mm) has recently been isolated (*146a*).

$$(Me_3Si)_2NR' + 2\,PCl_3 \rightarrow 2\,Me_3SiCl + R'N(PCl_2)_2$$

$$3\,R'N(PCl_2)_2 + 4\,SbF_3 \rightarrow 3R'N(PF_2)_2 + 4\,SbCl_3$$

($R = Me$, Et)

It is interesting to note that there is apparently no reaction between heptamethyldisilazane and trifluorophosphine (*293*).

Alkyl and arylaminobisdifluorophosphines are colorless, mobile liquids which are much more volatile than their chloro analogs and only hydrolyze slowly in air. They are stable at room temperature in sealed glass ampoules over a period of several months, in sharp contrast to the fairly rapid decomposition of the structurally related μ-oxobisdifluorophosphine F_2POPF_2 (Section VI).

The identity of $RN(PF_2)_2$ compounds can be confirmed by their quantitative reaction with hydrogen chloride (*237*) and by their characteristic fluorine and phosphorus NMR spectra (*239*) (Section XI).

$$RN(PF_2)_2 + 3\,HCl \rightarrow 2\,PF_2Cl + RNH_2 \cdot HCl$$

Although no stable complex can be obtained with boron trifluoride, these aminofluorophosphines do act as bidentate ligands toward metal carbonyls (*144*) (Section IX).

D. ALKYL- OR ARYLDIALKYLAMINOFLUOROPHOSPHINES, $RPF(NR'_2)$

The first report of compounds with this type of structure concerned the trifluoromethyl derivative $CF_3PF(NMe_2)$ (*227*), which is obtained either by Eq. (1) controlled aminolysis of difluorotrifluoromethylphosphine or Eq. (2) by fluorination of $CF_3PCl(NMe_2)$ (synthesized by partial

$$3\ CF_3PF_2 + 3\ Me_2NH \rightarrow 2\ CF_3PF(NMe_2) + [Me_2NH_2]^+[CF_3PF_4H]^- \tag{1}$$

$$CF_3PCl_2 \xrightarrow{Me_2NH} CF_3PCl(NMe_2) \xrightarrow{SbF_3} CF_3PF(NMe_2) \tag{2}$$

aminolysis of CF_3PCl_2). In Eq. (1) only two moles of $CF_3PF(NMe_2)$ are obtained from three moles of CF_3PF_2 on account of the formation of the novel anion $[CF_3PF_4H]^-$ (*49*).

On the other hand, fluorination of alkyl- and aryldialkylaminochlorophosphines, $RPCl(NR'_2)$, with antimony (or arsenic) trifluoride under similar conditions to reaction (2) affords only the pentavalent fluorophosphorane $RPF_3(NR'_2)$ (*288, 290*) via the same type of redox reaction discussed previously in Section III,A for alkyl- and arylhalophosphines.

$$3\ RPCl(NR'_2) + 3\ MF_3 \rightarrow 3\ RPF_3(NR'_2) + 2\ M + MCl_3$$
$$(M = \text{As or Sb};\ R = \text{alkyl or aryl})$$

If milder conditions are employed some trivalent phosphorus compound can be isolated (*87*), and when fluorination is carried out under nonoxidizing conditions, e.g., by sodium fluoride in tetramethylene sulfone solution, good yields of the alkyl- or aryldialkylaminofluorophosphines are obtained (*288, 290*).

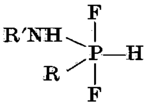
$$RPCl(NR'_2) + NaF \xrightarrow[\text{sulfone}]{\text{tetramethylene}} RPF(NR'_2) + NaCl$$

A detailed study by Drozd *et al.* (*87*) has shown that antimony trifluoride and even antimony pentafluoride may be used successfully in the fluorination of $RPCl(NR'_2)$ to $RPF(NR'_2)$ if the reactions are carried out in ether or dibutylaniline solution. Low-temperature reactions between secondary amines and alkyl- or aryldifluorophosphines

$$RPF_2 \xrightarrow[-30^\circ \text{ to } -40^\circ C]{R_2'NH} RPF(NR'_2)$$

offer an alternate route to these compounds (*87*). Primary amines, on the other hand, readily afford 1:1 adducts $RPF_2 \cdot R'NH_2$, which are distillable liquids and have been shown to be pentacoordinate phosphorus compounds (*88–90*) having axial fluorine atoms (VIII). Allylamine reacts

$$RPF_2 + R'NH_2 \rightarrow RPF_2H(NHR')$$



(VIII)

to give very small amounts of the allylaminofluorophosphine in addition to (VIII). It was not possible, however, to synthesize the tricoordinate compound $RPF(NHR')$ ($R = Me$, $R' = i\text{-}C_4H_9$) by elimination of HF from (VIII) by heating with potassium fluoride (*87*).

The interconversion of a dimethylamino to a di-*n*-butylamino derivative of methylfluorophosphine has been achieved by the following route (*87*), although the intermediate chlorofluorophosphine cannot be isolated. Similarly treatment of the reaction mixture formed by the

$$MePF(NMe_2) \xrightarrow{HCl} [MePFCl] \xrightarrow{n\text{-}Bu_2NH} MePF(NBu_2)$$

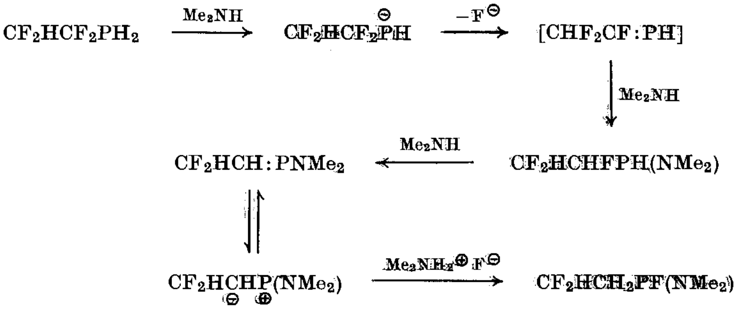
addition of hydrogen fluoride to phenyldichlorophosphine with diethylamine produces a 15% yield of phenyldiethylaminofluorophosphine (*87*). The latter is also obtained directly from phenyldifluorophosphine and diethylamine (*288*).

A particularly interesting synthesis of this type of compound has been reported (*118*). The reaction between 1,1,2,2-tetrafluoroethylphosphine

$$PhPCl_2 \xrightarrow{HF} [PhPFCl] \xrightarrow{Et_2NH} PhPF(NEt_2)$$

$$PhPF_2 \xrightarrow{Et_2NH} PhPF(NEt_2)$$

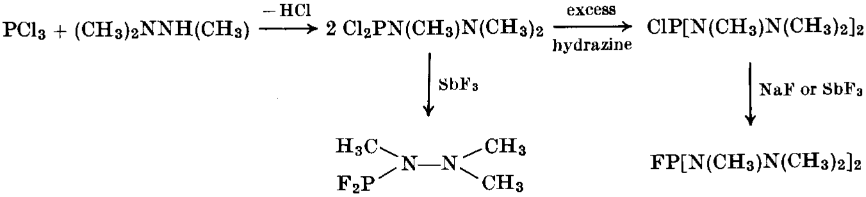
and dimethylamine affords a 64% yield of 2,2-difluoroethyl-*N*,*N*-dimethylphosphoramidous fluoride $CF_2HCH_2PF(NMe_2)$. The postulated mechanism outlined below involves a *phosphaalkene* intermediate:



The known alkyl- or aryldialkylaminofluorophosphines $RPF(NR'_2)$ are listed in Table IV. They are all colorless, mobile liquids, usually stable on distillation in an inert atmosphere, and may be stored at room temperature in sealed glass tubes over several months. In contrast to the spontaneously inflammable alkyl- or aryldifluorophosphines from which they are derived, they are only slowly oxidized in air.

E. HYDRAZINO- AND HYDROXYLAMINOFLUOROPHOSPHINES

Fluorination of the products from the reaction between 1,1,2-trimethylhydrazine and phosphorus trichloride affords the corresponding trimethylhydrazinofluorophosphines $F_2PN(CH_3)N(CH_3)_2$ and $FP[N(CH_3)N(CH_3)_2]_2$ (*115*), e.g.,

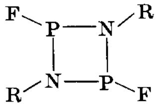


The bishydrazino derivative, which cannot be prepared by reacting $F_2P[N(CH_3)N(CH_3)_2]_2$ with excess 1,1,2-trimethylhydrazine, tends to disproportionate at its boiling point to the monohydrazino compound.

Analogous reactions using *O,N*-dimethylhydroxylamine gave the much less stable compounds $F_2P(NCH_3OCH_3)$ and $FP(NCH_3OCH_3)_2$ (*115*), whose formulas were established mainly by IR and NMR spectroscopy and molecular weight measurements.

F. 1,3-DIALKYL-2,4-DIFLUORODIAZADIPHOSPHETIDINES, $[RNPF]_2$

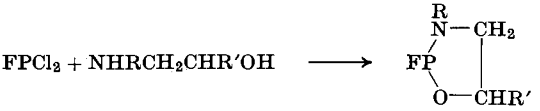
Several attempts to synthesize this type of ring compound



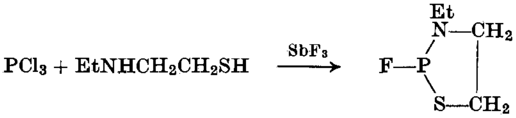
($R = Me, Et$) were unsuccessful (*141*), the isolable products being alkylaminobisdifluorophosphines $RN(PF_2)_2$. However, very recently the first example of this class of compounds has been obtained ($R =$ t-Bu; m.p. 17–18°C; b.p. 23.5/4mm) (*250a*). It seems very likely that the ring structure is stabilized by the presence of the bulkyl tertiary-butyl group. The cyclic structure has been confirmed by NMR studies (*250a*) (Section XI, A).

G. OTHER FLUOROPHOSPHINES CONTAINING P–N BONDS

Recently Martynov *et al.* (*179*, *203*) have synthesized some cyclic aminofluorophosphines containing phosphorus–oxygen or phosphorus–sulfur bonds by the following routes.



R = Me, Et
R′ = Me, Et, H



The compound $(MeO)PFNEt_2$ has been identified by its NMR spectrum in the products from the SbF_3 fluorination of mixtures of Et_2NPCl_2 and $MeOPCl_2$ (*291*), and there is a brief report (*91*) of other compounds of this type (see Table IV).

H. REACTIONS

The reactions of dimethylaminodifluorophosphine have been studied in some detail and are summarized in Fig. 3.

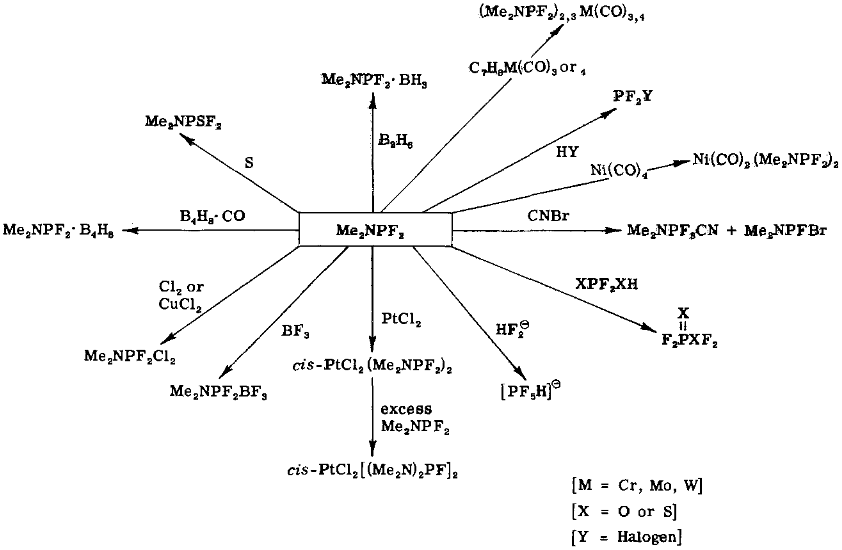


FIG. 3. Some reactions of Me_2NPF_2. From E. D. Morris and C. E. Nordman, *Inorg. Chem.* 8, 1673 (1969) with permission.

1. *Disproportionation Reactions*

There is no significant disproportionation of dialkylaminodifluorophosphines R_2NPF_2, when the compounds are heated to 60°C (e.g., $R = Me$, no disproportionation after 24 hours; $R = Et$, 0.9% after 7 days; $R_2 = C_5H_{10}$, 2.5% after 7 days) (*241*, *245*). The pyrrolidino derivative, however, does undergo disproportionation to an observable extent even at room temperature (*13*). Similarly a sample of bis(dimethylamino)-

$$2\,C_4H_8NPF_2 \rightarrow (C_4H_8N)_2PF + PF_3$$

fluorophosphine was found to disproportionate after several months storage at room temperature (*290*).

$$2\,(Me_2N)_2PF \rightarrow Me_2NPF_2 + (Me_2N)_3P$$

The exchange of groups on phosphorus is greatly facilitated by prolonged heating of dialkylaminodifluorophosphines with platinous halides (*241*, *245*) or gallium trichloride, and to a lesser extent by cuprous chloride (*30*, *65*) (see also Section IX). For example,

$$PtCl_2 + 4\,R_2NPF_2 \xrightarrow[\text{heating}]{\text{prolonged}} cis\text{-}[PtCl_2[(R_2N)_2PF]_2] + 2\,PF_3$$

Chlorodifluorophosphine may be obtained by heating mixtures of dimethylaminodifluorophosphine and phosphorus trichloride (*138*), but there is no evidence for Me_2NPFCl when excess dimethylaminodifluorophosphine is used.

$$Me_2NPF_2 + PCl_3 \rightarrow Me_2NPCl_2 + PF_2Cl$$

2. *Phosphorus–Nitrogen Bond Cleavage*

The phosphorus–nitrogen bond is readily cleaved by hydrogen halides (*47*, *107*, *118*, *236*, *277*, *213*, *237*).

$$R_2NPF_2 + 2HX \rightarrow PF_2X + R_2NH_2X \qquad (3)$$

$(X = Cl, Br, I)$

$$RN(PF_2)_2 + 2\,HCl \rightarrow 2\,PF_2Cl + RNH_3Cl \qquad (4)$$

$$RPF(NR'_2) + 2\,HCl \rightarrow [RPFCl] + R'_2NH_2Cl \qquad (5)$$

$(R = CH_3, CF_3, CF_2HCH_2)$

Reaction (3) offers a particularly useful route for the synthesis of PF_2I (see Section IV), while in reaction (5) the mixed fluorochlorophosphines are not isolable, but their presence may be established by IR, NMR, or chemical means (*227*, *87*).

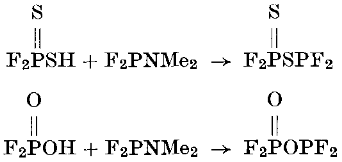
The reaction between dialkylaminodifluorophosphines and hydrogen fluoride has not been reported, but other studies (*238*, *249*) using bifluoride ion suggests that the resulting trifluorophosphine (or any unreacted dialkylaminodifluorophosphine) will react further with the dimethylammonium bifluoride salt to afford the hydridopentafluorophosphate ion $[PF_5H]^\ominus$.

$$Me_2NPF_2 + 3\,HF \rightarrow PF_3 + Me_2NH_2{}^\oplus HF_2{}^\ominus$$

$$Me_2NPF_2 + 3\,HF_2{}^\ominus \rightarrow Me_2NH_2{}^\oplus + [PF_5H]^\ominus + 3\,F^\ominus$$

$$PF_3 + HF_2{}^\ominus \rightarrow [PF_5H]^\ominus$$

Two interesting examples of phosphorus–nitrogen bond cleavage have been reported by Cavell *et al.* (*48*), (*50b*) who found that dimethylaminodifluorophosphine reacts with difluorophosphoric acid or difluorophosphorothioic acid $F_2P(X)XH$ ($X = O$ or S) to give compounds of empirical formula $[F_2PX]_2$, which contain phosphorus in both tervalent and pentavalent oxidation states, e.g. (see also Section VII, E),



$$F_2P(=S)SH + F_2PNMe_2 \rightarrow F_2P(=S)SPF_2$$

$$F_2P(=O)OH + F_2PNMe_2 \rightarrow F_2P(=O)OPF_2$$

3. *Oxidation*

Molecular chlorine or bromine readily oxidize dialkylaminodifluorophosphines to the mixed dihalogenodifluorodimethylaminophosphoranes $Me_2NPF_2X_2$ ($X = Cl, Br$) (*138, 65, 86*). $Me_2NPF_2Cl_2$ is also obtained by treating dimethylaminodifluorophosphine with cupric chloride along with the corresponding dimethylaminodifluorophosphine cuprous complex (*64*). Treatment of the fluorophosphorane with sulfur dioxide affords high yields of the dimethylphosphoramidic difluoride (*138*).

$$Me_2NPF_2 + Cl_2 \rightarrow Me_2NPF_2Cl_2 \xrightarrow{SO_2} Me_2NPOF_2$$

$$Me_2NPF_2 + CuCl_2 \rightarrow Me_2NPF_2Cl_2 + [CuClMe_2NPF_2]_4$$

In certain cases disproportionation of the products can take place (*86*), e.g.,

$$Et_2NPF_2 + Br_2 \rightarrow Et_2NPF_2Br_2 \rightarrow Et_2NPF_4 + Et_2NPF_3Br$$

Bisdimethylaminofluorophosphine and alkyl- or aryldialkylaminofluorophosphines can also be readily oxidized by halogens (*86*)

$$(Me_2N)_2PF + X_2 \rightarrow (Me_2N)_2PFX_2$$

$$RPF(NR'_2) + X_2 \rightarrow RPF(NR'_2)X_2$$

$$(R = Me, Ph;\ R' = Me, Et;\ X = Cl, Br)$$

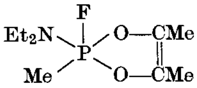
The pseudohalogen cyanogen bromide undergoes cleavage of the carbon–bromine bond when treated with dimethylaminodifluorophosphine

$$2\,Me_2NPF_2 + CNBr \rightarrow Me_2NPF_3CN + Me_2NPFBr$$

Methyldiethylaminofluorophosphine can be oxidized directly to the fluorophosphorane $MePF_3(NEt_2)$ with antimony trifluoride in the absence of solvent (*87*); however, the corresponding piperidyl and pyrrolidyl derivatives are unaffected. $MePFNEt_2$ and 2,3-butanedione

$$3\,MePF(NEt_2) + 2\,SbF_3 \rightarrow 3\,MePF_3(NEt_2) + 2\,Sb$$

form an adduct whose structure has been established as a cyclic five-coordinate phosphorus compound (*85*) rather than the four-coordinate



methylphosphonofluoridic ester.

Addition of sulfur to CF_3PFNMe_2 or PF_2NMe_2 affords the corresponding pentavalent phosphorus sulfide (*79*). For example,

$$Me_2NPF_2 + S \rightarrow Me_2NP(S)F_2$$

VI. Fluorophosphines Containing Phosphorus–Oxygen Bonds (Fluorophosphites)

A. μ-Oxobisdifluorophosphine, F_2POPF_2

Three independent syntheses of μ-oxobisdifluorophosphine (b.p. −18.3°C, m.p. −132.1° to −131.8°C) were reported almost simultaneously (*274*, *192*, *272*). Parry and co-workers (*274*) obtained F_2POPF_2 in 72% yield by reacting cuprous oxide and the newly synthesized difluoroiodophosphine (Section IV). Lustig *et al.* (*192*) identified the same

$$2\,PF_2I + Cu_2O \rightarrow F_2POPF_2 + 2\,CuI$$

compound as a side product in the preparation of tetrafluorodiphosphine, and subsequently found that 67% yields of F_2POPF_2 are obtained by addition of O_2 to P_2F_4. It has been suggested (*274*) that μ-oxobisdifluorophosphine may also be formed by hydrolysis of the latter:

$$2\,F_2PPF_2 + H_2O \rightarrow 2\,PF_2H + F_2POPF_2$$

Riess and Van Wazer (*272*) were able to characterize F_2POPF_2 in the products from the reaction between P_4O_6 and $BF_3 \cdot Et_2O$.

μ-Oxobisdifluorophosphine decomposes at a rate of about 1% per day at 25°C and is totally converted to trifluorophosphine when brought into contact with an adsorbent surface (e.g., asbestos) under the same

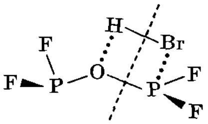
$$F_2POPF_2 \rightarrow PF_3 + (POF)_n$$

conditions. It is thus much less thermally stable than the structurally related alkylaminobisdifluorophosphines $RN(PF_2)_2$ (*236*).

Hydrogen bromide and μ-oxobisdifluorophosphine react at 25°C in the vapour phase to give bromodifluorophosphine and OPF_2H (*50*). A

$$F_2POPF_2 + HBr \rightarrow OPF_2H + PF_2Br$$

four-center intermediate (IX) has been postulated involving initial attack of the proton toward oxygen rather than phosphorus, followed by breaking of the P–O–P bond and rapid rearrangement of F_2POH to



(IX)

OPF_2H. The identity of the latter is confirmed by the observation of a very large directly bonded phosphorus–hydrogen coupling constant ($^1J_{PH} = 878$ Hz). It is interesting to note that the analogous trifluoromethyl derivative $(CF_3)_2POH$ does not undergo the same rearrangement to $(CF_3)_2HPO$ (*119*); indeed the latter compound is completely converted into $(CF_3)_2POH$ (*120*). It was originally thought that the strong withdrawal of electrons from phosphorus by the CF_3 groups reduced the bonding power of the lone-pair toward the proton, but in view of the failure to isolate F_2POH, it seems that other factors, e.g., steric interference or possible fluorine → phosphorus π bonding, may also be important.

B. μ-Oxodifluorophosphine Hexafluoropropanes and Difluorophosphine Carboxylates

Lustig (*194*) has described syntheses of 2-iodo- and 2-bromo(μ-oxodifluorophosphine)hexafluoropropane, $(CF_3)_2C(OPF_2)X$ ($X = Br, I$) from hexafluoroacetone and the appropriate difluorohalogenophosphine PF_2X. The mechanism is believed to involve the 1,3-dipolar intermediate

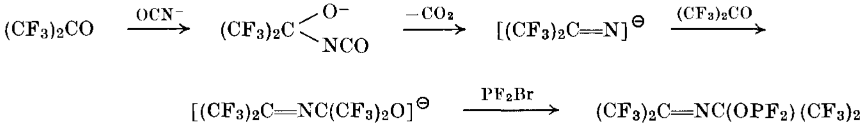
$$(CF_3)_2CO + PF_2X \rightarrow (CF_3)_2C(OPF_2)X$$
$$(X = Br, I)$$

$(CF_3)_2C^{\ominus}O\text{–}P^{\oplus}F_2X$, which rearranges by transfer of positive halogen from phosphorus to carbon (*194*).

The hydrido derivative may be prepared from the iodo compound by treatment with mercury and hydrogen iodide. Similarly the cyano derivative is formed by nucleophilic substitution of the bromine atom of bromodifluorophosphine with the 2-cyanoperfluoroisopropoxide ion (*193*). A different reaction occurs with the cyanate ion, carbon dioxide being liberated at the first stage, presumably forming an imine anion $[(CF_3)_2C{=}N]^{\ominus}$, which, in turn, gives an aza anion with hexafluoroacetone, and on subsequent treatment with PF_2Br affords the azopentene derivative $(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$ (*193*).

$$(CF_3)_2C(OPF_2)I + HI + 2\,Hg \rightarrow (CF_3)_2C(OPF_2)H + Hg_2I_2$$

$$NaCN + (CF_3)_2CO \rightarrow Na^{\oplus}[(CF_3)_2C(CN)O]^{\ominus} \xrightarrow{PF_2Br} (CF_3)_2C(OPF_2)CN + Na^+Br^-$$



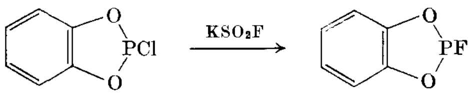
A new class of carboxylate compounds, $RfCOOPF_2$, is formed by treating difluorohalogenophosphines with silver carboxylates (*105*)

$$RfCO_2Ag \xrightarrow{PF_2X} RfCOOPF_2 + AgX$$
$$(Rf = CF_3, C_2F_5, C_3F_7, CH_3;\ X = Cl, Br, I)$$

C. FLUOROPHOSPHITES (PHOSPHOROFLUORIDITES), $(RO)_nPF_{3-n}$

The main synthetic route to these compounds is via fluorination of the corresponding chlorophosphite usually with SbF_3 (*136, 284, 201, 202, 260, 304*), AsF_3 (*136*), NaF (*284*), or potassium fluorosulfinate (*284, 295*).

$$ROPCl_2 \xrightarrow{MF_3} ROPF_2$$



The reactions are invariably strongly exothermic. Cyclic monofluorophosphites containing 5-, 6-, 7-, 9-, and 13-membered rings and the deutero compound CD_3OPF_2 have been obtained by this method (*268, 93*). Mixed alkylarylmonofluorophosphites are more conveniently obtained by treatment of an alkyldifluorophosphite with the sodium salt of the phenol (*136*), for example

$$\mathrm{ROPF_2 + NaOPh \rightarrow (RO)PF(OPh)}$$

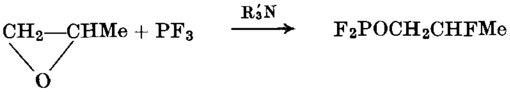
Fluorophosphites are also among the products from reactions between (*a*) trimethylphosphite and tungsten hexafluoride (*251*), (*b*) alcohols and dichlorofluorophosphine (*55, 67, 205*), (*c*) phosphorus pentafluoride or trifluorophosphine and trimethylphosphite (*35*), and (*d*) epoxides and trifluorophosphine in the presence of a tertiary amine (*150*), but these are of less importance from a preparative viewpoint. The attempted fluorination of $PhOPCl_2$ with anhydrous hydrogen fluoride led to cleavage of the phosphorus–oxygen bond (*136*). Table VI lists the known members of this class of compounds and their method of preparation.

$$\mathrm{WF_6 + (MeO)_3P \xrightarrow{0^\circ} (MeO)_2PF + other\ products}$$

$$\mathrm{PFCl_2 \xrightarrow{ROH} PF(OR)_2}$$

$$\mathrm{PF_5\ or\ PF_3 \xrightarrow{P(OMe)_3} PF_{\mathit{n}}(OMe)_{3-\mathit{n}}}$$

$(n = 1, 2)$



$$\mathrm{PhOPCl_2 \xrightarrow{3HF} PhOH + PF_3 + 2\ HCl}$$

D. ALKYLPHOSPHONOFLUORIDOUS ESTERS (ALKOXYALKYLFLUOROPHOSPHINES), RPF(OR′)

Relatively few examples of this type of compound are known (Table VI). Alcohols react with alkyldifluorophosphines at –40° to –50°C (in the presence of a dialkylaniline) to afford only small amounts of these tricoordinate compounds, the main products being the pentacoordinate alkoxyalkyldifluorophosphoranes (*94, 96, 97, 140*). The yields can be improved, however, by using stronger base, e.g., triethylamine.[3] The products are difficult to purify, although when ammonia is used the pure product can be obtained in 25–35% yield.

$$\mathrm{RPF_2 + R'OH \rightarrow RPHF_2(OR')}$$

$$\mathrm{RPF_2 + R'OH \rightarrow RPHF_2(OR') \xrightarrow[-HF]{NH_3\,(-40^\circ C)} RPF(OR')}$$

---

[3] The first alkylphosphonofluoridothioites MePF(SR) (R = Et, Bu) has recently been obtained by this route using $MePF_2$ and the appropriate thiol (*97b, 94*).

A series of methylphosphonofluoridous esters has been synthesized recently using either the low-temperature reaction between methyldifluorophosphine and the sodium alcoholate, or via antimony trifluoride fluorination of the corresponding chloridous ester (*185*). Alkylphos-

$$RPF_2 + NaOR' \xrightarrow{-50°C} RPF(OR') + NaF$$

$$3\,RPCl(OR') + SbF_3 \rightarrow 3\,RPF(OR') + SbCl_3$$

phonofluoridous esters are mobile liquids which are stable when stored at low temperatures. It is interesting to note that it has proved impossible to eliminate HF from $RPHF_2(OR')$ even when distilling the fluorophosphoranes with potassium fluoride (*96*).

