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TRIFLUOROPHOSPHINE COMPLEXES OF TRANSITION METALS

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I. Introduction

Transition metal carbonyl chemistry originated with the discovery of $[Ni(CO)_4]$ in 1890. Although the first trifluorophosphine coordination complex was prepared the following year by Moissan (*263*) by treating

phosphorus pentafluoride with platinum black, its identity was not recognized at the time, and almost 60 years passed before interest in PF_3 as a ligand arose.

In 1949, Chatt (*62*) suggested that the trans influence of ligands like ethylene, carbon monoxide, and, to a lesser extent, trialkylphosphines in square-planar platinum(II) complexes was related to back donation of *d*-electron density from the transition metal to suitable empty orbitals of the ligands. It was proposed that such back bonding should be enhanced in PF_3 complexes because of the presence of the highly electronegative fluorine atoms.

Soon afterwards, Chatt and Williams (*63*) tested this idea by bubbling PF_3 over heated platinum(II) chloride and isolated the crystalline complexes $[PtCl_2(PF_3)_2]$ and $[PtCl_2(PF_3)]_2$. Carbon monoxide was also readily displaced from $[Ni(CO)_4]$ by PF_3 and later work showed that all possible $[Ni(CO)_x(PF_3)_{4-x}]$ complexes can be formed. In the same year Wilkinson (*361*) achieved the first synthesis of the volatile liquid complex $[Ni(PF_3)_4]$ which exhibited considerably greater thermal stability than $[Ni(CO)_4]$.

The close similarity between transition metal PF_3 complexes and their CO analogues is indicated by a variety of studies (*72, 174, 272*), and has been rationalized in terms of a bonding scheme for PF_3 involving (1) a σ-donor component from donation of the phosphorus lone pair electrons to the metal, and (2) a symmetry-allowed π bond involving back donation of metal *d* electrons into empty 3*d* orbitals on phosphorus.

Experimental methods to study the nature of the metal–phosphorus bond in transition metal–phosphine complexes usually reveal only its overall nature, and the degree of d_π–d_π participation can only be inferred after assumptions have been made about the σ component. This area has been controversial (*248*) and a review by Pidcock (*299*) gives an excellent account of all the factors involved. Clearly the degree of any π bonding will be affected by the nature of the metal and its oxidation state, its attendant ligands, and the type of phosphines involved. The formation of $[BH_3 \cdot PF_3]$ and $[AlCl_3 \cdot PF_3]$ indicates that back donation is not a prerequisite for the existence of trifluorophosphine complexes; however, these compounds are extremely unstable compared to their transition metal–PF_3 counterparts and σ bonding alone is unlikely to account for the extensive range of PF_3 transition metal complexes now known (*vide infra*). Likewise, in metallate salts of the type $[M(PF_3)_x]^{n-}$ some mechanism is almost certainly necessary for removal of the negative charge. Further insight into the nature of PF_3 bonded to transition metals has come both from theoretical calculations and gas-phase photo-

electron spectroscopic measurements on the volatile complexes (see Section V).

This article is concerned with synthetic, structural, and spectroscopic aspects of an extensive range of transition metal PF_3 complexes including a wide variety of organometallic derivatives. Often, PF_3 can stabilize novel systems which have no precedent with other phosphine ligands. Likewise, the presence of ^{31}P and ^{19}F nuclei (both $I = \frac{1}{2}$, 100% abundant) offers NMR spectroscopic advantages in structural assignments and in the study of inter- and intramolecular ligand-exchange processes. This review covers publications up to early 1984 and complements previous articles (*72, 174, 272, 273, 292, 323*) covering the period up to 1975.

II. Binary Compounds

The first zero-valent binary transition metal–trifluorophosphine complex to be reported was $[Ni(PF_3)_4]$ made by Wilkinson in 1951 (*361*) by the interaction of $[Ni(PX_3)_4]$ (X = Cl, Br) with PF_3 (50–100 atm, 100°C) (method A). This is not a generally useful route, however, and although it was shown by using $^{32}PCl_3$ that the mechanism of the reaction involves ligand exchange rather than halogen exchange, the latter can be readily achieved (method B) using SbF_3 or KSO_2F as fluorinating agents.

$$Ni(PX_3)_4 \xrightarrow{PF_3} Ni(PF_3)_4 \qquad (X = Cl, Br)$$

$$Ni(PCl_3)_4 \xrightarrow[KSO_2F]{SbF_3 \text{ or}} Ni(PF_3)_4$$

By far the most extensively used synthetic route involves the technique of "reductive fluorophosphination" developed by T. Kruck and co-workers (*174*), who have made many important contributions to the development of the field of transition metal–PF_3 chemistry. In this method the appropriate metal halide is heated in an autoclave (usually copper-lined) with reducing agents, e.g., copper or zinc, in the presence of PF_3(50–500 atm) (method C). For example,

$$MCl_3 \xrightarrow{Cu/PF_3} M(PF_3)_5 \qquad (M = Ru, Os)$$

$$RhCl_3 \xrightarrow{Cu/PF_3} Rh_2(PF_3)_8$$

$$ReCl_5 \xrightarrow{Cu/PF_3} Re_2(PF_3)_{10}$$

$$MX_2 \xrightarrow{Cu/PF_3} M(PF_3)_4 \qquad (M = Ni, Pd, Pt; X = Cl, I)$$

$$WF_6 \xrightarrow{Cu/PF_3} W(PF_3)_6$$

A few complexes have been made by reduction of their oxides in the presence of PF_3 under extremely forcing conditions (method D) (e.g., 300°C, 4000 atm).

$$MO_3 \xrightarrow{Mg/PF_3} M(PF_3)_6 \qquad (M = Mo, W)$$
$$NiO \longrightarrow Ni(PF_3)_4$$

In some cases the presence of a metal reducing agent is superfluous since PF_3 can act as both a reducing agent and as a ligand (method E).

$$MCl_n \xrightarrow{PF_3} M(PF_3)_4 + PF_3Cl_2 \qquad (n = 2, 4; M = Pd, Pt)$$

Likewise, the direct synthesis of $[M(PF_3)_4]$ (M = Ni, Pd, Pt) complexes has been achieved from the appropriate metal powder (method F), or alternatively under very mild conditions from highly reactive forms of the metal (e.g., Ni) generated either from the decomposition of nickel oxalate or nickel tetracarbonyl or activated by sulfide (method G).

$$M(s) + 4PF_3 \xrightarrow[250\ atm/100^\circ]{PF_3} M(PF_3)_4 \qquad (M = Ni, Pd, Pt)$$

Not surprisingly, in recent years the technique of metal vapor synthesis, in which the metal vapor and PF_3 are cocondensed at liquid nitrogen temperatures, has found general application since PF_3 is readily condensible (in contrast to CO) and the high volatility of the resulting metal–PF_3 complexes facilitates their isolation (method H).

$$M(vap) \xrightarrow{PF_3} M(PF_3)_4 \qquad (M = Ni, Pd)$$
$$Cr(vap) \xrightarrow{PF_3} Cr(PF_3)_6$$
$$Fe(vap) \xrightarrow{PF_3} Fe(PF_3)_5$$

Interestingly, no PF_3 complex has been obtained so far using Mn vapor and there is a very recent report of the formation of the uranium complex $[U(PF_3)_6]$ using this technique, although the formulation is based solely on its mass spectrum (*302*).

Other synthetic routes involving mild conditions and not requiring specialized apparatus involve displacement of carbon monoxide from metal carbonyls (method I) or coordinated organic ligands (arenes,

η^5-cyclopentadienyl, η^3-allyl, etc.) (method J), e.g.,

$$Fe(CO)_5 \xrightarrow[h\nu]{PF_3} Fe(PF_3)_5$$

$$Ru_3(CO)_{12} \xrightarrow{PF_3} Ru(PF_3)_5$$

$$Ni(\eta^5\text{-}C_5H_5)_2 \xrightarrow{PF_3} Ni(PF_3)_4$$

$$M(\eta^6\text{-}C_6H_6)_2 \xrightarrow{PF_3} M(PF_3)_6 \quad (M = Cr, Mo)$$

$$Cr(\eta^3\text{-}C_3H_5)_3 \xrightarrow{PF_3} Cr(PF_3)_6$$

Dinuclear complexes have been made by photolysis of the related hydrido complex (*vide infra*) (method K) or by interaction of halogeno PF_3–metal derivatives with the trifluorophosphine metallate salt (method L).

$$IrH(PF_3)_4 \xrightarrow{h\nu} Ir_2(PF_3)_8$$

$$[RhCl(PF_3)_2]_2 \xrightarrow[PF_3]{KRh(PF_3)_4} Rh_2(PF_3)_8$$

Binary complexes are listed in Table I, together with references to physical and spectroscopic measurements made on them.

III. Hydrides

An interesting feature of hydrido transition metal–PF_3 complexes is that apart from a few dinuclear systems (Section VI) only mononuclear systems are so far known and there is as yet no corresponding chemistry analogous to that of polynuclear carbonyl hydrido compounds. The trifluorophosphine metal hydrido compounds are usually highly acidic and can readily form metallate ions such as $[M(PF_3)_m]^{x-}$ and $[MH(PF_3)_n]^{y-}$.

The reductive fluorophosphination of metal halides in the presence of copper and hydrogen gas at high temperature and pressure offers a useful synthetic route for a number of hydrido trifluorophosphine metal complexes (method A).

$$ReCl_5 \xrightarrow{Cu/PF_3/H_2} ReH(PF_3)_5$$

$$MCl_3 \xrightarrow{Cu/PF_3/H_2} MH_2(PF_3)_4 \quad (M = Ru, Os)$$

$$CoX_2 \xrightarrow{Cu/PF_3/H_2} CoH(PF_3)_4 \quad (X = Cl, Br, I)$$

$$M'Cl_3 \xrightarrow{Cu/PF_3/H_2} M'H(PF_3)_4 \quad (M' = Rh, Ir)$$

TABLE I

BINARY TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	δ_P[a]	ϕ_F[b]	$^1J_{PF}$[c]	Remarks	Reference
$Cr(PF_3)_6$[d]	(H) (I) (J)	Colorless	193 subl., $30/10^{-3}$, dec. >300	—	−8.4	1271	IR (*175, 176, 183, 215, 228*) NMR (*183*) MS (*228*) Raman (*228*)	*125, 174–176, 183 215, 228, 340, 341*
$Fe(PF_3)_5$[e]	(C) (H) (I) (J)	Yellow	44, 45, subl. $30/10^{-3}$, (dec. >270	−163.5	−1.9 +11.0	1275 1218[f]	IR (*70, 191, 218, 219*) NMR (*191, 218*) Raman (*218*) MS (*105, 218*) Var. temp. ^{19}F NMR (*251*)	*70, 118, 174, 191 218, 219, 251, 325, 340, 341*
$Ni(PF_3)_4$[g,h]	(A) (B) (C) (D) (F) (G) (I) (H) (J)	Colorless	−55, dec. >155, (0/33.8) (14/69.3) (25/120.5) (67.8/730) (70.5/760) v.p. 0/32.5 0/34	+137.7	+16.8	1347	NMR (*11, 61, 71, 191, 233, 235, 249, 254, 274, 275, 258, 305, 312, 334–336*) IR (*92–95, 108, 178, 191, 215, 230–233, 275, 324, 331, 360, 363, 364*) Raman (*93, 108, 231, 233, 363, 364*) MS (*181, 267, 268, 335*)	*68, 71, 75, 108, 128, 174, 178, 180, 191, 233, 264, 274, 275, 286, 287, 312, 324, 325, 334, 340, 341, 361, 364*
$Mo(PF_3)_6$[i,j]	(C) (D) (I) (J)	Colorless	196, dec. <250, subl. $20/10^{-3}$, v.p. 1.5 torr at 295 K	—	−2.6	1246	IR (*73, 176, 183, 215, 228*) NMR (*10, 183*) MS (*228*) Raman (*228*)	*73, 128, 174, 176, 183, 215, 228*

$Ru(PF_3)_5$[k]	(C) (I)	Colorless	30, subl. $25/10^{-3}$, dec. >155	−148.5	−2.4 +11.2	1320 1209[f]	NMR (*218*) IR (*218, 350*) Raman (*218*) Var. temp. ^{19}F NMR (*251*)	*174, 218, 350*
$Rh_2(PF_3)_8$[l]	(C) (K)	Orange-red	92.5, dec. >100, subl. $20/10^{-3}$	−114 ± 2	+2.98	1342	NMR (*17*) IR (*17*) Variable temp. ^{19}F NMR (*19*)	*17, 174, 182*
$Pd(PF_3)_4$[m]	(C) (D) (E) (H) (I) (J)	Colorless liquid	−41, dec. > −20	−95.5	+14.92	1350	NMR (*177, 336*) IR (*108, 177, 179, 331, 336, 360*) Raman (*108*)	*108, 174, 177, 179, 180, 331, 336, 341*
$W(PF_3)_6$[n]	(C) (D) (I)	Colorless	214, subl. $40/10^{-3}$, dec. >320, v.p. 1.5 torr at 295 K	—	0.5	1241	IR (*183, 210, 228*) NMR (*183*) Raman (*228*)	*174, 183, 210, 228* *128*
$Re_2(PF_3)_{10}$	(C)	Colorless	182, subl. $70/10^{-3}$, dec. >228	—	—	—	—	*174, 186*
$Os(PF_3)_5$	(C)	Colorless		—	−8.0	1250[f]	IR (*218*) Var. temp. ^{19}F NMR (*251*) Raman (*218*)	*174, 218, 251*
$Ir_2(PF_3)_8$[o]	(K) (L)	Yellow	105, 113–116, subl. $20/10^{-3}$	—	+5.2 +5.8	1230 1238	NMR (*17, 221*) IR (*17, 221*) MS (*220, 221*) Variable temp. ^{19}F NMR (*19*)	*17, 221*

(*continued*)

TABLE I (*continued*)

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	δ_P[a]	ϕ_F[b]	$^1J_{PF}$[c]	Remarks	Reference
$Pt(PF_3)_4$[p]	(C) (E) (F)	Colorless liquid	−15, dec. >90, (38/100) (85.5/730) (86/730)	−97.8	+11.5	1320	NMR (*177, 318*) IR(*108, 177, 179, 360*) Raman (*108*)	*108, 166, 177, 174, 179, 180, 287 287*
$U(PF_3)_6$	(H)	—	—	—	—	—	MS (*302*)	*302*

[a] In ppm relative to 85% H_3PO_4.
[b] In ppm relative to $FCCl_3$.
[c] In Hz.
[d] Magnetic susceptibility (*175*), He(I) PES (*139*).
[e] Dipole moment, optical density (*218*); ionization potential (*267*); magnetic susceptibility (*219*); He(I) PES (*139*); Mössbauer spectrum (*199*).
[f] $(^1J_{PF} + 4J_{PF'})$.
[g] Ionization potential (*267*); magneto optical properties, Faraday effect (*255, 317, 318, 319*); electron diffraction (*5, 246*); He(I) PES (*14, 122, 145, 267*).
[h] ^{61}Ni NMR, see text (*129*).
[i] He(I) PES (*139*).
[j] $^1J_{MOP} = 279$ Hz (*10*).
[k] He(I) PES (*139*).
[l] Magnetic susceptibility (*182*); stereochemical nonrigidity by NMR (*19*); X-ray structure determination (*19, 326*) a red complex of uncertain composition, $Rh_3(PF_3)_9$ or $Rh_3(PF_3)_8(PF_2)$, was obtained by heating either $Rh_2(PF_3)_8$ or $HRh(PF_3)_4$ (*17, 182*).
[m] He(I) PES (*14*).
[n] He(I) PES (*139*).
[o] Stereochemical nonrigidity (*19*).
[p] d_x^{20}2.4069, d_D^{20}1.3613 (*318*), magneto optical properties (*318*); He(I) PES (*14, 122, 145*); electron diffraction (*246, 310, 311*).

In some cases H_2 can interact directly with binary metal–trifluorophosphine complexes under mild conditions with or without addition of PF_3 or UV irradiation (method B), and group IV hydrides have also been utilized (method C).

$$Fe(PF_3)_5 \xrightarrow{H_2} FeH_2(PF_3)_4$$

$$Rh_2(PF_3)_8 \xrightarrow[25°C]{H_2} RhH(PF_3)_4$$

$$Rh_2(PF_3)_8 \xrightarrow{Ph_3MH} RhH(PF_3)_4 \qquad (M = Si, Ge)$$

There is a single report of the direct reaction between a metal, PF_3, and hydrogen at elevated temperature and pressure (method D) to give a 97% yield of the desired hydrido complex (*180*).

$$Co + PF_3 + H_2 \longrightarrow CoH(PF_3)_4$$

Transition metal carbonyl complexes can be suitable precursors, for example, treatment of hydrido complexes or their alkali salts with PF_3 under UV irradiation followed if necessary by acidification of the reaction mixture (method E). Interestingly, vanadium forms the hydrido trifluorophosphine complex $[VH(PF_3)_6]$, whereas with CO, the paramagnetic $[V(CO)_6]$ is formed.

$$CoH(CO)_4 \xrightarrow{PF_3} CoH(PF_3)_4$$

$$V(CO)_6^- \xrightarrow[\text{ii. } H^+]{\text{i. } PF_3/h\nu} VH(PF_3)_6$$

$$MnH(CO)_5 \xrightarrow[h\nu]{PF_3} MnH(PF_3)_5$$

A related synthetic method involves hydrolysis of the metallate salt made by another route (method F).

$$KRe(PF_3)_5 \xrightarrow{H_3PO_4} ReH(PF_3)_5$$

$$KM(PF_3)_4 \xrightarrow{H^+} MH(PF_3)_4 \qquad (M = Co, Rh)$$

There is one report (method G) of the ready hydrogenation of an η^3-allyl metal PF_3 system under very mild conditions in the presence of PF_3.

$$Rh(\eta^3\text{-}C_3H_5)(PF_3)_3 \xrightarrow[PF_3]{H_2} RhH(PF_3)_4$$

TABLE II

HYDRIDO–TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mm Hg)	δ_P[a]	ϕ_F[b]	J_{PF}[c]	Remarks	Reference
$VH(PF_3)_6$	(E)	—	Subl. $60/10^{-2}$, dec. 135	—	—	—	IR, MS {(216)[d] NMR[e]	*216*
$MnH(PF_3)_5$[f]	(E)	Colorless	18.5	—	—	—	IR (*259*)	*185, 259*
$FeH_2(PF_3)_4$[g]	(A) (B)	Colorless	−71, (87/760) dec. 220	−148	trans +2.9 cis +3.2	1235 (trans) 1270 (cis)	^{19}F NMR (*217*) ^{31}P NMR (*217*) IR (*217*) MS (*198*) Variable temp. ^1H, ^{19}F, and ^{31}P NMR (*199, 253*)	*118, 174 198, 217*
$CoH(PF_3)_4$[h]	(A) (D) (E) (F)	Very pale yellow	−51, (80/730), dec. 250	−147.7	2.6 (ax), 0.7 (eq)	1230[i]	IR (*15, 210*) Variable temp. ^1H and ^{19}F NMR (*251, 252*) Raman (*15*) MS (*313*)	*68, 180, 202, 209, 210, 351*
$RuH_2(PF_3)_4$[j]	(A) (B)	Colorless	−76, dec. 290	−101	trans +5.05 cis +3.57	1320 (trans) 1240 (cis)	^{19}F NMR (*217*) ^{31}P NMR (*217*) IR (*217*) Variable temp. ^1H, ^{19}F, and ^{31}P NMR (*199, 253*)	*217*
$RhH(PF_3)_4$[k]	(A) (B) (C) (F) (G)	Colorless	−40, (89/725)	−133.4	0.7 (ax) 4.8 (eq)	1293[i]	IR (*208*) Variable ^1H and ^{19}F NMR (*19, 251*)(*252*)	*17, 182, 208, 209 293*

$ReH(PF_3)_5$	(A) (E)	Colorless —	42 Subl. 20/10, dec. > 160	—	—	—	IR (*185*) ^1H NMR (*185*)	*185*
$OsH_2(PF_3)_4$[l]	(A)	Colorless	−72, dec. 340	—	trans 6.55 cis 7.8	1275 (trans) 1225 (cis)	^1H and ^{19}F NMR (*217*) IR (*217*) Variable temp. ^1H and ^{19}F NMR (*251, 252*)	*217*
$IrH(PF_3)_4$[m]	(A)	Colorless	−39, (95/730), dec. 245	−93.5	20.3 (ax), 15.6 (eq)	1244[i]	IR (*203*), Variable temp. ^1H and ^{19}F NMR (*251, 252*)	*174, 203, 209*

[a] In ppm against 85% H_3PO_4 as external reference.

[b] In ppm against $FCCl_3$ as internal reference.

[c] In Hz.

[d] Magnetic susceptibility, ^1H NMR (*216*).

[e] Detailed NMR on $[V(PF_3)_6]^-$ and Nb analogue (see text) (*114, 307, 308, 309, 321*).

[f] ^{55}Mn NMR (*201*), He(I) PES (*139, 141*).

[g] He(I) PES (*141*), Mössbauer spectrum (*198*), variable temp. ^1H and ^{19}F NMR of the anion $[FeH(PF_3)_4]^-$ (*251, 252*).

[h] Density (*15*), molecular conductance (*209*), ΔH (*313*), ^1H NMR (*21, 203*), ^{59}Co NMR of $[Co(PF_3)_4]^-$ (*234*) He(I) PES (*139, 141*), negative ion MS (*313*), neutron scattering spectrum (*359*), X-ray structure (*115*).

[i] $J_{PF} + 3J_{PF'}$.

[j] Free energy of activation for exchange (*253*), variable temp. ^1H and ^{19}F NMR of the anion $[RuH(PF_3)_5]^-$ (*251, 252*), molecular conductance in aqueous solution (*217*).

[k] Molecular conductance in aqueous solution (*209*), ^1H NMR (*251*), activation energy of ^{19}F exchange (*19*), He(I) PES (*139*), Molecular structure (*46*).

[l] Molecular conductance in aqueous solution (*217*), ^1H and ^{19}F NMR of the anion $[OsH(PF_3)_4]^-$ (*251, 252*).

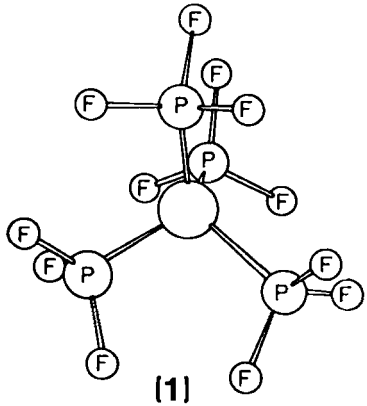
[m] Molecular conductance in aqueous solution (*209*), He(I) PES (*139*).

Hydrido trifluorophosphine complexes are listed in Table II together with their methods of preparation.

IV. Structures

A. Mononuclear Complexes

A variety of spectroscopic techniques (e.g., ^{19}F and ^{31}P NMR, IR, Raman) have been applied to $[M(PF_3)_4]$ (M = Ni, Pd, Pt) and $[M(PF_3)_4]^-$ complexes (M = Co, Rh, Ir) and have been interpreted in terms of a regular tetrahedral arrangement of PF_3 ligands around the central metal atom. These conclusions have been confirmed by electron diffraction studies on $[Ni(PF_3)_4]$ and $[Pt(PF_3)_4]$ (**1**) (*5, 246, 310, 311*), in which the PF_3 groups undergo free rotation about the metal–phosphorus bond. Although the Ni—P bond length in $[Ni(PF_3)_4]$ is exceptionally short, this is not the case for the platinum complex, in which the Pt—PF_3 bond length is not significantly shorter than in other platinum phosphorus complexes.



[1]

The tetrahedral environment around nickel in $[Ni(PF_3)_4]$ makes the electrical field gradient tensor zero and its ^{61}Ni NMR spectrum shown in Fig. 1 exhibits minimum quadrupole line broadening. Both the directly bounded ^{61}Ni–^{31}P coupling ($^1J_{NiP}$ = 482 Hz) and the two-bond ^{61}Ni–^{19}F coupling ($^2J_{NiF}$ = 28 Hz) have been recorded (*129*).

The ^{59}Co NMR spectrum of the isoelectronic tetrahedral $[Co(PF_3)_4]^-$ anion has also been recorded.

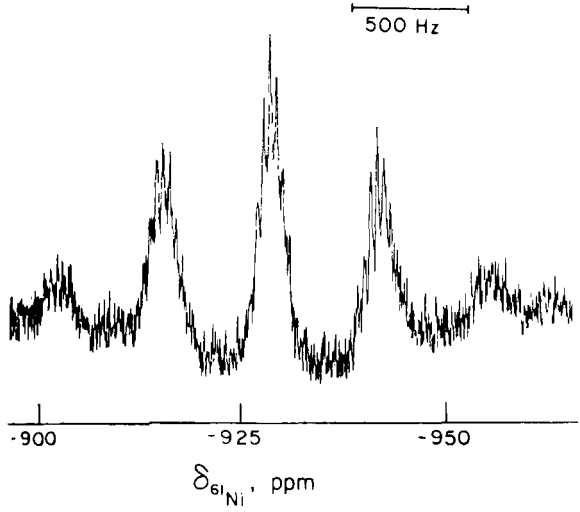


FIG. 1. Natural-abundance ^{61}Ni NMR spectrum of Ni(PF_3) recorded at 35.727 MHz. [Reproduced from reference (*129*) by permission.]

The almost certainly regular octahedron proposed for $[M(PF_3)_6]$, (M = Cr, Mo, and W) and $[VH(PF_3)_6]$, based on spectroscopic data, has not yet been substantiated by X-ray or electron diffraction methods; however, the well-resolved ^{51}V and ^{93}Nb NMR spectra of the anions $[M'(PF_3)_6]^-$ (M' = V, Nb), and the ^{95}Mo NMR spectrum of $[Mo(PF_3)_6]$ indicate that the metal atoms are certainly in a high symmetrical environment.

The beautiful ^{93}Nb NMR spectrum shown in Fig. 2 for the niobium complex $[Nb(PF_3)_6]^-$ exhibits a binomial septet arising from the one-bond metal–phosphorus coupling ($^1J_{NbP}$ = 1050 Hz) and further fine splitting arising from the two-bond metal–fluorine coupling ($^2J_{NbF}$ = 55 Hz). Chemical shift data have been compared to $[Nb(CO)_6]^-$ and interpreted as indicating that PF_3 is a slightly weaker π acceptor than CO (*vide infra*) (*307*).

No structural data are available for the pentakis(trifluorophosphine) complexes $[M(PF_3)_5]$ (M = Fe, Ru, Os), which almost certainly have trigonal-bipyramidal structures. Detailed ^{19}F and ^{31}P NMR studies indicate clearly that these molecules are fluxional even at temperatures as low as −160°C and the barrier to intramolecular ligand exchange between equatorial and axial positions of the trigonal bipyramid is less than ~20 kJ/mol (*251*). Figure 3 shows the temperature-dependent ^{19}F NMR spectrum of $[Ru(PF_3)_5]$, which is typical for all the MP_5

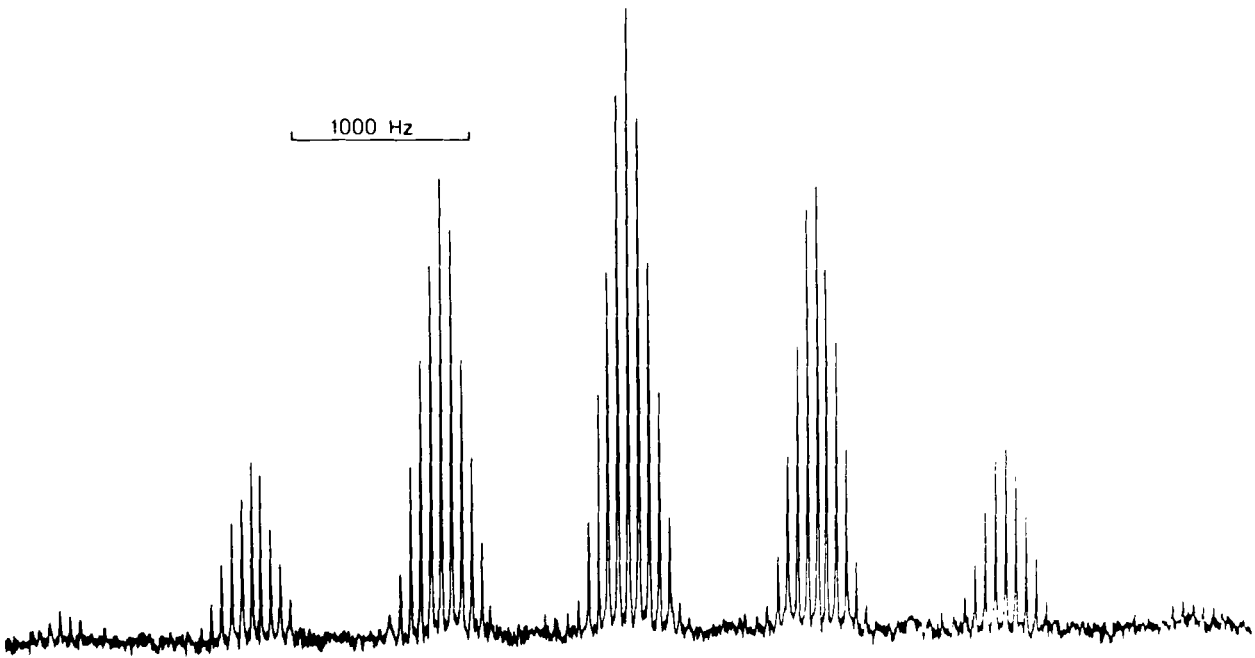


FIG. 2. The 22.00-MHz ^{93}Nb spectrum of $[Et_4N][Nb(PF_3)_6]$. [Reproduced from reference (*307*) by permission.]

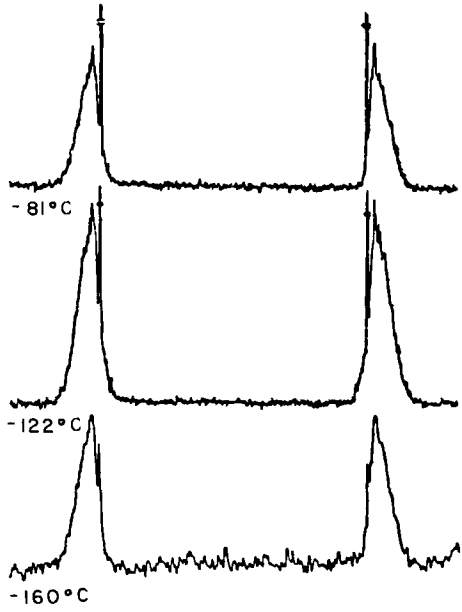


FIG. 3. ^{19}F (84.66 MHz) NMR spectra for $Ru(PF_3)_5$ in $CHClF_2$ taken at three temperatures. [Reproduced from reference (*251*) by permission.]

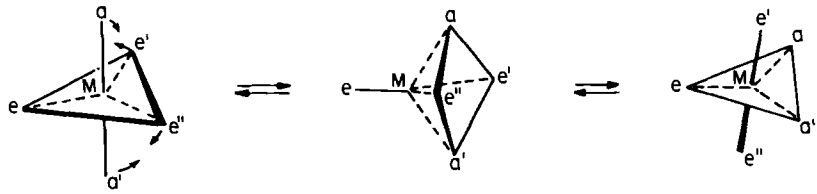


FIG. 4. Possible intramolecular ligand-exchange mechanism in $M(PF_3)_5$ complexes.

complexes. The possible mechanism for the PF_3 ligand interchange first proposed by Berry for other five-coordinate systems is depicted in Fig. 4.

The crystal structure of $[CoH(PF_3)_4]$ (Fig. 5) has been determined from X-ray data collected at $-125°C$. It can be described either as a distorted trigonal bipyramid with the hydrogen atom occupying an axial position, or alternatively as a tetrahedral array of PF_3 groups with hydrogen on one of the faces of the tetrahedron. The Co—P [2.052(5) Å average] bond distance is exceptionally short. The analogous $[RhH(PF_3)_4]$ (Fig. 6) has a similar structure which has been determined in the gas phase by electron diffraction (*46*).

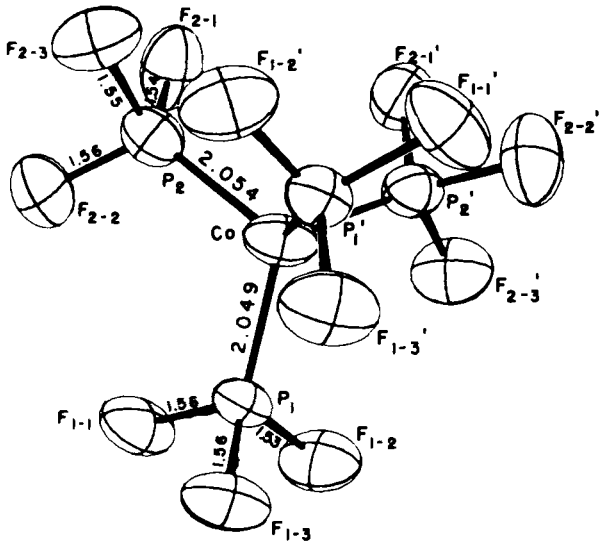


FIG. 5. A drawing of the $CoH(PF_3)_4$ molecule, with the H atom omitted. The 50% probability ellipsoids are shown. [Reproduced from reference (*115*) with permission.]

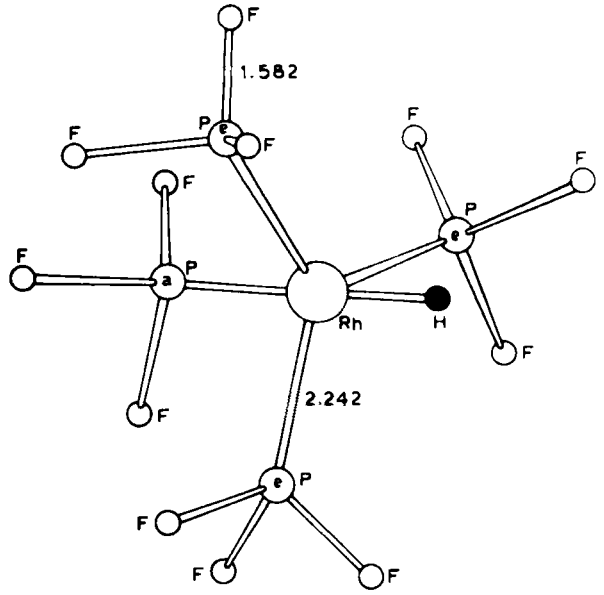


FIG. 6. The structure of $RhH(PF_3)_4$ as determined in the gas phase by electron diffraction. [Reproduced from references (*46, 292*) with permission.]

The $[MH(PF_3)_4]$ complexes (M = Co, Rh, Ir) and the isoelectronic species $[M'H(PF_3)_4]^-$ (M' = Fe, Ru, Os) are all stereochemically non-rigid, and detailed multinuclear NMR spectroscopic studies have been carried out and activation parameters determined. It has been proposed that the phosphorus environments are interchanged by a "tetrahedral tunnelling" rearrangement mechanism. Some typical temperature-dependent ^1H and ^{19}F NMR spectra are shown in Fig. 7.

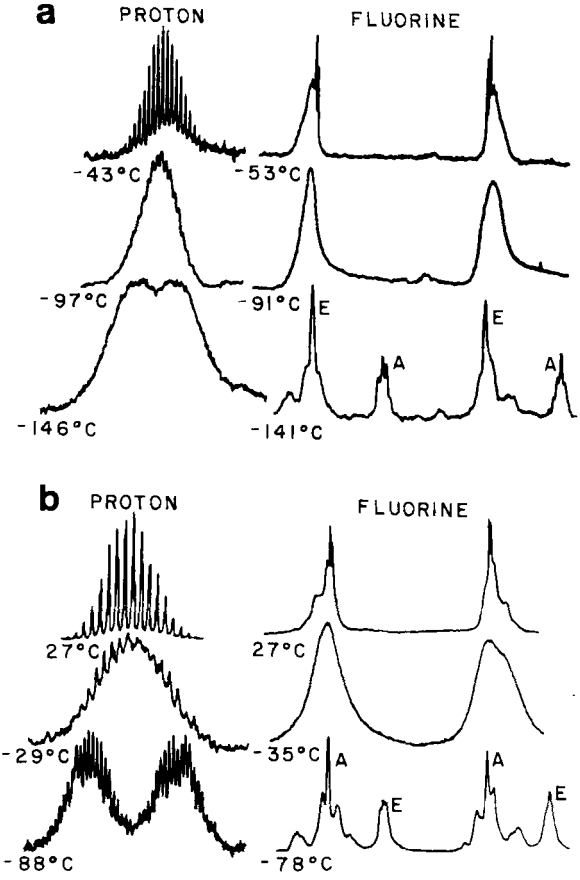
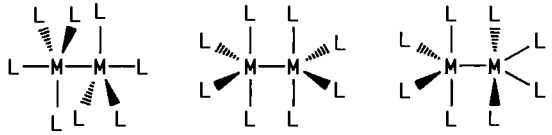


FIG. 7. (a) Temperature dependence of the ^1H (90 MHz) and ^{19}F (84.66 MHz) NMR spectra for $RuH(PF_3)_4^-$ in $CHClF_2$. A and E indicate axial and equatorial fluorine resonances. (b) Temperature dependence of the ^1H (90 MHz) and ^{19}F (84.66 MHz) NMR spectra for $IrH(PF_3)_4$. The ^{19}F spectra were taken in CH_2Cl_2, the 27°C ^1H spectrum in toluene-d_8, and the two low-temperature ^1H spectra in acetone-d_6. A and E indicate axial and equatorial fluorine resonances. [Reproduced from reference (*251*) with permission.]

Complexes of the type $[MH_2(PF_3)_4]$ (M = Fe, Ru, Os) have been assigned a cis structure on the basis of NMR spectroscopic data.