E. Reactions

Difluorophosphites are colorless, volatile liquids with unpleasant smells which do not rapidly attack glass in the absence of moisture, but are violently hydrolyzed by water. Monofluorophosphites, in general, are less rapidly hydrolyzed. Difluorophosphites fail to add sulfur even under forcing conditions (*136*); however diethylfluorophosphite $(EtO)_2PF$ is oxidized to a phosphorofluoridothiolate with alkylsulphenyl chlorides (*260*). The reaction of difluorophosphites with chlorine or

$$(EtO)_2PF + RSCl \rightarrow (EtO)P(O)F(SR) + EtCl$$

bromine at low temperatures affords alkyl halides and good yields of the corresponding halogenophosphonic difluorides (*95*). This reaction represents a more convenient route to the latter compounds than direct fluorination of OPX_3; for example,

$$BuOPF_2 + Br_2 \xrightarrow{-70°C} OPBrF_2$$

$$(i\text{-}Amyl)OPF_2 + Cl_2 \xrightarrow{-50°C} OPClF_2$$

The corresponding reaction with iodine or ICl, however, gives a more complex mixture of products including the expected alkyl iodide. Monofluorophosphites are converted by chlorine into alkylphosphorochlorofluoridates (RO)P(O)FCl (*137*), and also undergo an Arbuzov

$$(RO)_2PF + Cl_2 \rightarrow RCl + (RO)P(O)FCl$$
$$(R = Et)$$

$$(CH_2O)_2PF + Cl_2 \rightarrow (ClCH_2CH_2O)P(O)FCl$$

reaction with methyl iodide (*55*) and methyl or phenyl acid chlorides (*304*). Similarly *N*-chloroimides readily eliminate alkyl chloride from

TABLE VI

Fluorophosphines Containing Phosphorus–Oxygen Bonds

Compound	Boiling point (°C/mm)	n_D	(°C)	d_4^{20}	Refs.	$\phi_F{}^a$	$\delta_P{}^b$	$J_{PF}{}^c$	Refs.
$\mathrm{F_2POPF_2}$	−18.3 (m.p. −132.1)	—	—	—	*(274, 192, 272)*	38.1	−111	1358	*(274)*
$\mathrm{MeOPF_2}$	−15.5 (m.p. −117.3)	—	—	—	*(201, 202)*	53.0	−110	1278	*(282)*
$\mathrm{CD_3OPF_2}$	−7–9	—	—	—	*(93)*	—	−110	1280	*(93)*
n-$\mathrm{PrOPF_2}$	44–45	1.3400	20	—	*(284)*	49.1	−111.5	1288	*(270)*
$\mathrm{ClCH_2CH_2OPF_2}$	82.7 (m.p. −88)	—	—	—	*(201)*	—	—	—	—
i-$\mathrm{PrOPF_2}$	36–38	1.3310	18	1.0325	*(136)*	—	—	—	—
n-$\mathrm{BuOPF_2}$	74–75	1.3631	20	1.0333	*(284, 136)*	49.2	−111.9	1288	*(270)*
$\mathrm{CH_2{=}CHCH_2OPF_2}$	42	—	—	—	*(284)*	48.7	−111.9	1290	*(270)*
$\mathrm{PhOPF_2}$	126–127	1.4613	18	1.2470	*(284)*				
	58/60	1.4575	27	—	*(136)*	44.5	−110.1	1326	*(270)*
$\mathrm{F_2POCH_2CH_2OPF_2}$	50/180	1.3523	26	—	*(284)*	48.9	−112.0	1301	*(270)*
$\mathrm{PF_2OC_6H_4OPF_2}$	59/12	1.4488	23	—	*(284)*	44.9	−109.8	1328	*(270)*
o-$\mathrm{MeC_6H_4OPF_2}$	147–150	1.4700	18	1.2152	*(136)*	—	—	—	—
m-$\mathrm{MeC_6H_4OPF_2}$	153–155	1.4630	18	1.2106	*(136)*	—	—	—	—
p-$\mathrm{MeC_6H_4OPF_2}$	154–155	1.4630	24	1.1997	*(136)*	—	—	—	—
$\mathrm{CF_3C(O)OPF_2}$	17.3	—	—	—	*(105)*	49.9	—	1389	*(105)*
$\mathrm{C_2F_5C(O)OPF_2}$	35.5	—	—	—	*(105)*	49.7	—	1389	*(105)*
n-$\mathrm{C_3F_7C(O)OPF_2}$	62.9	—	—	—	*(105)*	49.7	—	1388	*(105)*
$\mathrm{MeC(O)OPF_2}$	24/120	—	—	—	*(105)*	54.4	—	1350	*(105)*
$\mathrm{(CF_3)_2C(OPF_2)H}$	30.7 (m.p. −90 ± 2)	—	—	—	*(194)*	50.5	—	1344	*(194)*
$\mathrm{(CF_3)_2C(OPF_2)I}$	74.4 (m.p. −98.4)	—	—	—	*(194)*	46.9	—	1384	*(194)*
$\mathrm{(CF_3)_2C(OPF_2)Br}$	—	—	—	—	*(194)*	45.9	—	1384	*(194)*
$\mathrm{(CF_3)_2C(OPF_2)CN}$	51.7 ± 0.6 (m.p. −90)	—	—	—	*(193)*	79.0	—	1380	*(193)*
$\mathrm{(CF_3)_2C{=}NC(OPF_2)(CF_3)_2}$	84.7 ± 1 (m.p. −58.7)	—	—	—	*(193)*	78.4	—	1176	*(193)*
$\mathrm{FP(OMe)_2}$	61–63	1.3673	20	1.0880	*(304)*	63.4	−131.6	1210	*(291)*
$\mathrm{FP(OEt)_2}$	101–103	1.3940	20	1.0350	*(304)*	58.9	−131.0	1209	*(291)*
$\mathrm{FP(OPr)_2}$	68–70/36	1.4000	20	0.9830	*(304)*	—	—	—	—
$\mathrm{FP(OPh)_2}$	119–120/3	1.5457	20	1.2167	*(136)*	—	—	—	—

FP(*i*-PrO)(PhO)	79–80/10	1.4760	18	1.0992	(*136*)	—	—	—	—
FP(BuO)(PhO)	99–101/9	1.4791	19	1.0852	(*136*)	—	—	—	—
FP(*o*-MeC_6H_4O)(PhO)	143–146/9	1.5444	18	1.1894	(*136*)	—	—	—	—
FP(*m*-MeC_6H_4O)(PhO)	145–147/7	1.5453	18	1.1897	(*136*)	—	—	—	—
FP(*o*-$MeC_6H_4O)_2$	138–140/5	1.5460	18	1.1742	(*136*)	—	—	—	—
FP(*m*-$MeC_6H_4O)_2$	140–141/3	1.5405	20	1.1617	(*136*)	—	—	—	—
FP(*p*-$MeC_6H_4O)_2$	147–148/5	1.5400	20	1.1599	(*136*)	—	—	—	—
$FP(OCH_2)_2$	26/18	1.4039	20	1.3552	(*268*)	—	—	—	
	48/170	1.4003	23.5	—	(*284*)	41.3	−123.8	1223	(*270*)
$FP(O_2C_3H_6)$	44/100	1.4035	20	1.2226	(*268*)	—	—	—	—
$FP(OCHMe)_2$	28/16	1.4020	20	1.1568	(*268*)	—	—	—	—
$FP(O_2C_4H_8)$	37/16	1.4160	20	1.1857	(*268*)	—	—	—	—
$FP(O_2C_8H_{18})$	61/1	1.4765	20	1.1241	(*268*)	—	—	—	—
$FP(O_2C_6H_{10})$	34/1	1.4586	20	1.2140	(*268*)	—	—	—	—
$FP(O_2C_6H_4)$	38/6, 36.5/6	1.5160	20	1.3592	(*268, 284*)	37.0	−123.1	1307	(*270*)
$FP(OCH_2CH_2)_2$	38/16	1.4450	20	1.2180	(*268*)	—	—	—	—
$FP[O(CH_2)_3]_2$	66/1	1.4270	20	1.0840	(*268*)	—	—	—	—
$FP[O(CH_2)_5]_2$	80/2	1.4798	20	1.1041	(*268*)	—	—	—	—
$FP(O_3C_6H_4)$	44–47/0.15	1.5390	25	—	(*284*)	—	—	—	—
MePF(OMe)	56–58/750	—	—	1.0150	(*185*)	—	—	—	—
MePF(OEt)	63–65	1.3967	20	1.0396	(*185, 96*)	—	−218	1079	(*96*)
MePF(OPr)	26–28/120	1.3990	20	—	(*185, 96*)	—	−214	1090	(*96*)
MePF(O-*i*-Bu)	47–48; 37–39/100	1.3907	20	—	(*185, 96*)	—	−216	1080	(*96*)
MePF(O-*i*-Pr)	67–69/750	1.3820	20	0.9300	(*185*)	—	—	—	—
MePF(OBu)	43–44/65	1.4000	20	0.9701	(*185*)	—	—	—	—
MePF(OCHEtMe)	49–50/125	1.4112	20	0.9702	(*185*)	—	—	—	—
$MePF(OC_6H_{11})$	53–55/26	1.4502	20	1.0483	(*185*)	—	—	—	—
MePF(OPh)	58–59/14	1.5020	20	1.1320	(*185*)	—	—	—	—
$EtPF(OC_6H_{11})$	75/25	1.4500	20	1.0332	(*185*)	—	—	—	—
BuPF(OEt)	30–32/12	1.4120	20	0.9203	(*185*)	—	—	—	—
$MePF(OCH_2CHMe_2)$	47–48/100	1.3990	20	0.9529	(*185, 96*)	—	—	—	—

---

[a] In ppm relative to CCl_3F.

[b] In ppm relative to H_3PO_4.

[c] In Hz.

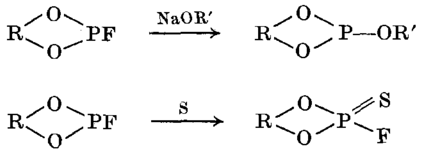
both di- and monofluorophosphites (*261*). Cyclic monofluorophosphites

$$(RO)_2PF + MeI \rightarrow MeP(O)F(OR) + RI$$

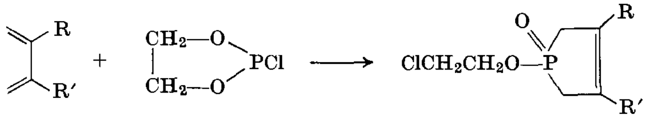
$$(RO)_2PF + R'COCl \rightarrow R'COP(O)F(OR) + RCl$$

$$(RO)PF_2 + R_2C{=}NCl \rightarrow R_2C{=}NP(O)F_2 + RCl$$

are found to be much less reactive toward nucleophilic reagents than their chloro analogs (*268*); for example, they do not react with alcohols in the presence of tertiary amines and esters are obtained only by reaction with the sodium alkoxide. Low yields of the amides are obtained from secondary amines in the presence of tertiary base and sulfur is added on prolonged heating (*268*).

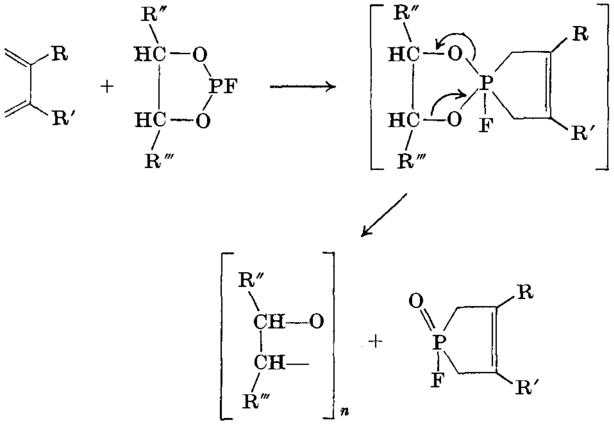


Petrov and co-workers (*100, 101, 269*) have studied the reaction between cyclic monofluorophosphites and 1 : 3 dienes. In contrast to the behavior of their chloro analogs which afford chloroalkyl esters of



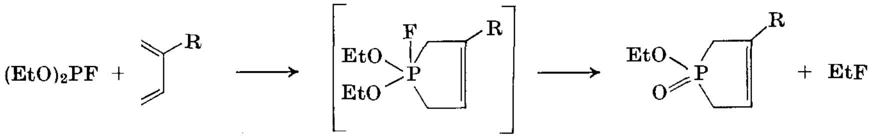
(6)

3-phospholene-1-oxide [Eq. (6)], the fluorophosphites yield 1-fluoro-3-phosphole-1-oxides with elimination of the substituted ethylene



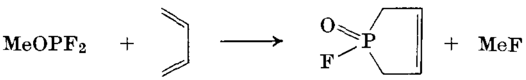
oxide. The different behavior is attributed to the relative strength of the phosphorus–chlorine and phosphorus–fluorine bonds. More recent work (*268*) suggests that in the first stage of the reaction phosphorus displays electrophilic character.

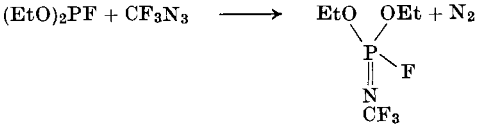
On the other hand, 1:3 dienes react with acyclic aliphatic monofluorophosphites in a sealed tube via the usual Arbuzov rearrangement eliminating the alkyl fluoride (*267*), and it has been suggested that in the *cyclic* esters the rigidity of the ring makes the P–O bond less stable.



(R = H, Me)

Butadiene also eliminates methyl fluoride from methyldifluorophosphite (*267*), while trifluoromethylazide adds to diethylfluorophosphite to produce the interesting pentavalent fluorophosphorane which contains a phosphorus–nitrogen double bond (*182*). MePF(OEt) behaves in a similar way (*182*) and also undergoes the Arbuzov rearrangement with methyl iodide (*184*).





$$MeP(OR')F + MeI \rightarrow Me_2P(O)F + R'I$$

Alkylphosphonofluoridous esters are easily oxidized to the pentavalent compounds on standing in dry air and also combine with sulfur in the presence of aluminium trichloride (*185*). Simultaneous elimination

$$RPF(OR') \xrightarrow{\text{air}} RP(O)F(OR')$$

$$RPF(OR') \xrightarrow{S/AlCl_3} RP(S)F(OR')$$

of an alkyl halide and formation of a P=O double bond occurs when dialkylaminomonofluorophosphites $(R_2N)(R'O)PF$ or MePF(OR) are treated with either halogen or alkyl halides (*91*, *97a*).

$$(R_2N)(R'O)PF + X_2 \rightarrow R_2NP(O)FX + R'X$$

$$(R_2N)(R'O)PF + R''X \rightarrow R''(R_2N)P(O)F + R'X$$

$$(X = Cl, Br;\ R = Me \text{ or } Et;\ R' = Me, Et, i\text{-}C_5H_{11})$$

Monofluorophosphites have recently been found to form 1:2 adducts with hexafluoroacetone (*92*).

VII. Other Fluorophosphines

A. DIFLUOROPHOSPHINE, PF_2H

Difluorophosphine, first reported in 1965, is a relatively stable gas [b.p. (extrapolated) –64.6°C, m.p. –124.2° to –123.6°C], which is formed in about 55% yield by reacting equal amounts of hydrogen iodide and difluoroiodophosphine (Section IV) in the presence of mercury (*276*). It has been suggested (*275*) that tetrafluorodiphosphine

$$PF_2I + HI + 2\ Hg \rightarrow PF_2H + Hg_2I_2$$

P_2F_4 (Section VII,B) is a precursor in this synthesis. The yield may be

$$2\ PF_2I \xrightarrow{Hg} F_2PPF_2 \xrightarrow{HI} PF_2I + PF_2H$$

improved considerably (90%) if phosphine is used instead of hydrogen iodide (*275*), and this method is similar to that used in the synthesis

$$PF_2I + 2\ Hg + PH_3 \rightarrow 2\ PF_2H + Hg_2I_2 + [PH]$$

of $(CF_3)_2PH$ (*127*) and CF_3PH_2 (*40*) from the corresponding trifluoromethyliodophosphines.

It is interesting to note that although PF_4H can be decomposed to HF and PF_3 it has not so far been possible to prepare PF_2H from PF_3H_2 (*27*).

Difluorophosphine is less that 5% decomposed at room temperature and saturation pressure over a period of 5 hours, and thus contrasts markedly with difluoroamine (NF_2H) which is very unstable.

Vapor pressure measurements lead to a Trouton constant of 24.7 cal deg^{-1} $mole^{-1}$ suggesting that association occurs in the condensed phase. Gas phase molecular weight measurements, however, indicate that the vapor is monomeric (*276*).

The basic hydrolysis was initially represented by the equation:

$$HPF_2 + H_2O \rightarrow PF_2OH + H_2$$

complicated by a secondary reaction, and was originally believed to suggest hydridic behavior for the hydrogen attached to phosphorus. It

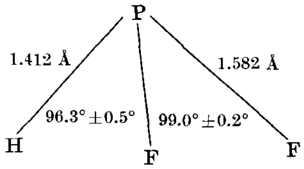
$$HPF_2 + 2\,H_2O \rightarrow HP(OH)_2 + 2\,HF \xrightarrow{\text{glass}} SiF_4$$

was found subsequently that hydrolysis of the deutero derivative PF_2D afforded deuterium-free hydrogen, indicating that the hydrogen is protonic in character (*276*)

$$\begin{tikzcd}
DPF_2 + 2\,OH^- \arrow[r] & DP(OH)_2 + 2\,F^- \arrow[d, "H_2O"] \\
& DPO(OH)_2 + H_2
\end{tikzcd}$$

Structure

The pyramidal structure of difluorophosphine has been established by microwave studies (*180*). The molecule has a dipole moment of 1.32 ± 0.01 Debyes (compared with 1.03 ± 0.01 D for PF_3 and 0.58 D for PH_3) which it resembles structurally. There is a slight increase in



the P–F bond length compared with trifluorophosphine (1.570 Å).

B. TETRAFLUORODIPHOSPHINE, P_2F_4

Early attempts to synthesize tetrafluorodiphosphine (b.p. −6.2° ± 0.4°C) by fluorination of P_2Cl_4 or P_2I_4 invariably led to the formation of trifluorophosphine (*104*, *128*), though theoretical considerations (*37*) suggested that the stability of P_2F_4 should be greater than P_2Cl_4 and comparable with N_2F_4.

The first successful synthesis of P_2F_4 by Parry *et al.* (*274*) involved the coupling of two PF_2 groups by reacting PF_2I and mercury at room temperature, e.g.,

$$2\,PF_2I + 2\,Hg \rightarrow P_2F_4 + Hg_2I_2$$

High yields are obtained when the pressure of PF_2I is about 50 mm; whereas at higher pressures the PF_2I undergoes disproportionation.

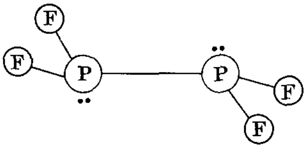
$$3\,PF_2I \rightarrow 2\,PF_3 + PI_3$$

There is some evidence that P_2F_4 is hydrolyzed by water to give PF_2H and F_2POPF_2 (*274*), and it may well also be an intermediate in the formation of PF_2H from PF_2I (see Section VII,A). EPR studies suggest that like N_2F_4, P_2F_4 yields MF_2 free radicals (*274*). PF_2 free radicals are also formed by electron impact on P_2F_4 (*305*), by γ-irradiation of ND_4PF_6 (*323a*) or by β-irradiation of trifluorophosphine in an SF_6 matrix (*101a*). The electron spin resonance spectrum of PF_2, generated by pyrolysis of PF_2H or P_2F_4 above 200° and trapped in an argon matrix at 20°K, shows 12 lines indicating that the radicals are randomly orientated and non rotating (*323c*). The data suggest that the unpaired electron in PF_2 is localized to a much greater extent on the central atom than it is in the NF_2 radical.

Structure

The identity of tetrafluorodiphosphine, established by molecular weight and mass spectral data, is confirmed by ^{19}F and ^{31}P NMR studies (*143*), which show that the molecule is an example of an XX′AA′X″X‴ nuclear spin system (X = fluorine, A = phosphorus) (see also Section XI).

The infrared and Raman spectra suggests that the trans structure



(X)

(X) is most likely, and the observation of two different vicinal fluorine–fluorine coupling constants from the analysis of the variable temperature ^{19}F NMR spectrum (Section XI), indicated that one rotamer must predominate (*143*). However semiempirical and extended Huckel LCAO-MO calculations suggest that the stability of the various conformations for P_2F_4 decreases in the order gauche > *cis* > *trans*– (*69a*).

C. PHOSPHINODIFLUOROPHOSPHINE, F_2PPH_2

This interesting compound has been obtained only recently by reacting a mixture of iododifluorophosphine and tetrafluorodiphosphine with phosphine. Apparently only small amounts of F_2PPH_2 are formed

$$PH_3 + PF_2I \rightarrow F_2PPH_2 + HI \qquad (6)$$

via Eq. (6) while Eq. (7) may explain the involvement of both PF_2I and P_2F_4.

$$\begin{tikzcd} PH_3 + PF_2I \arrow[r] & F_2PPH_2 + HI \arrow[d, "P_2F_4"] \\ & F_2PI + F_2PH \end{tikzcd} \qquad (7)$$

The identity of phosphinodifluorophosphine was confirmed by proton, fluorine, and phosphorus NMR studies (Section XI) and by observation of the parent ion in the mass spectrum (*275*).

D. TRIS(DIFLUOROPHOSPHINO)PHOSPHINE, $P(PF_2)_3$

This unusual compound is a product from the decomposition of tetrafluorodiphosphine (*305*) and has been identified by (1) its mass

$$P_2F_4(g) \xrightarrow[3\ \text{torr}]{900°} \begin{array}{c}\text{Transparent yellow}\\ \text{solid} + \text{other}\\ \text{fractions}\end{array} \rightarrow \begin{array}{c}P(PF_2)_3\ \text{colorless}\\ \text{liquid}\\ (\text{m.p.}\ -68°C)\end{array}$$

spectrum which showed the parent ion peak ($m/e = 238$) and (2) the characteristic almost first-order ^{19}F and ^{31}P NMR spectra.

The compound decomposes in the vapor phase above 10°C. It is interesting to speculate as to whether all four phosphorus atoms are coplanar in this molecule.

E. MIXED VALENCE FLUOROPHOSPHINES $F_2PXP(X)F_2$ ($X = O, S$)

1. *Difluorothiophosphoryl-μ-thiodifluorophosphine*, $F_4P_2S_2$

This moderately stable liquid (b.p. 85.7°), has been obtained recently from the reaction between SPF_2I and a stoichiometric amount of mercury, or more conveniently by reaction dimethylaminodifluorophosphine with dithiodifluorophosphoric acid (*50b*).

$$2SPF_2I + Hg \rightarrow F_2PSP(S)F_2 + HgI_2$$

$$2SPF_2SH + F_2PNMe_2 \rightarrow F_2PSP(S)F_2 + Me_2NH_2{\cdot}PS_2F_2$$

Although $F_4P_2S_2$ reacts almost quantitatively with hydrogen chloride to give PF_2Cl and SPF_2SH, it was not possible to add sulphur to $F_2PSP(S)F_2$ to give the known fully pentavalent compound $(SPF_2)_2S$ (*50b*).

2. *Difluorophosphoryl-μ-oxodifluorophosphine* $F_4P_2O_2$

This compound (m.p. –31°, b.p. 48°–50°), which is much less thermally stable than its sulfur analog has been obtained independently by Cavell (*50b*) and Des Marteau (*78a*) by the following routes:

$$2\,OPF_2Br + \text{excess Hg} \longrightarrow F_2POP(O)F_2 + Hg_2Br_2$$

$$OPF_2OH + Me_2NPF_2 \longrightarrow F_2POP(O)F_2 + Me_2NH_2\cdot PO_2F_2$$

The structures of both these mixed valence compounds have been confirmed by NMR studies (Section XI, A).

VIII. Coordination Complexes

BONDING IN FLUOROPHOSPHINE COMPLEXES

Interest in the coordinating ability of fluorophosphines stems from Chatt's studies (*52*, *53*) on trifluorophosphineplatinum(II) complexes. This clarified early work on the $[PtF_2\cdot PF_3]_2$ complex (*210*) and together with Wilkinson's synthesis of $Ni(PF_3)_4$ (*325*), suggested that trifluorophosphine and carbon monoxide have somewhat similar characteristics as ligands. The large number of transition metal carbonyl compounds reflects the great interest in carbon monoxide as a ligand and more recently a wide range of analogous trifluorophosphine and fluorophosphine (R_nPF_{3-n}) complexes have been synthesized (Table VII).

The presence of highly electronegative fluorine atoms on phosphorus in trifluorophosphine significantly lowers its ability to donate its lone-pair electrons to an acceptor atom or molecule and it behaves as a very weak base. The donor properties can be considerably enhanced if one or more fluorines are replaced by other groups, e.g., in Me_2NPF_2.

Phosphines PX_3 ($X =$ alkyl or aryl, RO-, halogen) generally exhibit a distinct preference for coordination with heavy Group VIII metals, i.e., those defined by Chatt, Ahrland, and Davies (*51*) as having class "b" character. Alternatively, using Pearson's classification (*259*), phosphines are considered to be "soft" bases and thus readily coordinate with "soft" acids, e.g., Group VIII metal ions and other transition metals in low- or zero-oxidation states.

The bonding in such complexes has been discussed in terms of (*i*) a σ-bond contribution arising from donation of the phosphorus lone-pair electrons into suitable empty orbitals of the acceptor atom or molecule and (*ii*) d_π–d_π bonding which involves donation of electrons from filled metal nd orbitals into empty phosphorus $3d$ orbitals (*69*) (Fig. 4). Such a process would operate synergically.

The importance of π bonding in phosphine complexes of transition metals in their usual oxidation states has recently been questioned (*262*, *321*, *1*, *98*) and the "soft" character of phosphorus ligands attributed to σ-bonding effects. It should be noted, however, that d_π–d_π bonding could become significantly more important in fluorophosphine–metal complexes on account of the presence of the electronegative fluorine atoms which will enhance back-donation of metal electrons by lowering the energy of the phosphorus 3*d* orbitals. This is most likely to be important when the metal itself is in a low- or zero-oxidation state.

Donor and acceptor properties of phosphines are related to the energy and form of the highest occupied and first virtual orbitals. Recently *ab initio* SCF-MO calculations (*131a*) on PH_3, PMe_3, and PF_3 show that the highest occupied orbital (the one localized on phosphorus), has roughly equal 3*s* and 3*p* components for PF_3 and about 60–70% *p*-character for PH_3 and PMe_3. Although the first ionization potential for PF_3 (12.31 eV) is distinctly larger than the other phosphines, the energy separation between the lone-pair orbital and the first empty orbital is nearly the same in all three phosphines, which means that PF_3 has the *lowest* lying virtual orbital.

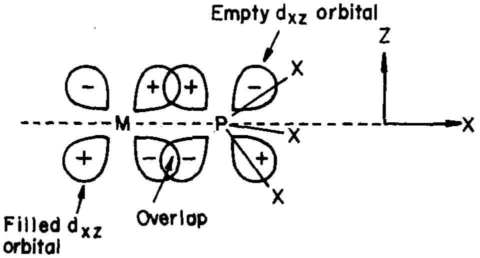


FIG. 4. Diagram showing the back bonding from a filled metal *d* orbital to an empty phosphorus 3*d* orbital in the PX_3 ligand, taking the internuclear axis as the *z* axis. An exactly similar overlap occurs in the *yz* plane using the d_{yz} orbitals (*69*).

The extensive range of very thermally stable complexes of fluorophosphines with transition metals in low-oxidation states (Section IX), which is to be contrasted with the nonexistence of analogous compounds containing nitrogen trifluoride, lends some support to the π-bonding theory. Other evidence cited in favor of this bonding picture includes the rather low dipole moment found for *cis*-$Pt(PF_3)_2Cl_2$ (*53*), the failure so far to obtain fluorophosphine complexes of transition metals in formal oxidation state higher than two, and the observation that while the P–F-stretching frequency in zero-valent metal fluorophosphine complexes (*155, 160, 171, 173*) and hydrido- or halogenotrifluorophosphine metal complexes (*164, 166*) invariably occur at higher wave numbers than the free ligand, corresponding values in fluorophosphine complexes containing stronger bases, e.g., $M(PF_3)_nL_{4-n}$ [M = Ni, Pt, L = AR_3;

A = N, P, As, Sb]; $M'[(CF_3)_nPF_{3-n}]_2L'_2$, [M' = Pt; L = Ph_3P, Ph_2MeP, $PPhMe_2$] (*173*, *174*, *247*, *160*), and anionic species $[M''(PF_3)_4^-]$, (M'' = Co, Rh, Ir) (*162*, *164*, *152*), are always much lower.

This has been rationalized by Kruck (*152*) who suggested that the F → P p_π–d_π bond in uncoordinated PF_3 is strengthened slightly when the ligand becomes coordinated to a zero-valent metal. The donor σ bond leads to a decrease in the electron density at phosphorus, but this is opposed by d_π–d_π bonding from metal to phosphorus.

When the metal carries a more negative charge, e.g., in anions $[M(PF_3)_4]^-$ or in fluorophosphine–metal complexes containing strongly donating substituents, there is an increase in the metal → phosphorus π bond which, in turn, decreases the p_π–d_π component of the P–F bond.

Force constant calculations for $Ni(PF_3)_4$ (*190*, *326*) indicate that K(P–F) is similar to that in free trifluorophosphine and the metal–phosphorus force constant (about 2.4 mdyne/Å), is only in the range expected for a single bond. Very recently, structural data for $Ni(PF_3)_4$ have become available from electron diffraction studies (*1a*, *279a*) (Section IX,C) and the phosphorus–fluorine bond length (1.561 ± 0.003Å) is indeed very similar to the free ligand value. On the other hand, the nickel–phosphorus distance (2.099 ± 0.003Å) is very much shorter than the values reported in other phosphine–nickel complexes, which suggests that the metal–phosphorus bond in $Ni(PF_3)_4$ may indeed have significant π-character. A σ-bond order of one has been estimated from the magnitude of the ^{59}Co–^{31}P coupling constant in the $[Co(PF_3)_4]^\ominus$ ion (*191*).[4]

The ease of substitution of metal–fluorophosphine complexes has also been related to the σ-donor and π-acceptor characteristics of the substituting ligand (*152*), since only ligands of high π-acceptor ability (e.g., CO, phosphites) can completely displace the coordinated fluorophosphines, whereas tertiary amines, phosphines, arsines, and stibines usually form partially substituted products (see Section IX, 6).

The similarity in the coordinating ability of CO and trifluorophosphine toward transition metals is illustrated by mass spectroscopic studies on $HCo(PF_3)_x(CO)_{4-x}$, which show that the Co–CO and Co–PF_3 bond energies are both 56 ± 15 kcal (*279*). Along the series $x = 4 \rightarrow 0$, the ΔH formation of the complex becomes progressively more negative by about 200 kcal/mole, which is approximately the difference between

---

[4] A very recent determination of the Co–P distances in $HCo(PF_3)_4$ [2.052(5) Å] indicates that there is considerably more multiple bonding than in other cobalt–PR_3 bonds where R is alkyl or aryl. (B. A. Frenz and J. A. Ibers, in press, personal communication May 1970.) However the synergic effect is less pronounced in the case of the third row transition metal complex $Pt(PF_3)_4$ (*200a*).

the heats of formation of PF_3 and CO. Analogous results are obtained for nickel (*147*).

As in the case of carbon monoxide, metallic nickel reacts readily with fluorophosphines R_nPF_{3-n} (R = F, CF_3, CCl_3, R_2N; $n = 1$ or 2), under mild conditions to form $Ni(R_nPF_{3-n})_4$ complexes (*160*, *234*, *240*). Furthermore, PF_3 and certain fluorophosphines are among few monodentate ligands which can completely displace carbon monoxide from metal carbonyls (*42*, *59*, *56–58*). Infrared and Raman studies on mixed carbonyl–fluorophosphine complexes, $Ni(CO)_{4-n}(R_yPF_{3-y})_n$ (R = CF_3; $y = 0$, 1, 2) (*190*, *125*, *23*, *24*, *42*), $Mo(CO)_{6-n}L_n$ (L = PF_3, CF_3PF_2, $(CF_3)_2PF$, CCl_3PF_2, R_2NPF_2; $n = 2$, 3) (*125*, *68*, *8*), $Fe(CO)_{5-n}(PF_3)_n$, and $Mn_2(CO)_{10-n}(PF_3)_n$ (*254*, *125*, *317*) indicate that the CO-stretching force constant (K_{co}), changes less on replacing carbon monoxide by a fluorophosphine ligand than by any other ligands (except possibly NO). This again underlines the similarity between CO and R_nPF_{3-n}.[5] Carbonyl-stretching frequencies have been used to list fluorophosphines in order of their decreasing π-acceptor ability (*8*, *117*). An alternative approach by Bigorgne (*21*, *22*) which relates carbonyl-stretching frequencies in phosphine–carbonyl compounds to changes in the σ^* parameter of the groups attached to phosphorus attributes the high ν_{CO} values in PF_3–metal–carbonyl complexes to the weak σ-donor ability of the ligand, but considerable differences of opinion have been expressed in the literature. Support for this view has also come from other workers (*5*, *6*, *80*). In one case the data used was subsequently reinterpreted using a π- rather than a σ-bonding approach (*309*). Others (*73*) suggested π-bonding between metals and phosphorus is probably important, the evidence coming from infrared band intensities rather than from frequencies.