B. Dinuclear Complexes

The structures of $[M_2(PF_3)_8]$ (M = Rh, Ir) consist of $M(PF_3)_4$ units joined together by a metal–metal bond, and could adopt any of the arrangements (I)–(III) involving axial–axial linkage (I) or equatorial–equatorial linkage (II and III). The ^{19}F NMR spectra of



(I) (II) (III)

(L = PF_3)

these complexes are temperature dependent and the problem has been simplified by ^{31}P decoupling experiments (see Fig. 8), which show that

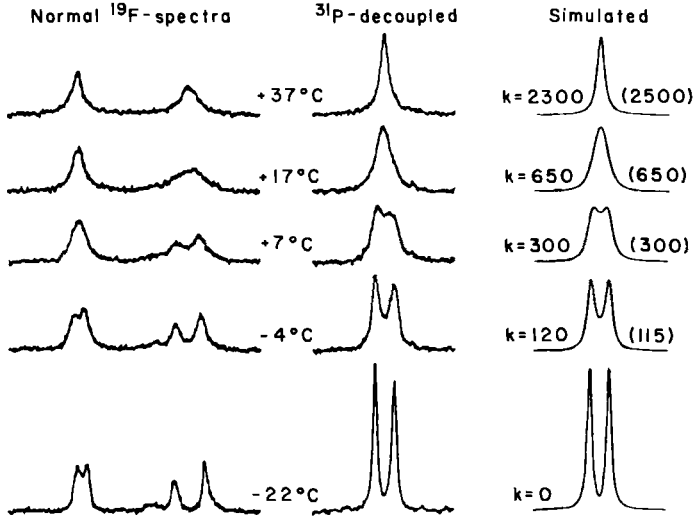


FIG. 8. Normal and ^{31}P-noise decoupled ^{19}F NMR spectra at 56.45 MHz of $Rh_2(PF_3)_8$ in C_5F_5Br at various temperatures with calculated NMR line shapes at rates (K) indicated. [Reproduced from reference (*19*) with permission.]

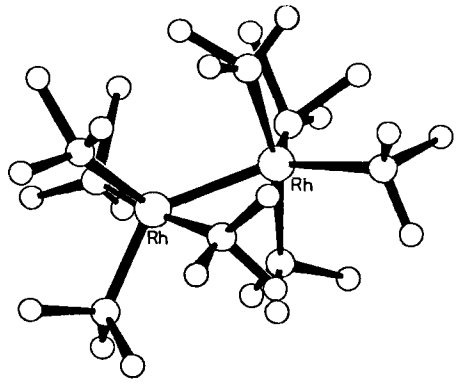


FIG. 9. Molecular structure of $[Rh_2(PF_3)_8]$ (*326*).

in the slow exchange limit two equally intense singlet signals are obtained, indicative of (**II**) or (**III**) rather than the 3:1 ratio expected for structure (**I**).

The $(PF_3)_4$ units can be either eclipsed (**II**) (D_{2h} microsymmetry) or staggered (**III**) (D_{2d} microsymmetry). The latter alternative, which is favored on steric grounds, has been confirmed by an unpublished X-ray study of a poor quality crystal of $[Rh_2(PF_3)_8]$ (Fig. 9) (*19, 326*). The accuracy of the molecular structure as shown above is limited by thermal motions and disorder of the fluorine atoms. The Rh—Rh distance [2.88(2) Å] is longer than in $[Rh_2(PF_3)_4(PPh_3)_2(\mu\text{-}PhC_2Ph)]$ (*vide infra*) and may be related to the ready cleavage of the metal–metal bond by H_2 or group IV hydrides.

V. Bonding

A. Trifluorophosphine

Before discussing the nature of the bonding in PF_3 and its transition metal complexes it is interesting to note that quantitative data on the gas-phase basicity of PF_3 have recently become available using the technique of ion cyclotron resonance spectroscopy. The proton affinity of PF_3 was originally determined as 160 ± 5 kcal/mol (*84*) and later improved to 158 ± 1 kcal/mol (*104*). The corresponding value for CO is 143 kcal/mol. Surprisingly, the order of gas-phase basicities of the group V trifluorides is found to be $NF_3 < AsF_3 < PF_3$ and this anomalous order has been attributed to the greater p_π–d_π overlap in PF_3 and PF_3H^+.

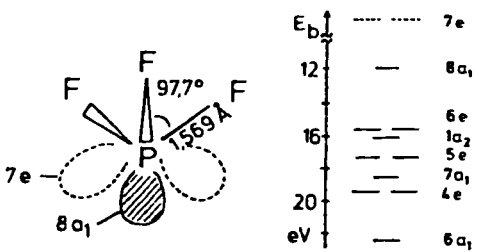


FIG. 10. Structure and ionization potentials of free PF_3.

COMPARISON OF EXPERIMENTAL AND THEORETICAL IONIZATION POTENTIALS FOR PH_3, $P(CH_3)_3$, AND PF_3

		Ionization potentials (eV)			
Molecule	Orbital	Expt.	SCM-Xα-DV	SCF-MO	SCF-Xα-SW
PH_3	$5a_1$	10.58	10.39	10.02[a]	10.61
	$2e$	13.50	13.09	13.70	13.42
	$4a_1$	21.2	20.43		20.55
$P(CH_3)_3$	$8a_1$	8.58	8.41	8.49	
	$6e$	11.31	10.67	12.04	
	$1a_2$		12.01	13.87	
	$5e$	12.7	12.11	14.63	
	$7a_1$		13.13	15.88	
	$4e$	15.8	13.07	15.89	
	$6a_1$		15.75	na	
	$3e$	19.6	19.53	na	
PF_3	$8a_1$	12.27	12.19	12.68	
	$6e$	15.88	15.00	18.32	
	$1a_2$	16.30	14.68	17.93	
	$5e$	17.46	16.00	19.67	
	$7a_1$	18.60	17.17	21.11	
	$4e$	19.50	17.83	21.45	

Early self-consistent field molecular orbital (SCF-MO) studies on PH_3, PF_3, and PMe_3 by Hillier and co-workers (*123, 144*) predicted ionization potential data which were in good agreement with the experimental values determined by UV photoelectron spectroscopy (*241*). More recently, the electronic structures of these phosphines have been reexamined (*67, 366*). Self-consistent multipolar Xα calculations (SCM-Xα-DV) by Xiao *et al.* (*366*) give excellent agreement between the theoretical and experimental ionization energies. When the transition-state procedure is used, the first ionization potentials of 10.39, 8.41, and 12.19 eV for PH_3, PMe_3, and PF_3 are calculated compared with the experimental values of 10.58, 8.58, and 12.27 eV (Fig. 10).

The nature of the frontier orbitals is also of interest and a Mulliken population analysis of the constituent orbitals establishes that the highest occupied molecular orbital (HOMO) of each phosphine consists primarily of a lone pair *sp* hybrid on phosphorus. The orbital energy ordering $PMe_3 < PH_3 < PF_3$ also parallels the percentage phosphorus *s*-character of the HOMO of PMe_3 (11% *s* and 60% *p*), PH_3 (14% *s*, 67% *p*) and PF_3 (29% *s*, 32% *p*). In each case the back lobe of the *sp* hybrid interacts with the substituent attached to phosphorus in a σ-bonding fashion.

Especially interesting is the π-symmetry *pd* hybrid that comprises the lowest unoccupied molecular orbital (LUMO) and the SCM-Xα-DV results show that there are several important quantitative differences in the PX_3 systems. The energy of the 7*e* (LUMO) in PF_3 is lower than that in either PH_3 or PMe_3, and this should enhance back bonding to PF_3 when complexed to a transition metal compared to PH_3 or PMe_3. Furthermore, the nature of the lowest unoccupied *e* orbital changes so that whereas in PH_3 3*e* is a hybrid of 36% *p* and 23% 3*d* on phosphorus, the corresponding percentages for PMe_3 are 14% and 10% (7*e*) and 44% and 23% for PF_3 (7*e*).

Thus contrary to the normally accepted view (*86, 124*) which ascribes π-acceptor properties of PF_3 to empty 3*d* orbitals, the π-acceptor orbital on phosphorus is mainly 3*p* in character. Mixing in 3*p* orbital character has the effect of directing the empty π orbital in the direction of the lone pair where the metal would bind. It is also worth noting that the 7*e* orbital for PF_3 has antibonding P—F character.

The most recent view on the π-accepting abilities of phosphines in transition metal–phosphine complexes is by Marynick (*247*) who has used approximate and *ab initio* MO theory to demonstrate that π accepting into σ^* orbitals is important for PF_3. Calculations on the model complex $[Cr(NH_3)_5(PF_3)]$ compared to $[Cr(NH_3)_5(PH_3)]$ showed

greater π-accepting ability for PF_3 even without *d* orbitals on phosphorus. The reasons for the enhanced π-accepting ability via σ^* orbitals of PF_3 are related to the highly polar P—F bonds which characteristically have low-lying σ^* orbitals. These σ^* orbitals are composed of 3*s* and 3*p* orbitals which overlap more effectively with metal 3*d* orbitals than do the 2*s* and 2*p* orbitals of amines.

B. Transition Metal–PF_3 Complexes

Molecular orbital (CNDO/2) theoretical calculations have been carried out on $[Cr(PF_3)_6]$, $[Ni(PF_3)_4]$, and $[Fe(PF_3)_5]$ (*320*), and the results compared with experimental ionization energies determined by UV photoelectron spectroscopic measurements of these complexes in the gas phase. The metal–phosphorus bonds show large $\sigma(P \rightarrow M)$ and $\pi(M \rightarrow P)$ charge transfers but small *total* charge transfers $(M \rightarrow P)$ which induce on the metal a small positive charge.

The high volatility of binary metal–PF_3 complexes and hydrides has enabled photoelectron data to be measured on the following complexes: $[M(PF_3)_6]$ (M = Cr, Mo, W) (*139, 276*); $[M(PF_3)_5]$ (M = Fe, Ru) (*139, 267, 276*); $[M(PF_3)_4]$ (M = Ni, Pd, Pt) (*122, 146, 267*); $[MH(PF_3)_4]$ (M = Co, Rh, Ir) (*139, 276*); $[MnH(PF_3)_5]$ (*139*); and $[FeH_2(PF_3)_4]$ (*141*).

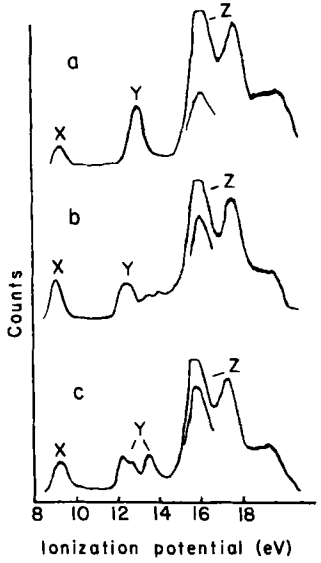


FIG. 11. He(I) photoelectron spectra of $[M(PF_3)_6]$ [M = Cr (a), Mo (b), and W (c)]. [Reproduced from reference (*139*) with permission.]

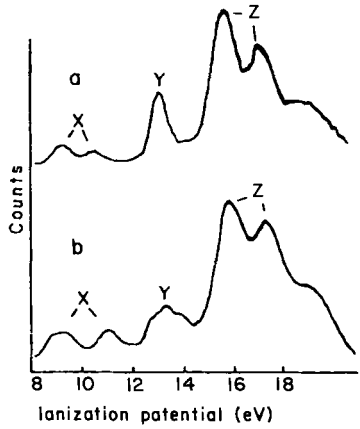


FIG. 12. He(I) spectra of $[M(PF_3)_5]$ [M = Fe (a) and Ru (b)]. [Reproduced from reference (*139*) with permission.]

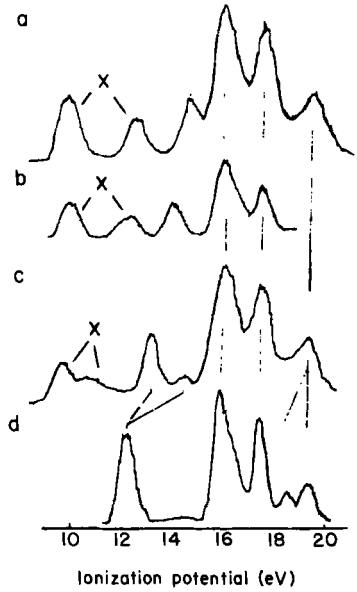


FIG. 13. He(I) Photoelectron spectra of (a) $[Pt(PF_3)_4]$, (b) $[Pd(PF_3)_4]$, (c) $[Ni(PF_3)_4]$, and (d) PF_3. [Reproduced from reference (*146*) with permission.]

Some typical He(I) photoelectron spectra are shown in Figs. 11–13, and the ionization energy data are summarized in Table III, together with relevant values for the corresponding carbonyl complexes.

The photoelectron spectra are usually easily assigned in view of the

TABLE III

IONIZATION POTENTIALS (eV) OF TRANSITION METAL TRIFLUOROPHOSPHINE AND HYDRIDOTRIFLUOROPHOSPHINE COMPLEXES. DATA FOR ANALOGOUS CARBONYL COMPLEXES ARE GIVEN IN PARENTHESES WHERE APPLICABLE

		$[M(PF_3)_6](O_h)$					$[M(PF_3)_5](D_{3h})$		$[MH(PF_3)_4](C_{3v})$			$[M(PF_3)_4](T_d)$		
Orbital		Cr	Mo	W	$[MnH(PF_3)_5](C_{4v})$		Fe	Ru	Co	Rh	Ir	Ni	Pd	Pt
Metal *d*	e_g				a_1	a_1'		a_1			t_2	9.69 (8.93)	9.9	9.83
	t_{2g}	9.29 (8.40)	9.17 (8.50)	9.30 (8.56)	b_1	e'	9.15 (8.60)	9.17 e	9.58 (8.90)	9.70	9.82 e	10.74 (9.76)	12.2	12.45
					e	(8.85) e''	10.43	11.07 e	10.56	11.79	11.95			
					b_2	9.47 (9.14)	(9.86)		(9.90)					
M—H					a_1	11.30 (10.55)		a_1	12.12 (11.5)					
M—P	t_{1u}		12.94	12.26 a_1		a_2'		a_1			t_2	13.17	13.7	14.54
	a_{1g}	12.84	13.48	12.64 e		12.93 a_1	13.08	12.8 a_1	13.25	13.83	14.18 a_1	14.65		
	e_g		13.93	13.52 e		e'		13.25 e						
						a_2''		13.65						
Fluorine lone pair		15.80	15.80	15.85	15.85		15.83	15.75	16.00	15.90	16.01	15.97	15.8	15.87
		17.36	17.36	17.44	17.43		17.24	17.18	17.46	17.42	17.42	17.48	17.4	17.53
		19.3	19.1	18.7	19.4		19.1	18.9	19.4	19.3	19.4			

widely separated bands. Thus the bands labeled X in the spectra of the octahedral d^6 $[M(PF_3)_6]$ complexes (Fig. 11) (M = Cr, Mo, W) can be clearly assigned to ionization of the filled t_{2g} orbital. Likewise, in the d^8 trigonal-bipyramidal $[M(PF_3)_5]$ complexes (M = Fe, Ru) (Fig. 12) the X bands arise from the e' $(d_{x^2-y^2}, d_{xy})$ and e'' (d_{xz}, d_{yz}) orbitals. Bands labeled Y and Z arise from the M—P σ orbitals and orbitals principally involving P—F and F lone pair electrons, respectively.

Figure 13 shows the photoelectron spectra of tetrahedral d^{10} $[M(PF_3)_4]$ complexes (M = Ni, Pd, Pt) where the X bands arise from filled metal t_2 and e orbitals. The figure shows how the orbital energies change relative to PF_3 itself. The photoelectron studies suggest that (1) in the $[M(PF_3)_4]$ series σ and π bonding are both strongest for Pt and weakest for Pd, (2) d-orbital ionization energies generally increase along a series and down a group, and (3) metal–phosphorus σ bonding increases across a series and down a group.

C. PF_3 Adsorbed on Metal Surfaces

An important link between the chemistry of transition metal complexes and that of metal surfaces has been established recently by studies of the chemisorption of PF_3 on a series of transition metals by Ertl and co-workers (*112, 227, 271*). Although strictly the chemisorption of PF_3 is beyond the scope of this article, a brief summary of the results is given below.

The electronic properties of PF_3 bonded to surfaces of Cr, Fe, Ni, Cu, Ru, Pd, Ir, and Pt have been investigated mainly by UV photoelectron spectroscopy, low-energy electron diffraction (LEED), and electron energy loss spectroscopy (*271*). Bond formation may be described as involving the coupling of the highest occupied PF_3 orbital (σ donor $8a_1$) to metallic s states and "back donation" of metallic d electrons into the empty π acceptor ($7e$) orbital. Of special importance is the observation that the observed lowering of the ionization energy of the $8a_1$ level shows behavior very similar to the properties of the corresponding zero-valent mononuclear PF_3 complex $[M(PF_3)_n]$, suggesting that the chemisorption bond should be considered as an essentially local phenomenon. Agreement is especially good with the face-centered cubic metals (Ni, Pd, Pt, and Ir), whereas large variations were found for body-centered cubic metals Cr and Fe. Figure 14 shows He(I) and He(II) data for PF_3/Fe (110) and $[Fe(PF_3)_5]$, and the data in Table IV list the relative ionization energies of chemisorbed PF_3 (in eV) (*271*).

Interactions of single transition metal atoms (e.g., Cr, Fe, Co, and Ni) with PF_3 (and CO) have been studied by an *ab initio* MO theory and the

TABLE IV

RELATIVE IONIZATION POTENTIALS OF CHEMISORBED PF_3 (IN eV) WITH RESPECT TO AN INTERNAL REFERENCE ($6a + 1a_1 = 16.1$ eV)[a]

Level	PF_3(free)	Cr(poly)	Fe(111)	Fe(110)	Ni(111)	Cu(110)	Ru(0001)	Pd(110)[b]	Pd(100)	Ir(100) (−5 × 1)	Ir(100) (−1 × 1)	Pt(111)	Peak
$8a_1$	12.27	12.75	13.1*	13.90	13.75	13.45	13.75	13.85	13.90	14.20	—	14.60	*a*
$6e$	15.88 } 16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	*b*
$1a_2$	16.30 }												
$5e$	17.46	17.60	17.30	17.40	17.40	17.30	17.35	17.40	17.30	17.45	17.50	17.40	*c*
$7a_1$	18.60												
$4e$	19.50	19.30	19.50	19.45	19.45	19.40	19.40	19.35	19.35	19.55	19.55	19.55	*d*
$6a_1$	22.55	22.50	22.60	22.65	22.60	22.55	22.60	22.60	22.60	22.70	22.75	22.75	*e*
Complex		$Cr(PF_3)_6$	$Fe(PF_3)_5$		$Ni(PF_3)_4$		$Ru(PF_3)_5$		$Pd(PF_3)_4$		$HIr(PF_3)_4$		$Pt(PF_3)_4$
$8a_1$		12.84	13.08		13.17(t_2)		12.8		13.7		14.18		14.54
					14.65(a_1)		13.25						
					−13.54(av)		13.65						
							−13.25(av)						

[a] The ionization potentials of the $8a_1$ levels of the corresponding mononuclear complexes are included for comparison.

[b] HeI data.

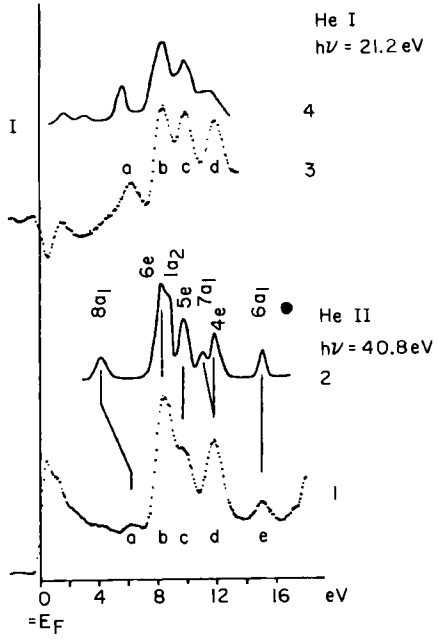


FIG. 14. Comparison of UPS data. (1) He(II) spectrum of PF_3/Fe(110); (2) He(II) spectrum of free PF_3; (3) He(I) difference spectrum (PF_3 covered clean surface) of PF_3/Fe(110); (4) He(I) spectrum $Fe(PF_3)_5$. The energy scales were adjusted in order to line up peak *b* with the ($6e + 1a_2$) maximum. [Reproduced from references (*112, 227, 271*) with permission.]

HOMO levels of both ligands ($8a_1$ for PF_3; 5σ for CO) move toward lower energies due to interaction with the metal 4*s* and $3dz^2$ orbitals (*163*). Calculations for $Ni(3d^{10})$ reveal that there is a more pronounced electron transfer to PF_3 than to CO (*162*). More recently a surface molecule approach to the adsorbate derived ionization energies for both PF_3 and CO on transition metal surfaces has been developed (*106*).

D. COMPARISON OF CO AND PF_3 AS LIGANDS

As mentioned in Section I, various physical evidence suggests that PF_3 and CO are very similar in their behavior toward transition metals (*72, 174, 272*). Mass spectroscopic data (*313*) on mixed CO/PF_3 metal complexes show that within experimental error the M—CO and M—PF_3 bond energies are the same. IR and Raman studies also indicate that the CO stretching force constants change less on PF_3 substitution

than with any other neutral 2*e* donor. The very small cone angle (*344*) of PF_3 compared with other phosphines (except for PH_3 and cage phosphines) is also likely to contribute significantly to its coordinating properties.

Jolly and co-workers (*7*) showed that the carbon 1*s* and oxygen 1*s* binding energies of a CO ligand in transition metal carbonyls are a good measure of the d_π–π^* back bonding involved. The Mo $3d_{5/2}$, C_{1s}, and O_{1s} binding energies measured by X-ray photoelectron spectroscopy (XPES) on complexes of the type $[M(CO)_5L]$ (L = CO, PX_3) are linearly related to each other and to the phosphorus lone pair ionization energy of the free PX_3. The XPES results indicate that both σ donor and π acceptor properties of PX_3 are important and that PF_3 seems to be a slightly better π acceptor than CO.

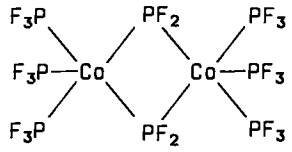
He(I) photoelectron spectroscopic data on mixed CO/PF_3 complexes of Fe(0) and Cr(0) (*142, 267*) show a steady increase in the metal 3*d*-orbital energies as PF_3 replaces CO, thus suggesting that there is a greater *overall* electron-withdrawing ability for PF_3. Similarly, where data are available for complexes of the type $[ML_n]$ (L = CO or PF_3; n = 4, 5, 6), $[MHL_n]$ (n = 4 or 5), and $[MH_2L_4]$, the metal *nd* ionization energies are always larger for the PF_3 derivative.

Detailed UV photoelectron spectra have been published on $[ML(CO)_5]$ [M = Cr, Mo, W; L = PX_3; X = F, Cl, Br (*96*) and M = Cr, Mo, W; L = PEt_3, PMe_3, $P(NMe_2)_3$, $P(OR)_3$, PF_3 (*367*)]. It was concluded that (i) the electron density on the metal increases along the series $PF_3 < CO < PCl_3 < PBr_3$ and in the order W < Mo < Cr, and (ii) PF_3 is similar but a somewhat poorer π acceptor than CO. A theoretical study of a series of complexes $[Ni(CO)_3L']$ using the nonempirical Hartree–Fock Slater transition state method suggested an order of σ donation as CO > PF_3 and for back bonding CO > PF_3 (*368*).

VI. Dinuclear Complexes Containing Bridging PF_2 Ligands

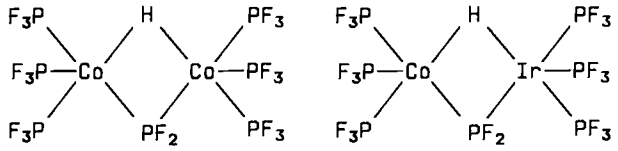
The first complex of this type was reported by Kruck and Lang (*205*) who obtained the red liquid compound $[Co_2(PF_3)_6(\mu\text{-}PF_2)_2]$ (**2**) by heating CoI_2 and copper at 170°C with high-pressure (400 atm) PF_3 (method A). The structure (**2**) was elucidated by ^{19}F NMR spectroscopy.

The structurally related bright-red crystalline iron compound $[Fe_2(PF_3)_6(\mu\text{-}PF_2)_2]$ has been obtained by Timms by metal vapor synthesis (method B) in which iron atoms and PF_3 are cocondensed at liquid nitrogen temperature (*340, 341*). A similar reaction using cobalt



(2)

was originally thought to afford $[Co_2(PF_3)_8]$ (*341*) but the product is more likely to be $[Co_2(PF_3)_6(\mu\text{-}PF_2)H]$ (**3**) (*342*). The latter has also been obtained by UV irradiation of the hydrido complex $[CoH(PF_3)_4]$ (method C) and when a mixture of $[CoH(PF_3)_4]$ and $[IrH(PF_3)_4]$ is used the mixed metal complex $[CoIr(PF_3)_6(\mu\text{-}PF_2)H]$ (**4**) results.



(3) (4)

Dinuclear iron complexes containing bridging PF_2 ligands have been made by UV irradiation of $[FeH_2(PF_3)_4]$ in the presence of iodine or ethylmercaptan (method D) (*198*). There is a very interesting report of the interaction of PF_3 with a uranium cathode at 77 K (method E) which affords a PF_3 complex of uranium formulated tentatively as containing a triple-bridging PF_2 system, viz $[U_2F_2(PF_3)_4(\mu\text{-}PF_2)_3]$, but no confirmatory structural or spectroscopic data are available (*9*). Complexes made by the above methods are listed in Table V.

VII. Polynuclear Complexes

In marked contrast to the large number of polynuclear metal carbonyl complexes known there are as yet relatively few reports of analogous polynuclear (i.e., containing more than two metal atoms) transition metal–PF_3 complexes. Trifluorophosphine can displace up to half the coordinated CO ligands in $[Ru_3(CO)_{12}]$ (method A) before the metal cluster is broken and mononuclear complexes are formed.

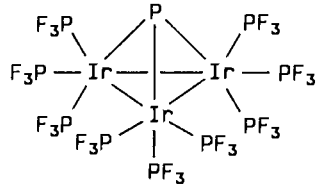
TABLE V

DINUCLEAR TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES CONTAINING PF_2-BRIDGING LIGANDS

Complex[a]	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[b]	$^1J_{PF}$[c,d]	Reference
$Fe_2(PF_3)_6(PF_2)_2$	(B) (C)	Bright-red	34	−0.7[e]	—	*198, 340, 341*
$Fe_2(PF_3)_6(PF_2)(SC_2H_5)$	(D)	Red	Oil	—	—	*198*
$Fe_2(PF_3)_6(PF_2)(I)$	(D)	Red	Oil	—	—	*198*
$Co_2(PF_3)_6(PF_2)_2$	(A)	Red	25, 50/10^{-3}	13.2[f]	1330	*205, 341; 342*
$Co_2(PF_3)_6(PF_2)(H)$	(C)	Red-violet	64, subl. 40/10^{-3}	7.0[g]	1290	*220*
$CoIr(PF_3)_6(PF_2)(H)$	(C)	Red oil	40/10^{-3}	—	—	*220*
$U_2F_2(PF_3)_4(PF_2)_3$	(E)	—	—	—	—	*9*

[a] The complexes $Cr_2(PF_3)_8(PF_2)_2$ and $CrFe(PF_3)_7(PF_2)_2$ have also been described briefly (*341*) as has $Fe_3(PF_3)_9(PF)_2$ (*256*).
[b] In ppm (relative to CCl_3F).
[c] In Hz.
[d] $^1J_{PF}$ quoted is only approximate.
[e] (PF_2) $\phi_F = -30.6; +36.7$ ppm.
[f] (PF_2) $\phi_F = 33.8$ ppm, $^1J_{PF} = 1230$ Hz.
[g] (PF_2) $\phi_F = 14.4$ ppm, $^1J_{PF} = 1160$ Hz.

Reductive fluorophosphination of $IrCl_3$ with copper at 80–200 atm PF_3 (method B) leads to the formation of the interesting orange-red crystalline μ-phosphidononakis(trifluorophosphine)triiridium compound $[Ir_3(PF_3)_9(\mu\text{-}P)]$ (**5**), containing the stable Ir_3P cluster.



(**5**)

Pyrolysis of $[Rh_2(PF_3)_8]$ at 170° (method C) evolves two molecules of PF_3 per dimer and gives a dark red volatile crystalline solid which has been formulated as $[Rh_3(PF_3)_8(\mu\text{-}PF_2)]$ or $[Rh_3(PF_3)_9]$ mainly on the basis of mass spectroscopic results. However, the possibility that this complex is in fact $[Rh_4(PF_3)_{12}]$ cannot be ruled out in view of the synthesis of the complex $[Rh_4(PF_3)_8(CO)_4]$ from the reaction between $[Rh(CO)_2Cl]_2$ and $[KRh(PF_3)_4]$ (method D).

Several other tetranuclear complexes containing different metals have been obtained from the reaction between metal carbonyl and metal trifluorophosphine complexes (method E) or by intermolecular ligand-exchange reactions (method F) between tetranuclear complexes. The following structures have been proposed on the basis of ^{19}F NMR and mass spectroscopic studies.

$$[RhCl(CO)_2]_2 + KRh(PF_3)_4 \longrightarrow Rh_4(PF_3)_8(CO)_4$$

$$[RhCl(PF_3)_2]_2 + Co_2(CO)_8 \longrightarrow Co_2Rh_2(CO)_8(PF_3)_4$$

$$[RhCl(PF_3)_2]_2 + TlCo(CO)_4 \longrightarrow Co_2Rh_2(CO)_8(PF_3)_4$$

$$Co_2Rh_2(CO)_{12} + Co_2Rh_2(CO)_8(PF_3)_4 \longrightarrow Co_2Rh_2(CO)_{10}(PF_3)_2$$

The trimetallic complex $[Fe_3(CO)_8(\mu\text{-}PPh)_2(PF_3)]$ has been obtained from the corresponding $[Fe_3(CO)_8(\mu\text{-}PPh)_2(MeCN)]$ compound by displacement of MeCN (method G). The structure, which is based on a square-pyramidal array of three iron and two phosphorus atoms, consists of isomers whose interconversion has been studied by variable-temperature ^{19}F and ^{31}P NMR spectroscopy. A trimetallic PF_3 complex containing mercury bonded to two metals results from the reactions

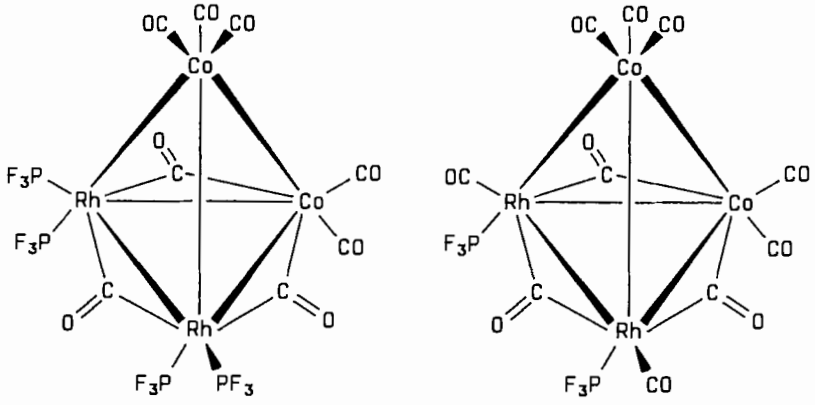
TABLE VI

POLYNUCLEAR TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES

Complex	Method of preparation	Colour	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Fe_3(CO)_8(\mu\text{-}PPh)_2(PF_3)$	(G)	Red	—	−174; −166[d]	1289, 1306	*173*
$Co_2Rh_2(PF_3)_4(CO)_8$	(E)	Deep-brown	—	10.3, 13.8[e]	1410, 1465	*155, 156*
$Co_2Rh_2(PF_3)_2(CO)_{10}$	(E) (F)	Deep-brown	—	11.9[f]	1459	*155, 156*
$Co_2Ir_2(PF_3)_4(CO)_8$	(E)	Dark-brown	—	—	—	*155, 156*
$Ru_3(PF_3)_x(CO)_{12-x}(x = 1\text{–}6)$	(A)	Red	—	—	—	*350*
$Rh_3(PF_3)_9$[g]	(C)	Red	—	—	—	*17*
$Rh_2Hg(PF_3)_8$	(H)	White	105–106	—	—	*17*
$Rh_4(PF_3)_8(CO)_4$	(E)	Dark-red	subl. $60/10^{-3}$	—	—	*155, 156*
$Os_3(PF_3)(CO)_8(Ph_2C_2)$	(A)	Violet	—	—	—	*113*
$Ir_2Hg(PF_3)_8$	(G)	Yellow	113–116	—	—	*17*
$Ir_3P(PF_3)_9$	(B)	Orange-red	subl. $80/10^{-3}$	—	—	*220*

[a] In ppm relative to CCl_3F.
[b] In Hz.
[c] Spectra complex and temperature dependent.
[d] Standard not given. (Mixture of isomers).
[e] ϕ_P[relative to $P(OMe)_3$] = 18.2 ppm.
[f] ϕ_P[relative to $P(OMe)_3$] = 26.9 ppm.
[g] See text for discussion of this formulation.

(method H) between potassium amalgam and $[RhCl(PF_3)_2]_2$ (in the presence of PF_3) or $[IrCl(PF_3)_4]$. Polynuclear complexes containing PF_3 are listed in Table VI.



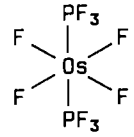
VIII. Halogeno–Metal Complexes

Probably the first metal–PF_3 complex to be synthesized was $[PtF_2(PF_3)]_2$, made by Moissan as early as 1891 (*263*) from the reaction of PF_5 with platinum black (method A); however, its identity was not recognized at that time. Much later, in 1951, Chatt and Williams (*63*) passed PF_3 over heated $PtCl_2$ (method B) to give both $[PtCl_2(PF_3)_2]$ and $[PtCl_2(PF_3)]_2$. This method is not generally applicable for halogeno–trifluorophosphine complexes, however, recently it has been extended to the bromo complex. Hydrolysis of the coordinated PF_3 in these complexes is rapid (*174*).

$$PtCl_2 \xrightarrow{PF_3} PtCl_2(PF_3)_2 \xrightarrow{H_2O} [PtCl_2(PF_2O)(PF_3)]^-$$

There is a very recent report (*51*) of the exothermic reaction between $[OsF_6]$ and PF_3 to give $[OsF_4(PF_3)_2]$ which is a monomeric nonelectrolyte and has been assigned the trans structure (**6**). This seems to be the first well-authenticated fluorometal to contain PF_3. It is also noteworthy in involving the high oxidation state Os(IV). No evidence has been found for the analogous Ir(IV) complex but a polymeric $[RuF_4(PF_3)]$ has been described (*50*).

Kruck and co-workers (*174*) have shown that reductive fluorophosphination of transition metal halides with high pressures of PF_3 in the



(6)

presence of copper metal at elevated temperatures is a general route to zero-valent metal–PF_3 complexes (see earlier sections), but this route can be used (method C) in certain circumstances to afford halogeno complexes.

$$ReCl_5 \xrightarrow{Cu/PF_3} ReCl(PF_3)_5$$
$$CoI_2 \xrightarrow{Cu/PF_3} CoI(PF_3)_4$$

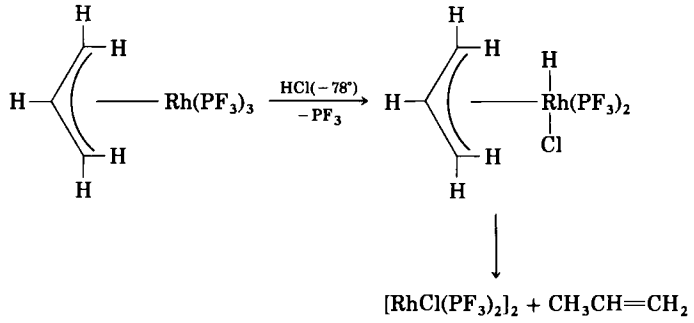
The dihalogenotetrakis(trifluorophosphine)iron complexes can readily be obtained by direct oxidation of $[Fe(PF_3)_5]$ with the appropriate halogen under mild conditions (method D). NMR studies establish that the halogens lie in cis-positions of the octahedron.

$$Fe(PF_3)_5 \xrightarrow{X_2} FeX_2(PF_3)_4 \qquad (X = Cl, Br, I)$$

Other synthetic routes reported involve the interactions of trifluorophosphine metallates and iodine (method E), displacement of carbon monoxide, alkenes, etc. by PF_3 from the corresponding halide complexes (method F), addition of PF_3 to dinuclear halogeno-bridged PF_3 complexes at low temperatures (method G), and treatment of a metal hydrido–PF_3 complex with iodoform (method H).

$$KIr(PF_3)_4 \xrightarrow{I_2} IrI(PF_3)_4$$
$$[RhCl(C_2H_4)_2]_2 \xrightarrow{PF_3} [RhCl(PF_3)_2]_2$$
$$[RhCl(PF_3)_2]_2 \xrightarrow{PF_3} RhCl(PF_3)_4$$
$$CoH(PF_3)_4 \xrightarrow{CHI_3} CoI(PF_3)_4$$

A particularly interesting synthetic route to complexes of the type $[RhX(PF_3)_2]$ (X = Cl, Br) is via the oxidative addition of HCl (or ^tBuBr) to the η^3-allylic rhodium(I) complex $[Rh(C_3H_5)(PF_3)_3]$ (method I) (Scheme 1), followed by alkene elimination.



SCHEME 1

At low temperatures the intermediate η^3-allylrhodium(III) hydride PF_3 complex was detected by ^1H and ^{19}F NMR spectroscopy and provided supportive evidence for the isomerisation of alkenes via an allyl–metal–hydride mechanism (*285, 293*).

The dinuclear complexes $[MX(PF_3)_2]_2$ (M = Rh, Ir; X = Cl, Br, I) are sufficiently volatile for their He(I) and He(II) photoelectron spectra to be recorded (*288, 289*) and the data have assisted in the assignments of bands in the photoelectron spectra of the corresponding carbonyl complexes for which transition state SCF-Xα-SW calculations of ionization energies have been made.

Another interesting feature of the dinuclear iridium complex $[IrCl(PF_3)_2]_2$ is its very dark color and metallic luster in the solid state, indicative of intermetallic bonding. A recent single-crystal structure determination (*149*) reveals that the structure consists of infinite zig-zag chains of iridium atoms with short inter- and intramolecular Ir $\cdots$ Ir contacts (see Figs. 15 and 16).