In short, although it clearly remains uncertain what relative importance should be attached to the σ and π contributions of the transition metal–phosphorus bond in metal–phosphine complexes, it is probably not without significance that fluorophosphines mainly stabilize the metal in an electronic configuration which maximizes the number of *d* electrons, i.e., in a low, zero, or formally negative oxidation state. Some metal salts have been reduced directly from a high to a zero-valent state by the coordinating fluorophosphine (Section IX).

The ready synthesis of complexes of the type $R_nPF_{3-n}BH_3$ (R = CF_3; $n = 2$, 1, 0) from diborane and the corresponding fluorophosphine (*38*, *39*, *255*) is unexpected in view of the preceding discussion, and the stability of $F_3P \cdot BH_3$ was first ascribed (*116*) to the hyperconjugative effect of electrons in the B–H bonds π bonding to phosphorus. This idea is supported by the nonexistence of $PF_3 \cdot BF_3$ (*31*).

---

[5] Very recent ^{55}Mn NMR data on the series $HMn(CO)_{5-x}(PF_3)_x$ are consistent with the assumption that PF_3 is a better σ-donor than CO (*206a*).

More recent work shows that although PF_3 does not form complexes with aluminum or boron trifluorides, it is possible to obtain the complex PF_3AlCl_3 (*2*) which above −20°C affords AlF_3 and PCl_3. This has led to the suggestion by Parry and co-workers (*256*) that although d_π–d_π bonding may be important in transition metal–fluorophosphine complexes, the ease of deformation of the Lewis acid may also play a significant role in complex formation with boron acceptors.

Calculations (*256*) suggest that the deformation energy of BF_3 is about three times as large as BH_3 and the latter should therefore more easily coordinate with weak bases. The formation of $AlCl_3 \cdot PF_3$ is attributed to the low deformation energy and the greater ease with which aluminum attains a four-coordinate structure. As expected the more basic fluorophosphine Me_2NPF_2 readily forms 1:1 complexes with both BF_3 and BH_3, and 2:1 complexes with aluminum and gallium trichloride. Neither PF_2OPF_2 nor $EtN(PF_2)_2$ form BF_3 adducts, however, although the former will give a stable monoborane adduct.

IX. Transition Metal–Fluorophosphine Complexes

A. PREPARATIVE METHODS

Many synthetic approaches have been employed and these are summarized below. Only in certain cases are the methods specific for a particular metal or ligand (Table VII).

1. *Directly from the Metal*

Trifluorophosphine complexes of nickel, palladium, and platinum have been obtained by direct reaction of PF_3 with the metal at elevated temperatures and pressures (*172*). Similarly several fluorophosphine complexes of zero-valent nickel can be made under very mild conditions (60°C) using metallic nickel formed by decarboxylation of nickel oxalate (*240*) or $Ni(CO)_4$ (*310*). Tetrakis(trifluorophosphine)cobalt hydride $HCo(PF_3)_4$ is obtained in almost quantitative yield from the metal, PF_3, and hydrogen (*172*), and when carbon monoxide is included in the

$$M + 4\,PF_3 \xrightarrow[\text{high pressure}]{\text{temperature}} M(PF_3)_4$$

$$(M = Ni, Pd, Pt)$$

$$Ni + R_nPF_{3-n} \xrightarrow{60°C} Ni(R_nPF_{3-n})_4$$

$$(R = F, CF_3, CCl_3, R_2N;\ n = 1 \text{ or } 2)$$

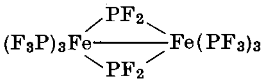
$$Co + \tfrac{1}{2}\,H_2 + 4\,PF_3 \xrightarrow[250°C]{200\ \text{atm}} HCo(PF_3)_4$$

$$\mathrm{Co} + \tfrac{1}{2}\,\mathrm{H_2} + 4\,\mathrm{PF_3} \xrightarrow{\mathrm{CO}} \mathrm{HCo(PF_3)_{4-\mathit{n}}(CO)_{\mathit{n}}}$$
$$(n = 1, 2, 3)$$

reaction mixture the corresponding mixed carbonyl–trifluorophosphine cobalt hydride complexes $\mathrm{HCo(PF_3)_n(CO)_{4-n}}$ are formed (*172*).

It is noteworthy that there is no evidence for formation of pentakis-(trifluorophosphine)iron(0) when iron [made thermally by decomposition of iron(II)oxalate or iron pentacarbonyl] and 600 atm trifluorophosphine are heated at 300°C. (*171*)

Timms (*316a*) has recently described very interesting syntheses of several metal–trifluorophosphine complexes using the technique of co-condensing vapors of transition metals (formed at temperatures between 1300° and 1700°) with $\mathrm{PF_3}$ at liquid nitrogen temperature. Chromium, nickel, cobalt, and iron vapors readily afford the known compounds $\mathrm{Cr(PF_3)_6}$ (70% yield), $\mathrm{Ni(PF_3)_4}$ (100%), $\mathrm{Co_2(PF_3)_8}$ (50%), and $\mathrm{Fe(PF_3)_5}$ (25%). In the latter case a new red, diamagnetic, crystalline, volatile dimeric compound is also obtained in 25% yield. Its structure is formulated as



$$\mathrm{(F_3P)_3Fe}\overset{\mathrm{PF_2}}{\underset{\mathrm{PF_2}}{\text{———}}}\mathrm{Fe(PF_3)_3}$$

on the basis of NMR and mass spectroscopic studies. The method also seems capable of producing a variety of organometallic fluorophosphine complexes, e.g., $\mathrm{C_6H_6Cr(PF_3)_3}$ is formed when chromium is co-condensed with $\mathrm{PF_3}$ and benzene (*316a*).

2. *By Direct Reaction with Metal Salts*

The strong reducing properties of certain fluorophosphines can, in certain cases, lead directly to fluorophosphine complexes of the metal in its zero-valent state (*173*, *234*, *247*), for example,

$$\mathrm{PtCl_2} \xrightarrow{\mathrm{PF_3}} \textit{cis}\text{-}\mathrm{(PF_3)_2\,PtCl_2} \xrightarrow[\mathrm{PF_3}]{\text{heat}} \mathrm{Pt_2(PF_3)_2Cl_4} \qquad (\textit{53})$$

$$\mathrm{MCl_4\ or\ MCl_2} \xrightarrow{\mathrm{PF_3}} \mathrm{M(PF_3)_4 + PF_3Cl_2} \qquad (\textit{173})$$
$$(\mathrm{M = Pd, Pt})$$

$$\mathrm{PdL'_2Cl_2} \xrightarrow{5\,\mathrm{PF_3}} \mathrm{Pd(PF_3)_4 + 2L' + PF_3Cl_2} \qquad (\textit{173})\ (\textit{313})$$
$$(\mathrm{L' = PhCN, CO})$$

whereas passing $\mathrm{PF_3}$ over heated $\mathrm{PtCl_2}$ affords *cis*-$\mathrm{(PF_3)_2PtCl_2}$ or dimeric $\mathrm{(PF_3)_2Pt_2Cl_4}$ the zero-valent complex $\mathrm{Pt(PF_3)_4}$ is obtained when high pressures of trifluorophosphine are used (*173*, *247*). Similarly $\mathrm{Fe(PF_3)_4I_2}$

TABLE VII

SOME FLUOROPHOSPHINE–TRANSITION METAL COMPLEXES

Complex	Method of preparation (section number)	Melting point (°C) or boiling point (°C/mm)	Refs.	$\phi_F{}^a$	$\delta_P{}^b$	$J_{PF}{}^c$	Refs.
Chromium							
$Cr(PF_3)_6$	IX, A, 7, 1	193	(*153, 154, 316a*)	—	—	—	—
$Cr(PF_3)_3(CO)_3$	IX, A, 5, 7, 9	34	(*153, 154*)	—	—	—	—
cis-$Cr(PF_3)_2(CO)_4$	IX, A, 5, 7	Liquid	(*145*)	−0.2	−173.2	1311	(*145*)
trans-$Cr(PF_3)_2(CO)_4$	IX, A, 5, 7	Liquid	(*145*)	1.1	−177.2	1318	(*145*)
cis-$(Me_2NPF_2)_2Cr(CO)_4$	IX, A, 5	55.6	(*145*)	28.1	−203.0	1128	(*145*)
trans-$(Me_2NPF_2)_2Cr(CO)_4$	IX, A, 5	—	(*145*)	27.8	−209.4	1123	(*145*)
cis-$(CCl_3PF_2)_2Cr(CO)_4$	IX, A, 5	Liquid	(*145*)	44.1	−211.2	1187	(*145*)
cis-$EtN(PF_2)_2Cr(CO)_4$	IX, A, 5	Liquid	(*144*)	47.8	−170.7	1301	(*144*)
cis-$(Cl_2CHPF_2)_2Cr(CO)_4$	IX, A, 5	Liquid	(*250*)	—	−235.0	—	(*250*)
$Cr(PF_3)_3C_6H_6$	IX, A, 1, 5, 6, 7	—	(*54, 152, 316a*)	—	—	—	—
$Cr(PF_3)(CO)_5$	IX, A, 7	—	(*252a*)	2.1	—	1315	(*252a*)
Molybdenum							
$Mo(PF_3)_6$	IX, A, 3, 5, 7	196	(*155, 59*)	—	—	—	—
$Mo(PF_3)_5(CO)$	IX, A, 7	45	(*59*)	—	—	—	—
cis-$Mo(PF_3)_4(CO)_2$	IX, A, 7	—	(*59*)	—	—	—	—
trans-$Mo(PF_3)_4(CO)_2$	IX, A, 7	—	(*59*)	—	—	—	—
cis-$Mo(PF_3)_3(CO)_3$	IX, A, 5, 7, 9	64	(*155, 59, 68*)	2.5	—	—	(*271*)
trans-$Mo(PF_3)_3(CO)_3$	IX, A, 5, 7	42	(*8, 59*)	3.0	−150.6	1300	(*12*)
cis-$Mo(PF_3)_2(CO)_4$	IX, A, 5, 7	27–28; 32	(*8, 59*)	2.9	−148.0	1305	(*9*)
trans-$Mo(PF_3)_2(CO)_4$	IX, A, 7	10	(*322, 59*)	4.0	—	1320	(*322*)
$Mo(PF_3)(CO)_5$	IX, A, 7	5	(*59*)	4.7	—	1310	(*322*)
$Mo(PhPF_2)_3(CO)_3$	IX, A, 5	—	(*292*)	46.1	−233.6	1113	(*271*)
trans-$Mo(CF_3PF_2)_3(CO)_3$	IX, A, 5	Vol. liquid	(*8*)	52.1, 56.3	—	—	(*10*)
cis-$Mo(CF_3PF_2)_2(CO)_4$	IX, A, 5	Vol. liquid	(*8*)	54.1	−199.0	1155	(*9*)
trans-$Mo[(CF_3)_2PF]_3(CO)_3$	IX, A, 5	Vol. liquid.	(*8*)	137, 143	—	—	(*10*)

cis-Mo[$(CF_3)_2PF]_2(CO)_4$	IX, A, 5	Vol. liquid	(*8*)	142.0	−184.0	976	(*9*)
trans-$Mo(CCl_3PF_2)_3(CO)_3$	IX, A, 5	95.5–96	(*8*)	46.5	—	—	(*10*)
cis-$Mo(CCl_3PF_2)_2(CO)_4$	IX, A, 5	38.5–39.5	(*8*)	47.1	−191.2	1196	(*9*)
cis-$Mo(Cl_2CHPF_2)_2(CO)_4$	IX, A, 5	Liquid	(*250*)	—	−211.2	—	(*250*)
cis-$Mo(CH_2ClPF_2)_3(CO)_3$	IX, A, 5	Liquid (b.p. 127/0.05)	— (*281*)	— —	— —	— —	— —
cis-$Mo(CH_2ClPF_2)_2(CO)_4$	IX, A, 5	Vol. liquid	(*9*)	51.5	−232.6	1120	(*9*)
cis-$Mo(MePF_2)_2(CO)_4$	IX, A, 4	Vol. liquid	(*250*)	46.2	−255.4	1065	(*250*)
cis-$Mo(Me_2NPF_2)_3(CO)_3$	IX, A, 5, 10	56–57	(*287, 11*)	—	—	—	—
cis-$Mo(Me_2NPF_2)_2(CO)_4$	IX, A, 5	Liquid	(*9*)	31.3	−180.5	1118	(*9*)
cis-$Mo(Et_2NPF_2)_3(CO)_3$	IX, A, 5	Liquid	(*287*)	29.2	−182.4	1104	(*271, 291*)
cis-$Mo(Et_2NPF_2)_2(CO)_4$	IX, A, 5	Liquid	(*8*)	29.8	−179.5	1100	(*9, 10*)
cis-$Mo(C_5H_{10}NPF_2)_3(CO)_3$	IX, A, 5, 10	100	(*287, 11*)	30.8	−177.4	1120	(*271*)
cis-$Mo(C_5H_{10}NPF_2)_2(CO)_4$	IX, A, 5, 10	38–38.5	(*8, 11*)	31.0	—	—	(*10*)
$Mo(C_5H_{10}NPF_2)_4(CO)_2$	IX, A, 7	142 (dec.)	(*287*)	26.9	−183.1	1079	(*271, 291*)
cis-Mo[$(Me_2N)_2PF]_3(CO)_3$	IX, A, 5	108–110	(*287*)	59.7	−182.3	1034	(*291*)
cis-$Mo(MePFNMe_2)_3(CO)_3$	IX, A, 5	127–128	(*290*)	77.7	−194.6	930	(*291*)
cis-$Mo(PhPFNEt_2)_3(CO)_3$	IX, A, 5	138–139	(*290*)	84.7	−185.5	990	(*291*)
trans-Mo[$(C_3F_7)_2PF]_3(CO)_3$	IX, A, 5	79.5–80	(*8*)	—	—	—	—
cis-$Mo(PrOPF_2)_3(CO)_3$	IX, A, 5, 7	(b.p. 125/0.05)	(*284*)	19.7	−157.5	1220	(*271*)
cis-$Mo(PhOPF_2)_3(CO)_3$	IX, A, 5	47	(*284*)	13.1	−150.1	1240	(*271*)
cis-$Mo(C_6H_4O_2PF)_3(CO)_3$	IX, A, 5	89.5–91	(*284*)	−1	−171.6	1270	(*271*)
cis-$Mo(PF_2H)_2(CO)_4$	IX, A, 5	—	(*12*)	—	—	—	—
cis-Mo[$EtN(PF_2)_2](CO)_4$	IX, A, 5	Liquid (b.p.60/10^{-3})	(*144*)	49.6	−144.8	1284	(*144*)
$Mo(PF_3)_3C_9H_{12}$	IX, A, 6	160	(*152*)	—	—	—	—
Tungsten							
$W(PF_3)_6$	IX, A, 3	214	(*158, 152*)	—	—	—	—
$WPF_3(CO)_5$	IX, A, 7	—	(*322*)	7.9	—	1245	(*322, 252a*)
cis-$W(PF_3)_2(CO)_4$	IX, A, 5, 7	Liquid	(*145*)	6.0	−122.0	1282	(*145*)
cis-$W(Me_2NPF_2)_2(CO)_4$	IX, A, 5	22–25	(*145*)	31.6	−156.1	1096	(*145*)
cis-$W(ClCH_2PF_2)_2(CO)_4$	IX, A, 5	Liquid	(*145*)	51.6	−201.5	1106	(*145*)
cis-W[$EtN(PF_2)_2](CO)_4$	IX, A, 5	14–15	(*144*)	51.4	−114.0	1277	(*144*)
***cis*-$W(CCl_3PF_2)_2(CO)_4$**	IX, A, 5	Liquid	(*145*)	47.6	−167.6	1171	(*145*)
cis-W[$(CF_3)_2PF]_2(CO)_4$	IX, A, 5	Liquid	(*145*)	136.9	−153.1	997	(*145*)
cis-$W(CF_3PF_2)_2(CO)_4$	IX, A, 5	Liquid	(*145*)	53.9	−170.9	1065	(*145*)
cis-$W(CCl_2HPF_2)_2(CO)_4$	IX, A, 5	Liquid	(*250*)	—	−164.2	—	(*250*)

TABLE VII—*cont.*

SOME FLUOROPHOSPHINE–TRANSITION METAL COMPLEXES

Complex	Method of preparation (section number)	Melting point (°C) or boiling point (°C/mm)	Refs.	ϕ_F[a]	δ_P[b]	J_{PF}[c]	Refs.
Manganese							
$Mn(PF_3)_5H$	IX, A, 10	18.5	*(169, 206)*	—	—	—	—
$Mn_2(CO)_9PF_3$ (axial)	IX, A, 7	90	*(61, 146)*	—	—	—	—
$Mn_2(CO)_8(PF_3)_2$ (diaxial)	IX, A, 7	81	*(61, 146, 254)*	—	—	—	—
$Mn_2(CO)_8(PF_3)_2$	IX, A, 7	45	*(61)*	—	—	—	—
$Mn_2(CO)_7(PF_3)_3$	IX, A, 7	38	*(61)*	—	—	—	—
$Mn_2(CO)_9(MeOPF_2)$ (axial)	IX, A, 10	—	*(61)*	—	—	—	—
$Mn_2(CO)_9[(MeO)_2PF]$ (axial)	IX, A, 10	—	*(61)*	—	—	—	—
$Mn(\pi\text{-}C_5H_5)(CO)_2PF_3$	IX, A, 7	—	*(311)*	—	—	—	—
$Mn(\pi\text{-}C_5H_5)_2(CO)_2(Et_2NPF_2)$	IX, A, 7	Liquid	*(121)*	—	—	—	—
$Mn(\pi\text{-}C_5H_5)(CO)_2(C_5H_{10}NPF_2)$	IX, A, 7	74–76	*(121)*	—	—	—	—
$Mn(CO)_4(PF_3)H$	IX, A, 7	−56 to −52	*(206)*	—	—	—	—
$Mn(CO)_3(PF_3)_2H$	IX, A, 7	−73 to −51	*(206)*	—	—	—	—
$Mn(CO)_2(PF_3)_3H$	IX, A, 7	<−108	*(206)*	—	—	—	—
$Mn(CO)(PF_3)_4H$	IX, A, 7	−56 to −24	*(206)*	—	—	—	—
$Mn(CO)_{5-x}(PF_3)_xCF_3$	IX, A, 10	—	*(206)*	—	—	—	—
$Mn(CO)_{5-x}(PF_3)_x(CF_3CO)$	IX, A, 7	—	*(206)*	—	—	—	—
$Mn(CO)_4PF_3(HCF_2CF_2)$	IX, A, 7, 10	—	*(206)*	—	—	—	—
$Mn_2PF_2I(CO)_8$	IX, A, 7	—	*(120a)*	38.2	—	1144	*(120a)*
Rhenium							
$Re(PF_3)_5Cl$	IX, A, 3	(153 dec.; sublimes 20/10^{-2})	*(169)*	—	—	—	—
$Re(PF_3)_5H$	IX, A, 3	Sublimes 20/10	*(169)*	—	—	—	—
$[Re(PF_3)_5]K$	IX, A, 10	210 dec.	*(169)*	—	—	—	—
$[Re(PF_3)_5]_2$	IX, A, 3	182	*(152)*	—	—	—	—
$Re_2(CO)_{10-x}(PF_3)_x$	IX, A, 7	—	*(61)*	—	—	—	—

Iron							
$Fe(PF_3)_5$	IX, A, 2, 3, 1	45 (dec. >270)	(*171, 157, 56, 316a*)	−1.9	−163.5	1275	(*171*)
$[Fe(NO)(PF_3)_3]K$	IX, A, 10	—	(*167*)	—	—	—	—
$Fe(NO)(PF_3)_3H$	IX, A, 4	(b.p. 80/720, dec.)	(*167*)	—	—	—	—
$Fe(CO)_x(PF_3)_{5-x}$	IX, A, 7	—	(*56, 317*)	6.22, 5.59	—	1329, 1322	(*252a*)
$Fe(PF_3)_4I_2$	IX, A, 10	—	(*171*)	—	—	—	—
$Fe(NO)_2(PF_3)_2$	IX, A, 3	b.p. 97/727 (dec. 118)	(*156*)	9.4	−174.3	1360	(*186*)
$Fe(PF_3)_4H_2$	IX, A, 3, 6	Liquid (m.p. −80)	(*152, 178a*)	2.9, 3.2	−148	1235, 1270	(*178a*)
$Fe(PF_2OEt)(PF_3)_4$	IX, A, 10	Liquid (b.p. 121)	(*176*)	1.0	−161.5	1260 (PF_3)	(*176*)
				15.1	−170.9	1235 (PF_2)	(*176*)
$(Fe(PF_3)_4PF_2O)^-M^+$	IX, A, 10	—	(*176*)	1.5	−162.0	1265 (PF_3)	(*176*)
				13.2	−135	1250 (PF_2)	(*176*)
$K_2Fe(PF_3)_4$	IX, A, 10	Dec. >205	(*152, 178a*)	—	—	—	—
$Fe(CO)_3(PF_3)[(CF_3)PF]$	IX, A, 7	—	(*319*)	—	—	—	—
$Fe(CO)_{5-x}(CF_3PF_2)_x$	IX, A, 7	—	(*319*)	—	—	—	—
$Fe(CO)_{5-x}[(CF_3)_2PF]_x$	IX, A, 7	—	(*319*)	—	—	—	—
$Fe(CO)_3[PF_{3-x}(OMe)_x]_2$	IX, A, 10	—	(*319*)	—	—	—	—
$Fe(CO)_4PF_{3-x}(OR)_x$	IX, A, 10	—	(*319*)	—	—	—	—
$Fe(CO)_x(PF_3)_{3-x}C_4H_6$	IX, A, 7	—	(*323a*)	—	—	—	—
$Fe(phen)_3[HFe(PF_3)_4]_2$	IX, A, 10	—	(*178a*)				
Ruthenium							
$Ru(PF_3)_5$	IX, A, 3	30 (dec. >155)	(*171*)	−2.4	−148.5	1320	(*171*)
$Ru(PF_3)_4H_2$	IX, A, 3	−76, dec. >290	(*152, 178a*)	5.05, 3.57	−101	1320, 1240	(*178a*)
$[Ru(PF_3)_4]K_2$	IX, A, 10	dec. 150 >	(*152, 178a*)	—	—	—	—
$Fe(phen)_3[HRu(PF_3)_4]_2$	IX, A, 10	—	(*178a*)	—	—	—	—
Osmium							
$Os(PF_3)_5$	IX, A, 3	—	(*171*)	—	—	—	—
$Os(PF_3)_4H_2$	IX, A, 3	−72 (dec. 340)	(*152, 178a*)	6.55, 7.8	—	1275, 1225	(*178a*)
$[Os(PF_3)_4]K_2$	IX, A, 10	—	(*152*)	—	—	—	—
$(Et_3NH)[HOs(PF_3)_4]$	IX, A, 10	—	(*178a*)	—	—	—	—
Cobalt							
$Co(PF_3)_4I$	IX, A, 2, 3, 10	Dec.>7	(*164, 175*)	—	—	—	—
$Co(PF_3)_4H$	IX, A, 3, 10	−51(b.p. 80/730)	(*164, 172, 175*)	7.6	−147.7	1315	(*186*)
$[Co(PF_3)_4]K$	IX, A, 10	—	(*164, 172, 175, 191*)	2.8	−159.2	1270	(*186*)
$[Co(PF_3)_4]_2$	IX, A, 3, 1	—	(*169, 316a*)	—	—	—	—
$[Co(PF_3)_3PF_2]_2$	IX, A, 3	Liquid (b.p. $50/10^{-3}$	(*170*)	13.2	—	1330	(*170*)

TABLE VII—*cont.*

SOME FLUOROPHOSPHINE–TRANSITION METAL COMPLEXES

Complex	Method of preparation (section number)	Melting point (°C) or boiling point (°C/mm)	Refs.	$\phi_F{}^a$	$\delta_P{}^b$	$J_{PF}{}^c$	Refs.
$Co(PF_3)_2(C_5H_5)$	IX, A, 5	−8 (b.p. 51/13)	(*165*)	—	—	—	—
$[Co(PF_3)_2(Ph_3P)_2]K$	IX, A, 10	Dec. >190	(*164*)	—	—	—	—
$Co(PF_3)_3(Ph_3P)H$ (and D)	IX, A, 6	174–175	(*164*)	—	—	—	—
$Co(PF_3)_2(Ph_3P)_2I$	IX, A, 2, 6	Dec. >144	(*164*)	—	—	—	—
$Co(PF_3)_3(CO)H$	IX, A, 7, 3	−67 (b.p. 80.5/715)	(*159*)	—	—	—	—
$[Co(PF_3)_3(CO)]K$	IX, A, 10	Dec. >100	(*159, 191*)	—	—	—	—
$CoNO(PF_3)_3$	IX, A, 3	−92 (b.p. 81/732)	(*57, 156*)	9.9	—	1375	(*186*)
$CoNO(PF_3)_{3-x}(CO)_x$	IX, A, 7	—	(*57*)	—	—	—	—
$Co[(MeO)_{3-x}PF_x]NO(CO)_2$	IX, A, 10	—	(*60*)	—	—	—	—
$Co(PF_3)_n(CO)_{4-n}H$	IX, A, 7	—	(*320, 159, 172*)	—	—	—	—
$Co(PF_3)_n(CO)_{4-n}CF_3$	IX, A, 7	—	(*320, 318*)	—	—	1368^d	(*318*)
$Co(PF_3)_n(CO)_{4-n}C_2F_5$	IX, A, 7	—	(*320*)	—	—	—	—
$Co(PF_3)_n(CO)_{4-n}C_3F_7$	IX, A, 7	—	(*320*)	—	—	—	—
$CoBr_2(Me_2NPF_2)_2$	IX, A, 2	—	(*66*)	—	—	—	—
$Co(PF_3)_4Me$	IX, A, 10	—	(*175*)	—	—	—	—
$Co(PF_3)_4Et$	IX, A, 10	—	(*175*)	—	—	—	—
$Co(PF_3)_3(C_8H_{13})$	IX, A, 5	—	(*243*)	—	—	—	—
$Co(Me_2NPF_2)_3(C_8H_{13})$	IX, A, 5	—	(*243*)	—	—	—	—
$Co(Et_2NPF_2)_3(C_8H_{13})$	IX, A, 5	—	(*243*)	—	—	—	—
$Co(PF_3)_4(PH_3)H$	IX, A, 6, 7	25	(*44*)	9.8	—	1117	(*44*)
Rhodium							
$Rh(PF_3)_4H$	IX, A, 3	−40 (b.p. 89/725)	(*175, 162*)	4.8	−133.4	1350	(*186*)
$[Rh(PF_3)_4]K$	IX, A, 10	—	(*175, 162*)	—	−141.5	1365	(*186*)
$[Rh(PF_3)_4]_2$	IX, A, 3	92.5	(*168*)				

$[RhPF_2(PF_3)_3]_2$	IX, A, 3	—	*(175)*				
$[RhCl(PF_3)_2]_2$	IX, A, 5	68–9	*(63, 17, 168)*	21.6	—	1310	*(63, 17)*
$[RhCl(PF_2NMe_2)_2]_2$	IX, A, 5, 6	112–13	*(63)*	40.1	—	1098	*(63)*
$[Rh(PF_3)_4]_2Hg$	IX, A, 10	97–9	*(17)*	—	—	—	—
$Rh(PF_3)_4SnPh_3$	IX, A, 10	85 (dec.)	*(17)*	—	—	—	—
$Rh(PF_3)_2\pi\text{-}C_5H_5$	IX, A, 10	—	*(17)*	—	—	—	—
$Rh(PF_3)_2(acac)$	IX, A, 10	—	*(17)*	—	—	—	—
$Rh(CCl_3PF_2)_3Cl$	IX, A, 7	108.5–111	*(241)*	56.8	—	—	*(241)*
$Rh(Me_2NPF_2)_3Cl$	IX, A, 7, 5	Dec. >50	*(241)*	39.2	—	—	*(241)*
$Rh(Et_2NPF_2)_3Cl$	IX, A, 7	—	*(241)*	—	—	—	—
$Rh(C_5H_{10}NPF_2)_3Cl$	IX, A, 7	Dec. >60	*(241)*	46.3	—	—	*(241)*
$Rh(NO)(PF_3)_3$	IX, A, 3, 6	−87	*(152, 63)*	3.8	—	—	*(63)*
trans-$[Rh(Ph_3P)_2(PF_3)Cl]$	IX, A, 6	159–161	*(17, 63, 168)*	15.4	—	1286	*(63)*
Iridium							
$Ir(Ph_3P)_2PF_3Cl$	IX, A, 6	134	*(18)*	—	—	—	—
$Ir(PF_3)_4I$	IX, A, 3	(Dec. 15)	*(166)*	—	—	—	—
$(Ir(PF_3)_4)K$	IX, A, 10	Dec. 225	*(166, 175)*	−0.8	−100.9	1320	*(186)*
$(Ir(PF_3)_4H)$	IX, A, 3	−39 (b.p. 95/732)	*(175, 163)*	6.4	−93.5	1325	*(186)*
$[IrCl(PF_3)_2]_2$	IX, A, 5	76–8	*(17)*	—	—	—	—
$[Ir(PF_3)_4]_2Hg$	IX, A, 10	100–2	*(17)*	—	—	—	—
$[Ir(PF_3)_4]SnPh_3$	IX, A, 10	113–14	*(17)*	—	—	—	—
$Ir(PF_3)_2\pi\text{-}C_5H_5$	IX, A, 10	—	*(17)*	—	—	—	—
Nickel							
$Ni(PF_3)_4$	IX, A, 1–6	−55.0 (b.p. 71)	*(232, 233, 160, 62, 58, 172, 310, 325, 316a, 240)*	16.8	−137.7	1347	*(173, 233, 271, 198)*
$Ni(MePF_2)_4$	IX, A, 4	(b.p. 66–68/3.5)	*(295)*	—	—	—	—
$Ni[(PhPF_2]_4$	IX, A, 4, 7	65–66	*(295, 281)*	55.8	−214.8	1113	*(271)*
$Ni(CF_3PF_2)_4$	IX, A, 1, 5, 7	−84 (b.p. ~164)	*(233, 240, 42)*	72.1	−184.8	1207	*(233, 198)*
$Ni(CCl_3PF_2)_4$	IX, A, 1, 5	120–122	*(233, 240)*	58.0	−169.9	1221	*(233, 198)*
$Ni(ClCH_2PF_2)_4$	IX, A, 5	Oil	*(240)*	62.0	−211.6	1140	*(240, 198)*
$Ni[(CF_3)_2PF]_4$	IX, A, 1, 5, 7	55–56 (b.p. ~218)	*(233, 240, 42)*	159.2	−156.7	1005	*(233, 198)*
$Ni(PF_2Cl)_4$	IX, A, 7, 10	Liquid (b.p. 64/0.5)	*(177, 113a)*	—	—	—	—
$Ni(n\text{-}PrOPF_2)_4$	IX, A, 7	(b.p. 140.5–143/0.5)	*(284)*	29.2	−146.0	1230	*(271)*