Anionic halogeno complexes listed in Table VII are usually obtained by addition of either tetraalkylammonium or tetraphenylarsonium halides to a dinuclear halogeno-bridged metal–PF_3 complex (method J) or, alternatively, by simple addition of PF_3 to dinuclear halogeno-bridged anions, e.g., of the type $[M_2X_6]^{2-}$ (M = Pt) (method K).

$$[RhCl(PF_3)_2]_2 \xrightarrow{R_4NCl} [R_4N][RhCl_2(PF_3)_2]$$

$$[Pt_2Br_6]^{2-} \xrightarrow{PF_3} [PtBr_3(PF_3)]^-$$

These synthetic routes are of interest since it is possible to oxidize these anionic species further with halogen to give rather rare examples

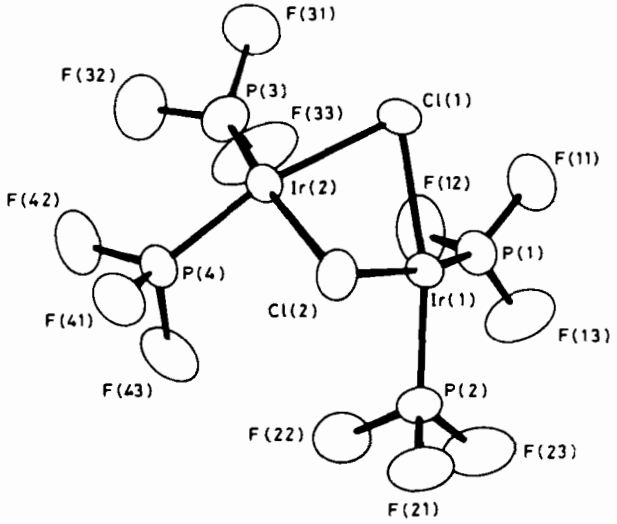


FIG. 15. The molecular structure of $[IrCl(PF_3)_2]_2$. Ir–P (av.), 2.134(5); Ir–Cl (av.), 2.413(5); P–F (av.), 1.517 Å. [Reproduced from reference (*149*) with permission.]

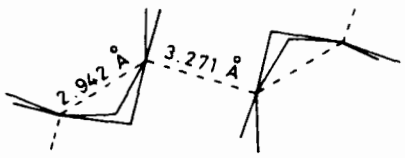


FIG. 16. The chain structure of $[IrCl(PF_3)_2]_2$.

of PF_3 complexes of metals in a high oxidation state (method L) (*87–90*).

$$[PtCl_3(PF_3)_2]^- \xrightarrow{Cl_2} [PtCl_5(PF_3)]^-$$
$$[RhBr_2(PF_3)_2]^- \xrightarrow{Br_2} [RhBr_4(PF_3)_2]^-$$

The measurement of $^1J_{PtP}$ for these anionic PF_3 complexes of metals in two oxidation states has been utilized to ascertain the importance of π bonding in these systems. Thus the ratio of $^1J_{PtP}$ in Pt(II) complexes of the type $[PtX_3(PF_3)]^-$ and Pt(IV) complexes $[PtX_5(PF_3)]^-$ (X = Cl, Br) is about 1:0.6, which is similar to related data for the corresponding trialkylphosphine and -phosphite complexes.

There is a single report (*168*) (method M) of the reaction between a metal fluoride–BrF_3 adduct and PF_3, in which the PF_3 acts as both a

reducing agent and a ligand. Halogeno–transition metal complexes containing PF_3 are summarized in Table VII.

IX. Transition Metal–Alkene Complexes

A variety of synthetic routes to monoene and polyene trifluorophosphine–transition metal complexes have been devised. Direct photochemically induced reaction of a metal–PF_3 complex with an activated alkene or diene (method A) has proved useful only for iron, the products being either $[Fe(PF_3)_4(alkene)]$ or $[Fe(PF_3)_3(diene)]$ (*194*). Mixed carbonyl–trifluorophosphine complexes of the type $[Fe(PF_3)_x(CO)_{3-x}(diene)]$ result from either thermal or photochemical reactions of dieneiron carbonyl complexes and PF_3 (*52, 53*) (method B). The compounds are fluxional.

$$Fe(PF_3)_5 \xrightarrow{diene} Fe(PF_3)_3(diene)$$

$$Fe(CO)_3(diene) \xrightarrow{PF_3} Fe(PF_3)_x(CO)_{3-x}(diene)$$

There is one report (*193*) of the formation of a hexa-1,3-dienemetal complex formed by a coupling reaction of the allyl ligands (method C) in the reaction of $[Fe(PF_3)_5]$ with allyl chloride.

$$Fe(PF_3)_5 \xrightarrow{CH_2=CH-CH_2Cl} Fe(PF_3)_3(C_6H_{10})$$

The most generally applicable route to diene or triene metal PF_3 complexes is via metal vapor synthesis (method D), in which the metal vapors are cocondensed with PF_3 and the polyene at liquid nitrogen temperatures.

$$Cr + PF_3 + \text{cycloheptatriene} \longrightarrow Cr(PF_3)_3(C_7H_8)$$

$$Ru + PF_3 + \text{butadiene} \longrightarrow Ru(PF_3)(C_4H_6)_2$$

$$Ni + PF_3 + \text{alkene} \longrightarrow Ni(PF_3)_3(\text{alkene})$$

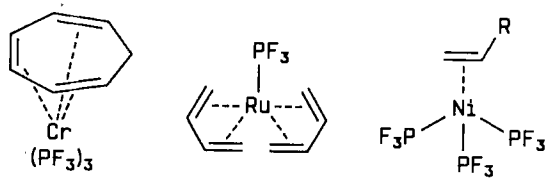


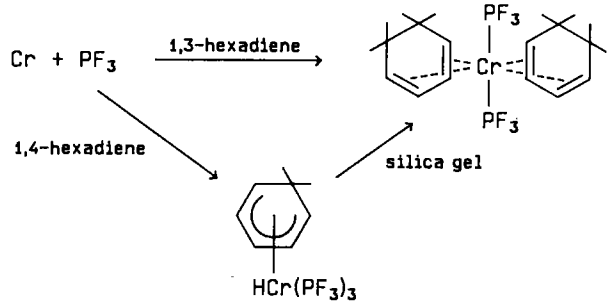
TABLE VII

HALOGENO–TRANSITION METAL–TRIFLUOROPHOSPHINE COMPLEXES

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$FeCl_2(PF_3)_4$	(D)	Yellow-orange	subl. $20/10^{-3}$ (dec. 45)	4.2, 12	1330	*200*
$FeBr_2(PF_3)_4$	(D)	Orange-red	subl. $20/10^{-3}$ (dec. 65)	4.4, 230	1355	*200*
$FeI_2(PF_3)_4$	(D)	Purple	subl. $30/10^{-3}$ (dec. 95)	1.6, 264	1310	*199, 200*[d]
$CoI(PF_3)_4$	(C) (H)	Red-brown	dec. 77	—	—	*174, 202*
$RhCl(PF_3)_4$	(G)	Yellow	stable at −78	—	—	*17, 18, 87, 291*
$RhBr(PF_3)_4$	(G)	Yellow	stable at −78	—	—	*17, 18, 87, 291*
$RhI(PF_3)_4$	(G)	Yellow	stable at −78	—	—	*17, 18, 87, 291*
$[RhCl(PF_3)_2]_2$[e]	(C) (F) (I)	Red	69–70	17.0	1328	*17, 18, 80, 87–89, 182, 282, 288, 291, 293*
$[RhBr(PF_3)_2]_2$[e]	(F) (I)	Red	61.5–62	15.9	1309	*17, 18, 87–89, 285, 289, 291*
$[RhI(PF_3)_2]_2$	(F)	Red	62.5	14.2	1316	*17, 18, 87, 289, 291*
$[RhCl_2(PF_3)_2][(CH_3)_4N]$	(J)	Pale-yellow	—	—	—	*17, 18, 87–89*
$[RhCl_2(PF_3)_2][(C_6H_5)_4As]$	(J)	Pale-yellow	—	—	—	*17, 18, 87–89*
$[RhCl_2(PF_3)_2][Bu_4N]$	(J)	Lemon	88–92	20.6	1298	*17, 18, 87–89*
$[RhBr_2(PF_3)_2][Bu_4N]$	(J)	Lemon	107–108	19.9	1392	*17, 18*
$[RhCl_4(PF_3)_2][Bu_4N]$[e]	(L)	Deep-yellow	130–132	34.5	1367	*87, 89*
$[RhBr_4(PF_3)_2][Bu_4N]$[e]	(L)	Deep-orange	169–172	29.5	1355	*87, 89*
$ReCl(PF_3)_5$	(C)	Colorless	153(dec.)(subl. $20/10^{-3}$)	—	—	*174, 186*
$[RuF_4(PF_3)]_n$	(B)	Rust-brown	—	—	—	*50*
$OsF_4(PF_3)_2$	(B)	Yellow	—	—	—	*51*

$PdCl_2(PF_3)_2$[e]	(B) (F)	—	—	34.5	1383	*87, 89*
$[PdCl_3(PF_3)][Bu_4N]$[f]	(K)	Golden-yellow	86–96	34.7	1408	*87*
$IrCl(PF_3)_4$	(F)	Pale-yellow	32.5	19.5	1252	*17*
$IrI(PF_3)_4$	(E)	Yellow	dec. >25	—	—	*174, 186*
$[IrCl(PF_3)_2]_2$[l]	(F)	Dark-blue	76–78	24.1	1270	*17, 149, 289*
$[PtF_2(PF_3)]_2$	(A)	—	—	—	—	*263*
$PtCl_2(PF_3)_2$[e]	(B)	Colorless	102	29.0[g]	1316	*63, 88, 89, 143, 312*
$[PtCl_2(PF_3)]_2$	(B)	Orange-yellow	155–156	—	—	*63, 88*
$PtBr_2(PF_3)_2$[e]	(B) (F) (M)	Colorless	97–100	33.9	1323	*87–89, 168*
$[PtCl_3(PF_3)][Bu_4N]$	(K)	Yellow	131–134	40.4[h,i]	1311	*91, 119*
$[PtBr_3(PF_3)][Bu_4N]$	(K)	Yellow	114–118	37.7[i,j]	1313	*91*
$[PtI_3(PF_3)][Bu_4N]$	(K)	Orange	130–131	33.1[i,k]	1320	*91*
$[PtI_3(PF_3)][(C_5H_{11})_4N]$	(K)	Orange	73–75	—	—	*91*
$[PtCl_5(PF_3)][Bu_4N]$	(L)	—	—	—	—	*90*
$[PtBr_5(PF_3)][Bu_4N]$	(L)	—	—	—	—	*90*

[a] In ppm relative to CCl_3F.
[b] In Hz.
[c] $^1J_{PF}$ listed is equal to $^1J_{PF} + n^3J_{PF'}$ for $(PF_3)_{n+1}$ complexes.
[d] Mössbauer spectrum (*199*), $\delta = 0.44$ (mm/sec), ε(mm/sec) = 0.26.
[e] Full NMR analysis (*89*).
[f] Relative signs determined.
[g] δ_P[relative to $P(OMe)_3$] = −68.0 ppm.
[h] $\delta_P = -50.2$ ppm, $^1J_{PtP} = 7464$ Hz.
[i] Pt chemical shift data available.
[j] $\delta_P = -52.1$ ppm, $^1J_{PtP} = 7257$ Hz.
[k] $\delta_P = -60.3$ ppm, $^1J_{PtP} = 6959$ Hz.
[l] X-Ray structure (*149*).

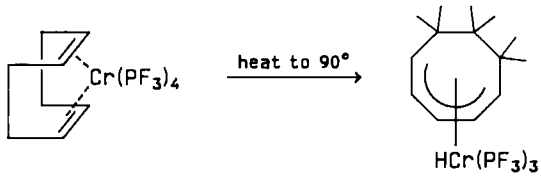


SCHEME 2

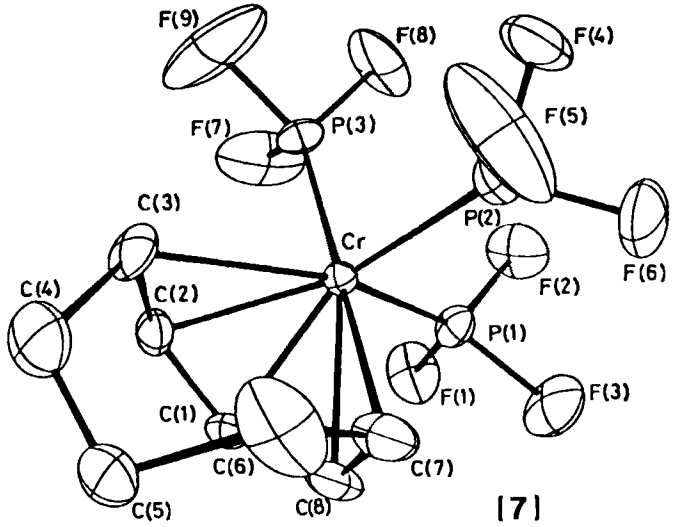
Interestingly, although the reaction of 1,3-cyclohexadiene, chromium atoms, and PF_3 yields bis(η^4-cyclohexadiene)bis(trifluorophosphine)chromium, the corresponding reaction with 1,4-cyclohexadiene yields the η^5-cyclohexadienyl hydrido tris(trifluorophosphine)-chromium complex, which rearranges in the presence of silica gel to form $[Cr(\eta^4\text{-}C_6H_8)_2(PF_3)_2]$ rather than (η^4-cyclohexadiene)tetrakis-(trifluorophosphine)chromium (*40*) (Scheme 2).

Similar reactions using 1,3-cyclooctadiene, chromium atoms, and PF_3 led only to the η^5-(cycloocta-1,3-dienyl) hydrido tris(trifluorophosphine)chromium complex $[Cr(C_8H_{11})(PF_3)_3H]$ (**7**), whose structure has been established by X-ray crystallography (*125*). (See also Section VIII). The chromium–phosphorus bond lengths [ave. 2.146(3) Å] are, as expected, particularly short.

Reaction of chromium atoms, 1,5-cyclooctadiene(1,5-cod), and PF_3 on the other hand yielded a separable mixture of $[Cr(C_8H_{11})(PF_3)_3H]$ and (η^4-cycloocta-1,5-diene)tetrakis(trifluorophosphine)chromium. The latter is readily converted to the former by warming a solution of it to 90°C (Scheme 3). This rearrangement is impaired under an atmosphere of PF_3 and the 1,5-cod is preferentially displaced to give $[Cr(PF_3)_6]$.



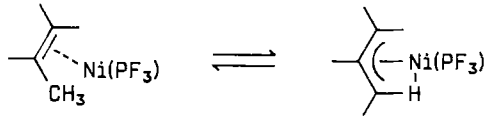
SCHEME 3



[7]

The [Ni(alkene)$(PF_3)_3$] complexes (alkene = $ClCH{=}CH_2$, $CH_3CH{=}CH_2$, $CF_3CH{=}CH_2$, and $FCH{=}CH_2$) made by metal vapor synthesis are much less thermally stable than the polyene complexes (*28*) and decompose readily to give [Ni$(PF_3)_4$], alkene, and nickel metal.

The propene complex is the most stable and of special interest is the failure to observe any evidence for metal hydride formation prior to thermal decomposition. This contrasts markedly with the temperature-dependent equilibrium between metal–propene and metal–allyl–hydride first observed by Bönnemann (*42*) for the related complex [Ni$(C_3H_6)(PF_3)$] and studied by variable-temperature NMR spectroscopy.



The η^4-cyclohexadiene complex [Ru(η^4-C_6H_8)$(PF_3)_3$], which is readily obtained by displacement of benzene (method E) from [Ru(η^4-C_6H_8)(η^6-C_6H_6)], is a fluxional molecule (*1*). The $^{31}P\{^1H\}$ NMR spectrum at room temperature (Fig. 17) exhibits a basic 1–3–3–1 quartet pattern (coupling to F) and shows the further complicated fine structure expected for an $[AX_3]_3$ spin system (X = F, A = P) indicative of

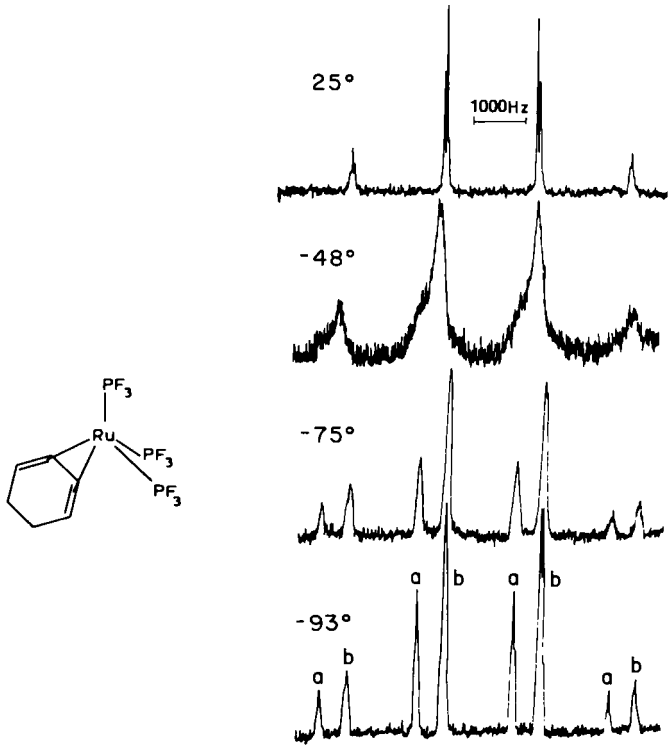


FIG. 17. Variable-temperature ^{31}P NMR spectra of $Ru(\eta^4\text{-}C_6H_8)(PF_3)_3$. [Reproduced from reference (*1*) with permission.]

equivalence of the three PF_3 ligands. The limiting NMR spectrum obtained at −93°C shows two overlapping quartet patterns in the ratio 1:2 with much further fine structure evident (*1*).

Other synthetic routes to alkene–metal complexes reported in the literature involve bridge cleavage reactions of halogeno complexes (method F), facile intermolecular scrambling reactions involving metal–alkene and metal–PF_3 complexes (*18, 81*) (method G) (Scheme 4), and the coupling together of two alkyne units to afford a metallocyclopentadiene derivative (method H).

Complexes obtained by all of the above routes are listed in Table VIII.

$$[RhCl(C_2H_4)_2]_2 + [RhCl(PF_3)_2]_2 \longrightarrow 2[RhCl(C_2H_4)(PF_3)]_2$$

SCHEME 4

TABLE VIII

ALKENE TRANSITION METAL COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	References
$Cr(PF_3)_4$(buta-1,3-diene)	(D)	Yellow-brown	205–210	—	—	*330*
$Cr(PF_3)_4$(cycloocta-1,5-diene)[d]	(D)	Yellow	—	3.3 16.7	1280 ± 25	*37*
$Cr(PF_3)_3$(cycloheptatriene)[e]	(D)	Orange-yellow	223 (subl. 150/760)	−7.3 −12.5	1264	*38, 343*
$Cr(PF_3)_2$(cyclohexa-1,3-diene)$_2$	(D)	Orange-red	—	0.7	1250	*40*
$Fe(PF_3)_4$(acrylonitrile)	(A)	Yellow	45–46 ($\sim 30/10^{-3}$)	—	—	*194*
$Fe(PF_3)_4$(crotonitrile)	(A)	Yellow	73–74 ($\sim 40/10^{-3}$)	—	—	*194*
$Fe(PF_3)_4$(styrene)	(A)	Yellow	28–29 ($\sim 40/10^{-3}$)	—	—	*194*
$Fe(PF_3)_4$(methylacrylate)	(A)	Orange	ca. −5 ($\sim 25/10^{-3}$)	—	—	*194*
$Fe(PF_3)_3$(methylmethacrylate)	(A)	Red	ca. 0 ($\sim 25/10^{-3}$)	—	—	*194*
$Fe(PF_3)_3$(crotonaldehyde)	(A)	Orange	ca. −15 ($\sim 25/10^{-3}$)	—	—	*194*
$Fe(PF_3)_3$(methyl vinyl ketone)	(A)	Yellow	ca. −20 ($\sim 25/10^{-3}$)	—	—	*194*
$Fe(PF_3)_3$(buta-1,3-diene)	(A) (B)	Yellow	118–119	4.8	1290	*52, 53, 197, 357*
$Fe(PF_3)_3$(isoprene)	(A)	Yellow	84–86; 65	5.8	1290	*52, 53, 197, 293*
$Fe(PF_3)_3$(*cis*-penta-1,3-diene)	(A) (B)	Yellow	55–58	5.8	1293	*52, 53, 197*
$Fe(PF_3)_3$(cyclopentadiene)	(A)	Yellow	112–114	—	—	*195*
$Fe(PF_3)_3$(*trans*-penta-1,3-diene)	(A) (B)	Yellow	97–98	3.8	1291	*52, 53, 197*
$Fe(PF_3)_3$(2,3-dimethylbutadiene)	(A) (B)	Yellow	88–89	6.5	1289	*52, 53, 197*
$Fe(PF_3)_3$(hexa-1,3-diene)	(C)	Yellow	85	—	—	*193*
$Fe(PF_3)_3$(*trans*,trans-hexa-2,4-diene)	(A) (B)	Yellow	34–35	—	—	*52, 53, 197*
$Fe(PF_3)_3$(*cis*,*trans*-hexa-2,4-diene)	(A)	Yellow	106	—	—	*197*
$Fe(PF_3)_3$(2,4-dimethyl-1,3-pentadiene)	(A) (B)	Yellow	116–119	5.4	1300	*52, 53, 197*
$Fe(PF_3)_3$(methylsorbate)	(A)	Yellow	42–44	—	—	*197*
$Fe(PF_3)_3$(1,3-cyclohexadiene)	(A) (B)	Yellow	102	—	1290	*197, 355*
$Fe(PF_3)_3$(1,3-cycloheptadiene)	(A)	Yellow	34–35	—	—	*197*
$Fe(PF_3)_3$(1,3-cyclooctadiene)	(A)	Yellow	31	—	—	*197*

(*continued*)

TABLE VIII (*continued*)

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	References
$Fe(PF_3)_3$(1,5-cyclooctadiene)[f]	(D)	Yellow	—	—	—	*54, 237*
$Fe(PF_3)_3$(norbornadiene)	(A)	Yellow	52–53	—	—	*197*
$Fe(PF_3)$(buta-1,3-diene)$_2$[g]	(D)	Orange-yellow	185–192	—	—	*126, 224, 343, 362*
$Fe(PF_3)_2(CO)$(buta-1,3-diene)	(B)	Yellow	—	6.6	1310	*52, 53, 357*
$Fe(PF_3)_2(CO)$(isoprene)	(B)	Yellow	—	—	—	*52, 53*
$Fe(PF_3)_2(CO)$(2,3-dimethylbuta-1,3-diene)	(B)	Yellow	—	8.3	1303	*52, 53*
$Fe(PF_3)_2(CO)$(*trans,trans*-2,4-hexadiene)	(B)	Yellow	—	6.9	1304	*52, 53*
$Fe(PF_3)_2(CO)$(*trans*-1,3-pentadiene)	(B)	Yellow	—	—	—	*52, 53*
$Fe(PF_3)_2(CO)$(*cis*-1,3-pentadiene)	(B)	Yellow	—	—	—	*52, 53*
$Fe(PF_3)_2(CO)$(1,3-cyclohexadiene)	(B)	Light-yellow	—	—	1302	*358*
$Fe(PF_3)_2(CO)$(2,4-dimethyl-1,3-pentadiene)	(B)	Yellow	—	—	—	*52, 53*
$Fe(PF_3)(CO)_2$(buta-1,3-diene)	(B)	Yellow	—	—	1300	*52, 53, 357*
$Fe(PF_3)(CO)_2$ (isoprene)	(B)	Yellow	—	7.4	1307	*52, 53*
$Fe(PF_3)(CO)_2$(2,3-dimethylbutadiene)	(B)	Yellow	—	8.0	1308	*52, 53*
$Fe(PF_3)(CO)_2$(*trans,trans*-2,4-hexadiene)	(B)	Yellow	—	10.4	1304	*52, 53*
$Fe(PF_3)(CO)_2$(*trans*-1,3-pentadiene)	(B)	Yellow	—	8.7	1305	*52, 53*
$Fe(PF_3)_x(CO)_{4-x}$(pentene)	(B)	—	—	—	1300	*78*
$Fe(PF_3)(CO)_2$(*cis*-1,3-pentadiene)	(B)	Yellow	—	8.2	1311	*52, 53*
$Fe(PF_3)(CO)_2$(1,3-cyclohexadiene)	(B)	Light-yellow	—	—	1316	*358*
$Fe(PF_3)(CO)_2$(2,4-dimethyl-1,3-pentadiene)	(B)	Yellow	—	10.4	1309	*52, 53*
$Fe(PF_3)_x(CO)_{3-x}$(trimethylenemethane)	(B)	Light-yellow	Liquid	6.4	1310	*74*
$Ni(PF_3)_x$(propene)	—	—	—	—	—	*42*
$Ni(PF_3)_3$(propene)	(D)	Yellow	liquid, (dec. −45°)	20.3	1270	*28*
$Ni(PF_3)_3(CF_3CH{=}CH_2)$	(D)	Yellow	liquid, (dec. −30°)	20.8	1305	*28*
$Ni(PF_3)_3(FCH{=}CH_2)$	(D)	Yellow	liquid, (dec. −96 to −45)	21.3	1284	*28*

$Ni(PF_3)_3(ClCH{=}CH_2)$	D	Yellow	liquid, (dec. −96 to −45)	—	—	*28*
$Ru(PF_3)(buta\text{-}1,3\text{-}diene)_2$[h]	(D)	Red-yellow	—	−2.91	1334	*262*
$Ru(PF_3)_3$(cyclohexadiene)	(E)	Pale-yellow	Liquid	3.5	1309	*1*
$Ru(PF_3)_2(PPh_3)$(buta-1,3-diene)	(B)	Pale-yellow	Oil	3.2	1307	*1*
$[RhCl(PF_3)(ethylene)]_2$	(G)	Yellow	50 (dec.)	24.6	1332	*28, 81*
$RhCl(PF_3)_2$(buta-1,3-diene)	(F)	Yellow	60	—	—	*294*
$RhCl(PF_3)_2$(1,3-pentadiene)	(F)	Yellow	60	—	—	*294*
$RhCl(PF_3)_2$(2-methylbuta-1,3-diene)	(F)	Yellow	Oil	—	—	*294*
$RhCl(PF_3)_2$(acrylonitrile)	(F)	Yellow	100 (dec.)	—	—	*294*
$Rh_2(PF_3)_5(CH_3O_2CC_2CO_2CH_3)_2$	(H)	Red	162	13.0, 15.6[i]	1337, 1376	*22*
$Rh_2(PF_3)_5(CH_3O_2CC_2H)_2$	(H)	Red	—	10.0, 13.9[i]	1337, 1360	*22*
$Rh_2(PF_3)_3(PPh_3)(CH_3CO_2C_2CO_2CH_3)_2$	(H)	Red	167	14.0, 17.2, 13.7	1353, 1391, 1345	*22*
$RhCl(PF_3)(SbPh_3)_2(C_8F_{12})$	(H)	Lemon-yellow	—	—	—	*238*
$[Rh(PF_3)(spp)_2][BF_4]$[j]	(F)	—	—	—	—	*24*
$[Rh(PF_3)(spas)_2][BF_4]$[k]	(F)	—	—	—	—	*24*
$[Ir(PF_3)(spp)_2][BF_4]$[j]	(F)	—	—	—	—	*24*
$[Ir(PF_3)(spas)_2][BF_4]$[k]	(F)	—	—	—	—	*24*
$IrCl(PF_3)$(cyclooctene)$_2$	(F)	Yellow	106–109	—	—	*17*
$Ir(acac)(PF_3)$(cyclooctene)	(F)	Yellow	—	—	—	*17*

[a] In ppm relative to CCl_3F.

[b] In Hz.

[c] ${}^1J_{PF}$ quoted = ${}^1J_{PF} + n^3J_{PF'}$ for $(PF_3)_{n+1}$ complexes.

[d] $Cr(PF_3)_3(\eta^5$-cyclooctadienyl)hydridotris(trifluorophosphine) also formed (see Section XIII).

[e] δ_P [in ppm relative $P(OMe)_3$] = 178.6, 206.7 (*343*).

[f] The analogous cyclooctatetraene complex is also known (*343*).

[g] X-Ray crystallographic structure done (*224*); Fe–PF_3 = 2.024 Å.

[h] δ_P = 172.5 ppm.

[i] Temperature-dependent spectra.

[j] spp = *o*-Styryldiphenylphosphine.

[k] spas = *o*-Styryldiphenylarsine.

TABLE IX

TRANSITION METAL ALKYNE COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b]	Temperature (°C)	References
$Rh_2(PF_3)_6(HC_2H)$	(B)	Yellow	60–61	7.1	1400	24	*20, 26*
$Rh_2(PF_3)_6(C_6H_5C_2H)$	(B)	Dark-brown	Oil	6.1	1385	−145	20, 26
$Rh_2(PF_3)_6(n\text{-}C_4H_9C_2H)$	(B)	Brown	Oil	6.5	1400	24	*20, 26*
$Rh_2(PF_3)_6(t\text{-}C_4H_9C_2H)$	(B)	Orange-brown	18	6.1	1400	−40	*20, 26*
$Rh_2(PF_3)_6(CH_3C_2CH_3)$	(B)	Yellow	118	7.5	1380	−70	*20, 26*
$Rh_2(PF_3)_6(n\text{-}C_3H_7C_2CH_3)$	(B)	Yellow	—	8.9	1405	24	*20*
$Rh_2(PF_3)_6(C_6H_5C_2CH_3)$	(A)	Orange	68	8.6	1405	24	*20, 26*
$Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$	(A)	Red	Oil	7.3	1385	−55	*20*
$Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$	(A)	Red	143–145	8.4	1415	−9	*20*
$Rh_2(PF_3)_6(C_6H_5C_2CO_2CH_3)$	(A)	Orange	Oil	9.0	1400	24	*20*
$Rh_2(PF_3)_6(p\text{-}NO_2C_6H_4C_2CO_2C_2H_5)$	(A)	Yellow	58	8.7	1405	24	*20, 26*
$Rh_2(PF_3)_6(CF_3C_2CF_3)$	(B)	Yellow	159	6.3 7.7	1395 1355	−104	*20*
$Rh_2(PF_3)_6(CH_3C_2CO_2CH_3)$	(B)	Yellow	—	8.6	1400	24	*20, 26*
$Rh_2(PF_3)_6(t\text{-}C_4H_9C_2\text{-}t\text{-}C_4H_9)$	(C)	Red	—	5.3	1402	24	*23*
$Rh_2(PF_3)_5(t\text{-}C_4H_9C_2\text{-}t\text{-}C_4H_9)$	(A)	Yellow	145–148	−1.5	1381	24	*23*
				12.1	1353	24	
				8.1	1375	24	
				14.1	1324	24	

$Rh_2(PF_3)_4(PPh_3)_2(C_6H_5C_2C_2H_5)$	(D)	Burgundy	164–165 (dec.)	5.6	1390	24	*21*
$Rh_2(PF_3)_4(PPh_3)_2(C_6H_5C_2C_6H_5)(Et_2O)$[c]	(D)	Burgundy	110–113 (dec.)	—	—	—	*21, 26*
$Rh_2(PF_3)_4(AsPh_3)_2(C_6H_5C_2C_6H_5)$	(D)	Red	189 (dec.)	5.7	1385	24	*21*
$Rh_2(PF_3)_4(PMePh_2)_2(C_6H_5C_2C_6H_5)$	(D)	Red	146–148	5.8	1385	24	*21*
$Rh_2(PF_3)_4(PPh_3)_2(C_6H_5C_2CH_3)$	(D)	Red	147–151 (dec.)	4.4, 5.7	1360, 1380	24	*21*
$Rh_2(PF_3)_4(AsPh_3)_2(C_6H_5C_2CH_3)$	(D)	Red	176–180	5.5 4.0, 5.2	1385 1360, 1390	24 −30	*21*
$Rh_2(PF_3)_4(PMePh_2)_6(C_6H_5C_2CH_3)$	(D)	Red	105	4.6, 5.8 3.2	1360, 1385 1410	24 110	*21*
$Rh_2(PF_3)_4(AsMePh_2)_2(C_6H_5C_2CH_3)$	(D)	Red	136–138	5.4 4.8, 5.8	1385 1365, 1385	55 24	*21*
$Rh_2(PF_3)_4(AsPh_3)_2(p\text{-}NO_2C_6H_4C_2CO_2C_2H_5)$	(D)	Red	174 (dec.)	4.4, 6.1 5.8	1385, 1405 1415	24 85	*21*
$Rh_2(PF_3)_2(diars)_2(C_6H_5C_2C_6H_5)$[d]	(D)	Red	196 (dec.)	−0.2	1375	24	*21*
$Rh_2(PF_3)_2(diars)_2(C_6H_5C_2CH_3)$[d]	(D)	Red	180–183	0.2	1360	24	*21*
$Rh_2(\eta^5\text{-}C_5H_5)_2(CO)(PF_3)(CF_3C_2CF_3)$[e]	(E)	Orange	155 (dec.)	8.2	1340		*103*
$Os_3(CO)_8(PF_3)(C_6H_5C_2C_6H_5)_2$	(E)	Violet	—	—	—	—	*113*

[a] In ppm relative to CCl_3F.

[b] $^1J_{PF}$ in Hz, all J_{PF} values are approximate and spectra are temperature dependent.

[c] X-Ray structure done (*21*).

[d] diars = $o\text{-}C_6H_4(AsMe_2)_2$.

[e] $\delta_P = 124.9$ ppm, $^1J_{PRh} = 360$ Hz (*103*).

X. Transition Metal–Alkyne Complexes

No mononuclear alkyne complexes containing PF_3 have been reported to date but a number of complexes of the type $[Rh_2(PF_3)_6(alkyne)]$ listed in Table IX have been obtained by heating a solution of $[Rh_2(PF_3)_8]$ in *n*-hexane under reflux in an inert atmosphere with an equimolar amount of the alkyne (method A). Care must be taken in the case of $MeCO_2C{\equiv}CCO_2Me$ and $HC{\equiv}CCO_2Me$ since reactions occur below room temperature to give the red complexes $[Rh_2(PF_3)_5(alkyne)_2]$ (see Section IX), while explosive polymerization of the alkyne occurs above room temperature. The $[Rh_2(PF_3)_5(alkyne)_2]$ compounds have been assigned a metallocyclopentadiene structure.

In a number of cases an excess of the alkyne can be condensed onto solid $[Rh_2(PF_3)_8]$ using a conventional high vacuum system (method B), and in one case addition of PF_3 to an $[Rh_2(PF_3)_5(alkyne)]$ complex has been reported (method C) (*23*).

$$Rh_2(PF_3)_8 \xrightarrow{\text{alkyne}} [Rh_2(PF_3)_6(alkyne)]$$

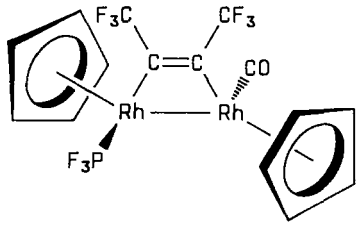
$$[Rh_2(PF_3)_5(alkyne)] \xrightarrow{PF_3} [Rh_2(PF_3)_6(alkyne)]$$

Complexes containing coordinated tertiary phosphines or arsines of the type $[Rh_2(PF_3)_4L_2(alkyne)]$ and $[Rh_2(PF_3)_2L'_2(alkyne)]$ (L = monodentate, L′ = bidentate ligand) are readily obtained by displacement of PF_3 from $[Rh_2(PF_3)_6(alkyne)]$ under mild conditions (method D). There are also reports of displacement of CO by PF_3 from an alkyne metal carbonyl complex (method E) e.g., (*113*).

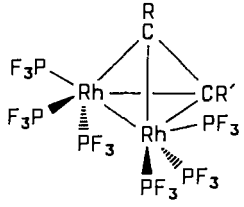
$$Os_3(CO)_9(PhCCPh)_2 \qquad Os_3(CO)_8(PF_3)(PhC{\equiv}CPh)$$

More recently, decarbonylation of the bridging η^1-alkyne complex $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CF_3CCCF_3)]$ with Me_3NO gave the η^2-complex, which, when treated with PF_3, afforded high yields of the η^1-alkyne mixed carbonyl–trifluorophosphine derivative (**8**), in which the ligands are mutually trans (*103*).

By contrast, the structures of the $[Rh_2(PF_3)_6(alkyne)]$ (**9**) complexes contain a bridging alkyne ligand lying over and perpendicular to the metal–metal bond, similar to that in $[Co_2(CO)_6(RCCR)]$. Variable-temperature ^{19}F NMR studies show that the PF_3 groups undergo intramolecular exchange leading to NMR equivalence at room temperature, and possible mechanisms for exchange have been discussed.



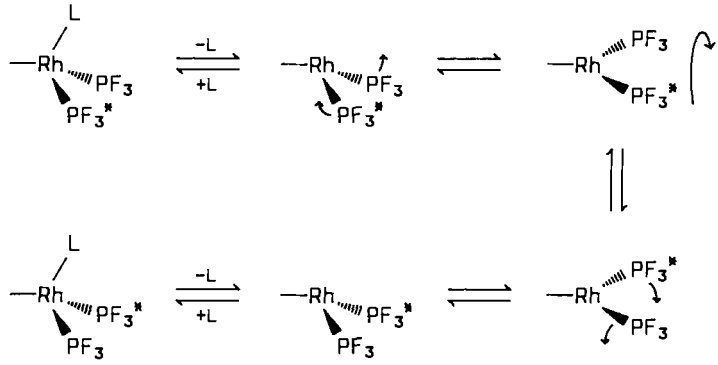
(8)



(9)

A single-crystal X-ray analysis of the complex $[Rh_2(PF_3)_4(PPh_3)_2(PhCCPh)]$ (*21*) confirmed that it has a similar structure and that the PPh_3 ligands are on the same side of the molecule as the bridging alkyne.