TABLE VII—*cont.*

SOME FLUOROPHOSPHINE–TRANSITION METAL COMPLEXES

Complex	Method of preparation (section number)	Melting point (°C) or boiling point (°C/mm)	Refs.	$\phi_F{}^a$	$\delta_P{}^b$	$J_{PF}{}^c$	Refs.
$Ni(PhOPF_2)_4$	IX, A, 4, 7	Oil	(*284*)	24.6	−139.6	1258	(*271*)
$Ni(C_6H_4O_2PF)_4$	IX, A, 4	129–130	(*284*)	13.9	−157.1	1290	(*271*, *198*, *196*)
$Ni[(OCH_2PF_2)_2]_n$	IX, A, 7	Dec. >250	(*284*)	—	—	—	—
$Ni[C_6H_4(OPF_2)_2]_n$	IX, A, 7	Dec. >300	(*284*)	—	—	—	—
$Ni(Me_2NPF_2)_4$	IX, A, 1, 7, 10	110.5–111.5	(*240*, *287*, *233*)	38.9	—	1125	(*271*, *233*, *198*)
$Ni(Et_2NPF_2)_4$	IX, A, 1, 7	46	(*240*, *287*, *233*)	38.6	−167.9	1115	(*271*, *233*, *198*)
$Ni(C_5H_{10}NPF_2)_4$	IX, A, 1, 7	164–165	(*240*, *287*, *233*)	39.9	—	1123	(*271*, *233*, *198*)
$Ni(PF_3)_3(P^*F_2OEt)$	IX, A, 10	Liquid (b.p. 110)	(*176*)	*30.2 17.5	*−142.5 −138.7	*1255 1340	(*176*)
$[Ni(PF_3)_3P^*F_2O]_2Ba$	IX, A, 10	—	(*176*)	*2.0	−123.0	*1250	(*176*)
$[Ni(PF_3)_3P^*F_2O](Me_4N)$	IX, A, 10	—	(*176*)	17.5	−142.0	1330	(*176*)
$Ni(PF_3)_2(Et_2NPF_2)_2$	IX, A, 10	Oil	(*177*)	—	—	—	—
$Ni(PF_3)(C_5H_{10}NPF_2)_3$	IX, A, 10	41	(*177*)	—	—	—	—
$Ni(PF_3)_2(n\text{-}Pr_2NPF_2)_2$	IX, A, 10	Oil	(*177*)	—	—	—	—
$Ni(Me_2NPF_2)_2(CO)_2$	IX, A, 7	Oil	(*287*)	43.4	−168.5	1149	(*271*, *198*)
$Ni(Et_2NPF_2)_2(CO)_2$	IX, A, 7	Oil	(*287*)	42.2	−168.8	1145	(*271*, *198*)
$Ni(C_5H_{10}NPF_2)_2(CO)_2$	IX, A, 7	39.5	(*287*)	43.1	−164.6	1148	(*271*, *198*)
$Ni[(Me_2N)_2PF]_2(CO)_2$	IX, A, 7	Oil	(*290*)	68.7	−181.0	1039	(*271*, *198*)
$Ni(MePFNMe_2)_2(CO)_2$	IX, A, 7	Oil	(*290*)	84.0	−184.4	940	(*291*)
$Ni(PhPFNEt_2)_3(CO)$	IX, A, 7	97	(*290*)	—	—	—	—
$Ni(Me_2NPF_2)_3(CO)$	IX, A, 7	Identified by NMR	(*198*, *248*)	41.6	—	1137	(*198*)
$Ni(Et_2NPF_2)_3(CO)$	IX, A, 7	NMR	(*198*, *248*)	40.6	—	1134	(*198*)
$Ni(C_5H_{10}NPF_2)_3(CO)$	IX, A, 7	NMR	(*198*, *248*)	41.5	—	1136	(*198*)
$Ni[(Me_2N)_2PF]_3(CO)$	IX, A, 7	NMR	(*198*, *248*)	64.0	—	1025	(*198*)

$Ni(Me_2NPF_2)(CO)_3$	IX, A, 7	NMR	*(198, 248)*	44.8	—	1157	*(198)*
$Ni(Et_2NPF_2)(CO)_3$	IX, A, 7	NMR	*(198, 248)*	43.6	—	1150	*(198)*
$Ni(C_5H_{10}NPF_2)(CO)_3$	IX, A, 7	NMR	*(198, 248)*	44.5	—	1157	*(198)*
$Ni(PF_3)_2(Ph_3P)_2$	IX, A, 6	213	*(174, 160)*	—	—	—	—
$Ni(PF_3)_3(Ph_3P)$	IX, A, 6	123–125	*(174, 160)*	—	—	—	—
$Ni(PF_3)_2[(Ph_2P)_2C_2H_4]$	IX, A, 6	203–205	*(160)*	—	—	—	—
$Ni(PF_3)[(PhO)_3P]_3$	IX, A, 6	89	*(160)*	—	—	—	—
$Ni(PF_3)_3$(pyridine)	IX, A, 6	—	*(174)*	—	—	—	—
$Ni(PF_3)_3(Ph_3As)$	IX, A, 6	140 (dec.)	*(174)*	—	—	—	—
$Ni(PF_3)_3(Ph_3Sb)$	IX, A, 6	96–7	*(174)*	—	—	—	—
$Ni(PF_3)_2$(dipy)	IX, A, 6	120 (dec.)	*(174)*	—	—	—	—
$Ni(PF_3)_2(Ph_3As)_2$	IX, A, 6	(157 (dec.)	*(174)*	—	—	—	—
$Ni(PF_3)_2(Ph_3Sb)_2$	IX, A, 6	180 (dec.)	*(174)*	—	—	—	—
$Ni(PF_3)(Ph_2PCl)_3$	IX, A, 6	114 (dec.)	*(174)*	—	—	—	—
$Ni(PF_3)_2$(*o*-phen)	IX, A, 6	225 (dec.)	*(174)*	—	—	—	—
$Ni_2(PF_3)_n$	—	In mass spec.	*(312)*	—	—	—	—
$Ni(CF_3PF_2)_3(CO)$	IX, A, 7	—	*(42)*	—	—	—	—
$Ni[(CF_3)_2PF]_3(CO)$	IX, A, 7	—	*(42)*	—	—	—	—
$Ni(CF_3PF_2)_2(CO)_2$	IX, A, 7	—	*(42)*	—	—	—	—
$Ni[(CF_3)_2PF]_2(CO)_2$	IX, A, 7	(b.p. 0/1.6)	*(42)*	—	—	—	—
$Ni(CF_3PF_2)_2(PF_3)_2$	IX, A, 6	(b.p. ~125)	*(42)*	—	—	—	—
$Ni(CF_3PF_2)(PF_3)_3$	IX, A, 6	—	*(42)*	—	—	—	—
$Ni(PF_3)_3CO$	IX, A, 7	−93 (b.p. 0/88)	*(58, 190)*	—	—	—	—
$Ni(PF_3)_2(CO)_2$	IX, A, 7	−93 (b.p. 0/56)	*(58, 190, 43)*	18.87	—	1357	*(252a)*
$Ni(PF_3)(CO)_3$	IX, A, 7	−(b.p. 0°/41)	*(58, 190)*	—	—	—	—
$NiBr_2(Me_2NPF_2)_2$	IX, A, 2	—	*(111)*	—	—	—	—
$Ni(PF_2Cl)_n(CO)_{4-n}$	IX,A,	—	*(113a)*	—	—	—	—
Palladium							
$Pd(PF_3)_4$	IX, A, 1, 2, 7	−41 (dec. >−20)	*(172, 173, 313)*	14.9	−94.5	~1350	*(173)*
$Pd(PF_3)_2(Ph_3P)_2$	IX, A, 6	156–158 (dec.)	*(173)*	—	—	—	—
$Pd(PF_3)CO(Ph_3P)_2$	IX, A, 6	—	*(173)*	—	—	—	—
Platinum							
$Pt(PF_3)_4$	IX, A, 1–3	−15 (b.p. 86/730)	*(161, 173, 172)*	11.5	−97.0	~1320	*(173)*
$Pt(CF_3PF_2)_4$	IX, A, 2	Vol. liquid	*(234, 247)*	68.1	−155.6	—	*(241)*
$Pt[(CF_3)_2PF]_4$	IX, A, 2	45–47	*(234, 247)*	150.9	−127.2	—	*(241)*
$Pt(PF_3)_2(Ph_3P)_2$	IX, A, 6	202 (dec.)	*(173)*	—	—	—	—
$Pt(PF_3)_3(Ph_3P)$	IX, A, 6	121	*(173)*	—	—	—	—

TABLE VII—*cont.*

SOME FLUOROPHOSPHINE–TRANSITION METAL COMPLEXES

Complex	Method of preparation (section number)	Melting point (°C) or boiling point (°C/mm)	Refs.	ϕ_F[a]	δ_P[b]	J_{PF}[c]	Refs.
$Pt(CF_3PF_2)_2(Ph_3P)_2$	IX, A, 6	153–155	(*247*)	—	—	—	—
$Pt(CF_3PF_2)_2(PhPMe_2)_2$	IX, A, 6	Oil	(*247*)	—	—	—	—
$Pt(CF_3PF_2)_2(Ph_2PMe)_2$	IX, A, 6	—	(*247*)	—	—	—	—
cis-$PtCl_2(PF_3)_2$	IX, A, 2	102	(*53*)	29.0	−68.0	1316	(*130*)
$(PtCl_2PF_3)_2$	IX, A, 2	155–156	(*53*)	—	—	—	—
cis-$PtCl_2(Me_2NPF_2)_2$	IX, A, 2	104–106	(*245, 241*)	52.3	−88.2	1128 (32)[e]	(*241*)
cis-$PtCl_2[(Me_2N)_2PF]_2$	IX, A, 2	212.5–214	(*245, 241*)	59.7	−86.5	1023 (27)	(*241*)
cis-$PtCl_2(Et_2NPF_2)_2$	IX, A, 2	108.5–110	(*245, 241*)	51.3	—	1130 (26)	(*241*)
cis-$PtCl_2[(Et_2N)_2PF]_2$	IX, A, 2	110–112	(*245, 241*)	—	—	—	(*241*)
cis-$PtCl_2(C_5H_{10}NPF_2)_2$	IX, A, 2	Dec. >150	(*245, 241*)	53.2	—	1138	(*241*)
cis-$PtCl_2[(C_5H_{10})_2NPF]_2$	IX, A, 2	181–183	(*245, 241*)	58.5	—	1028 (32)	(*241*)
cis-$PtBr_2[(Me_2N)_2PF][Me_2NPF_2]$	IX, A, 2	136–137	(*245, 241*)	—	—	—	—
cis-$PtBr_2[(Me_2N)_2PF]_2$	IX, A, 2	229–238 (dec.)	(*245, 241*)	57.2	—	1027 (29)	(*241*)
cis-$PtBr_2(Et_2NPF_2)_2$	IX, A, 2	80–83	(*245, 241*)	49.6	—	1125 (27)	(*241*)
cis-$PtBr_2(C_5H_{10}NPF_2)_2$	IX, A, 2	Dec. >100	(*245, 241*)	52.3	—	1129	(*241*)
cis-$PtBr_2[(C_5H_{10}N)_2PF]_2$	IX, A, 2	184–185	(*245, 241*)	55.6	—	1028 (37)	(*241*)
$PtCl_2(PF_3)(PEt_3)$	IX, A, 6	104	(*130*)	34.7	−71.0	1299	(*130*)
Copper							
$CuCl(Me_2NPF_2)_4$	IX, A, 2	—	(*65*)	53.0	—	—	(*65*)

[a] In ppm relative to CCl_3F.

[b] In ppm relative to H_3PO_4.

[c] In Hz.

[d] Average value (see Section XI).

[e] Numbers in parentheses are approximate values in Hz for $^2(\mathrm{PMP'})$.

and PF_3 at 300 atm/100°C form $Fe(PF_3)_5$ (*171*). The more strongly reducing trifluoromethylfluorophosphines CF_3PF_2 and $(CF_3)_2PF$ give good yields of zero-valent complexes of platinum even at 60°C (*234, 247*).

$$PtCl_2 + 5\ R_nPF_{3-n} \xrightarrow{60°C} Pt(R_nPF_{3-n})_4 + R_nPF_{3-n}Cl_2$$
$$(R = CF_3;\ n = 1, 2)$$

$$K_2PtCl_4 + 5\ (CF_3)_2PF \xrightarrow{60°C} Pt((CF_3)_2PF)_4 + (CF_3)_2PFCl_2 + 2\ KCl$$

Coordination and partial reduction of the metal salt occurs in the reaction between dimethylaminodifluorophosphine and cupric chloride,

$$2\ CuCl_2 + Me_2NPF_2 \rightarrow 2\ CuCl + Me_2NPF_2Cl_2$$
$$CuCl + Me_2NPF_2 \rightarrow CuCl\cdot F_2PNMe_2$$

the product being the tetrameric copper(I) complex $[CuCl\cdot F_2PNMe_2]_4$, which has a dissociation pressure of about 2 mm at 27°C (*65*).

There is also evidence for a slower process involving group exchange on the coordinated ligand (*65*). Cuprous chloride itself reacts with dimethylaminodifluorophosphine to give both 1:1 and 2:1 complexes. Platinum(II) halides are not reduced by dialkylaminodifluorophosphines, but give instead the stable *cis*-$(R_2NPF_2)_2PtX_2$ derivatives ($R = Me, Et, R_2 = C_5H_{10}; X = Cl, Br$). Prolonged heating in the presence of excess ligand, however, leads to quantitative evolution of trifluorophosphine and formation of the corresponding bis(dialkylamino)fluorophosphine derivatives (*245*). The cis configuration has been established by NMR studies (see also Section XI, C,5).

$$CuCl_2 + 2\ nMe_2NPF_2 \rightarrow \text{complex} \rightarrow CuCl_2[(Me_2N)_2PF]_n + n\ PF_3$$

$$PtX_2 + 2\ R_2NPF_2 \rightarrow cis\text{-}(R_2NPF_2)_2PtX_2$$
$$PtX_2 + 4\ R_2NPF_2 \rightarrow cis\text{-}[(R_2N)_2PF]_2PtX_2 + 2\ PF_3$$

$$cis\text{-}(R_2NPF_2)_2PtX_2 + 2\ R_2NPF_2 \rightarrow cis\text{-}[(R_2N)_2PF]_2PtX_2 + 2\ PF_3$$

Cobalt(II) and nickel(II) bromides react with Me_2NPF_2 to give the complexes $MBr_2\cdot 2Me_2NPF_2$, which readily dissociate back to the free ligand and the metal halide with no apparent rearrangement of the ligand (*66, 111*). Certain metal difluorides react with trifluorophosphine to afford complexes of the type $MF_2\cdot PF_3$ ($M = Os, Ir, Pd$) (*126*), which have not been studied in any detail. Similarly little is known about the black, insoluble complexes of formula $2MO_4\cdot PF_3$ ($M = Ru, Os$) formed directly from the tetroxides (*126*).

3. *By Reaction with Metal Halides in the Presence of a Reducing Agent*

Kruck and co-workers have used this method extensively for synthesizing transition metal-trifluorophosphine complexes. The scope of this approach may be seen from the following equations and the data summarized in Table VII. Usually this "reductive fluorophosphination" is carried out at elevated temperatures using high pressures of trifluorophosphine and copper or zinc as the reducing agent. The subject has been reviewed (*152*). The $CoI_2/PF_3/Cu$ reaction in the absence of hydrogen can in certain circumstances afford the binuclear complex $[(F_3P)_3CoPF_2]_2$ containing bridging PF_2 groups (*170*).

$$MX_m \xrightarrow[100^\circ\text{–}250^\circ C]{Cu/PF_3/\text{high pressure}} M(PF_3)_n + CuX \quad (X = Cl, I)$$

(M = Cr, Mo, W; Fe, Ru, Os; Ni, Pd, Pt) (*152*) (*157*) (*161*) (*172*) (*171*) (*173*) (n = 6,5,4)

$$M'X_m \xrightarrow{Cu/PF_3/H_2} H_xM'(PF_3)_n + CuX$$

(M' = Co, Rh, Ir; Fe, Ru, Os, $x = 1$ or 2; $n = 4$) (*158*) (*162*) (*172*) (*152*)

$$M''X_m \xrightarrow{Cu/PF_3} XM''(PF_3)_n + CuX$$

(M'' = Co; X = I, $n = 4$) (*164*) (*152*)
(M'' = Re, X = Cl, $n = 5$) (*166*) (*152*)

$$[M'''(NO)_2X]_2 \xrightarrow{Cu/PF_3} M'''(NO)_n(PF_3)_{4-n}$$

(M''' = Fe, X = Br. $n = 2$, M''' = Co, Rh; X = Cl, $n = 1$) (*166*) (*152*)

4. *By Fluorination of Halogenophosphine–Metal Complexes*

Exchange of chlorine by fluorine can be easily effected by reacting the chlorophosphine–metal complex with antimony trifluoride (*250*), arsenic trifluoride (*281*), zinc fluoride (*281*), potassium fluorosulfinate (*281*, *284*, *295*), or potassium fluoride in tetramethylene sulfone (*250*). For example,

$$Ni(PCl_3)_4 + 12\ KSO_2F \rightarrow 12\ KCl + 12\ SO_2 + Ni(PF_3)_4$$

$$Ni(PhOPCl_2)_4 + 8\ KSO_2F \rightarrow 8\ KCl + 8\ SO_2 + Ni(PhOPF_2)_4$$

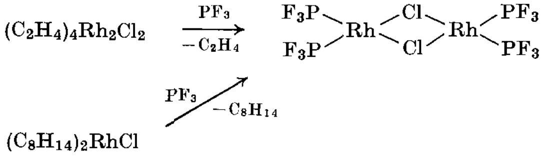
$$3\ Ni(PhPCl_2)_4 + 8\ AsF_3 \rightarrow 3\ Ni(PhPF_2)_4 + 8\ AsCl_3$$

$$Mo(CO)_3(PCl_3)_3 + 9\ KSO_2F \rightarrow 9\ KCl + 9\ SO_2 + Mo(CO)_3(PF_3)_3$$

This method is particularly useful in those cases where the fluorophosphine itself is unstable with respect to disproportionation to the corresponding fluorophosphorane and cyclic polyphosphine (Section III).

5. *By Displacement of Coordinated Organic Compounds*

The red, volatile, dimeric tetrakis(trifluorophosphine)–μ,μ'-dichlorodirhodium complex is easily obtained by displacement of ethylene or cyclooctene from the corresponding olefin–metal complex (*63*, *17*).



Norbornadiene likewise is readily displaced from complexes of the type $C_7H_8M(CO)_4$ (M = Cr, Mo, W) under mild conditions and this synthetic route is particularly useful for obtaining the *cis*-$L_2M(CO)_4$ isomer (L = fluorophosphine) (*8–10*, *144*, *145*, *250*).

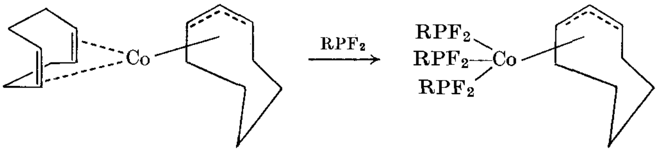
$$C_7H_8M(CO)_4 + 2\,L \rightarrow cis\text{-}L_2M(CO)_4 + C_7H_8$$

$(M = Cr;\ L = PF_3,\ CCl_3PF_2,\ ClCH_2PF_2,\ Me_2NPF_2)$

$[M = Mo;\ L = PF_3,\ CF_3PF_2,\ (CF_3)_2PF,\ ClCH_2PF_2,\ PF_2NMe_2,\ PF_2NEt_2,\ PF_2NC_5H_{10},\ CCl_2HPF_2,\ CCl_3PF_2;\ L_2 = EtN(PF_2)_2$

$(M = W;\ L = PF_3,\ CCl_3PF_2,\ CF_3PF_2,\ ClCH_2PF_2)$

Cycloocta-1,5-diene has also been displaced from a cobalt complex by fluorophosphines (*243*).



(R = F, Me_2N–, Et_2N–)

Cycloheptatrienemolybdenum tricarbonyl, $C_7H_8Mo(CO)_3$, has been used extensively as a route to trisubstituted fluorophosphine–carbonyl complexes $L_3Mo(CO)_3$; however, the stereochemistry of the resulting complex seems to depend on the reaction conditions and in certain cases trans rather than cis isomers are obtained (*8*, *10*, *281*, *284*, *286*, *290*).

$$C_7H_8Mo(CO)_3 + 3\,L \rightarrow L_3Mo(CO)_3 + C_7H_8$$

[L = PF_3, CF_3PF_2, $(CF_3)_2PF$, CCl_3PF_2,
Et_2NPF_2, $C_5H_{10}NPF_2$, Me_2NPF_2, $ClCH_2PF_2$,
n-$PrOPF_2$, $PhOPF_2$, $C_6H_4O_2PF$, $MePFNMe_2$,
$PhPFNMe_2$, $(Me_2N)_2PF$]

Hexakistrifluorophosphinechromium (and molybdenum) complexes are formed by treating the corresponding dibenzene metal derivative with PF_3 at high pressure (*153*, *155*). Different products are obtained from benzenetricarbonylchromium and PF_3, depending on whether the reaction is carried out at elevated temperatures and pressures or with UV irradiation (*54*, *155*). Mesitylenemetal tricarbonyl complexes behave similarly.

$$M(C_6H_6)_2 + 6\,PF_3 \longrightarrow M(PF_3)_6 + 2\,C_6H_6$$
(M = Cr, Mo)

$$C_6H_6Cr(CO)_3 + 3\,PF_3 \xrightarrow{UV} C_6H_6Cr(PF_3)_3 + 3\,CO$$

$$C_9H_{12}Cr(CO)_3 + 3\,PF_3 \xrightarrow[\text{high pressure}]{100°C} (PF_3)_3Cr(CO)_3 + C_9H_{12}$$

A facile route to tetrakisfluorophosphine complexes of zero-valent nickel, NiL_4, which avoids the separation difficulties encountered in displacing carbon monoxide from nickel carbonyl, involves displacement

$$\pi\text{-}(C_5H_5)_2Ni + 4\,L \rightarrow NiL_4 + 2\,[C_5H_5]$$

[L = PF_3, CF_3PF_2, CCl_3PF_2, $ClCH_2PF_2$,
$(CF_3)_2PF$, Me_2NPF_2, Et_2NPF_2,
$C_5H_{10}NPF_2$]

of both cyclopentadienyl rings from nickelocene (*232*, *233*, *240*). When cobaltocene is used one of the rings remains intact (*165*).

$$\pi\text{-}(C_5H_5)_2Co + 2\,PF_3 \rightarrow \pi\text{-}C_5H_5Co(PF_3)_2$$

6. *By Displacement of Coordinated Phosphine Ligands*

An early synthesis of $Ni(PF_3)_4$ involved the displacement of phosphorus trichloride from $Ni(PCl_3)_4$ (*325*). More recent studies using ^{32}P-labeled PCl_3 show that the mechanism involves ligand exchange rather than halogen exchange (*62*). A similar displacement of PCl_3

$$Ni(P^*Cl_3)_4 + 4\,PF_3 \rightarrow Ni(PF_3)_4 + 4\,P^*Cl_3$$

probably operates in the synthesis of complexes of the type *cis*-$[PtCl_2(PEt_3)PF_3]$ from $Pt_2Cl_4(PEt_3)_2$ by treatment with trifluorophosphine in the presence of a trace amount of PCl_3 (*130*). No reaction

$$Pt_2Cl_4(PEt_3)_2 + 2\,PF_3 \rightarrow 2\,\textit{cis}\text{-}[PtCl_2(PEt_3)PF_3]$$

is observed in the absence of the phosphorus trichloride. Rapid redistribution of groups attached to nickel is known in the case of complexes of the type $Ni(PF_3)_n(CO)_{4-n}$ (*58*) and $HCo(PF_3)_n(CO)_{4-n}$ (*320*) and the products can be separated by vapor phase chromatography. A similar but much slower process is observed in mixed carbonyl–dialkylaminodifluorophosphine complexes of nickel (*248*) (see also Section XI). Tris(trifluorophosphine)triphenylstibinenickel(0) can undergo group redistribution to give the disubstituted product

$$2\,Ni(PF_3)_3SbPh_3 \rightarrow Ni(PF_3)_4 + Ni(PF_3)_2(SbPh_3)_2 \qquad (174)$$

Mixed phosphine–fluorophosphine (*160, 247, 164, 173, 174*), phosphite–fluorophosphine (*174*), tertiary amine–fluorophosphine (*174*), carbonyl–fluorophosphine (*160, 173, 56, 58, 59*), tertiary arsine–fluorophosphine (*174, 175*), and stibine–fluorophosphine complexes are readily formed directly from the appropriate fluorophosphine–metal complex. Only in the case of carbon monoxide, chlorophosphines, and phosphites is it possible to completely displace all the fluorophosphine ligands from the metal. Some typical examples are quoted below:

(*a*) $M(PF_3)_n + xCO \rightarrow M(PF_3)_{n-x}(CO)_x + xPF_3$
$(M = Ni, Fe, Cr, Mo, Pt;\ x = 1\text{–}6,\ n = 4, 5, \text{ or } 6)$

$HM(PF_3)_y \xrightarrow{CO} HM(PF_3)_{y-x}(CO)_x$
$(M = Co,\ y = 4;\ M = Mn,\ y = 5)$

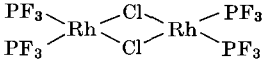
(*b*) (*i*) $(CF_3PF_2)_4Pt + 2R_nPR'_{3-n} \rightarrow (CF_3PF_2)_2Pt(R_nPR'_{3-n})_2 + 2\,CF_3PF_2$
$(R = Ph,\ R' = Me;\ n = 3, 2, 1)$

(*ii*) $Pt(PF_3)_4 + R_3P \rightarrow Pt(PF_3)_{4-n}(R_3P)_n$
$(R = Ph,\ n = 1, 2;\ R = PhO\text{-},\ n = 4)$
$Ni(PF_3)_4 + L_n \rightarrow Ni(PF_3)_{4-n}(L)_n + nPF_3$
$(L = Ph_3A;\ A = P, As, Sb,\ n = 1, 2;\ L = \text{pyridine},\ n = 1;\ L = PCl_3,\ n = 4]$
$Ni(PF_3)_4 + L_2' \rightarrow Ni(PF_3)_2L_2 + 2\,PF_3$
$(L_2' = 2,2'\text{-dipyridyl},\ o\text{-phen})$

(*iii*) $HCo(PF_3)_4 + L'' \rightarrow HCo(PF_3)_3L + PF_3$
$(L'' = Ph_3P, PH_3, AsPh_3, SbPH_3)$

(*iv*) $[(PF_3)_4Rh_2Cl_2] + R_2PR' \rightarrow (R_2PR')_2PF_3RhCl$
$(R = Ph \text{ or } Me)$
$(Ph_3P)_3RhCl + XPF_2 \rightarrow (Ph_3P)_2(XPF_2)RhCl + Ph_3P$
$(X = F, CCl_3, Me_2N\text{-})$

Rather surprisingly difluorotrichloromethylphosphine completely displaces trifluorophosphine from $(PF_3)_4Rh_2Cl_2$ (*63*).



$$+\ 6\,CCl_3PF_2 \longrightarrow 2(CCl_3PF_2)_3RhCl + 4\,PF_3$$

7. *Displacement of Carbon Monoxide*

Displacement of carbon monoxide from metal carbonyls has been widely used as a synthetic route to fluorophosphine–metal complexes.

Clark and co-workers have shown that trifluorophosphine can replace all the CO groups from certain metal carbonyl complexes (*56*, *58*, *59*). Other fluorophosphines behave similarly, the reactions usually being thermally or photochemically induced (*320*, *57*, *121*, *284*, *287*, *61*). In the case of $HCo(CO)_4$, however, substitution by PF_3 occurs rapidly and spontaneously even at −20°C (*320*).

Some typical examples of carbonyl displacement reactions are quoted below:

(*a*) $Ni(CO)_4 + xL \rightarrow Ni(CO)_{4-x}L_x + xCO$
$[x = 4;\ L = PF_3, CF_3PF_2, (CF_3)_2PF, R_2NPF_2, ROPF_2, (RO)_2PF, PF_2Cl;$
$L_x = [F_2POROPF_2]_n]$
$[x = 3;\ L = PF_3, CF_3PF_2, (CF_3)_2PF, PF_2Cl]$
$[x = 2;\ L = PF_3, CF_3PF_2, (CF_3)_2PF, R_2NPF_2, RPFNR'_2, (R_2N)_2PF, PF_2Cl]$
$[x = 1;\ L = PF_3, (CF_3)_2PF, PF_2H, PF_2Cl]$

(*b*) $M(CO)_6 \xrightarrow{L'} Mo(CO)_{6-n}L'_n$
$(M = Mo,\ L' = PF_3, ROPF_2, R_2NPF_2;\ M = Cr,\ L' = PF_3)$
$Fe(CO)_5 \rightarrow Fe(CO)_{5-n}L'_n$
$L = (PF_3, CF_3PF_2)$

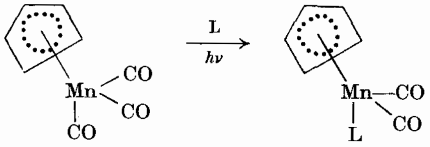
$$Co_2(CO)_8 + 2\ HF + 6\ PF_3 \xrightarrow{500\ atm} 2\ HCo(CO)(PF_3)_3 + COF_2 + 5\ CO$$

$$Co_2(CO)_8 + H_2 + 6PF_3 \xrightarrow[70°C]{200\ atm} 2\ HCo(CO)(PF_3)_3$$

$$RCo(CO)_4 \xrightarrow{PF_3} RCo(PF_3)_x(CO)_{4-x}$$
$(R = H, Me, C_2F_5, C_3F_7)$

$$NOCo(CO)_3 \xrightarrow{PF_3} NOCo(CO)_{3-n}(PF_3)_n$$

(*c*)

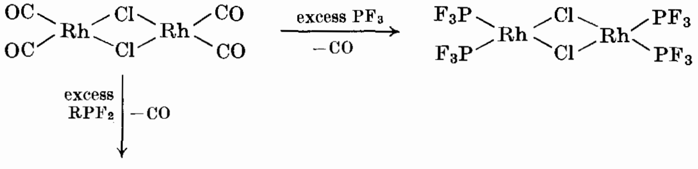


$(L = Et_2NPF_2, C_5H_{10}NPF_2, PF_3)$

$$AMn(CO)_5 \xrightarrow{PF_3} AMn(CO)_{5-x}(PF_3)_x$$
$(A = H \text{ or } Rf;\ x = 1 \rightarrow 5)$

$$Mn_2(CO)_{10} \xrightarrow{PF_3} Mn_2(CO)_{10-y}(PF_3)_y;\ PF_2I \text{ gives } (CO)_4MnPF_2IMn(CO)_4$$
$(y = 1, 2, 3)$

(*d*)



$(RPF_2)_3RhCl$

$(R = CCl_3, R_2N)$

Complete displacement of CO from $[Rh(CO)_2Cl]_2$ is possible using fluorophosphines RPF_2, the reaction with trifluorophosphine affording $[(PF_3)_2RhCl]_2$ (*250*).