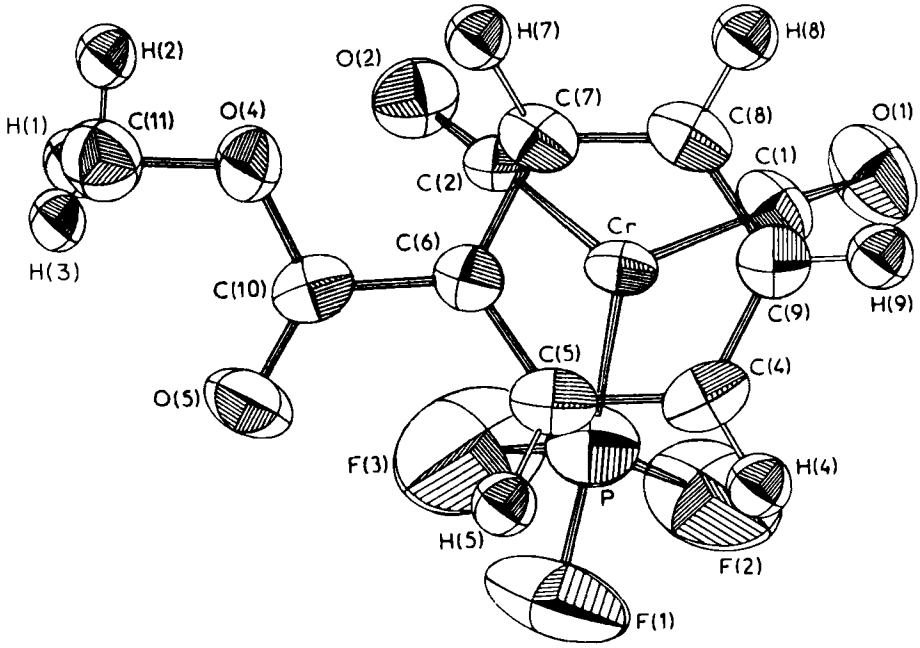
Interestingly this type of complex is stereochemically rigid at around room temperature but undergoes an intramolecular exchange of PF_3 on warming. Such a process suggested the formation of a coordinatively unsaturated intermediate by phosphine dissociation (Scheme 5). Support for this comes from the synthesis of $[Rh_2(PF_3)_5(^tBuCC^tBu)]$, which reacts reversibly with PF_3 at room temperature to form $[Rh_2(PF_3)_6(^tBuCC^tBu)]$.



SCHEME 5. Proposed mechanism for fluxional behaviour of $[Rh_2(PF_3)_4L_2(alkyne)]$ (21).

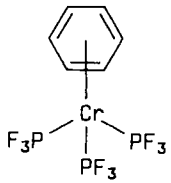
XI. Transition Metal–Arene Complexes

The first reported arene–transition metal trifluorophosphine complex $[Cr(\eta^6\text{-}C_6H_6)(PF_3)_3]$ was obtained by UV irradiation of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ with PF_3 (method A), whereas the corresponding thermal reaction afforded instead the mixed carbonyl trifluorophos-

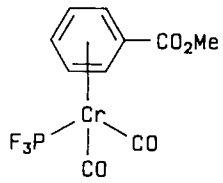


[11]

phine complex (*174*). The ^{19}F NMR spectrum of $[Cr(\eta^6\text{-}C_6H_6)(PF_3)_3]$ (**10**) has been fully analyzed (*277*) and is consistent with the complex having C_{3v} symmetry. The crystal and molecular structure of the related complex $[Cr(\eta^6\text{-}C_6H_5CO_2Me)(CO)_2(PF_3)]$ (**11**), made by a similar synthetic route (*97, 315, 316*), has been determined by a single crystal X-ray study. The Cr—P distance of 2.123(3) Å is very much shorter than other known chromium(0)–trivalent phosphorus distances [e.g., 2.252(1) Å in $\{Cr(CO)_4[P(OMe)_3]_2\}$, 2.346(3) Å in $[Cr(CO)_5(PH_3)]$, and 2.422(1) Å in $[Cr(CO)_5(PPh_3)]$] and this has been attributed to



(**10**)



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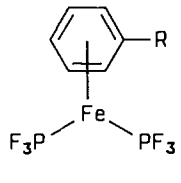
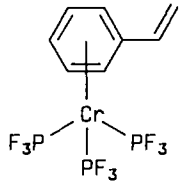


(R = H, Me)

(**12**)

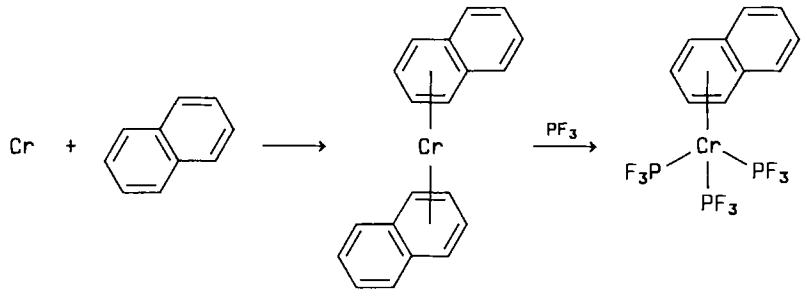


(**13**)

the π-acceptor properties of PF_3. The Cr—P bond length in $[Cr(C_8H_{11})(PF_3)_3H]$ is also very short [ave. 2.146(3) Å] (see Section IX).

More recently, the technique of metal vapor synthesis has been generally used (method B) to synthesize a variety of arene–metal–PF_3 complexes, and the method has been extended to include pyridine acting as an η^6-bonded ligand. The report from Skell's group (*362*) of [Fe(η^6-toluene)$(PF_3)_3$] using this route was followed shortly thereafter by Timms's preparation of $[Fe(\eta^6\text{-}C_6H_6)(PF_3)_2]$ (**12**), and styrene has also been successfully utilized in the preparation of [Cr(η^6-styrene)$(PF_3)_3$] (**13**) (*39*). This synthetic method is attractive because the metal can often be sublimed from a spiral of tungsten or molybdenum wire heated electrically and the vapor deflected into the bottom half of a liquid nitrogen cooled vacuum vessel. PF_3 and the arene are then condensed at −196°C and subsequently unreacted ligands are pumped off on warming to room temperature. The arene–metal–PF_3 complexes are invariably volatile and can be sublimed from the reaction vessel. Electron beam and laser techniques are also useful in these metal vapor syntheses (*16, 125*).

The metal vapor synthesis can also be used to obtain bisarenemetal complexes, which then readily react with PF_3 to displace one arene ring (method C). This route has been used effectively in the synthesis of [Cr(η^6-naphthalene)$(PF_3)_3$] (*225, 226*) (Scheme 6).



SCHEME 6

Interestingly, the presence of the acceptor PF_3 ligands in [Cr(η^6-naphthalene)$(PF_3)_3$] makes the coordinated naphthalene become activated toward attack by nucleophiles. Thus treatment with stabilized carbanions and either I_2 or Ce(IV) salts affords high yields of the α-substituted naphthalenes (*102*) (Scheme 7).

A rather unusual synthetic route to an η^6-arene–metal–trifluorophosphine complex has been described in which displacement

TABLE X

η^6-ARENE TRANSITION METAL COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Cr(PF_3)_3(C_6H_6)$[c]	(A)(B)	Pale-yellow	dec. >220	−12.4	1295	*174, 257, 277, 338, 339*
$Cr(PF_3)_3(C_6F_6)$	(B)	Pale-yellow	—	—	—	*257*
$Cr(PF_3)_3$(mesitylene)	(B)	Cream	dec. >130	−11.1	1250	*257*
$Cr(PF_3)_3$(cumene)	(B)	Pale-green	47–48	−12.7	1284	*257*
$Cr(PF_3)_3$(styrene)	(B)	—	Oil	—	—	*39*
$Cr(PF_3)_3$(styrene)$_n$	(B)	Red	—	—	—	*39*
$Cr(PF_3)_3$(pyridine)	(B)	—	—	—	—	*338*
$Cr(PF_3)_3$(naphthalene)	(C)	Yellow-orange	153 ± 1	—	—	*102, 225, 226*
$Cr(PF_3)(CO)_2$(benzonorbornadiene)	(D)	Yellow	—	—	—	*161*
$Cr(PF_3)(CO)_2(C_6H_5CO_2Me)$[d]	(A)	Yellow-orange	—	—	—	*97, 315, 316*
$Cr(PF_3)(CO)_2[C_6H_4(CO_2Me)_2]$	(A)	Yellow-orange	88	—	—	*97, 315, 316*
$Fe(PF_3)_2(C_6H_6)$	(B)	Red	dec. >50	−0.4	1305	*257*
$Fe(PF_3)_2$(toluene)	(B)	Red	Liquid	—	—	*362*
$Mo(PF_3)_3$(mesitylene)[e]	(A)	Colorless	dec. 160 (subl. 100/10^{-3})	—	—	*174*

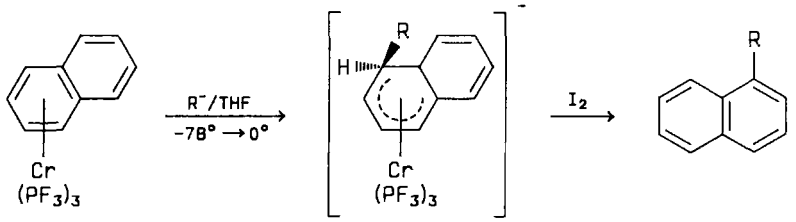
[a] In ppm relative to CCl_3F.

[b] In Hz.

[c] Except for $Cr(PF_3)_3(C_6H_6)$, $^1J_{PF}$ as listed is actually $|^1J_{PF} + 2^3J_{PF'}|$ for the $(PF_3)_3$ complexes and $^1J_{PF} + {}^3J_{PF'}$ for the $(PF_3)_2$ complexes. A full NMR spectroscopic analysis has been carried out (*277*).

[d] Single-crystal X-ray structure done; Cr—PF_3 = 2.123(3) Å.

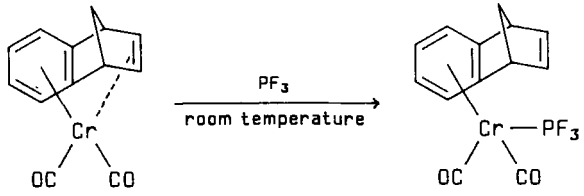
[e] This complex is also formed when $Mo(PF_3)_6$ and mesitylene are irradiated with UV light (*174*).



(R = CMe_2CN, CH_2CN)

SCHEME 7

of the complexed exocyclic carbon–carbon double bond of η^8-benzonorbornadiene(dicarbonyl)chromium occurs only in the presence of good π-acceptor ligands (Scheme 8) (method D). The known transition metal–arene complexes containing trifluorophosphine are summarized in Table X.



SCHEME 8

XII. Transition Metal η^3-Allyl Complexes

A variety of different preparative routes to this class of compounds have been utilized and the known complexes are listed in Table XI.

There is only one report to date of the simple addition of PF_3 to an η^3-allyl–metal complex containing no other ligands (method A), namely,

$$Cr(\eta^3\text{-}C_3H_5)_3 \xrightarrow{PF_3} Cr(\eta^3\text{-}C_3H_5)_3(PF_3)$$

However, the complex slowly converts to $[Cr(PF_3)_6]$. A related route (method B) involves the displacement of one or more coordinated η^3-allyl ligands, viz.,

$$Ta(\eta^3\text{-}C_3H_5)_4 \xrightarrow[20°C]{PF_3} Ta(\eta^3\text{-}C_3H_5)(PF_3)_5$$

TABLE XI

TRANSITION METAL η^3-ALLYL COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Cr(\eta^3\text{-}C_3H_5)_3(PF_3)$	(A)	Dark-green	—	—	—	*183*
$Fe(\eta^3\text{-}C_3H_5)(PF_3)_3$	(G)	Purple	Unstable	—	—	*338*
$Fe(\eta^3\text{-}C_3H_5)(PF_3)_3Br$	(D)	Red-brown	Subl. $25/10^{-1}$	—	—	*193*
$Fe(\eta^3\text{-}C_3H_5)(PF_3)_3I$	(D)	Red-brown	110 (dec.), subl. $45/10^{-3}$	—	—	*193*
$Co(\eta^3\text{-}C_3H_5)(PF_3)_3$	(B) (E) (F) (G)	Yellow	22 (55/760)	10.7	1268	*56, 220, 338*
$Co(\eta^3\text{-1-methylallyl})(PF_3)_3$(*anti*)	(C) (F)	Yellow	45	11.3	1268	*56, 220*
$Co(\eta^3\text{-1-methylallyl})(PF_3)_3$(*syn*)	(C) (F)	Yellow	0	10.6	1265	*56, 220*
$Co(\eta^3\text{-1-methyl-2-chloroallyl})(PF_3)_3$	(C)	Yellow	65 (subl. 60/1)	—		*220*
$Co(\eta^3\text{-1,1-dimethylallyl})(PF_3)_3$	(F)	Orange	56	12.5	1265	*56*
$Co(\eta^3\text{-1,2-dimethylallyl})(PF_3)_3$(*anti*)	(F) (G)	Orange	98	11.8	1268	*56*
$Co(\eta^3\text{-1,3-dimethylallyl})(PF_3)_3$(*syn,syn*)	(C) (F)	Orange	−12	11.4	1290	*56, 220*
$Co(\eta^3\text{-2-ethylallyl})(PF_3)_3$	(F)	—	—	11.3	1268	*56*
$Co(\eta^3\text{-cycloheptatrienyl})(PF_3)_3$	(C) (J)	Yellow	80/1	−13.6	1316	*56, 338, 343*
$Co(\eta^3\text{-1-methyl-2-ethylallyl})(PF_3)_3$	(C)	Red	35	—	—	*220*
$Co(\eta^3\text{-1,1,2-trimethylallyl})(PF_3)_3$	(C)	Yellow	Subl. $25/10^{-3}$	—	—	*220*
$Co(\eta^3\text{-cycloheptadienyl})(PF_3)_3$	(F) (I)	Orange	−15	14.3	1273	*56*
$Co(\eta^3\text{-cyclooctenyl})(PF_3)_3$	(C) (F)	Orange	35	11.6	1265	*56, 220*
$Co(\eta^3\text{-cyclohexenyl})(PF_3)_3$	(C)	Red oil	Subl. $/10^{-3}$	—	—	*55, 220*
$Co(\eta^3\text{-}C_3H_5)(PF_3)_2(PPh_3)$	(F)	Orange	145–147	12.9	1278	*55*
$Co(\eta^3\text{-1-methylallyl})(PF_3)_2(PPh_3)$(*anti*)	(F)	Orange	114–115	13.4 11.6	1288 1265	*55*
$Co(\eta^3\text{-1-methylallyl})(PF_3)_2(PPh_3)$(*syn*)	(F)	Red-orange	125–126	13.5 11.0	1287 1268	*55*
$Co(\eta^3\text{-1,1-dimethylallyl})(PF_3)_2(PPh_3)$	(F)	Red-brown	153–157	13.9 11.8	1323 1304	*55*
$Co(\eta^3\text{-1,2-dimethylallyl})(PF_3)_2(PPh_3)$(*anti*)	(F) (G)	Orange	150–152	13.3 12.0	1290 1274	*55*
$Co(\eta^3\text{-1,3-dimethylallyl})(PF_3)_2(PPh_3)$(*syn,syn*)	(F)	Red	114–115	11.6	1277	*55*

$Co(\eta^3\text{-2-ethylallyl})(PF_3)_2(PPh_3)$	(F)	Orange	96–98	11.6	1282	*55*
$Co(\eta^3\text{-2-ethylallyl})(PF_3)(PPh_3)_2$	(F)	Red	145–152	7.4	1308	*55*
$Co(\eta^3\text{-cyclooctenyl})(PF_3)_2(PPh_3)$	(F)	Red	137–139	12.9	1281	*55*
$Co(\eta^3\text{-cycloheptadienyl})(PF_3)_2(PPh_3)$	(I)	Red	116–118	16.3 14.7	1297 1287	*55*
$Co(\eta^3\text{-1-methylallyl})(C_4H_6)(PF_3)$(*anti*)	(C)	Yellow	85–87	13.2	1308 (RT)	*58*
				13.0 12.4	1313 1316 (−20°C)	
$Co(\eta^3\text{-1,1,3-trimethylallyl})(PF_3)_3$	(C)	Orange	—	12.8	1269	*157*
$(Ni(\eta^3\text{-}C_3H_5)(PF_3)H)$[d]	—	—	—	—	—	*42*
$RuCl_2(PF_3)(\eta^3\text{-}C_{10}H_{16})$[e,f]	(H)	Orange	130–131 (dec.)	22.0	1374	*140, 148*
$Rh(\eta^3\text{-}C_3H_5)(PF_3)_3$[g]	(B) (C) (E)	Yellow	Liquid	8.1	1342[h]	*82, 277, 295*
$Rh(\eta^3\text{-1-methylallyl})(PF_3)_3$	(C) (E)	Yellow	−20	8.2 (*syn*) 8.2 (*anti*)	1340, 1341[h]	*82, 295*
$Rh(\eta^3\text{-2-methylallyl})(PF_3)_3$	(E)	Yellow	−20	8.3	1340[h]	*82, 295*
$Rh(\eta^3\text{-cyclohexenyl})(PF_3)_3$	(C)	Yellow	0	8.4	1346[h]	*82, 295*
$Rh(\eta^3\text{-1,1-dimethylallyl})(PF_3)_3$	(E)	Yellow	0	9.6	1340[h]	*59, 82, 295*
$Rh(\eta^3\text{-1,2-dimethylallyl})(PF_3)_3$	(E) (G)	Yellow	35	8.7 (*syn*) 8.7 (*anti*)	1347, 1342[h]	*59, 82, 295*
$Rh(\eta^3\text{-1,3-dimethylallyl})(PF_3)_3$	(C)	Yellow	−15	9.3 (*syn,syn*) 9.3 (*anti,syn*)	1342[h] 1340	*82, 295*
$Rh(\eta^3\text{-1-ethyl-3-methylallyl})(PF_3)_3$	(C)	Yellow	0	9.2 (*syn,syn*)	1333[h]	*82, 295*
$Rh(\eta^3\text{-allyl})(PF_3)(PPh_3)_2$	(H)	Yellow	140–150	8.3	1381	*280*
$Rh(\eta^3\text{-2-methylallyl})(PF_3)(PPh_3)_2$	(H)	Yellow	116–120	—	—	*280*
$Rh(\eta^3\text{-1-methylallyl})(PF_3)(PPh_3)_2$	(H)	Orange	145–155	10.5	1373	*280*
$Ta(\eta^3\text{-allyl})(PF_3)_5$	(B)	Ruby-red	20 (dec.)	—	—	*187*

[a] In ppm relative to CCl_3F.
[b] In Hz.
[c] Except where stated, $^1J_{PF}$ listed is equal to $^1J_{PF} + n^3J_{PF}$ for $(PF_3)_{n+1}$ complexes.
[d] Low-temperature species in equilibrium with the propene-Ni-PF_3 complex (*42*).
[e] An X-ray crystallographic study has been made (*148*); Ru—PF_3 = 2.237 Å.
[f] η^3-$C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl.
[g] A full NMR spectroscopic analysis has been made (*277*); $^1J_{PF} = -1422$ Hz; $^3J_{PF} = +40$ Hz.
[h] All spectra are temperature dependent.