There is an interesting report of carbonyl substitution in the reaction between phosphorus pentafluoride and $MeSiH_2Co(CO)_4$ (*114*, *7*). There is evidence that PF_5 is reduced by the silicon–hydrogen bonds yielding $HCo(CO)_4$, the fluorosilane, and trifluorophosphine; the latter subsequently displaces carbon monoxide from the hydridocarbonyl complex.

The same products are obtained, together with $MeSiF_2Co(CO)_4$ when mixtures of cobalt carbonyl, phosphorus pentafluoride, and methylsilane react at room temperature (*114*).

$$2\,MeSiH_3 + Co_2(CO)_8 \rightarrow 2\,MeSiH_2Co(CO)_4 + H_2$$

$$MeSiH_2Co(CO)_4 + PF_5 \rightarrow MeSiF_2H + PF_3 + HCo(CO)_4$$

$$\begin{tikzcd} HCo(CO)_4 \arrow[r, "PF_3"] \arrow[d, "MeSiF_2H"] & HCo(CO)_n(PF_3)_{4-n} \qquad (n = 1, 2, 3) \\ MeSiF_2Co(CO)_4 + H_2 & \end{tikzcd}$$

8. By Displacement of Coordinated Nitrogen or Hydrogen

Dimethylaminodifluorophosphine readily displaces nitrogen or hydrogen from the cobalt complexes $HCoN_2(Ph_3P)_3$ and $H_3Co(Ph_3P)_3$ (*243*).

$$HCoN_2(Ph_3P)_3 + 2\,Me_2NPF_2 \rightarrow HCo(Me_2NPF_2)_2(Ph_3P)_2 + N_2 + Ph_3P$$

$$H_3Co(Ph_3P)_3 + 2\,Me_2NPF_2 \rightarrow HCo(Me_2NPF_2)_2(Ph_3P)_2 + H_2 + Ph_3P$$

9. By Displacement of Coordinated Ammonia

Only one report of this type of displacement has appeared (*153*, *154*).

$$Cr(NH_3)_3(CO)_3 + 3\,PF_3 \xrightarrow[20°C]{300\text{ atm}} Cr(PF_3)_3(CO)_3 + 3\,NH_3$$

The cis isomer apparently is formed exclusively.

10. From Other Fluorophosphine–Transition Metal Complexes

a. Cleavage of the P–C Bond of a Coordinated Fluorophosphine Ligand. Dialkylaminodifluorophosphine–molybdenum carbonyl complexes are formed by cleavage of the phosphorus–carbon bond of the corresponding difluorotrichloromethylphosphine–molybdenum carbonyl complex by secondary amines at room temperature (*11*).

$$(CCl_3PF_2)_nMo(CO)_{6-n} + nR_2NH \rightarrow nCCl_3H + (R_2NPF_2)_nMo(CO)_{6-n}$$
$$(n = 2, 3)$$

b. Cleavage of the P–F Bond of a Coordinated Fluorophosphine. Controlled aminolysis or alcoholysis of the phosphorus–fluorine bond of coordinated trifluorophosphine likewise produces the corresponding aminofluorophosphine or fluorophosphite compound (*319*, *177*, *60*, *178*, *61*).

$$\mathrm{Ni(PF_3)_4} \xrightarrow{\mathrm{R_2NH}} \mathrm{Ni(PF_3)_{4-n}(R_2NPF_2)_n}$$

$$(\mathrm{R} = \mathrm{Me, Et}, n\text{-}\mathrm{Pr}, \mathrm{C_5H_{10}};\ n = 2, 3, 4)$$

$$\mathrm{Mn_2(CO)_9PF_3} \xrightarrow{\mathrm{MeOH}} \mathrm{Mn_2(CO)_9PF_{3-n}(OMe)_n}$$

$$(n = 1, 2, 3)$$

$$\mathrm{Co(NO)(PF_3)_3} \xrightarrow{\mathrm{NaOMe}} \mathrm{Co(NO)(PF_3)_n(PF_2OMe)_{3-n}}$$

$$\mathrm{Fe(CO)_x(PF_3)_{5-x}} \xrightarrow{\mathrm{ROH}} \mathrm{Fe(CO)_x(PF_2OR)_{5-x}}$$

$$\mathrm{M(PF_3)_n} \xrightarrow{n\mathrm{M'X}} \mathrm{M(PF_2X)_n} + n\mathrm{M'F}$$

$$(\mathrm{M} = \mathrm{Ni, Pt, Fe, Cr};\ \mathrm{M'} = \text{alkali metal};$$
$$\mathrm{X} = \mathrm{OR, R, NR_2})$$

Alternatively by treating trifluorophosphine complexes with barium hydroxide in tetrahydrofuran, one fluorine atom can be replaced, and barium salts containing anionic fluorophosphine–transition metal complexes can be obtained (*176*) and subsequently alkylated using $[\mathrm{Et_3O}][\mathrm{BF_4}]$ to give high yields of the volatile liquid mixed trifluorophosphine–(difluorophosphite) complexes.

$$\begin{tikzcd}
2\,\mathrm{Ni(PF_3)_4} + \mathrm{Ba(OH)_2} \arrow[r] & 2\,\mathrm{Ni(PF_3)_3(PF_2OH)} + \mathrm{BaF_2} \arrow[d, "\mathrm{Ba(OH)_2}"] \\
 & \mathrm{Ba^{2+}[Ni(PF_3)_3PF_2O^-]_2} + 2\,\mathrm{H_2O}
\end{tikzcd}$$

$$\mathrm{Fe(PF_3)_5} \xrightarrow{\mathrm{Ba(OH)_2}} \mathrm{Ba^{2+}[Fe(PF_3)_4PF_2O^-]_2}$$

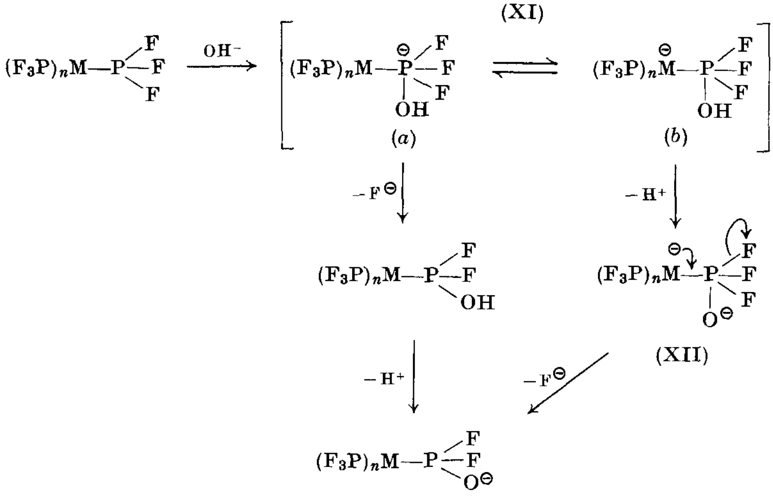
$$\mathrm{Ba[M(PF_3)_nPF_2O]} + 2\,\mathrm{Et_3O{\cdot}BF_4} \rightarrow 2\,\mathrm{M(PF_3)_n(PF_2OEt)} + \mathrm{Ba(BF_4)_2} + 2\,\mathrm{Et_2O}$$

$$(\mathrm{M} = \mathrm{Fe}, n = 4;\ \mathrm{M} = \mathrm{Ni}, n = 3)$$

When dimethyl sulfate in diethyl ether is used as alkylating agent, there is considerable decomposition and a mixture of $\mathrm{Ni(PF_3)_4}$ and $\mathrm{Ni(PF_3)_3PF_2OR}$ compounds (R = Me, Et, Pr, Bu) results (*176*).

It is noteworthy that the mixed trifluorophosphine–difluorophosphite complexes are more thermally stable than the parent trifluorophosphine complexes. The phosphorus–fluorine bond is apparently not susceptible to further attack by $\mathrm{Ba(OH)_2}$.

The mechanism has been discussed and two possible schemes proposed. In (*a*) initial nucleophilic attack of the $\mathrm{OH^-}$ ion at phosphorus is followed by elimination of fluoride ion and loss of a proton under the influence of the base.



Alternatively, in (*b*) the proton may be lost initially from (XI) affording a doubly negatively charged anion (XII), which, in turn, eliminates fluoride ion. Since POF_3 is never observed in these reactions, however, the possibility of the $(PF_3)_nM^{2-}$ ion being a reaction intermediate can be ruled out even though this ion is known to exist in the case when M = Fe (*152*). These studies on hydroxide ion attack on metal–trifluorophosphine complexes are particularly interesting in relation to analogous studies with metal carbonyls for which scheme (*b*) operates. In the latter case there is subsequent loss of carbon dioxide and formation of the carbonylate anion $M(CO)_n^{2-}$.

c. Cleavage of the P–N or P–halogen Bond of a Coordinated Fluorophosphine. The ready fission of the phosphorus–nitrogen bond in dialkylaminodifluorophosphine–metal complexes enables other fluorophosphine–metal derivatives to be readily obtained (*177*, *178*), and these may

$$Ni(Me_2NPF_2)_4 + 8\,HCl \rightarrow Ni(PF_2Cl)_4 + 4\,Me_2NH_2Cl$$

$$Ni(PF_2Cl)_4 + 4\,MeOH \rightarrow Ni(PF_2OMe)_4 + 4\,HCl$$

$$M(PF_2X)_n \xrightarrow{\text{HA or }A^-} M(PF_2A)_n$$

undergo further transformations which are of general synthetic applicability.

d. From Hydrido Derivatives. Hydrido derivatives containing trifluorophosphine are usually strong acids and hydridotetrakis(trifluorophosphine)cobalt(I) reacts with diazomethane at −50°C in ether to give high yields of the methyldiethyloxonium salt $[Et_2OMe][Co(PF_3)_4]$. This complex is stable at 0°C, but above 100°C is quickly converted to the methyl- and ethylcobalt complexes $RCo(PF_3)_4$ (R = Me, Et) (*175*).

$$CH_2N_2 + HCo(PF_3)_4 + Et_2O \xrightarrow{-50^\circ C} [Et_2OMe][Co(PF_3)_4] \xrightarrow{100^\circ C} \underset{(94\%)}{MeCo(PF_3)_4} + \underset{(6\%)}{EtCo(PF_3)_4}$$

Iodoform also reacts with hydridotetrakis(trifluorophosphine)cobalt (I) in pentane at 0°C (*164*) and the acidic hydrogen is also easily replaced

$$HCo(PF_3)_4 + CI_3H \rightarrow ICo(PF_3)_4 + CH_2I_2$$

by treatment with base or sodium (or potassium) amalgam to give crystalline salts, which on acidification regenerate the hydride (*164, 175*). The

$$HM(PF_3)_4 + B \rightarrow BH^+M(PF_3)_4^-$$

$$HM(PF_3)_4 + K/Hg \rightarrow K^+[M(PF_3)_4]^- + \tfrac{1}{2}H_2$$

$$H_2M'(PF_3)_4 + K/Hg \rightarrow 2K^+[M'(PF_3)_4]^{2-}$$

(M′ = Fe, Ru, Os)

$$KM(PF_3)_4 + D^+ \rightarrow DM(PF_3)_4$$

(M = Co, Rh, Ir)

method is useful for preparing deuterium analogs, and very recently the novel trimethylsilylammonium cation has been obtained using this route (*19*).

$$Me_3SiNMe_2 + HCo(PF_3)_4 \rightarrow [Me_3SiN(H)Me_2]^{\oplus}Co(PF_3)_4^{\ominus}$$

Iodotetrakistrifluorophosphineiridium is formed by treating the potassium salt with iodine (*166*), and reduction of $Fe(NO)_2(PF_3)_2$ with

$$KIr(PF_3)_4 + I_2 \xrightarrow[-80^\circ C]{Et_2O} IIr(PF_3)_4 + KI$$

K/Hg in ether gives the air-sensitive potassium salt, which may be quantitatively converted to $HFe(NO)(PF_3)_3$ on acidification (*156*, *167*).

$$Fe(NO)_2(PF_3)_2 \xrightarrow{K/Hg} K^{\oplus}[Fe(NO)(PF_3)_3]^{\ominus} \xrightarrow{H^+} HFe(NO)(PF_3)_3$$

The orange, sublimable complex formed when hydridotetrakis(trifluorophosphine)rhodium decomposes on standing at room temperature is believed to have the same dimeric structure as its cobalt analog (*175*).

$$2\,HRh(PF_3)_4 \rightarrow [(PF_3)_2RhPF_2]_2 + 2\,HF$$

B. PHYSICAL PROPERTIES

Most of the metal(0) complexes and their hydrido-, halogeno-, and mixed carbonyl- or nitrosylfluorophosphine analogs are appreciably volatile, and the vapors often have a strong oppressive odor necessitating careful handling. Many liquid fluorophosphine–metal complexes are known and usually they can be distilled without significant decomposition (see Table VII).

A striking feature of fluorophosphine–transition metal complexes is their high thermal stability, and this often contrasts markedly with the corresponding carbonyl derivative, e.g., $HCo(CO)_4$ decomposes to an appreciable extent below room temperature, whereas $HCo(PF_3)_4$ is stable up to 250°C. The only exceptions appear to be some 4*d* metal complexes, e.g., $Pd(PF_3)_4$ and $HRh(PF_3)_4$, which are both somewhat unstable at room temperature, and halogenometal derivatives [e.g., $ICo(PF_3)_4$], which readily loses trifluorophosphine, or halogenotrifluorophosphine complexes of the 5*d* metals which tend to polymerize]. Replacement of one or more PF_3 groups with aryl phosphines considerably increase the thermal stability of the complex (*152*).

In contrast to the often strongly reducing properties of the uncoordinated fluorophosphines R_nPF_{3-n} (Section III), the corresponding metal complexes are usually stable in air and are only slowly hydrolyzed by water. $Ni(PF_3)_4$ can be steam-distilled without significant loss, although treatment with stronger nucleophiles causes phosphorus–fluorine bond cleavage. Trifluorophosphine complexes of Pt(II), on the other hand, are often very sensitive to hydrolysis (*53*), whereas the corresponding dialkylaminofluorophosphine derivatives $(R_2NPF_2)_2PtX_2$ and particularly $[(R_2N)_2PF]_2PtX_2$ are stable in air over much longer periods (*241*).

C. Stereochemistry

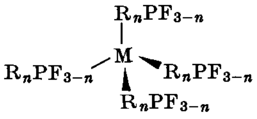
No X-ray studies on fluorophosphine–transition metal complexes have yet been reported, in detail, although it is mentioned in reference (*254*) that the manganese–manganese bond length in $Mn_2(CO)_8(PF_3)_2$ is identical with the value in $Mn_2(CO)_{10}$ (*265*), which again demonstrates the similar coordinating ability of trifluorophosphine and carbon monoxide. Only two dimensional X-ray data on $Ni(PF_2NC_5H_{10})_4$ have been reported and a rough estimate of the nickel–phosphorus bond length has been made assuming the complex is tetrahedral (*118a*).[6]

The Raman spectrum of $Ni(PF_3)_4$ (*326*, *190*) has been interpreted in terms of a regular tetrahedral arrangement of the PF_3 groups about nickel. Tetrahedral stereochemistry is also suggested by IR and Raman studies on several nickel(0) and platinum(0) complexes ML_4 [M = Ni, Pt; L = PF_3, CF_3PF_2, $(CF_3)_2PF$] (*241*) (XIII) and by analysis of the ^{19}F and ^{31}P NMR spectra of certain NiL'_4 complexes ($L' = PF_3$, CCl_3PF_2,

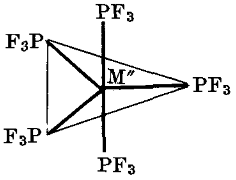
---

[6] See footnote p. 412.

R_2NPF_2, $ClCH_2PF_2$, CF_3PF_2, $C_6H_4O_2PF$) (*240*, *196*, *198*) and $M'(PF_3)_4^{\ominus}$ ions ($M' = Co, Rh, Ir$) (*186*).



(XIII)



(XIV)

These results have been confirmed only very recently in the case of $Ni(PF_3)_4$ by two independent electron diffraction studies (*1a*, *279a*). The four PF_3 groups are arranged tetrahedrally around the nickel atom (see Fig. 5) and undergo essentially free rotation about the Ni–P bonds. The molecular parameters are

$$\begin{aligned} \text{Ni–P} &= 2.099 \pm 0.003\text{Å} \\ \text{P–F} &= 1.561 \pm 0.003\text{Å} \\ \theta\text{NiPF} &= 118.4 \pm 0.3^\circ \\ \theta\text{FPF} &= 99.3^\circ \end{aligned}$$

The P–F bond length is very similar to the free ligand value, and the nickel–phosphorus bond length is very short indeed since the normally accepted covalent radius of phosphorus is 1.10Å and that of atomic

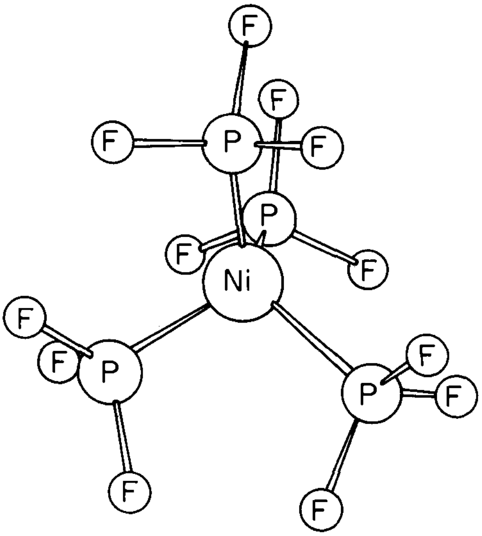
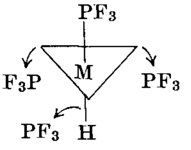


FIG. 5. Structure of Tetrakistrifluorophosphine nickel (0).

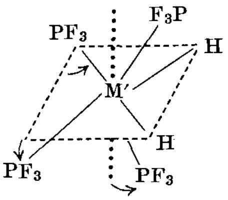
nickel probably about 1.2–1.3Å. Most nickel–phosphorus bond lengths in phosphine complexes of Ni(O) or Ni(II) are shorter than the sum of the two radii (typically in the 2.20–2.30Å range) but the extremely short value in $Ni(PF_3)_4$ seems strongly suggestive of a π-contribution to the metal–phosphorus bond. (See also p. 412).

The IR spectra of the five-coordinate $M''(PF_3)_5$ complexes ($M'' =$ Fe, Ru, Os) are consistent with a trigonal-bipyramid structure (XIV) and the dipole moment of the iron derivative is found to be zero (*171*). The ^{19}F and ^{31}P NMR indicate that all five PF_3 groups are apparently equivalent because the molecule is undergoing an *intra*molecular inversion process (see Section XI,D).

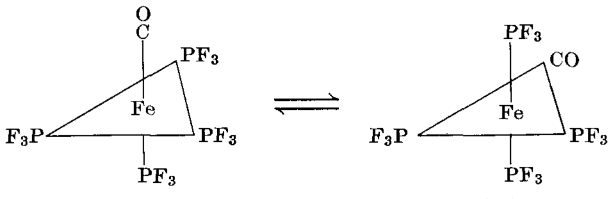
Infrared and NMR studies suggest C_{3v} symmetry (based on a trigonal-bipyramid) for all the $HM(PF_3)_4$ complexes (M = Co, Rh, Ir) (XV) and $HFe(NO)(PF_3)_3$; and C_{2v} symmetry in the case of the dihydro complexes $H_2M'(PF_3)_4$ (XVI) ($M' =$ Fe, Ru, Os). The PF_3 ligands may be displaced slightly toward the hydrogen atoms (*152, 178a*). The "fluxional" behavior of several pentacoordinate metal–fluorophosphine complexes has been studied in considerable detail by Bigorgne (*317*), Sheline (*125*), and Clark (*318, 319*). In contrast to the octahedral $M(CO)_x(PF_3)_{6-x}$ systems (M = Cr, Mo, W) where the various isomers can be isolated by gas–liquid partition chromatography, the corresponding $Fe(CO)_x(PF_3)_{5-x}$ compositions *cannot* be separated into isomers because of the intramolecular inversion process. The infrared spectrum of a very carefully purified sample of $Fe(CO)(PF_3)_4$ shows *two* strong bands in the CO-stretching region, indicating the presence of two isomers having C_{3v} and C_{2v} symmetry that are in equilibrium. Haas and Sheline (*125*) have calculated



(XV)



(XVI)



(C_{3v}) (C_{2v})

the percentage abundance of all the various $Fe(CO)_x(PF_3)_{5-x}$ isomers, but their assignment of frequencies differs from those of Tripathi and Bigorgne (*317*).

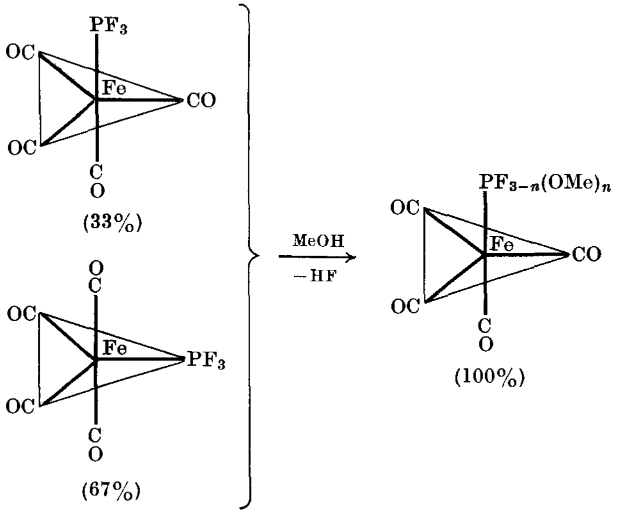
Alcoholysis studies on $Fe(CO)_x(PF_3)_{5-x}$ compounds ($x = 4, 3, 2$) support these conclusions and the products contain mainly *one* isomer. In the case where $x = 1$ or 0, however, the isomeric composition is affected much less (*319*). For example,

$$\underset{\substack{\text{(mixtures of}\\ \text{isomers)}}}{Fe(CO)_4(PF_3)} \xrightarrow{\text{MeOH}} \underset{\text{(one isomer)}}{Fe(CO)_4PF_{3-n}(OMe)_n}$$

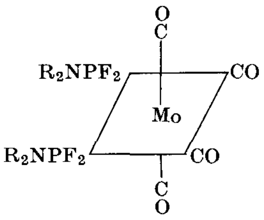
The $PF_{3-n}(OMe)_n$ ligands show a strong preference for axial positions within the trigonal-bipyramid structure.

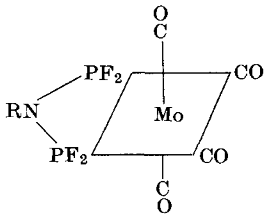
Substitution of the bulkier trifluoromethylfluorophosphines CF_3PF_2 or $(CF_3)_2PF$ into $Fe(CO)_5$ occurs at equatorial sites, and the isomeric composition moves toward the corresponding structures. This suggests that the axial position adopted by the ligands after solvolysis is controlled by electronic rather than steric factors (*319*).

The infrared spectra of hydrido and perfluoroalkylcobalt carbonyl–fluorophosphine complexes $RCo(CO)_x(PF_3)_{4-x}$ ($R = H, CF_3, C_2F_5, C_3F_7$) have also been interpreted in terms of the presence of nonisolable isomers (*320*). This contrasts with a report (*159*) that pure $HCo(CO)(PF_3)_3$ can be obtained directly from dicobalt octacarbonyl. As discussed in Section XI,D, there is convincing evidence from ^{19}F NMR studies of stereochemical nonrigidity in $CF_3Co(PF_3)(CO)_3$.



Geometric isomers can be readily isolated in the case of hexacoordinate polyfluoroalkyl- and perfluoroarylmanganese carbonyl–trifluorophosphine complexes $RfMn(CO)_{5-n}(PF_3)_n$, whereas the corresponding hydrides $HMn(CO)_{5-n}(PF_3)_n$ cannot be resolved (206). This may be due to the small size of the hydride ligand, which lowers the activation energy of the intramolecular inversion process. Axial and equatorial substitution of trifluorophosphine into $Mn_2(CO)_{10}$ gives isolable isomers (*61*). The stereochemistry of many $L_nM(CO)_{6-n}$ complexes (L = fluorophosphine; M = Cr, Mo, W) has been determined from analysis of the CO-stretching region of the infrared or Raman spectra (*8*, *59*, *125*, *284*, *287*). Spectroscopic (*287*, *144*, *9*) and displacement (*11*) studies indicate that in aminofluorophosphine–metal complexes coordination always occurs via the phosphorus atom rather than nitrogen.



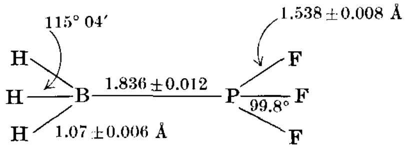


X. Other Fluorophosphine Complexes

A. FLUOROPHOSPHINE–BORANE COMPLEXES

The known fluorophosphine–borane adducts are listed in Table VIII. Trifluorophosphine–borane can be made directly from diborane and excess trifluorophosphine (*255*) or by displacement of carbon monoxide from $BH_3 \cdot CO$ (*255*), which it closely resembles.

The structure of $PF_3 \cdot BH_3$ has been recently established by microwave studies on several isotopic species (*181*). The shortening of 0.032 Å of the P–F bond compared with PF_3 itself may result from a lowering of the lone-pair repulsion on coordination, and this may also account for the widening of the FPF bond angle (*181*). The phosphorus–boron bond length is the shortest known for this type of complex and this



correlates with the higher value for the heat of dissociation ($\Delta H = 24.5$ kcal) compared with other phosphine complexes of boron acceptors.

Trifluorophosphine–borane has also been prepared in the gas phase reaction between boroxine and trifluorophosphine, but the method is somewhat hazardous and probably best carried out with small amounts of material (*16*). Kinetic studies indicate a first-order dependence on the

$$B_3O_3H_3 + PF_3 \rightarrow BH_3PF_3 + B_2O_3 \qquad (8)$$

pressure of boroxine, but the rate is essentially independent of trifluorophosphine concentration suggesting that the rate-determining step involves the slow decomposition of $B_3O_3H_3$ to BH_3 followed by a rapid

$$B_3O_3H_3 \rightarrow BH_3 + B_2O_3 \qquad \text{(slow)}$$

$$BH_3 + PF_3 \rightarrow BH_3PF_3 \qquad \text{(fast)}$$

TABLE VIII

FLUOROPHOSPHINE–BORANE COMPLEXES

Complex	Melting point (°C)	Boiling point (°C/mm)	Refs.
BH_3PF_3	−116.1	−61.8	(*16, 255, 181*)
BD_3PF_3	−115.1	−59.8	(*255*)
$BH_3CF_3PF_2$	—	—	(*39*)
$BH_3(CF_3)_2PF$	—	—	(*39, 38*)
BH_3PF_2H	—	6.2	(*276*)
$BH_3Me_2NPF_2$	−56.7	119.4	(*148*)
$BH_3P_2F_4$	—	—	(*214*)
$BH_3PF_2OPF_2$	—	—	(*50*)
$BH_3MeNHPF_2$	−65 ± 3	129 (est)	(*148*)
$BH_3(MeNH)_2PF$	—	Involatile liquid	(*148*)
$BH_3(Me_2N)_2PF$	—	—	(*148*)
$BMe_3(Me_2N)_2PF$	—	—	(*107*)
$B_4H_8PF_3$	—	−47.7/6.1	(*306, 39, 251a*)
$B_4H_8PF_2NMe_2$	−18	27.7/2.5	(*314, 187, 50a*)
$B_2H_42PF_3$	−114.3	−44/33	(*75, 76*)
$(BH_3)_2(PF_2)_2CH_2$	—	—	(*29*)
$B_4H_8PF_2H$	−80.4 to −79.3	90.2	(*50a*)

heterogeneous reaction with trifluorophosphine. Reaction (8) is exothermic to the extent of about 21 kcal.

BH_3PF_3 and oxygen react in the gas phase to form $H_2B_2O_3$, hydrogen, trifluorophosphine, and B_2O_3 (*16*).

$F_3P{\cdot}BH_3$ is a spontaneously inflammable gas which is appreciably dissociated at room temperature. Trifluorophosphine is readily displaced by trimethylamine (*255*), and treatment with ammonia between −111 °C and room temperature leads to complete cleavage of phosphorus–fluorine bonds; although at −78°C there is evidence for formation of $(NH_2)_2PF{\cdot}BH_3$.

$$F_3P{\cdot}BH_3 + Me_3N \longrightarrow Me_3N{\cdot}BH_3 + PF_3$$

$$F_3PBH_3 \xrightarrow{NH_3} [(NH_2)_2PF{\cdot}BH_3] \rightarrow (NH_2)_3P{\cdot}BH_3$$

Methylaminodifluorophosphine–borane, $MeNHPF_2{\cdot}BH_3$, and bis(methylamino)fluorophosphine–borane, $(MeNH)_2PF{\cdot}BH_3$, are formed when methylamine reacts with the trifluorophosphine borane adduct (*148*). The uncoordinated $(MeNH)_2PF$ is as yet unknown.

$$2\,MeNH_2 + F_3P{\cdot}BH_3 \xrightarrow[Et_2O]{-111°C} MeNHPF_2{\cdot}BH_3 + MeNH_3F$$

$$2\,MeNH_2 + MeNHPF_2{\cdot}BH_3 \xrightarrow[Et_2O]{25°C} (MeNH)_2PF{\cdot}BH_3 + MeNH_3F$$

Corresponding reactions with dimethylamine afford $Me_2NH{\cdot}BH_3$, $Me_2NPF_2{\cdot}BH_3$, or $(Me_2N)_2PF{\cdot}BH_3$, depending on the reaction conditions (*148*). The last two can be more easily made directly from Me_2NPF_2 or $(Me_2N)_2PF$, and coordination via phosphorus rather than nitrogen is indicated by NMR and other studies (*107*).

Displacement reactions indicate that the order of increasing base strength with respect to BH_3 is $F_3P < MeNHPF_2 \sim Me_2NPF_2 < Me_3N \sim Me_2NH < (MeNH)_2PF \sim (Me_2N)_2PF$.

The decomposition of fluorophosphine–borane adducts $L{\cdot}BH_3$ [$L = PF_3, CF_3PF_2, (CF_3)_2PF$] to B_2H_6 and free fluorophosphine is found to occur by a similar mechanism to that known for $BH_3{\cdot}CO$ (*39*).

$$LBH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BH_3 + L$$

$$BH_3 + L{\cdot}BH_3 \xrightarrow{k_3} B_2H_6 + L$$

$$(k_2 \gg k_3)$$

First-order rate constants for the initial association at different temperatures enable a value for the dissociation energy of diborane to be obtained. A similar rate law is suggested for $B_4H_8PF_3$ (*39*).

Bis(trifluorophosphine)–diborane (*4*) (m.p. −114.3°C) is obtained from trifluorophosphine and the dimethyl ether adduct of triborane (*7*) at −15°C (*75, 76*). The complex decomposes to give hexaborane (*12*) and pentaborane (*9*). Treatment with hydrogen affords quantitative yields

$$2\ B_2H_4(PF_3)_2 \rightarrow i\text{-}B_4H_8(PF_3)_2 + 2\ PF_3$$

$$B_2H_4(PF_3)_2 + i\text{-}B_4H_8(PF_3)_2 \rightarrow B_6H_{12} + 4PF_3$$

$$B_6H_{12} + B_2H_4{\cdot}(PF_3)_2 \rightarrow B_5H_9 + B_3H_7 + 2\ PF_3$$

of trifluorophosphine–borane, and reaction with diborane (*6*) gives an almost 100% yield of tetraborane (*10*).

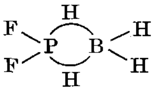
$$B_2H_4(PF_3)_2 + H_2 \rightarrow 2\ BH_3{\cdot}PF_3$$

$$B_2H_4{\cdot}(PF_3)_2 + B_2H_6 \rightarrow B_4H_{10} + 2\ PF_3$$

Difluorophosphine and diborane react at 25°C to give HPF_2BH_3 (*276*), which shows unusual stability in sharp contrast to the high degree of dissociation found for both $PH_3{\cdot}BH_3$ and $F_3P{\cdot}BH_3$. The order of base strength for the three phosphines toward borane is found to be $H_3P < F_3P \ll F_2PH$. The unusual stability of $PF_2H{\cdot}BH_3$ is rather difficult to rationalize. ^{1}H, ^{19}F, and ^{11}B NMR studies indicate that

$(PF_2)^+(BH_4)^-$

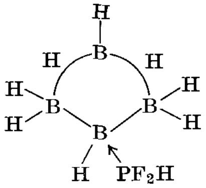
(XVII)



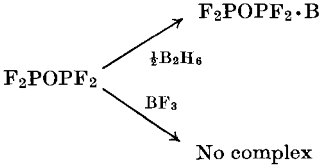
(XVIII)

structures (XVII) and (XVIII) can be ruled out. Arguments based on hyperconjugation (*116*) would predict that PF_3 should be a better acceptor than PF_2H.

An alternative suggestion (*276*) invoked an internal hydrogen bond between the H of PF_2H and the two fluorine atoms. This would allow closer approach between phosphorus and boron and reduce the effective positive charge on hydrogen allowing the phosphorus lone-pair electrons to form a strong P–B bond. A subsequent microwave determination of the bond lengths and bond angles in PF_2H (*180*), however, does not support the internal hydrogen bond hypothesis (Section VII). PF_2H is also a strong base towards B_4H_8 forming a 1:1 adduct which is more stable than either $OC{\cdot}B_4H_8$ or $F_3P{\cdot}B_4H_8$ (*50a*). The structure (shown below) assigned on the basis of ^{11}B NMR studies is very similar to that established for $Me_2NPF_2{\cdot}B_4H_8$ using X-ray methods (*187*).



μ-Oxobisdifluorophosphine F_2POPF_2, like its alkylamino analog $RN(PF_2)_2$ (*236*), does not form a stable BF_3 adduct (*50*), and this has been attributed to the high deformation energy required to convert the planar boron trihalide into the tetrahedral complex. The ready formation of the monoborane adduct, on the other hand, is due to the lower deformation energy of BH_3 (*50*). The coordination of only *one* BH_3 group



may result from electron interchange between PF_2 units by way of the π system of the oxygen, since this enhances the base strength of the coordinated phosphorus and correspondingly reduces that of the uncoordinated phosphorus.

This hypothesis is supported by the fact that $(PF_2)_2CH_2$ binds *two* BH_3 groups rather strongly (*29*).

$$F_2PCH_2PF_2 \xrightarrow{B_2H_6} H_3B.PF_2CH_2PF_2.BH_3$$

Tetrafluorodiphosphine affords only a monoborane adduct when reacted with diborane at room temperature. The product which collects

$$P_2F_4 + \tfrac{1}{2}B_2H_6 \rightarrow F_2PPF_2 \cdot BH_3$$

at −100°C as a white crystalline solid shows no detectable P_2F_4 (compare the ready dissociation of $F_3P \cdot BH_3$), suggesting that the diphosphine is a stronger base than trifluorophosphine. Slow decomposition of $F_2PPF_2 \cdot BH_3$ gives $PF_3 \cdot BH_3$ and a yellow solid presumed to be $[PF]_x$ polymer (*214*). NMR evidence indicates rapid exchange of BH_3 units between the two phosphorus atoms.

The formation of only the monoborane adduct may result from partial double bond interaction (p_π–d_π) between the phosphorus atoms of P_2F_4 which enhances the basicity of one at the expense of the other, as was found for F_2POPF_2 (*50*).

Although tetraborane(8) has not been isolated, it is known from its trifluorophosphine and dimethylaminodifluorophosphine adducts. The former complex can be made directly from pentaborane(11) and the

$$B_5H_{11} \xrightarrow{2PF_3} B_4H_8 \cdot PF_3 + BH_3PF_3$$

$$B_5H_{11} \xrightarrow{CO} B_4H_8CO \xrightarrow{Me_2NPF_2} B_4H_8 \cdot Me_2NPF_2 + CO$$

latter by displacement of carbon monoxide from B$_4$H$_8$·CO (*306*, *314*). Dimethylaminodifluorophosphine–tetraborane(8) (m.p. −18°C) is more stable than the other complexes and its structure has been elucidated by X-ray diffraction (Fig. 5) (*187*). Coordination as expected is via the phosphorus atom, and as in the uncoordinated ligand the P–N–C$_2$ skeleton is essentially planar, but the P–N bond is even shorter than the free ligand value. ^{19}F NMR measurements on Me$_2$NPF$_2$·B$_4$H$_8$ indicate the presence of *two* isomers (*50a*).

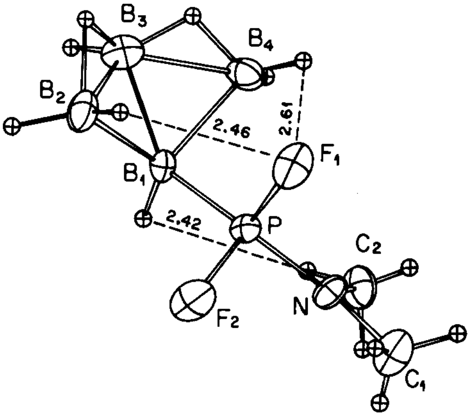


Fig. 6. Structure of Me$_2$NPF$_2$·B$_4$H$_8$. From M. D. La Prade and C. E. Nordman, *Inorg. Chem.* 8, 1669 (1969) with permission.

INTRAMOLECULAR DISTANCES AND ANGLES

Bond distances (Å)

P–B$_1$	1.856 (8)	B$_1$–B$_3$	1.687 (12)
B$_1$–B$_2$	1.844 (11)	B$_2$–B$_3$	1.759 (13)
B$_1$–B$_4$	1.826 (11)	B$_3$–B$_4$	1.753 (14)

B–H (av, regular) 1.08 (0.98–1.15)
B–H (av, bridge) 1.19 (1.10–1.40)

P–F$_1$	1.581 (4)	N–C$_1$	1.483 (13)
P–F$_2$	1.586 (5)	N–C$_2$	1.470 (9)
P–N	1.593 (6)	C–H	0.8–1.0

Angles (deg)

B$_1$–B$_2$–B$_3$	55.6 (5)	F$_1$–P–B$_1$	116.6 (3)
B$_1$–B$_4$–B$_3$	55.9 (5)	F$_2$–P–B$_1$	113.1 (3)
B$_2$–B$_3$–B$_4$	114.1 (7)	F$_1$–P–F$_2$	96.4 (3)
B$_2$–B$_1$–B$_4$	107.6 (6)	F$_1$–P–N	107.1 (3)
P–B$_1$–B$_2$	97.4 (5)	F$_2$–P–N	103.3 (3)
P–B$_1$–B$_4$	97.8 (4)	P–N–C$_1$	121.0 (5)
P–B$_1$–B$_2$	135.2 (5)	P–N–C$_2$	123.7 (5)
N–P–B$_1$	117.6 (3)	C$_1$–N–C$_2$	115.1 (6)

B. FLUOROPHOSPHINE COMPLEXES OF NONTRANSITION METAL HALIDES

As discussed in Section VIII, no complex is formed between PF_3 and boron trifluoride (*52, 53*). Similarly neither F_2POPF_2 or $EtN(PF_2)_2$ are basic enough to coordinate to BF_3 (*50, 236*). Me_2NPF_2, however, gives a solid 1 : 1 adduct with BF_3, which is completely dissociated in the vapor phase (*47, 107*). Infrared and NMR studies have been interpreted in terms of coordination being via nitrogen rather than phosphorus (*107*). This is unexpected since the coplanar arrangement of the two carbon atoms, the nitrogen and phosphorus in Me_2NPF_2, suggests that there is nitrogen → phosphorus p_π–d_π bonding which would enhance the donor character of phosphorus. Parry (*256*) has proposed that there may be a strong dependence of phosphorus coordination on the B–P internuclear distance and that coordination via nitrogen is less distance-dependent.

$$EtN(PF_2)_2 \xrightarrow{BF_3} \text{No complex}$$

$$Me_2NPF_2 \xrightarrow{BF_3} Me_2NPF_2 \cdot BF_3$$

A novel trifluorophosphine–tris(difluoroboryl)borane complex $B_4F_6 \cdot PF_3$ (m.p. 55°C, b.p. 74°C) is formed by reacting the high-temperature species boron monofluoride with PF_3 on a cold surface (*316*). The crystal structure has recently been determined by X-ray diffraction and is shown in Fig. 7 (*74*).

Although Chatt and Williams (*53*) observed no reaction when trifluorophosphine was passed over Al_2Cl_6 at temperatures up to 250°C or when PF_3 was passed into a cyclohexane solution of Al_2Br_6, later work by Alton (*2*) using a sealed tube and 8 atm pressure of PF_3 quantitatively afforded $PF_3 \cdot AlCl_3$. Its identity was confirmed by a low-temperature molecular weight determination, displacement of the PF_3 by tertiary amine, and the combining ratios of PF_3 and $AlCl_3$. Halogen exchange readily occurs even at low temperatures, but is inhibited in the presence of excess trifluorophosphine. No simple complex could be isolated from Al_2Me_6–PF_3 mixtures, although there is evidence of a reaction.

$$xF_3P \cdot AlCl_3 \rightarrow xPCl_3 + [AlF_3]_x$$

Halogen exchange is also found using the more basic dimethylaminodifluorophosphine which initially forms an adduct with aluminum trichloride (*256*). In the presence of excess ligand trifluorophosphine and the bis(dimethylamino)fluorophosphine complex is formed, and halogen exchange gives Me_2NPCl_2 and AlF_3. Similar behavior is found

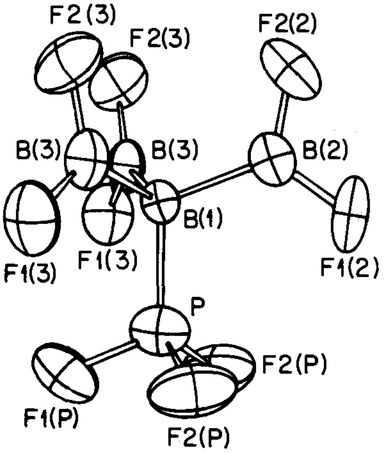


FIG. 7. The $B_4F_6 \cdot PF_3$ molecule, which is bisected by a crystallographic mirror plane which contains F1(P), P, B(1), B(2), F1(2), and F2(2). The thermal elipsoids have been reduced to 30% probability contours for the sake of clarity. From B. G. De Boer *et al.*, *Inorg. Chem.* **8**, 836 (1969) with permission.

B(2)–F1(2)	1.330 (10)	F1(2)–B(2)–F2(2)	113.6 (7)
B(2)–F2(2)	1.276 (10)	F1(3)–B(3)–F2(3)	112.8 (5)
B(3)–F1(3)	1.319 (6)	Av	113.2 ± 1
B(3)–F2(3)	1.293 (7)	B(1)–B(2)–F1(2)	123.6 (7)
Av	1.305 ± 0.015	B(1)–B(2)–F2(2)	122.8 (7)
Thermal correction = 0.009, 0.051		B(1)–B(3)–F1(2)	124.5 (5)
B(1)–B(2)	1.685 (10)	B(1)–B(3)–F2(3)	122.7 (5)
B(1)–B(3)	1.668 (7)	Av	123.4 ± 1
Av	1.677 ± 0.015	B(2)–B(1)–B(3)	108.3 (4)
(Thermal correction = 0.001, 0.013)		B(3)–B(1)–B(3)	109.5 (5)
B(1)–P	1.825 (7)	B(2)–B(1)–P	111.1 (5)
	1.825 ± 0.015	B(3)–B(1)–P	109.8 (3)
(Thermal correction = 0.005, 0.026)		Av	109.7 ± 1
P–F1(P)	1.525 (6)	B(1)–P–F1(P)	115.2 (3)
P–F2(P)	1.496 (4)	B(1)–P–F2(P)	117.2 (2)
Av	1.511 ± 0.015	Av	116.2 ± 1
(Thermal correction = 0.013, 0.066)		F1(P)–P–F2(P)	101.5 (2)
		F2(P)–P–F2(P)	101.8 (3)
		Av	101.7 ± 1

using $GaCl_3$, but at a slower rate and at higher temperatures halogen exchange gives $GaCl_2F \cdot (Me_2N)_2PCl$ (*256*). It has been suggested that

$$MCl_3 + 2\ Me_2NPF_2 \rightarrow [MCl_3 \cdot 2\ Me_2NPF_2] \rightarrow [(Me_2N)_2PF]_2MCl_3 + PF_3$$
$$(M = Al, Ga)$$

disproportionation and halogen exchange is promoted by metal ions of small size and high charge which have no *d* electrons (*256*). Other factors, however, must be important in view of the almost quantitative redistribution of groups attached to phosphorus in a series of R_2NPF_2–Pt(II) complexes (*245*) (Section IX).

XI. Nuclear Magnetic Resonance Spectra

Since both fluorine and phosphorus have nuclear spin $I = \frac{1}{2}$ in 100% natural abundance, nuclear magnetic resonance studies have not surprisingly occupied an important place in the development of the chemistry of tervalent phosphorus fluorides.

A. ANALYSIS OF SPECTRA

The ^{19}F and ^{31}P NMR spectra of the simple fluorophosphines R_nPF_{3-n} are always first-order and the phosphorus–fluorine coupling constant $^1J_{PF}$ is found to lie between 1000 and 1450 Hz depending on the nature of R, with the parent PF_3 having the largest $^1J_{PF}$ value known. The ^{19}F NMR spectrum of $P(PF_2)_3$ is also almost first-order (*305*), but more complicated spin systems are known, for example, in the case of tetrafluorodiphosphine P_2F_4 (*143*), alkyl- or arylaminobis(difluorophosphines) $RN(PF_2)_2$ (R = Me, Et, Ph, *m*-ClC_6H_4) (*237*, *239*), and F_2PSPF_2 (*223*), which have all been analyzed as examples of $XX'AA'X''X'''$ spin systems [X = fluorine, A = phosphorus]. Similarly μ-oxobisdifluorophosphine PF_2OPF_2 has been treated as an $X_2AA'X_2'$ spin system, with the assumption that the remote $J_{XX'}$ coupling constant is zero (*274*). This is not the case, however, for either $RN(PF_2)_2$ or F_2PPF_2 (*239*, *143*); in the former case there are two distinctly different fluorine–fluorine coupling constants, $^4J_{FF'}$, while in the latter one of the two different vicinal $^3J_{FF}{'}$ coupling constants is almost zero. Furthermore, the temperature independence of the ^{19}F NMR spectrum of P_2F_4 down to −140°C suggests that one isomer predominates (see also Section VII).

Analysis of the NMR spectra also leads to the evaluation of the phosphorus–phosphorus coupling constant and provides evidence concerning the relative signs of the directly bonded $^1J_{PF}$ and the remote ($^2J_{PF}{'}$ or $^3J_{PF'}$) phosphorus–fluorine coupling constants (see Table IX).

Recently the ^1H, ^{19}F, and ^{31}P NMR spectra of F_2PPH_2 were found to be first-order (*275*), even though an $AA'KQXX'$ spin system requires two distinct AX coupling constants. A single $^3J_{HF}$ coupling constant would result if both rapid rotation about the phosphorus–phosphorus axis and inversion through the P atom of the PH_2 group occurs, but since two remote coupling constants are found in F_2PPF_2 (*143*) and H_2PPH_2 (*195*), it appears more likely that the deceptively simple spectrum results from the magnitude of $J_{\mathrm{FF}'}$ being very much larger than $^3J_{\mathrm{HF}}$.

A preliminary report (*223*) describes the temperature dependence of $^2J_{\mathrm{PP}'}$ in F_2PSPF_2. There is a steady increase in $^2J_{\mathrm{PP}'}$ from 302 Hz at −1°C to 393 Hz at −120°C and this has been attributed to either P–S–P bond angle changes in excited vibrational states of the molecule or to internal rotation about the P–S bond. $EtN(PF_2)_2$ also shows a temperature dependence ^{19}F NMR spectrum (*249a*) as does $F_2PSP(S)F_2$ (*50b*). At 40°C the ^{19}F spectrum of the latter consists of two doublets associated with the presence of pentavalent, four-coordinate $-P(S)F_2$ and tri-coordinate tervalent $-SPF_2$ units. At lower temperatures the two sets of peaks broaden at different rates, probably due to differences in the rates of rotation about the P(III)–S and P(V)–S bonds. At −90° each of the four lines is split into a doublet and each of the components of the doublet is further split into a triplet, in agreement with the $F_2PSP(S)F_2$ formulation but not compatible with either the diphosphine disulphide structure, $F_2P(S)P(S)F_2$, or the dithio-bridged compound $F_2P{-}S{-}S{-}PF_2$ (*50b*).

TABLE IX

NMR PARAMETERS FOR SOME $X_2AA'X_2'$ AND $XX'AA'X''X'''$ SPIN SYSTEMS[a]

Compound	$^1J_{\mathrm{PF}}$	$J_{\mathrm{PF}'}$	$J_{\mathrm{PP}'}$	$J_{\mathrm{FF}'}$	Refs.
F_2PPF_2	(−)1198.5	(+)67.5	(+)227.4	34.4 0.0	(*143*) (*69b*)
F_2PPH_2	(−)1203	(+)82	211	—	(*275*)
F_2POPF_2	(−)1358	(+)14	4	0	(*274*)
F_2PSPF_2	—	—	302[c]	—	(*223*)
$F_2PNMePF_2$	(−)1264	(+)47	(+)437	11.7 1.7	(*239*)
$F_2PNEtPF_2$[b]	(−)1261	(+)52	+446	11.1 2.2	(*239*)
$F_2PNPhPF_2$	(−)1252	(+)40	(+)371	10.0 4.4	(*239*)
$F_2PN(m\text{-}ClC_6H_4)PF_2$	(−)1285	(+)41.5	(+)372	11.6 2.6	(*239*)

[a] In Hz.

[b] Double resonance experiments (*197*) show that $^2J_{\mathrm{PP}'}$ is *opposite* in sign from $^1J_{\mathrm{PF}}$.

[c] Value at −1°C, ^{19}F NMR spectrum shows a temperature dependence.

The ^{19}F NMR spectrum of the recently synthesized 1,3-ditertiarybutyl-2,4-difluorodiazadiphosphetidine (which is an XAA′X′ spin system; X = fluorine, A = phosphorus) has been analysed and the transannular phosphorus–phosphorus coupling constant found to be 92.5 Hz (*250a*).

Table IX lists the various spin–spin coupling constants obtained from analysis of some of these more complicated NMR spin systems of the $X_2AA'X_2$ or $XX'AA'X''X'''$ type.

B. RELATIVE SIGN DETERMINATIONS

Pople and Santry (*264*) showed that single-bond coupling constants between fluorine and first-row elements should be negative because of the large separation of the fluorine 2*s* and 2*p* orbitals, and this has recently been confirmed in phosphorus fluorides (*72*, *200*). Double resonance studies on $(CF_3)_2PF$ and CF_3PF_2 show that $^1J_{PF}$ and $^2J_{PCF}$ are of *opposite* sign, whereas $^3J_{FF'}$ has the *same* sign as $^1J_{PF}$. Since $^1J_{PF}$ lies in the 500–1450 Hz region in all phosphorus–fluorine compounds, it seems that it will always be negative.

Double resonance experiments on $EtN(PF_2)_2$ and $EtN(PF_2)_2Mo(CO)_4$ show that $^2J_{PP'}$ is *opposite* in sign to $^1J_{PF}$ in both cases (*197*) and, therefore, $^2J_{PP'}$ is positive. Similar studies on the *cis*-$(CCl_3PF_2)_2Mo(CO)_4$ complex indicate that in this case $^2J_{PP'}$ is negative (*197*). The negative coupling constant has been explained by simple molecular orbital arguments (*199*) and the analogous trans coupling predicted to be positive (*199*) and subsequently this was confirmed experimentally (*20*).

The knowledge of the sign of $^2J_{PP'}$ in *cis*-$EtN(PF_2)_2M(CO)_4$ ($M = Mo$) enables the increase in magnitude along the series $Cr < Mo < W$ to be understood (see Section XI,D) because the coupling can be considered to contain both positive (via nitrogen) and negative (via the metal) contributions (*199*). Johanssen has reported the relative signs of $^1J_{PF}$, $^1J_{PH}$, and $^2J_{HF}$ in PF_2H (*142*).

C. CHEMICAL SHIFTS AND COUPLING CONSTANTS

1. *Phosphorus-31 Chemical Shifts* (δ_P)

a. In Free Ligands. Tricoordinate phosphorus fluorides R_nPF_{3-n}, all show a characteristic low-field phosphorus chemical shift [δ_P in the range -97 to -255 ppm relative to 85% H_3PO_4 as standard], the resonance of the parent trifluorophosphine occurring at highest field (see Tables II–VI). This low-field phosphorus shift can be used with confidence to distinguish tricoordinate phosphorus fluorides from other species present in mixtures (*226*). "$EtPF_2$" and "EtPFCl" said to be formed simultaneously in the fluorination of ethyldichlorophosphine (*134*) had δ_P values (+30 ± 3 and −26 ± 2 ppm, respectively), which were clearly out of line with other compounds of this type, but a later study (*289*) showed that the products were, in fact, ethyltetrafluorophosphorane $EtPF_4$ and its hydrolysis product $EtPOF_2$.

Tetelbaum *et al.* (*315*) have suggested that a correlation exists between δ_P for compounds of the type XPF_2 (where the group X is alkyl, aryl, or halogenoalkyl) and the Taft σ^* parameter for X. While it is true that the lowest-field chemical shifts (−200 to −250 ppm) occur for the alkyl derivatives, values for other fluorophosphines sometimes show irregular variations (Tables II–VI) even within fairly closely related compounds.

Early empirical approaches relating δ_P of phosphorus compounds to their molecular structure were generally unsatisfactory, but more recently theoretical treatments based on Ramsey's equation have appeared (*188*, *189*, *124*) and the phosphorus chemical shift is found to depend mainly on the paramagnetic term in the shielding expression which arises from a field-induced mixing of the ground state with low-lying excited states. Using an average energy approximation, the chemical shift may be related to the properties of individual bonds, e.g., ionic character, hybridization, and double bonding. The topic is included in part of a recent monograph (*70*) and has been extended very recently by Ionin (*135*).

In view of the lack of accurate structural data on fluorophosphines and their complexes, it is not surprising that chemical shifts are not yet well understood.

Trifluorophosphine has the highest field ^{31}P chemical shift (δ_P) of all the phosphorus trihalides or fluorophosphines R_nPF_{3-n} (*123*) and the unexpected order for δ_P in the PX_3 series (X = halogen) was originally discussed (*122*) in terms of opposing effects of ionic and double character of the P–X bond. A relationship apparently exists between δ_P and the electronegativity of the substituent atom for some RPF_2 compounds (R = F, RO-, R_2N-), the values being considerably lower for the R_2N derivatives than the RO compounds.

On the other hand, Sheluchenko *et al.* (*301*) found no simple correlation between δ_P and the inductive effect of the X group for a series of fluorophosphines of the type RPFX (X = OR, NR_2, SR, Cl), and while the main criterion for determining the phosphorus shift seems to be the atoms to which phosphorus is bonded, at present there is no quantitative understanding of the ^{31}P shift data summarized in Tables II–VI.

b. In Complexes. ^{31}P chemical shift measurements have been made on several fluorophosphine–transition metal complexes (*271, 145, 144, 9*) (Table VII), and usually there is a significant shift to low-field from the free ligand value when the metal is in its zero-valent state. In complexes of metals within the same group this low-field shift is greatest for the lighter elements (e.g., δ_P becomes more negative in the order $Cr > Mo > W$) (*242*), possibly reflecting a decrease in the average excitation energy term on descending the group. For third-row transition elements in zero-oxidation state δ_P is usually close to the free ligand value and occasionally to slightly higher field (*242*). The bidentate fluorophosphine $EtN(PF_2)_2$ is unusual in that only the chromium complex of the Group VI derivatives has a lower δ_P value than the free ligand (*144*), but variations within the group are as expected.

^{31}P NMR shift measurements on nickel and molybdenum carbonyl–fluorophosphine complexes $M(CO)_xL_y$ ($M = Ni, Mo$; $L = PF_2X$) (*271*) have been discussed in terms of an increase in the paramagnetic term on coordination. It has been proposed that there is evidence for appreciable π bonding between phosphorus and the metal. A further suggestion that there is a correlation between the coordination shift [δ_P (complex)-δ_P (ligand)], and the carbonyl-stretching frequency in these complexes was not borne out by other studies (*242*) using a wider variety of fluorophosphines.

Fewer data are available on fluorophosphine complexes of metals in higher oxidation states. In Pt(II) complexes (*241, 242*) δ_P occurs at higher field than the free ligand, whereas the behavior in Rh(I) complexes (*242, 250*) is more variable.

^{31}P shifts in dialkylaminofluorophosphine complexes with boron acceptors occur at higher field than the uncoordinated fluorophosphine (*107, 242*).

2. *Fluorine-19 Chemical Shifts*

These will only be considered briefly. Available data are summarized in Tables II–VII. Here again the paramagnetic contribution dominates the shielding, and since σ and π-bond changes may often be self-cancelling any general quantitative understanding is lacking, and comparisons are best made within structurally similar series. The fluorine chemical shifts of a series of XPF_2 compounds ($X = F$, RO-, R_2N-) decrease regularly with the electronegativity of X (*270*), as is found for the analogous chlorofluorophosphines $PF_{3-n}Cl_n$ (*133, 219a*). This is in the opposite direction to the behavior of δ_P. No simple correlations, however, are apparent from data on a variety of compounds of the type RR′PF [$R = Me, Ph$; $R' = F, Cl, OR, SR, NR_2$] (*301*). It is interesting to note that there is a much better correlation between the phosphorus and fluorine shifts in pentavalent phosphorus fluorides XYP(O)F with the nature of the substituents X and Y (*300*), and this may reflect smaller bond-angle changes at phosphorus within the whole series.

Complexes. A characteristic feature of the ^{19}F NMR spectra of fluorophosphine–transition metal complexes is the appearance of the resonance at much lower field compared with the free ligand value, and this can be used as a diagnostic test for complex formation (*9*, *10*, *233*, *271*). Small changes in the chemical shift for a series of chromium, molybdenum, and tungsten complexes (*145*) are probably not significant, particularly since solvent effects have not been studied. This low-field ^{19}F shift on coordination is similar to that observed in the ^{19}F NMR spectrum of perfluoroalkyl–transition metal complexes (*263*). There is no apparent relationship between the coordination shift and the nature of the substituents on phosphorus, although it is noticeable that monofluorophosphines show bigger deviations from the free ligand value (*233*, *271*) than difluorophosphines.

The ^{19}F chemical shift of PF_2X ligands plotted against the coordination shift in $Ni(PF_2X)_4$ and $Mo(CO)_3(PF_2X)_3$ complexes suggests that the paramagnetic term is larger for molybdenum (*271*).

3. *Magnitude of Phosphorus-Fluorine Coupling Constants in Fluorophosphines and Their Complexes*

a. Ligands. The largest directly bonded phosphorus–fluorine coupling constant is observed in the parent trifluorophosphine ($^1J_{PF} = 1440$ Hz), while the magnitudes of $^1J_{PF}$ for a series of difluorophosphines RPF_2 seem to be largely determined by changes in hybridization, and usually obey Walsh's rule. Thus the *absolute* value increases with the electronegativity of the substituent. For example, $^1J_{PF}$ for a series of YPF_2 compounds decreases along the series (see Tables II–VI) $Y = F > RO \simeq CX_3 > R_2N > R$, ($X =$ halogen; $R =$ alkyl, aryl) and similarly in difluorohalogenophosphines PF_2X, $^1J_{PF}$ gets smaller in magnitude for $X = F > Cl > Br > I$ (*204*).

Mavel (*204*) has found a good correlation between $^1J_{PF}$ and the Taft σ_I parameter of X for a somewhat limited series of XPF_2 compounds, and likewise there is a relationship between $^1J_{PF}$ and the sum of δ_I coefficients of X and Y in PFXY derivatives. Inspection of data (Tables II–IV), however, for a much wider range of compounds indicates the limitations of this simplified approach.

Fewer data are available on monofluorophosphines, RR′PF, and invariably they have smaller $^1J_{PF}$ coupling constants than the corresponding RPF_2 compounds, although the general trends outlined above are also applicable.

b. Complexes. The absolute magnitude of $^1J_{PF}$ is lowered by 10–150 Hz when the fluorophosphine becomes coordinated to a transition metal (Table VII) (*10, 233, 9, 271, 198*), but some literature values (*271, 233*) are not exact because a full analysis of the spectra has not been carried out. The $EtN(PF_2)_2$ complexes are anomalous and have a larger $^1J_{PF}$ value than the uncoordinated ligand (*144*). Within a series of Group VI metal–fluorophosphine complexes $^1J_{PF}$ decreases in the order $Cr > Mo > W$ (*145, 242*).

The difference between $^1J_{PF}$ in a series of nickel complexes $Ni(CO)_xL_{4-x}$ ($L = R_nPF_{3-n}$; $x = 3, 2, 1$) and that of the free ligand has been discussed in relation to the orbital energies involved (*198*).

4. *Spin–Spin Coupling Constants and σ-Bond Orders*

The ^{59}Co NMR spectra of the tetrahedral $[Co(PF_3)_4]^{\ominus}$ and $[Co(CO)_4]^{\ominus}$ anions have been recorded (*191*) and values obtained for the $^1J(^{59}Co–^{31}P)$ (1222 ± 25 Hz) and $^1J(^{59}Co–^{13}C)$ (287 ± 13 Hz) coupling constants. Approximate values for the σ-bond order were calculated and together with shift data suggested that bonding to the ligand π orbitals is more important in the carbonylate ion than bonding to the phosphorus 3*d* orbitals of the tetrakis(trifluorophosphine)cobaltate, and that the cobalt–phosphorus σ-bond order apparently is greater than the cobalt–carbon σ-bond order (*191*).

5. *Evaluation of Phosphorus–Phosphorus Coupling Constants in Fluorophosphine–Transition Metal Complexes*

a. Octahedral Complexes. A recent development in phosphine complexes of transition metals has been the evaluation of phosphorus–phosphorus coupling constants $^2J_{PMP'}$, through the metal atom (*242*). Most of the work on fluorophosphine complexes has been done with octahedral carbonyl complexes of zero-valent chromium, molybdenum, and tungsten (*9, 144, 145, 242, 129*) of the type *cis*-$L_2M(CO)_4$ (M = Group VI metal), e.g. $M = Mo$; $L = PF_3$, CF_3PF_2, CCl_2HPF_2, CH_2ClPF_2, PF_2H, $RN(PF_2)_2$, $ROPF_2$, R_2NPF_2, etc., and in a few cases *trans*-$L_nM(CO)_{6-n}$ (*242, 322*).

These represent $[X_nA]_2$ or $[X_nA]_3$ spin systems [using the notation of Haigh (*25*)] and the particular advantage of this type of system is that the phosphorus–phosphorus coupling constant ($J_{AA'}$) can be easily and accurately evaluated because J_{AX} (in this case, directly bonded phosphorus–fluorine coupling constant $^1J_{PF}$ in the 1000–1300 Hz range) is always so much larger that $J_{AA'}$ (here the phosphorus–phosphorus coupling $^2J_{\mathrm{PMP'}}$). This has enabled a detailed study to be made of the various factors affecting the magnitude and sign of $^2J_{\mathrm{PMP'}}$ (*9*, *242*, *144*, *145*), and this topic has been reviewed recently (*242*). Table X summarizes the various couplings obtained from the ^{19}F and/or ^{31}P NMR spectra of several fluorophosphine–Group VI metal complexes, from which the following points of interest emerge:

(1) Except for the case of the chelating ligand $\mathrm{EtN(PF_2)_2}$ which is discussed separately (Section V), the magnitude of $^2J_{\mathrm{PMP'}}$ for a given fluorophosphine ligand *decreases* in the order Cr > Mo > W for the *cis*-$\mathrm{(R_nPF_{3-n})_2M(CO)_4}$ complexes.

(2) There is a relationship between $^2J_{\mathrm{PMP'}}$ and the electron-withdrawing power of the R group in$\mathrm{R_nPF_{3-n}}$. For example, in the molybdenum complexes *cis*-$\mathrm{(RPF_2)_2Mo(CO)_4}$ which represent the most complete series, $^2J_{\mathrm{PMP'}}$ decreases in magnitude in the order $\mathrm{R = F > CF_3 \sim CCl_3 > CCl_2H > CH_2Cl > CH_3 \approx H}$. This can be understood in terms of a decrease in both the *s* character of the phosphorus hybrid orbital which is forming the σ bond to the metal and the amplitude of the phosphorus *s* orbital at the nucleus, $\psi_s(0)^2$, as the electron-withdrawing power of the substituted group R decreases.

TABLE X

Phosphorus–Phosphorus Coupling Constants ($^2J_{\mathrm{PMP'}}$) in Fluorophosphine–Group VI Complexes[a]

Complex	L	Cr	Mo	W	Refs.
cis-$\mathrm{L_2M(CO)_4}$	$\mathrm{CH_3PF_2}$	—	40 ± 3	—	(*250*)
	$\mathrm{ClCH_2PF_2}$	59.5 ± 1	42.5 ± 0.5	33.0 ± 1	(*9, 145*)
	$\mathrm{Cl_2CHPF_2}$	66.0 ± 1	47.5 ± 0.5	37.0 ± 0.5	(*250*)
	$\mathrm{CCl_3PF_2}$	67.0 ± 1	48.0 ± 0.5[b]	38.0 ± 0.5	(*9, 145*)
	$\mathrm{CF_3PF_2}$	—	48.5 ± 1.0	—	(*9, 145*)
	$\mathrm{PF_3}$	77.0 ± 0.5[c]	55.0 ± 0.2[e]	38.5 ± 0.5[f]	(*9, 145*)
	$\mathrm{R_2NPF_2}$ (R = Me, Et)	62.0 ± 2	38.0 ± 2	—	(*9, 145*)
	$\mathrm{(CF_3)_2PF}$	—	41.0 ± 1	—	(*9*)
	$\mathrm{EtN(PF_2)_2}$	78.5	121.0[d]	155.3	(*144*)
	$\mathrm{PF_2H}$	—	40.0 ± 0.5	—	(*12*)
cis-$\mathrm{L_3M(CO)_3}$	$\mathrm{PF_3}$	—	56.4 ± 1.2	—	(*129, 242*)
	$\mathrm{PhOPF_2}$	—	55.2	—	(*129, 242*)

[a] In Hz.

[b] $-$ve (*197*) *sign.*

[c] Trans isomer $^2J_{\mathrm{PMP}} = 34.0 \pm 0.5$ Hz (*145a*).

[d] +ve (*197*) *sign.*

[e] Trans isomer 312 Hz.

[f] Trans isomer 315 Hz (*252a*).

(3) ${}^1J_{\mathrm{PF}}$ becomes smaller in magnitude (actually less negative) when the fluorophosphine becomes attached to the metal, and the remote phosphorus–fluorine coupling constant ${}^3J_{\mathrm{PF'}}$ is usually less than 5 Hz in the cis complexes, but distinctly larger (~30 Hz) in the trans derivatives *(145, 322)*.

(4) In the special case of complex of the chelating $\mathrm{EtN(PF_2)_2}$ ligand *cis*-$\mathrm{EtN(PF_2)_2M(CO)_4}$, ${}^2J_{\mathrm{PMP'}}$ actually increases in magnitude along the series Cr > Mo > W, but this may be understood when the appropriate sign of ${}^2J_{\mathrm{PMP'}}$ is taken into consideration *(242)* (Section XI,B).

b. Tetrahedral Complexes. By comparison with the octahedral complexes, fully substituted tetrahedral derivatives of the type $\mathrm{ML_4}$ (where M = Ni, Pd, or Pt and L is a fluorophosphine $\mathrm{R_{3-\mathit{n}}PF_{\mathit{n}}}$) present a formidable problem for exact NMR analysis. The NMR spectra in the general case of the $[\mathrm{AX}_n]_4$ tetrahedron only involve four basic coupling constants J_{AX} $(={}^1J_{\mathrm{PF}})$, $J_{\mathrm{AX'}}$ $(={}^3J_{\mathrm{PF'}})$, $J_{\mathrm{AA'}}$ $(={}^2J_{\mathrm{PP'}})$, and $J_{\mathrm{XX'}}$ $(={}^4J_{\mathrm{FF'}})$.

TABLE XI

PHOSPHORUS–PHOSPHORUS COUPLING CONSTANTS (${}^2J_{\mathrm{PMP'}}$) IN ZERO-VALENT NICKEL–FLUOROPHOSPHINE COMPLEXES

Complex	${}^2J_{\mathrm{PMP'}}$ (Hz)	Refs.
$\mathrm{Ni(PF_3)_4}$	3 ± 1	*(198)*
$\mathrm{Ni(CF_3PF_2)_4}$	$\leqslant 5$	*(198)*
$\mathrm{Ni[(CF_3)_2PF]_4}$	<5	*(198)*
$\mathrm{Ni[CCl_3PF_2]_4}$	21 ± 1	*(198)*
$\mathrm{Ni(CH_2ClPF_2)_4}$	<10	*(198)*
$\mathrm{Ni(Me_2NPF_2)_4}$	$\leqslant 10$	*(198)*
$\mathrm{Ni(C_6H_4O_2PF)_4}$	17.7 ± 0.2	*(196, 198)*
$\mathrm{Ni(R_2NPF_2)_\mathit{x}(CO)_{4-\mathit{x}}}$	≈ 0	*(198)*

A full analysis of the simplest system, namely $[\mathrm{AX}]_4$, typified by the complex $\mathrm{Ni(PFO_2C_6H_4)_4}$ (neglecting interaction with remote protons) has been reported *(196)*, while partial analyses of more complicated complexes of the type $\mathrm{NiL_4}$ [$\mathrm{L = PF_3, CF_3PF_2, (CF_3)_2PF, CCl_3PF_2, CH_2ClPF_2}$, and $\mathrm{Me_2NPF_2}$] *(198, 240)* give only slightly less accurate values for all the above spin–spin coupling constants. NMR parameters for mixed carbonyl–fluorophosphine complexes of nickel have also been obtained *(198)*. Table XI summarizes data for the tetrahedral complexes. ${}^1J_{\mathrm{PF}}$ and ${}^3J_{\mathrm{PF'}}$ have opposite signs; however, the magnitude of the latter (20–40 Hz) is significantly larger than the values found for cis substituted octahedral complexes (1–5 Hz) and closer to the values in the trans isomers.

The low values of $^2J_{PMP'}$ in these compounds have been related to rather small differences in molecular orbital energies (*198*), and as a result there is apparently no simple relation between $^2J_{PMP'}$ and the nature of R within a series of RPF_2–Ni complexes.

c. Other Complexes. i. Rhodium (I) complexes. The ^{19}F NMR spectra of several rhodium(I)–fluorophosphine complexes of the type $[(RPF_2)_2RhCl]_2$ (R = F, CCl_3, Me_2N-, Et_2N-) have been analyzed as $X_nAA'X_n'$ spin systems (X = fluorine, A = phosphorus, $n = 2$ or 3), and the phosphorus–phosphorus coupling constant obtained (*250*).

These values also show a steady decrease in the magnitude of $^2J_{PMP'}$ with the electron-withdrawing power of the R group directly paralleling the observations in octahedral complexes of zero-valent Cr, Mo, and W discussed previously. A further correlation not possible in other zero-valent complexes [except for W] is found (*250*) between the phosphorus–phosphorus coupling constant ($^2J_{PP'}$) and $^1J_{RhP}$ the metal–phosphorus coupling constant.

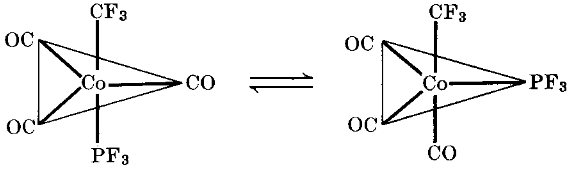
ii. Platinum(II) complexes. The ^{19}F and ^{31}P NMR spectra of several complexes of the type $(R_2NPF_2)_2PtX_2$ and $[(R_2N)_2PF]_2PtX_2$ (R = Me, Et, $R_2 = C_5H_{10}$; X = Cl, Br) have been analyzed as $X_2AA'X_2'$ and $XAA'X'$ spin systems, respectively (*245*), and the relatively small phosphorus–phosphorus coupling constant (in the 25–37 Hz range) shows that the complexes have the cis rather than trans stereochemistry. In the case of the $(R_2N)_2PF$ complexes which were formed by heating the R_2NPF_2 compounds, it is interesting to note that until very recently only $(Me_2N)_2PF$ was known as the free ligand (*241*).

D. APPLICATION OF NMR SPECTROSCOPY TO STRUCTURAL PROBLEMS

1. *Stereochemical Nonrigidity in Fluorophosphine–Metal Complexes*

Stereochemically nonrigid compounds (fluxional molecules) represent an important current area of interest in the field of organometallic chemistry. Five-coordinate fluorophosphoranes R_nPF_{5-n} (Section III) and $Fe(CO)_5$ provide excellent examples of this type of behavior on account of "pseudorotation" of atoms or groups about the central atom (*216*). Similarly fluorine-19 NMR studies (*171*) on $M(PF_3)_5$ complexes (M = Fe, Ru) indicate apparent equivalence of all five PF_3 ligands. A clear-cut case involving nonrigidity has been reported recently by Clark (*318*) for the complex $CF_3Co(PF_3)(CO)_3$. The ^{19}F NMR spectrum at 30°C shows a doublet of quartets for the CF_3 resonance and a widely spaced broad doublet for the PF_3 group. At lower temperatures the spectrum becomes broadened, but below −30°C again becomes resolvable, and at

$-70°C$ consists of lines attributable to two isomers (XIX) and (XX) present to a comparable extent both of which are thought to have axial CF_3 groups. As expected the room temperature spectrum has shift

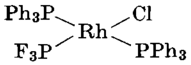


(XIX) (XX)

and spin-coupling parameters which are the average of the values found for the two isomers. The energy of activation for interconversion of the two isomers is estimated to be about 11 kcal (*318*). A very recent study on the fluxional behavior of some PF_3-substituted derivatives of butadienetricarbonyl iron (0) underlines the usefulness of ^{19}F NMR spectroscopy as a tool for studying the dynamic behavior of organometallic compounds (*323b*).

2. *Intermolecular Exchange in a Rh(I) Complex*

The ^{19}F NMR spectrum of a carefully purified sample of *trans*-$PF_3(Ph_3P)_2RhCl$ shows the characteristic low-field shift discussed earlier. The spectrum consists of a widely spaced doublet (from coupling with phosphorus), each line of which is split further into a doublet (coupling

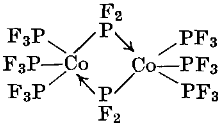


(XXI)

with ^{103}Rh) of triplets (coupling with two equivalent Ph_3P groups). Addition of small amounts of triphenylphosphine immediately collapses the triplet pattern as the free and coordinated triphenylphosphine molecules undergo exchange, but the smaller doublet pattern due to ^{19}F–^{103}Rh spin coupling is preserved. When a pressure of PF_3 is maintained above a solution of (XXI), the spectrum changes to a simple widely spaced doublet indicating loss of ^{103}Rh–^{19}F coupling because of exchange of coordinated and uncoordinated PF_3 (*63*).

3. *Structural Assignment*

The structure of the red liquid complex (XXII), bis(μ-difluorophosphino)hexakis(trifluorophosphine) dicobalt has been confirmed by its characteristic ^{19}F NMR spectrum which exhibits two doublets (from coupling with phosphorus) of relative intensity 9:2 (*170*). The chemical shift of the coordinated PF_3 groups (+13.2 ppm relative to CCl_3F) is significantly downfield from the free ligand value, and similarly $^1J_{PF}$ (1330 Hz) is much reduced in magnitude (see also Section XI,C,4). The doublet resonance of the fluorine atoms of the bridging phosphorus is split further into a septet pattern from spin-coupling with the six terminal PF_3 groups ($^3J_{PF} = 28$ Hz). The magnitude of the directly bonded phosphorus–fluorine coupling constant (1230 Hz) is in the range expected for a difluorophosphine group.



(XXII)

4. *Establishment of the Coordinating Site in Dialkylaminodifluorophosphine Complexes*

In principle dialkylaminodifluorophosphines R_2NPF_2, can form complexes in which either nitrogen or phosphorus is acting as the donor atom. The phosphorus–phosphorus coupling constant $^2J_{(PMP')}$ in several *cis*-$(R_2NPF_2)_2Mo(CO)_4$ complexes (see Section XI,C) is found to be comparable in magnitude with values obtained in other bisfluorophosphine molybdenum tetracarbonyl complexes (e.g., PF_3, CCl_3PF_2) in which phosphorus must be the donor atom (*9*). This provides strong evidence against nitrogen being the donor atom since the phosphorus–phosphorus coupling constant over four bonds would be very much smaller. The ^{31}P NMR spectrum of dimethylaminodifluorophosphine–borane, $Me_2NPF_2 \cdot BH_3$, shows a triplet of 1:1:1:1 quartets indicating that phosphorus is the donor atom. In the analogous BF_3 complex no fine structure appears in the triplet pattern and in the absence of an exchange process, this lends support to other evidence which suggests that nitrogen is the donor atom (*107*).

5. *Redistribution Reactions*

a. Group Redistribution within a Fluorophosphine Ligand. Platinous(II) chloride and dialkylaminodifluorophosphines R_2NPF_2 readily afford the cis square-planar complexes *cis*-$(R_2NPF_2)_2PtCl_2$. The ^{19}F NMR spectra of these compounds are of the $X_2AA'X_2'$ type and since $J_{AX} \gg J_{AA'}$ may be accurately analyzed (*245*). $^2J_{PMP'}$ is found to be in the 22–28 Hz range and this small value by analogy with other studies confirms the cis stereochemistry. Extending the reaction time leads to redistribution of groups on phosphorus and formation of *cis*-$[(R_2N)_2PF]_2$-$PtCl_2$, whose ^{19}F NMR spectrum again is analysed as an XAA′X′ spin system to give rather similar values for $^2J_{PMP'}$. A further characteristic feature of these spectra is the lower value for $^1J_{PF}$ in the monofluoroderivatives and a correspondingly high value for $^2J_{PtF}$ (*241*) (see also Section XI,C).

b. Ligand Redistribution. The ^{19}F NMR spectra of complexes of the type $NiL_2(CO)_2$ ($L = R_2NPF_2$, etc.), which had stood at room temperature for a period of months, showed clear evidence for the presence of compounds of the type $NiL(CO)_3$ and $Ni(L)_3(CO)$, showing that redistribution of ligands had occurred (*248*). The identification of each component of the mixture (shown in Fig. 8) is facilitated by the difference in ^{19}F chemical shifts of the complexes and the variations in complexity of the spectrum as the number of ligands attached to nickel varies. A detailed analysis of the spectrum shows that $^2J_{PMP'}$ is close to zero in all cases (*198*). Clark (*58*) has observed similar redistribution reactions

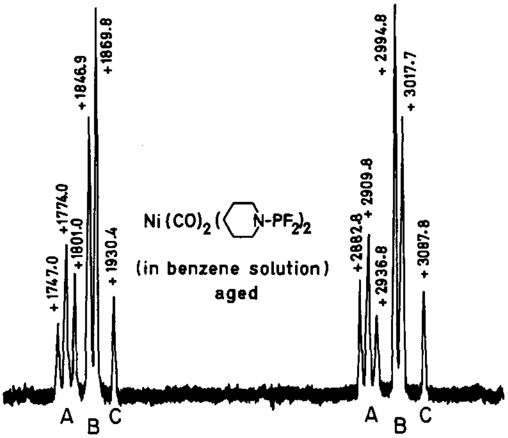


FIG. 8. ^{19}F NMR spectrum at 56.4 MHz/sec of $Ni(CO)_2(C_5H_{10}NPF_2)_2$ (B) and its redistribution products, $Ni(CO)(C_5H_{10}NPF_2)_3$ (A) and $Ni(CO)_3$-$(C_5H_{10}NPF_2)$ (C). Figures are in Hz, relative to CCl_3F as internal standard (*248*).

$$2\,NiL_2(CO)_2 \xrightarrow[\text{redistribution}]{\text{slow}} Ni(CO)_3L + Ni(CO)L_3$$

$[L = Me_2NPF_2, Et_2NPF_2, (Me_2N)_2PF,$
$C_5H_{10}NPF_2]$

as $Ni(PF_3)_n(CO)_{4-n}$ complexes and separated the various species by vapor phase chromatography. The rate of rearrangement in the PF_3 case is very much faster than that observed in the dialkylaminodifluorophosphine case.

ACKNOWLEDGMENTS

I wish to thank Professors B. Anderson (Oslo), R. Schmutzler (Braunschweig), and Drs. R. Keat (Glasgow), D. H. Rankin (Edinburgh), J. A. Salthouse (Manchester), and P. L. Timms (Bristol) for communicating some of their unpublished results; also Mr. J. R. Swain for reading the manuscript and making several suggestions. I am also indebted to E. F. and M. Nixon for clerical assistance, and finally I thank my wife Kim for her patience and encouragement.

REFERENCES

1. Allen, F. H., and Pidcock, A., *J. Chem. Soc. A* p. 2700 (1968).

1a. Almenningen, A., Anderson, B., and Astrup, E. E., *Acta. Chem. Scand.* In Press and personal communication.

2. Alton, E. R., *Dissertation Abstr.* **21**, 3620 (1961).

3. Anderson, H. H., *J. Am. Chem. Soc.* **69**, 2495 (1947).

4. Ang, H. G., and Schmutzler, R., *J. Chem. Soc. A* p. 702 (1969).

5. Angelici, R. J., and Ingemanson, C. M., *Inorg. Chem.* **8**, 83 (1969).

6. Angelici, R. J., and Malone, M. D., *Inorg. Chem.* **6**, 1731 (1967).

7. Baay, Y. L., Berry, A., Gondal, S. K., Hagen, A. P., and MacDiarmid, A. G., *3rd Organometal. Symp., Munich, 1967.*

8. Barlow, C. G., Nixon, J. F., and Webster, M., *J. Chem. Soc. A* p. 2216 (1968).

9. Barlow, C. G., Nixon, J. F., and Swain, J. R., *J. Chem. Soc. A* p. 1082 (1969).

10. Barlow, C. G., and Nixon, J. F., *Inorg. Nucl. Chem. Letters* **2**, 323 (1966).

11. Barlow, C. G., Jefferson, R., and Nixon, J. F., *J. Chem. Soc. A* p. 2692 (1968).

12. Barlow, C. G., Personal communication.

13. Barlow, C. G., and Nixon, J. F., *J. Chem. Soc. A* p. 228 (1966).

14. Barlow, C. G., and Nixon, J. F., Unpublished results.

15. Barlow, M. G., Green, M., Haszeldine, R. N., and Higson, H. G., *J. Chem. Soc. B* p. 1025 (1966).

16. Barton, L., *J. Inorg. Nucl. Chem.* **30**, 1683 (1968).

17. Bennett, M. A., and Patmore, D. J., *Chem. Commun.* p. 1510 (1969)

18. Bennett, M. A., and Milner, D. L., *Chem. Commun.* p. 581 (1967); *J. Am. Chem. Soc.* **91**, 6983 (1969).

19. Berry, A. D., Bergerund, J. R., Highsmith, R. A., MacDiarmid, A. G., and Nasta, M. A., *Organometal. Symp. Bristol, 1969.*

20. Bertrand, R. D., Ogilvie, F., and Verkade, J. G., *Chem. Commun.* p. 756 (1969).

21. Bigorgne, M., *J. Organometal. Chem.* **2**, 68 (1964).

22. Bigorgne, M., *J. Inorg. Nucl. Chem.* **26**, 107 (1964).

23. Bigorgne, M., *Bull. Soc. Chim. France* p. 1986 (1960).

24. Bigorgne, M., and Bénard, J., *Rev. Chim. Minerale* p. 831 (1966).
25. Bishop, E. O., *Ann. Rev. NMR Spectroscopy* **1**, 91 (1968).
26. Bishop, E. O., Carey, P. R., Swain, J. R., and Nixon, J. F., *J. Chem. Soc. A*. p. 1074 (1970).
27. Blaser, B., and Worms, K. H., *Z. Anorg. Chem.* **361**, 15 (1968).
28. Blaser, B., and Worms, K. H., *Z. Anorg. Chem.* **360**, 117 (1968).
29. Bokerman, G. N., and Parry, R. W., *Am. Chem. Soc. Meeting., Chicago 1967.*
30. Bond, A. C., and Cohn, K. W., quoted by Parry (*256*).
31. Booth, H. S., and Cassidy, M. C., *J. Am. Chem. Soc.* **62**, 2369 (1940).
32. Booth, H. S., and Frary, S. G., *J. Am. Chem. Soc.* **61**, 2934 (1939).
33. Brockway, L. O., and Wall, F. T., *J. Am. Chem. Soc.* **56**, 2373 (1934).
34. Brown, D. H., Crosbie, K. D., Fraser, G. W., and Sharp, D. W. A., *J. Chem. Soc. A* p. 551 (1969).
35. Brown, D. H., Crosbie, K. D., Fraser, G. W., and Sharp, D. W. A., *J. Chem. Soc. A* p. 872 (1969).
36. Brown, R. D., and Peel, J. B., *Australian J. Chem.* **21**, 2605 (1968).
37. Brown, R. D., and Harcourt, R. D., *Australian J. Chem.* **16**, 737 (1963).
38. Burg, A. B., and Brendel, G., *J. Am. Chem. Soc.* **80**, 3198 (1958).
39. Burg, A. B., and Chin-Fu, Y., *J. Am. Chem. Soc.* **88**, 1147 (1966).
40. Burg, A. B., and Nixon, J. F., *J. Am. Chem. Soc.* **86**, 356 (1964).
41. Burg, A. B., Slota, P. J., Mahler, W., and Juvinall, G. L., *W.A.D.C. Tech. Rept.* (1956).
42. Burg. A. B., and Street, G. B., *Inorg. Chem.* **5**, 1532 (1966).
43. Burg, A. B., and Street, G. B., *J. Am. Chem. Soc.* **85**, 3522 (1963).
44. Campbell, J. M., and Stone, F. G. A., *Angew Chem.* **81**, 120 (1969).
45. Cavell, R. G., and Dobbie, R. C., *Inorg. Chem.* **7**, 690 (1968).
46. Cavell, R. G., and Dobbie, R. C., *Inorg. Chem.* **7**, 101 (1968).
47. Cavell, R. G., *J. Chem. Soc.* p. 1992 (1964).
48. Cavell, R. G., Charlton, T. L., and Pinkerton, A. A., *Chem. Commun.* p. 424 (1969).
49. Cavell, R. G., and Nixon, J. F., *Proc. Chem. Soc.* p. 299 (1964).
50. Centofanti, L. F., and Parry, R. W., *Inorg. Chem.* **5**, 1005 (1968).
50a. Centofanti, L. F., Kodama, G., and Parry, R. W., *Inorg. Chem.* 8, 2072 (1969).
50b. Charlton, T. L., and Cavell, R. G., *Inorg. Chem.* **8**, 2436 (1969).
51. Chatt, J., Ahrland, S., and Davies, N. R., *Quart. Rev.* **12**, 265 (1958).
52. Chatt, J., *Nature* **165**, 637 (1950).
53. Chatt, J., and Williams, A. A., *J. Chem. Soc.* p. 3061 (1951).
54. *Chem. News.* October p. 52 (1964).
55. Childs, A. F., and Williams, L. T. D., British Patent 810,930 (1959); U.S. Patent 2,957,017 (1960).
56. Clark, R. J., *Inorg. Chem.* **3**, 1395 (1964).
57. Clark, R. J., *Inorg. Chem.* **6**, 299 (1967).
58. Clark, R. J., and Brimm, E. O., *Inorg. Chem.* **4**, 651 (1965).
59. Clark, R. J., and Hoberman, P. I., *Inorg. Chem.* **4**, 1771 (1965).
60. Clark, R. J., and Morgan, K. A., *Inorg. Chim. Acta* **2**, 93 (1968).
61. Clark, R. J., Hargaden, J. P., Haas, H., and Sheline, R. K., *Inorg. Chem.* **1**, 673 (1968).
62. Clark, R. J., Hoberman, P. I., and Brimm, E. O., *J. Inorg. Nucl. Chem.* **27**, 2109 (1968).

63. Clement, D. A., Sexton, M. D., and Nixon, J. F., *Chem. Commun.* p. 1509 (1969) and unpublished results.

64. Clune, J. E., and Cohn, K., *Inorg. Chem.* **1**, 2067 (1968).

65. Cohn, K., and Parry, R. W., *Inorg. Chem.* **7**, 46 (1968).

66. Cohn, K., quoted by Parry (*256*).

67. Cook, H. G., Ilett, J. D., Saunders, B. C., Stacey, G. J., Watson, H. G., Wilding, J. G. E., and Woodcock, S. J., *J. Chem. Soc.* p. 2921 (1949).

68. Cotton, F. A., *Inorg. Chem.* **3**, 702 (1964).

69. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 2nd ed., Chapter 27, Wiley, New York, 1968.

69a. Cowley, A. H., White, W. D., and Damasco, M. C., *J. Am. Chem. Soc.* **91**, 1922 (1969).

69b. Cowley, A. H., and White, W. D., *J. Am. Chem. Soc.*, 1917 (1969).

69c. Cowley, A. H., and Taylor, M. W., *J. Am. Chem. Soc.* **91**, 1929 (1969); **91**, 1026 (1969).

70. Crutchfield, M. M., Dungan, C. H., Letcher, J. H., Mark, V., and Van Wazer, J. R., *Topics Phosphorus Chem.*, **5**, 19 (1967).

71. Cullen, W. R., Dawson, D. S., and Dhaliwal, P. S., *Can. J. Chem.* **45**, 683 (1967).

72. Cunliffe, A. V., Finer, E. G., Harris, R. K., and McFarlane, W., *Mol. Phys.* **12**, 497 (1967).

73. Darensbourg, D. J., and Brown, T. L., *Inorg. Chem.* **7**, 959 (1968).

74. De Boer, B. G., Zalkin, A., and Templeton, D. H., *Inorg. Chem.* **8**, 836 (1969).

75. Deever, W. R., Lory, E. R., and Ritter, D. M., *Inorg. Chem.* **8**, 1263 (1969).

76. Deever, W. R., and Ritter, D. M., *J. Am. Chem. Soc.* **89**, 5073 (1967).

77. Delwaulle, M. L., and Bridoux, M., *Compt. Rend. Acad. Sci.* **248**. 1342 (1959).

78. Delwaulle, M. L., and Francois, F., *Compt. Rend. Acad. Sci.* **223**, 796 (1946); *J. Chim. Phys.* **46**, 87 (1949).

78a. Des Marteau, D. D., *J. Am. Chem. Soc.* **91**, 6211 (1969).

79. Dobbie, R. C., Doty, L. F., and Cavell, R. G., *J. Am. Chem. Soc.* **90**, 2015 (1968).

80. Dobson, G. R., and Houk, L. W., *Inorg. Chim. Acta* **1**, 287 (1967).

81. Drozd, G. I., Ivin, S. Z., and Sheluchenko, V. V., *Zh. Obshch. Khim.* **38**, 1655 (1968).

82. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., Tetel'baum, B. I., and Varshavskii, A. D., *Zh. Obshch. Khim.* **38**, 567 (1968).

83. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., and Tetel'baum, B. I., *Zh. Obshch. Khim.* **37**, 958 (1967).

84. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., Tetel'baum, B. I., Luganskii, G. M., and Varshavskii, A. D., *Zh. Obshch. Khim.* **37**, 1343 (1967).

85. Drozd, G. I., Ivin, S. Z., and Sheluchenko, V. V., *Zh. Obshch. Khim.* **38**, 1906 (1968).

86. Drozd, G. I., Sokalskii, M. A., Sheluchenko, V. V., Landau, M. A., and Ivin, S. Z., *Zh. Obshch. Khim.* **39**, 936 (1969); **39**, 935 (1969)

87. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., Tetel'baum, B. I., Luganskii, G. M., and Varshavskii, A. D., *Zh. Obshch. Khim.* **37**, 1631 (1967).

88. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., and Tetel'baum, B. I., *Zh. Obshch. Khim.* **37**, 957 (1967).

89. Drozd, G. I., Ivin, S. Z., and Sheluchenko, V. V., *Zh. Vses. Khim. Obshchestva im. D.I. Mendeleeva* **12**, 472 (1967).

90. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., and Landau, M. A., *Zh. Obshch. Khim.* **38**, 1653 (1968).

91. Drozd, G. I., Sokalskii, M. A., Ivin, S. Z., Sosova, E. P., and Strukov, O. G., *Zh. Obshch. Khim.* **39**, 936 (1969).

92. Drozd, G. I., and Ivin, S. Z., *Zh. Obshch. Khim.* **39**, 1179 (1969).

93. Drozd, G. I., Strukov, O. G., Sergeeva, E. P., Ivin, S. Z., and Dubov, S. S., *Zh. Obshch. Khim.* **39**, 937 (1969).

94. Drozd, G. I., Ivin, S. Z., Sheluchenko, V. V., and Tetel'baum, B. I., *Radiospek. Krant. Met. Strukt. Issled.* p. 204 (1967).

95. Drozd, G. I., and Ivin, S. Z., *Zh. Obshch. Khim.* **38**, 1907 (1968).

96. Drozd, G. I., Ivin, S. Z., Kulakova, V. N., and Sheluchenko, V. V., *Zh. Obshch. Khim.* **38**, 576 (1968).

97. Drozd, G. I., Ivin, S. Z., and Sheluchenko, V. V., *Zh. Vses, Khim. Obshchestva im. D.I. Mendeleeva* **12**, 474 (1967).

97a. Drozd, G. I., Ivin, S. Z., and Strukov, O. G., *Zh. Obshch. Khim.* **39**, 1418 (1969).

97b. Drozd, G. I., and Ivin, S. Z., *Zh. Obshch. Khim.* **39**, 1417 (1969).

98. Dumdahl, S. S., and Drago, R. S., *J. Am. Chem. Soc.* **90**, 6669 (1968).

98a. Eland, J. D., Green, J. C., Orchard, A. F., and Turner, D. W., unpublished results quoted in *131a*.

99. Emeleus, H. J., and Onak, T., *J. Chem. Soc. A* p. 1291 (1966).

100. Evtikhov, Zh. L., Razumova, N. A., and Petrov, A. A., *Dokl. Akad. Nauk. SSSR* **177**, 108 (1967).

101. Evtikhov, Zh. L., Razumova, N. A., and Petrov, A. A., *Zh. Obshch. Khim.* **38**, 465 (1969).

101a. Fessenden, R. W., and Schuler, R. H., *J. Chem. Phys.* **45**, 1845 (1966).

102. Fild, M., and Schmutzler, R., *J. Chem. Soc. A* p. 840 (1969).

103. Fild, M., and Schmutzler, R., Personal communication.

104. Finch, A., *Can. J. Chem.* **37**, 1793 (1959).

105. Flaskerud, G. G., Pullen, K. E., and Shreeve, J. M., *Inorg. Chem.* **8**, 728 (1969).

106. Flaskerud, G. C., and Shreeve, J. M., *Fluorine Symp., Goettingen 1968.*

107. Fleming, M. A., Ph.D. Dissertation, Univ. of Michigan, 1963.

108. Fleming, M. A., Wyma, R., and Taylor, R. C., *Spectrochim. Acta* **18**, 1387 (1962).

109. Fluck, E., *Z. Naturforsch.* **19b**, 869 (1964).

110. Fraser, G. W., Peacock, R. D., and Watkins, P. M., *Chem. Commun.* p. 1257 (1968).

111. Gilje, J. W., quoted by Parry (*121*).

112. Gillespie, R. J., *J. Chem. Soc.* p. 4672 (1963); *Angew Chem., Intern. Ed. Engl.* **6**, 819 (1967).

113. Gilliam, O. R., Edwards, H. D., and Gordy, W., *Phys. Rev.* **75**, 1014 (1949).

113a. Glemser, O., Niecke, E., and Müller, A., *Angew. Chem.* **78**, 593 (1966).

114. Gondal, S. K., MacDiarmid, A. G., Saalfield, F. E., and McDowell, M. V., *Inorg. Nucl. Chem. Letters* **5**, 351 (1969).

115. Goya, A. E., Rosario, M. D., and Gilje, J. W., *Inorg. Chem.* **8**, 725 (1969).

116. Graham, W. A. G., and Stone, F. G. A., *J. Inorg. Nucl. Chem.* **3**, 164 (1956).

117. Graham, W. A. G., *Inorg. Chem.* **7**, 315 (1968).

118. Green, M., Haszeldine, R. N., Isles, B. R., and Roswell, D. G., *J. Chem. Soc.* p. 6879 (1965).

118a. Greenberg, B., Amendola, A., and Schmutzler, R., *Naturwissenschaft.* **50,** 593 (1963).

119. Griffiths, J. E., and Burg, A. B., *J. Am. Chem. Soc.* **84,** 3442 (1962); **82,** 1507 (1961).

120. Griffiths, J. E., and Burg, A. B., *Proc. Chem. Soc.* p. 12 (1961).

120a. Grobe, J., and Kober, F., *Z. Naturforsch.* **24b,** 1660 (1969).

121. Grunbaum, J., and Nixon, J. F., Unpublished results.

122. Gutowsky, H. S., and McCall, D. W., *J. Chem. Phys.* **22,** 162 (1954).

123. Gutowsky, H. S., McCall, D. W., and Slichter, C. P., *J. Chem. Phys.* **21,** 279 (1953).

124. Gutowsky, H. S., and Larmann, J. P., *J. Am. Chem. Soc.* **87,** 3815 (1965).

125. Haas, H., and Sheline, R. K., *J. Chem. Phys.* **47,** 2996 (1967).

126. Hair, M. L., and Robinson, P. L., *J. Chem. Soc.* p. 106 (1958); unpublished results quoted in *Progr. Inorg. Chem.* p. 236 (1960).

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

128. Harris, G. S., and Payne, D. S., *Quart. Rev.* **15,** 173 (1961).

129. Harris, R. K., and Finer, E. G., *Bull. Soc. Chim. France* p. 2805 (1968).

130. Heaton, B. T., Ph.D. Thesis, Univ. of Sussex, 1967.

131. Hersh, O. L., *Dissertation Abstr.* **24,** 2286 (1963).

131a. Hillier, I. H., and Saunders, V. R., *Chem. Commun.* p. 316 (1970).

132. Holmes, R. R., and Wagner, R. P., *J. Am. Chem. Soc.* **84,** 357 (1962).

133. Holmes, R. R., and Gallagher, W. P., *Inorg. Chem.* **2,** 433 (1963).

134. Hovroka, A., and Weaver, E. E., *Am. Chem. Soc. Meeting, Buffalo, 1952.*

135. Ionin, B. I., *Zh. Obshch. Khim.* **38,** 1659 (1968).

136. Ivanova, Zh. M., *Zh. Obshch. Khim.* **34,** 858 (1964).

137. Ivanova, Zh. M., Stukalo, E. A., and Derkach, G. I., *Zh. Obshch. Khim.* **38,** 551 (1968).

138. Ivanova, Zh. M., *Zh. Obshch. Khim.* **35,** 164 (1965).

139. Ivanova, Zh. M., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31,** 3991 (1961).

140. Ivin, S. Z., Zinov'-ev, Y. M., Kulakova, V. N., and Drozd, G. I., *Izobret. Prom. Obrat. Tov. Znak.* **43,** 21 (1966).

141. Jefferson, R., Nixon, J. F., and Painter, T. M., *Chem. Commun.* p. 622 (1969).

142. Johanssen, R. B., *J. Chem. Phys.* **47,** 3088 (1967).

143. Johnson, F. A., and Rudolph, R. W., *J. Chem. Phys.* **47,** 5449 (1967).

144. Johnson, T. R., and Nixon, J. F., *J. Chem. Soc. A* p. 2518 (1969).

145. Johnson, T. R., M.Sc. Thesis, Sussex Univ. (1968).

145a. Johnson, T. R., Lynden-Bell, R. M., and Nixon, J. F., *J. Organometal. Chem.* **21,** 15 (1970).

146. Kasenally, A. S., Nyholm, R. S., Parker, D. J., Stiddard, M. H. B., Hodder, O. J. R., and Powell, H. M., *Chem. Ind.* (*London*) p. 2097 (1965).

146a. Keat, R. Personal communication.

147. Kiser, R. W., Krassoi, M. A., and Clark, R. J., *J. Am. Chem. Soc.* **89,** 3654 (1967).

148. Kodama, G., and Parry, R. W., *Inorg. Chem.* **4,** 410 (1965).

149. Kolditz, L., and Bauer, K., *Z. Anorg. Chem.* **302,** 241 (1959).

150. Kolka, A. J., U.S. Patent 2,866,809 (1958).

151. Komkov, I. P., Ivin, S. Z., Karawanov, K. W., and Smirnov, L. J., *Zh. Obshch. Khim.* **32,** 301 (1962).

152. Kruck, T., *Angew. Chem., Intern. Ed. Engl.* **6**, 53 (1967).
153. Kruck, T., *Z. Naturforsch.* **19b**, 165 (1964).
154. Kruck, T., *Ber.* **97**, 2018 (1964).
155. Kruck, T., and Prasch, A., *Z. Naturforsch.* **19b**, 670 (1964).
156. Kruck, T., and Lang, W., *Angew. Chem.* **76**, 787 (1964).
157. Kruck, T., and Prasch, A., *Angew. Chem.* **76**, 892 (1964).
158. Kruck, T., Lang, W., and Engelmann, A., *Angew. Chem.* **77**, 132 (1965).
159. Kruck, T., and Lang, W., *Ber.* **98**, 3060 (1965).
160. Kruck, T., and Baur, K., *Ber.* **98**, 3070 (1965).
161. Kruck, T., and Baur, K., *Angew. Chem.* **77**, 505 (1965).
162. Kruck, T., Lang, W., and Derner, N., *Z. Naturforsch.* **20b**, 705 (1965).
163. Kruck, T., and Lang, W., *Angew. Chem.* **77**, 860 (1965).
164. Kruck, T., and Lang, W., *Z. Anorg. Chem.* **343**, 181 (1966).
165. Kruck, T., Hieber, W., and Lang, W., *Angew. Chem.* **78**, 208 (1966).
166. Kruck, T., Engelmann, A., and Lang, W., *Ber.* **99**, 2473 (1966).
167. Kruck, T., and Lang, W., *Ber.* **99**, 3794 (1966).
168. Kruck, T., Derner, N., and Lang, W., *Z. Naturforsch.* **21b**, 1020 (1966).
169. Kruck, T., and Englemann, A., *Angew. Chem. Intern. Ed. Engl.* **9**, 836 (1966).
170. Kruck, T., and Lang, W., *Angew. Chem.* **79**, 474 (1967).
171. Kruck, T., and Prasch, A., *Angew. Chem.* **356**, 118 (1968).
172. Kruck, T., Baur, K., and Lang, W., *Ber.* **101**, 138 (1968).
173. Kruck, T., and Baur, K., *Z. Anorg. Chem.* **364**, 192 (1969).
174. Kruck, T., Baur, K., Glinka, K., and Stadler, M., *Z. Naturforsch.* **23b**, 1147 (1968).
175. Kruck, T., Lang, W., Derner, N., and Stadler, M., *Ber.* **101**, 3816 (1968).
176. Kruck, T., Höfler, M., Baur, K., Junkes, P., and Glinka, K., *Ber.* **101**, 3827 (1968).
177. Kruck, T., Höfler, M., Jung, H., and Blume, H., *Angew. Chem., Intern. Ed. Engl.* **8**, 522 (1969).
178. Kruck, T., and Höfler, M., *Angew. Chem.* **79**, 582 (1967).
178a. Kruck, T., and Prasch, A., *Z. Anorg. Chem.* **371**, 1 (1969).
179. Kruglyak, U. L., Malekin, S. I., and Martynov, I. V., *Zh. Obshch. Khim.* **39**, 466 (1969).
180. Kuczkowski, R. L., *J. Am. Chem. Soc.* **90**, 1705 (1968).
181. Kuczowski, R. L., and Lide, D. R., *J. Chem. Phys.* **46**, 357 (1967).
182. Kulakova, V. N., Zinovev, Y. M., Makarov, S. P., Shpanskii, V. A., and Soborovskii, L. Z., *Zh. Obshch. Khim.* **39**, 385 (1969).
183. Kulakova, V. N., Zinovev, Y. M., and Soborovskii, L. Z., *Zh. Obshch. Khim.* **29**, 3957 (1959).
184. Kulakova, V. N., Zinovev, Y. M., and Soborovskii, L. Z., *Zh. Obshch. Khim.* **39**, 838 (1969).
185. Kulakova, V. N., Zinovev, Y. M., and Soborovskii, L. Z., *Zh. Obshch. Khim.* **39**, 579 (1969).
186. Lang, W., Ph.D. Thesis, Munich, 1967.
187. La Prade, M. D., and Nordman, C. E., *Inorg. Chem.* **8**, 1669 (1969).
188. Letcher, J. H., and Van Wazer, J. R., *J. Chem. Phys.* **45**, 2916 (1966); **45**, 2926 (1966).
189. Letcher, J. H., and Van Wazer, J. R., *J. Chem. Phys.* **44**, 815 (1966).
190. Loutelier, A., and Bigorgne, M., *Bull. Soc. Chim. France* **11**, 3186 (1965).
191. Lucken, E. A. C., Noack, K., and Williams, D. F., *J. Chem. Soc. A* p. 148 (1967).

192. Lustig, M., Ruff, J. K., and Colburn, C. B., *J. Am. Chem. Soc.* **88**, 3875 (1966).

193. Lustig, M., *Inorg. Chem.* **7**, 2054 (1968).

194. Lustig, M., and Hill, W. E., *Inorg. Chem.* **6**, 1448 (1967).

195. Lynden-Bell, R. M., *Trans. Farad. Soc.* **57**, 888 (1961); *Mol. Phys.* **6**, 601 (1963).

196. Lynden-Bell, R. M., *Mol. Phys.* **15**, 523 (1968).

197. Lynden-Bell, R. M., McFarlane, W., Nixon, J. F., and Roberts, J., Unpublished results.

198. Lynden-Bell, R. M., Nixon, J. F., and Schmutzler, R., *Coordination Conf. Paris, 1969*; *J. Chem. Soc. A*, p. 565 (1970).

199. Lynden-Bell, R. M., and Nixon, J. F., unpublished results, quoted in Nixon and Pidcock (*242*).

200. Mannett, S. L., Ellemann, D. D., Cowley, A. H., and Burg, A. B., *J. Am. Chem. Soc.* **89**, 4544 (1967).

200a. Marriott, J. C., Salthouse, J. A., Ware, M. J., and Freeman, J. M., *Chem. Commun.* p. 595 (1970).

201. Martin, D. R., Cooper, W. D., Spessard, D. R., and Booth, H. S., *J. Am. Chem. Soc.* **74**, 809 (1952).

202. Martin, D. R., and Pizzolato, P. J., *J. Am. Chem. Soc.* **72**, 4584 (1950); *Inorg. Syn.* **4**, 141 (1953).

203. Martynov, I. V., Kruglyak, Y. L., and Malekin, S. I., *Zh. Obshch. Khim.* **38**, 2343 (1968).

204. Mavel, G., *J. Chim. Phys.* **65**, 1692 (1968).

205. McCombie, H., and Saunders, B. C., *Nature* **157**, 776 (1946).

206. Miles, W. J., and Clark, R. J., *Inorg. Chem.* **7**, 1801 (1968).

206a. Miles, W. J., Garrett, B. B., and Clark, R. J., *Inorg. Chem.* **8**, 2817 (1969).

207. Miller, J. M., *J. Chem. Soc. A* p. 828 (1967).

208. Mirri, A., *J. Chem. Phys.* **47**, 2823 (1967).

209. Mirri, A., Scappini, F., and Favero, P. G., *Spectrochim. Acta* **21**, 965 (1965).

210. Moissan, H., *Bull. Soc. Chim. France* **5**, 454 (1891); *Compt. Rend. Acad. Sci.* **102**, 763 (1886).

211. Morino, Y., Kuchitzu, K., and Moritani, T., *Inorg. Chem.* **8**, 867 (1969).

212. Morris, E. D., and Nordman, C. E., *Inorg. Chem.* **8**, 1673 (1969).

213. Morse, J. G., Cohn, K., Rudolph, R. W., and Parry, R. W., *Inorg. Syn.* **10**, 147 (1967).

214. Morse, K. W., and Parry, R. W., *J. Am. Chem. Soc.* **89**, 172 (1967).

215. Muetterties, E. L., Bither, T. A., Farlow, M. W., and Coffmann, D. D., *J. Inorg. Nucl. Chem.* **16**, 52 (1961).

216. Muetterties, E. L., and Schunn, R. A., *Quart. Rev.* **20**, 245 (1966).

217. Müller, A., Niecke, E., and Glemser, O., *Z. Anorg. Chem.* **350**, 256 (1967).

218. Müller, A., Glemser, O., and Niecke, E., *Z. Naturforsch.* **21b**, 732 (1966).

219. Müller, A., Niecke, E., Krebs, B., and Glemser, O., *Z. Naturforsch.* **23b**, 588 (1968).

219a. Müller, A., Niecke, E., and Krebs, B., *Mol. Phys.* **14**, 591 (1968).

220. Murray, M., and Schmutzler, R., *Chem. Ind.* (*London*) p. 1730 (1968).

221. Murray, M., and Schmutzler, R., *Z. Chem.* **7**, 241 (1968).

222. Nagarajan, G., and Durig, J. R., *Montash.* **98**, 1545 (1967).

223. Newmark, R. A., Nordman, A. D., and Rudolph, R. W., *Chem. Commun.* p. 893 (1969).

224. Nixon, J. F., Keat, R., and Painter, T. M., Unpublished results.

225. Nixon, J. F., *J. Chem. Soc.* p. 2469 (1964).

226. Nixon, J. F., and Schmutzler, R., *Spectrochim. Acta* **20**, 1835 (1964).

227. Nixon, J. F., and Cavell, R. G., *J. Chem. Soc.* p. 5983 (1964).

228. Nixon, J. F., and Schmutzler, R., Unpublished observations.

229. Nixon, J. F., *Chem. Ind.* (*London*) p. 1555 (1963).

230. Nixon, J. F., *J. Inorg. Nucl. Chem.* **27**, 1215 (1965).

231. Nixon, J. F., *J. Chem. Soc.* p. 777 (1965).

232. Nixon, J. F., *Chem. Commun.* p. 34 (1966).

233. Nixon, J. F., *J. Chem. Soc. A* p. 1136 (1967).

234. Nixon, J. F., and Sexton, M. D., *Inorg. Nucl. Chem. Letters* **4**, 275 (1968).

235. Nixon, J. F., and Swain, J. R., *Chem. Commun.* p. 997 (1968).

236. Nixon, J. F., *J. Chem. Soc. A*, p. 2689 (1968).

237. Nixon, J. F., *Chem. Commun.* p. 669 (1967).

238. Nixon, J. F., and Swain, J. R., *Inorg. Nucl. Chem. Letters* p. 295 (1969).

239. Nixon, J. F., *J. Chem. Soc. A* p. 1087 (1969).

240. Nixon, J. F., and Sexton, M. D., *J. Chem. Soc. A* p. 1089 (1969).

241. Nixon, J. F., and Sexton, M. D., Unpublished results.

242. Nixon, J. F., and Pidcock, A., *Ann. Rev. NMR Spectroscopy* **2**, 345 (1969).

243. Nixon, J. F., and Peppiat, R., Unpublished results.

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

245. Nixon, J. F., and Sexton, M. D., *Chem. Commun.* p. 827 (1969).

246. Nixon, J. F., and Jefferson, R., Unpublished results.

247. Nixon, J. F., and Sexton, M. D., *J. Chem. Soc. A* p. 321 (1970).

248. Nixon, J. F., Murray, M., and Schmutzler, R., *Intern. Coordination Colloq., Paris, 1969*; *Z. Naturforsch* **25b**, 110 (1970)

249. Nixon, J. F., and Swain, J. R., *J. Chem. Soc. A* p. 2075 (1970).

249a. Nixon, J. F., Unpublished results.

250. Nixon, J. F., Swain, J. R., Unpublished results.

250a. Nixon, J. F., and Wilkins, B., *Z. Naturforsch.* **25b**, 649 (1970).

251. Noble, A. M., Walker, D. W., and Winfield, J. M., *Fluorine Symp. Goettingen, 1968.*

251a. Nordman, A. D., and Schaeffer, R., *J. Am. Chem. Soc.* **88**, 1143 (1966).

252. Nöth, H., *Ber.* **96**, 1109 (1963); **96**, 1298 (1963).

252a. Ogilvie, F., Clark, R. J., and Verkade, J. G., *Inorg. Chem.* **8**, 1904 (1969).

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

254. Parker, D. J., and Stiddard, M. H. B., *J. Chem. Soc. A* p. 695 (1966).

255. Parry, R. W., and Bissot, T. C., *J. Am. Chem. Soc.* **78**, 1524 (1956).

256. Parry, R. W., *In* "Coordination Chemistry" (S. Kirchener, ed.), p. 207, 1969.

257. Parry, R. W., and Centofanti, L. F., *Fluorine Symp., Goettingen, 1968.*

258. Pauling, L., and Brockway, L. O., *J. Am. Chem. Soc.* **57**, 2684 (1935).

259. Pearson, R. G., *J. Am. Chem. Soc.* **85**, 3533 (1963).

260. Petrov, K. A., Sokolsky, G. A., and Polees, B. M., *Zh. Obshch. Khim.* **26**, 3681 (1956).

261. Petrov, K. A., Neimysheva, A. A., Fomenko, M. G., Chernushevich, L. M., and Knuntsevich, A. D., *Zh. Obshch. Khim.* **31**, 516 (1961).

262. Pidcock, A., Richards, R. E., and Venanzi, L. M., *J. Chem. Soc. A* p. 1707 (1966).

263. Pitcher, E., Buckingham, A. D., and Stone, F. G. A., *J. Chem. Phys.* **36**, 124 (1962).

264. Pople, J. A., and Santry, D. P., *Mol. Phys.* **8**, 1 (1964).

265. Powell, H. M., Unpublished results, quoted in Parker and Stiddard (*254*).

266. Rahskys, J. W., Taft, R. W., and Sheppard, W. A., *J. Am. Chem. Soc.* **90**, 5236 (1968).

266a. Rankin, D. W. H. Personal communication (1970).

267. Razumova, N. A., Evtikhov, Z. L., Zubtsova, L. I., and Petrov, A. A., *Zh. Obshch. Khim.* **38**, 2342 (1968).

268. Razumova, N. A., Evtikhov, Z. L., and Petrov, A. A., *Zh. Obshch. Khim.* **38**, 1117 (1968). **39**, 1419 (1969).

269. Razumova, N. A., Evtikhov, Z. L., Voznesenskaya, A. K., and Petrov, A. A., *Zh. Obshch. Khim.* **39**, 176 (1969).

270. Reddy, G. S., and Schmutzler, R., *Z. Naturforsch.* **20b**, 104 (1965).

271. Reddy, G. S., and Schmutzler, R., *Inorg. Chem.* **6**, 823 (1967).

272. Riess, J. G., and Van Wazer, J. R., *J. Am. Chem. Soc.* **88**, 2339 (1966).

273. Roesky, H. W., *Ber.* **100**, 2142 (1967).

273a. Roesky, H. W., *Inorg. Nucl. Chem. Letters* p. 891 (1969).

274. Rudolph, R. W., Taylor, R. C., and Parry, R. W., *J. Am. Chem. Soc.* **88**, 3729 (1966).

275. Rudolph, R. W., and Schiller, H. W., *J. Am. Chem. Soc.* **90**, 3581 (1968).

276. Rudolph, R. W., and Parry, R. W., *Inorg. Chem.* **4**, 1339 (1965); **6**, **1070** (1967); *J. Am. Chem. Soc.* **89**, 1621 (1967).

277. Rudolph, R. W., Morse, J. G., and Parry, R. W., *Inorg. Chem.* **5**, 1464 (1966).

278. Ruff, J. K., *Inorg. Chem.* **2**, 813 (1963).

279. Saalfield, F. E., McDowell, M. V., Gondal, S. K., and MacDiarmid, A. G., *J. Am. Chem. Soc.* **90**, 3684 (1968).

279a. Salthouse, J. A. Personal communication.

280. Santry, D. P., and Segal, G. A., *J. Chem. Phys.* **47**, 158 (1967).

281. Schmutzler, R., *Advan. Chem. Ser.* **37**, 150 (1963).

282. Schmutzler, R., *Advan. Fluorine Chem.* **5**, 31 (1965).

283. Schmutzler, R., *Chem. Ind.* (*London*) p. 1868 (1962).

284. Schmutzler, R., *Ber.* **96**, 2435 (1963).

285. Schmutzler, R., *J. Inorg. Nucl. Chem.* **25**, 335 (1963).

286. Schmutzler, R., *Inorg. Chem.* **3**, 410 (1964).

287. Schmutzler, R., *Inorg. Chem.* **3**, 415 (1964).

288. Schmutzler, R., *Angew. Chem.* **76**, 570 (1964).

289. Schmutzler, R., *J. Chem. Soc.* p. 4551 (1964).

290. Schmutzler, R., *J. Chem. Soc.* p. 5630 (1965).

291. Schmutzler, R., Unpublished results.

292. Schmutzler, R., *Ber.* **98**, 552 (1965).

293. Schmutzler, R., *Chem. Commun.* p. 19 (1965).

294. Schrader, G., and Bayer, O., U.S. Patent 2,146,356; German Patent 664,438; French Patent 807,769.

295. Seel, F., Ballreich, K., and Schmutzler, R., *Ber.* **94**, 1173 (1961).

296. Seel, F., and Rudolph, K., *Z. Anorg. Chem.* **363**, 233 (1968).

297. Seel, F., Rudolph, K., and Gombler, W., *Angew. Chem.* **79**, 686 (1967).

298. Seel, F., Rudolph, K., and Budenz, R., *Z. Anorg. Chem.* **341**, 196 (1965).

299. Seel, F., Jones, H., Riehl, L., and Langer, J., *Angew. Chem.* **67**, 32 (1955).

300. Sheluchenko, V. V., Landau, M. A., Dubov, S. S., Neimysheva, A. A., and Knunyants, I. L., *Dokl. Akad. Nauk. SSSR* **177**, 376 (1967).

301. Sheluchenko, V. V., Dubov, S. S., Drozd, G. I., and Ivin, S. Z., *Zh. Strukt. Khim.* p. 909 (1968).

302. Shreeve, J. M., *J. Inorg. Nucl. Chem.* p. 3375 (1968).

303. Shreeve, J. M., *Am. Chem. Soc. Meeting, Atlantic City, 1968.*

304. Soborovskii, L. Z., and Golobov, Y. G., *Zh. Obshch. Khim.* **34**, 1141 (1964).

305. Solan, D., and Timms, P. L., *Chem. Commun.* p. 1540 (1968).

306. Spielman, J. R., and Burg, A. B., *Inorg. Chem.* **2**, 1139 (1963).

307. Sterlin, R. N., Yatsenko, R. D., Pinkina, L. N., and Knunyants, I. L., *Izv. Akad. Nauk SSSR* p. 1991 (1960).

308. Sterlin, R. N., Yatsenko, R. D., Pinkina, L. N., and Knunyants, I. L., *Khim. Nauka Prom.* **4**, 810 (1959).

309. Stewart, R. P., and Treichel, P. M., *Inorg. Chem.* **7**, 1942 (1968).

310. Street, G. B., and Burg, A. B., *Inorg. Nucl. Chem. Letters* **1**, 47 (1965).

311. Stroheimer, W., and Muller, F. J., *Z. Naturforsch.* **22b**, 451 (1967).

312. Sullivan, R. E., and Kiser, R. W., *Chem. Commun.* p. 1425 (1968).

313. Svatos, G. F., and Flagg, E. E., *Inorg. Chem.* **4**, 422 (1965).

314. Ter Haar, G., Fleming, M. A., and Parry, R. W., *J. Am. Chem. Soc.* **84**, 1767 (1962).

315. Tetelbaum, B. I., Sheluchenko, V. V., Dubov, S. S., Drozd, G. I., and Ivin, S. Z., *Zh. Vses. Khim. Obshchestva im. D.I. Mendeleeva* **12**, 351 (1967).

316. Timms, P. L., *J. Am. Chem. Soc.* **89**, 1629 (1967).

316a. Timms, P. L., *Chem. Commun.* p. 1033 (1969) and Personal communication.

317. Tripathi, J. B., and Bigorgne, M., *J. Organometal. Chem.* **9**, 307 (1967).

318. Udovich, C. A., and Clark, R. J., *J. Am. Chem. Soc.* **91**, 526 (1969).

319. Udovich, C. A., Clark, R. J., and Haas, H., *Inorg. Chem.* **8**, 1066 (1969).

320. Udovich, C. A., and Clark, R. J., *Inorg. Chem.* **8**, 939 (1969).

321. Venanzi, L. M., *Chem. Britain* p. 162 (1968).

322. Verkade, J. G., Personal communication.

323. Vilkov, L. V., and Khaikin, L. S., *Dokl. Akad. Nauk SSSR* **168**, 810 (1966).

323a. Wan, J. K. S., Morton, J. R., and Bernstein, H. J., *Can. J. Chem.* **44**, 1957 (1966).

323b. Warren, J. D., and Clark, R. J., *Inorg. Chem.* **9**, 373 (1970).

323c. Wei, M. S., Current, J. H., and Gendell, J., *J. Chem. Phys.* **52**, 1592 (1970).

324. Wilkins, C. J., *J. Chem. Soc.* p. 2726 (1951).

325. Wilkinson, G., *Nature* **168**, 514 (1951); *J. Am. Chem. Soc.* **73**, 5501 (1951).

326. Woodward, L. A., and Hall, J. R., *Nature* **181**, 831 (1958); *Spectrochim. Acta* **16**, 654 (1960).