A useful general synthetic approach involves the insertion of allene or dienes into the metal–hydrogen bond of transition metal hydrido–trifluorophosphine complexes (method C).

$$RhH(PF_3)_4 + \text{allene} \longrightarrow Rh(C_3H_5)(PF_3)_3$$

$$CoH(PF_3)_4 + \text{butadiene} \longrightarrow Co(C_4H_7)(PF_3)_3$$

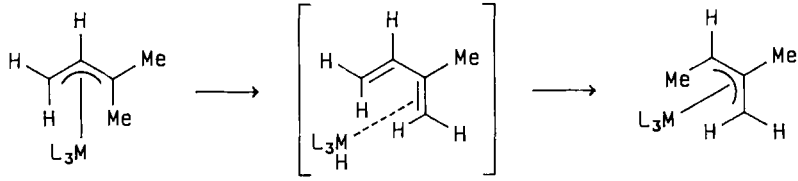
Oxidative addition of an allyl halide to a zero-valent complex (method D) or treatment of a trifluorophosphine metallate complex with an allylic halide followed by loss of PF_3 (method E) have also been briefly reported.

$$Fe(PF_3)_4 + \text{allylX} \longrightarrow Fe(C_3H_5)(PF_3)_3X \quad (X = Br, I)$$

$$KCo(PF_3)_4 + \text{allylX} \xrightarrow[-PF_3]{-KX} Co(C_3H_5)(PF_3)_3$$

A fairly general synthetic route involves the PF_3-induced displacement of ligands such as dienes and phosphines coordinated to metal allyl complexes (method F), and it has also been possible in certain complexes to interconvert η^3-allyl–metal–PF_3 complexes by an intramolecular thermal rearrangement (method G).

Thus when the η^3-1,1-dimethylallyltris(trifluorophosphine) complexes of cobalt or rhodium are gently warmed a rearrangement to the η^3-1,2-isomer occurs (*56, 295*). The postulated mechanism involves a diene–metal hydride intermediate (Scheme 9). The small PF_3 ligand can also be added directly to coordinatively unsaturated η^3-allylic systems or to chloro-bridged structures (method H).



SCHEME 9. (M = Co, Rh; L = PF_3)

$$Rh(C_3H_5)(PPh_3)_2 \xrightarrow{PF_3} Rh(C_3H_5)(PPh_3)_2(PF_3)$$

$$[RuCl_2C_{10}H_{16}]_2 \xrightarrow{PF_3} [RuCl_2(C_{10}H_{16})(PF_3)]$$

($C_{10}H_{16}$ = 2,7-dimethyl-2,6-diene-1,8-diyl)

The molecular structure of the latter compound has been determined

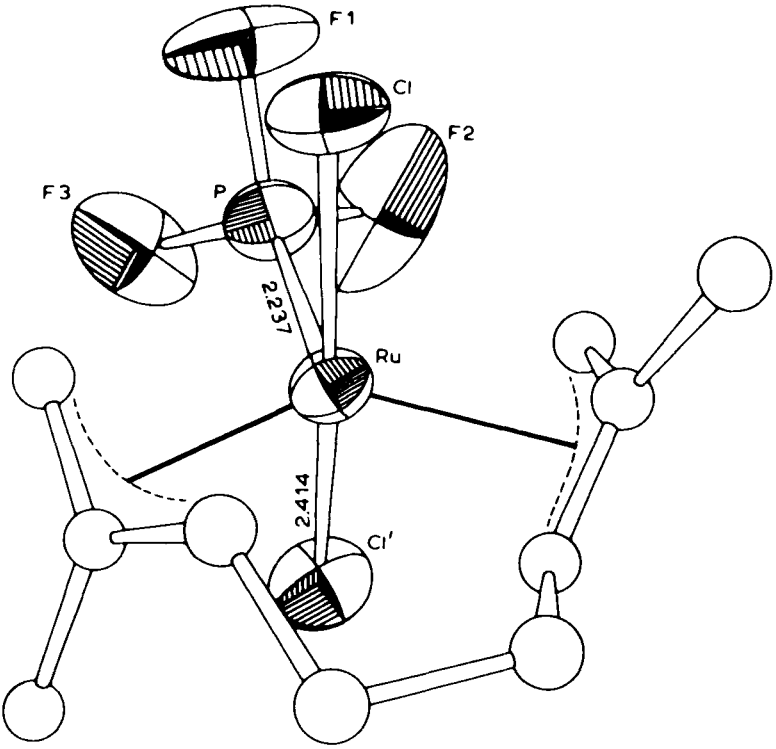


FIG. 18. Molecular structure of the complex $RuCl_2(PF_3)(C_{10}H_{16})$. [Reproduced from reference (*148*) with permission.]

(Fig. 18) and is a rare example of a PF_3 complex of a metal formally in oxidation state IV.

Addition of PF_3 to an η^5-heptadienyl metal PF_3 complex can lead to the corresponding η^3-allylic complex (method I). Finally, the method of metal vapor synthesis (see Sections IX and X) has not found general application for allylic systems (method J), but in one case, cocondensation of Fe, PF_3, and $[Sn(allyl)_4]$ gave the unstable paramagnetic complex $[Fe(PF_3)_3(\eta^3\text{-allyl})]$.

XIII. Transition Metal η^5-Cyclopentadienyl and Related Complexes

A common synthetic approach to this class of compounds involves thermally or UV induced substitution of coordinated CO or N_2 from a

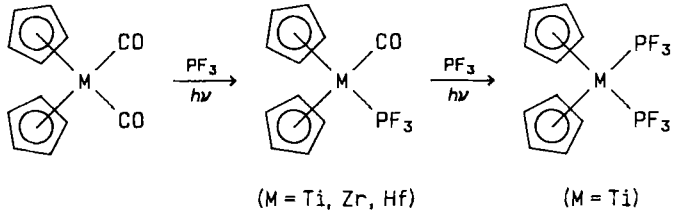
cyclopentadienyl metal complex by PF_3, or, alternatively, by $[Ni(PF_3)_4]$ as a source of PF_3 (method A).

$$Mn(\eta^5\text{-}C_5H_5)(CO)_3 \xrightarrow{PF_3} Mn(\eta^5\text{-}C_5H_5)(CO)_2(PF_3)$$
$$Rh(\eta^5\text{-}C_5Me_5)(CO)_2 \xrightarrow{Ni(PF_3)_4} Rh(\eta^5\text{-}C_5Me_5)(PF_3)_2$$

The gas-phase negative ion chemistry of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ has been studied by ion cyclotron resonance spectroscopy and the first observed example of a ligand displacement of an anionic transition metal complex involves the use of PF_3 in the formation of $[Co(\eta^5\text{-}C_5H_5)(PF_3)]^-$ and $[Co(\eta^5\text{-}C_5H_5)(PF_3)_2]^-$ (*84*). These results indicate that PF_3 is a stronger π acceptor than CO.

$$[Co(\eta^5\text{-}C_5H_5)CO]^- + PF_3 \longrightarrow [Co(\eta^5\text{-}C_5H_5)PF_3]^- + CO$$

A particularly interesting example of CO displacement involves the photochemical reaction of the early transition metal complexes $[M(\eta^5\text{-}C_5H_5)_2(CO)_2]$ (M = Ti, Zr, Hf) with PF_3 (Scheme 10). In the case of (M = Hf) this complex represented the first hafnocene–phosphine complex to be reported. A slightly better synthetic route to the mono(trifluorophosphine)titanium(II) complex involves displacement of PEt_3 from $[Ti(\eta^5\text{-}C_5H_5)_2(CO)(PEt_3)]$.



SCHEME 10

A single-crystal X-ray diffraction study on $[Ti(\eta^5\text{-}C_5H_5)_2(PF_3)_2]$ was the first structural determination of a PF_3 complex of an early transition metal. The structure (Fig. 19) reveals a number of features of interest. There are two crystallographically independent molecules in the unit cell, one residing on a mirror plane, but no apparent conformational differences between them. The Ti—P bond lengths range from 2.340(6) to 2.349(6) Å, which are considerably shorter than the value of 2.585(1) Å found in the related complex $[Ti(\eta^5\text{-}C_5H_5)_2(CO)(PEt_3)]$. Two independent methods of estimating a normal Ti—P bond distance give values of 2.48 and 2.53 Å, indicating that the

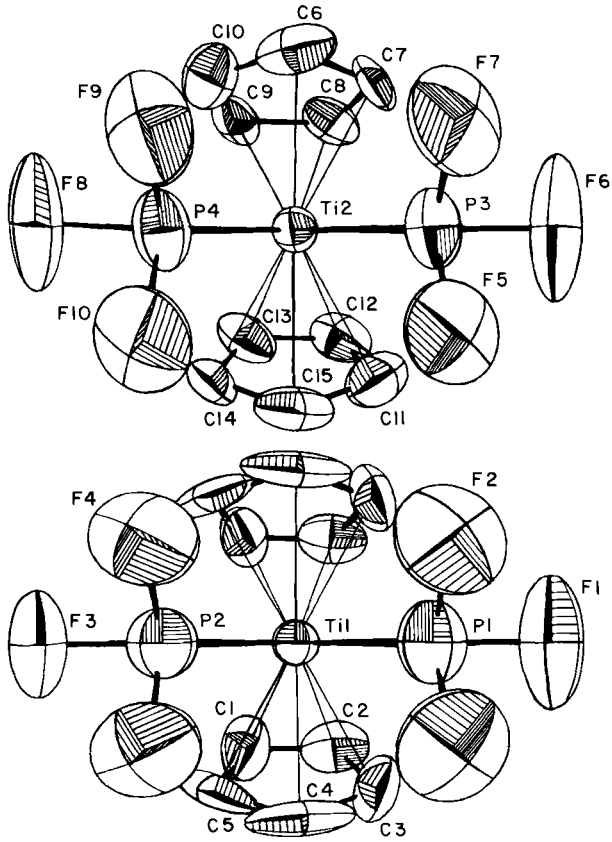
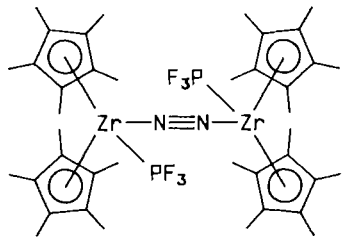


FIG. 19. Views of the two crystallographically independent molecules of $Cp_2Ti(PF_3)_2$. [Reproduced from references (*109, 329*) with permission.]

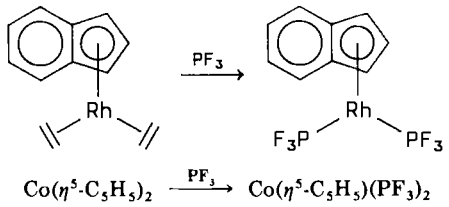
Ti—PF_3 bond distance in $[Ti(C_5H_5)_2(PF_3)_2]$ is perhaps 0.15 Å less than expected (*109, 329*). Similarly, the novel green dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2]$ (**14**) has been obtained by displacement of the



(**14**)

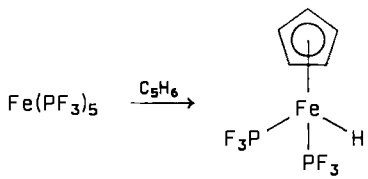
terminally coordinated N_2 molecules in $[\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2]$ (method A), although it exhibits low stability in solution, decomposing within minutes at room temperature (*245*).

Ethylene can be displaced by PF_3 from $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ (*284*) and from $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ (*158*) (method B), and there is one report of displacement of one $\eta^5\text{-}C_5H_5$ ring from a bis($\eta^5\text{-}C_5H_5$) metal complex (method C).



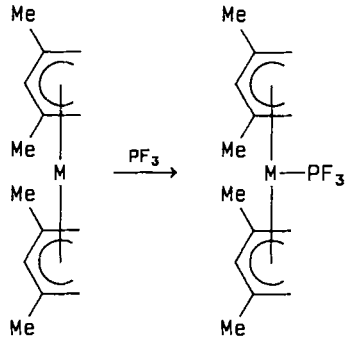
Other routes involve treatment of a metal–trifluorophosphine halide with either sodium or lithium cyclopentadienide (method D), or direct reaction between a metal–PF_3 complex and cyclopentadiene (method E).

This latter reaction is exemplified by the reaction of $[Fe(PF_3)_5]$ with cyclopentadiene, which, in contrast with the analogous iron carbonyl system, gives the stable hydrido complex $[Fe(\eta^5\text{-}C_5H_5)(PF_3)_2H]$.



More recent developments have utilized metal vapor synthesis (method F) involving cocondensation at low temperature of the metal, cyclopentadiene (or other dienes), and PF_3. The hydrido–cyclooctadienyl complex $[Cr(\eta^5\text{-}C_8H_{11})(PF_3)_3H]$ (*125*) (see Section IX) made in this fashion exhibits variable-temperature NMR spectra which establish the existence of an exchange between the hydrido atom and a methylenic hydrogen bound to an sp^3 carbon adjacent to the diene unit.

Direct addition of PF_3 to η^5-pentadienyl metal complexes offers an alternative synthetic route (method G) and this has been reported in the case of the formation of bis(2,4-dimethylpentadienyl)trifluorophosphine complexes of titanium and vanadium $[M(C_7H_{11})_2PF_3]$ (M = Ti, V) (Scheme 11) (*111*).



(M = Ti, V)

SCHEME 11

The formation of the 17-electron paramagnetic vanadium complex is not surprising in view of the known corresponding carbonyl complex, however the 16-electron titanium derivative is unexpected in view of the ready formation of the 18-electron biscarbonyl and bistrifluorophosphine metal complexes containing the η^5-cyclopentadienyl ligand. The solid-state structure of the PF_3 adduct of bis[2,4-dimethyl-(pentadienyl)]titanium has recently been determined (*111*) and is shown in Fig. 20. The corresponding vanadium complex is isomorphous. The metal–PF_3 distances are 2.326(Ti) and 2.275(V) Å.

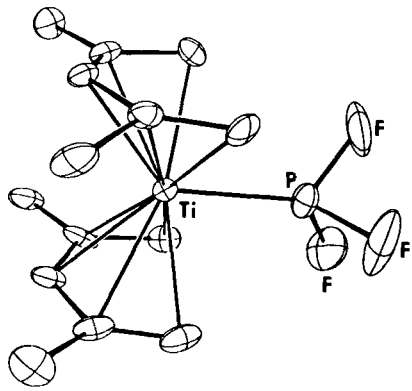


FIG. 20. The solid-state structure of the trifluorophosphine adduct of bis(2,4-dimethylpentadienyl)titanium. The corresponding vanadium compound is isomorphous. [Reproduced from reference (*111*) with permission.]

TABLE XII

TRANSITION METAL η^5-CYCLOPENTADIENYL AND RELATED COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Ti(\eta^5\text{-}C_5H_5)_2(CO)(PF_3)$	(A)	Orange	—	—	—	*109, 329*
$Ti(\eta^5\text{-}C_5H_5)_2(PF_3)_2$[d]	(A)	Yellow-orange	Sublimes	—	—	*109, 329*
$Ti(\eta^5\text{-}C_7H_{11})_2(PF_3)$[e]	(G)	Lime-green	Sublimes	21.8	1340	*111*
$V(\eta^5\text{-}C_7H_{11})_2(PF_3)$[f]	(G)	Blue-green	Sublimes	—	—	*111*
$V(\eta^5\text{-}C_5H_5)(NO)_2(PF_3)$	(A)	—	—	—	—	*270*
$V(\eta^5\text{-}C_5H_5)(CO)_x(PF_3)_{4-x}$[g]	(A)	Yellow	—	—	—	*306, 308, 309, 321*
$CrH(PF_3)_3(\eta^5\text{-cyclohexadienyl})$	(F)	Orange	—	—	—	*40*
$CrH(PF_3)_3(\eta^5\text{-cyclooctadienyl})$[h]	(F)	Orange[i]	—	7.7, 3.9	1280 ± 25	*125*
$Mn(PF_3)_3(\eta^5\text{-}C_5H_5)$	(A)	Yellow	165–167 (subl. $40/10^{-3}$)	14.4, −0.4	—	*201*
$Mn(PF_3)_2(CO)(\eta^5\text{-}C_5H_5)$	(A)	Yellow	Subl. $40/10^{-3}$	13.2, −1.2	—	*201, 127*
$Mn(PF_3)(CO)_2(\eta^5\text{-}C_5H_5)$	(A)	Yellow	—	3.7	1279	*127, 201, 266, 333*
$FeH(PF_3)_2(\eta^5\text{-}C_5H_5)$	(E)	Orange	$40/10^{-3}$	—	—	*196*
$Fe(PF_3)_2(\eta^5\text{-}C_5H_5)(C_4H_4N)$	(G)	—	—	—	—	*110*
$Fe(PF_3)_2(\eta^5\text{-}C_5H_5)K$	—	White	—	—	—	*196*
$Fe(PF_3)_2(\eta^5\text{-}C_5H_5)(Et_3NH)$	—	Colorless	—	—	—	*196*
$Fe(PF_3)(CO)(\eta^5\text{-}C_5H_5)(I)$	(A)	Brown	102–103	—	—	*170*
$Co(PF_3)_2(\eta^5\text{-}C_5H_5)$	(C) (F)	Deep-red	−8, 51/13	—	—	*132, 188*
$ZrH_2(PF_3)[\eta^5\text{-}C_5(CH_3)_5]_2$	(G)	Red-brown	Unstable	—	—	*243*
$\{Zr(\eta^5\text{-}C_5Me_5)_2PF_3\}_2N_2$	(A)	Metallic-green	—	—	—	*245*

$Hf(\eta^5\text{-}C_5H_5)_2(CO)(PF_3)$	(A)	—	—	—	—	*328*
$Nb(\eta^5\text{-}C_5H_5)(PF_3)_4$	(A)	Red-brown	—	—	1330	*308*
$Mo(PF_3)(CO)_2(\eta^5\text{-}C_5H_5)CH_3$	(A)	Yellow	—	—	—	*170*
$Mo_2(PF_3)_2(CO)_4(\eta^5\text{-}C_5H_5)_2$	(A)	Dark-red	175 dec.	—	—	*170*
$Mo_2(PF_3)(CO)_5(\eta^5\text{-}C_5H_5)_2$	(A)	Dark-red	159–160	—	—	*170*
$Rh(PF_3)_2(\eta^5\text{-}C_5H_5)$	(E) (D)	Orange	−8	1.1	1308	*17, 159, 278, 284*
$Rh(PF_3)_2(\eta^5\text{-}C_9H_7)$	(B)	Orange	Oil	4.8	1332	*158*
$Rh(PF_3)_2[\eta^5\text{-}C_5(CH_3)_5]$	(A)	Orange	88–89	10.8	1334	*170*
$Ir(PF_3)_2[\eta^5\text{-}C_5(CH_3)_5]$	(A)	Yellow	90–92	16.6	1250	*170*
$Ir(PF_3)(PF_2)(F)[\eta^5\text{-}C_5(CH_3)_5]$	(A)	Pale-yellow	~104	4.4	1177	*170*

[a] Relative to CCl_3F.

[b] In Hz.

[c] $^1J_{PF}$ for the $(PF_3)_2$ complexes is equal to $^1J_{PF} + {}^3J_{PF}$, and equals $^1J_{PF} + 2^3J_{PF}$, for the $(PF_3)_3$ complex.

[d] Single-crystal structure done.

[e] $\delta_P = 209.6$.

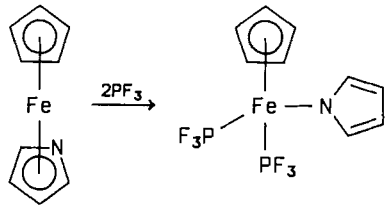
[f] $\mu_{eff} = 1.6$ BM; EPR data available.

[g] V chemical shift and J_{VP} coupling data reported.

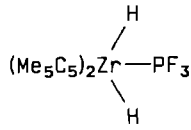
[h] A 1% yield of $Cr(PF_3)_4$(1,5-cyclooctadiene) is also reported (*125*).

[i] A single-crystal X-ray study has been carried out (see Section IX for details).

Another interesting example of addition of PF_3 to an η^5-cyclopentadienyl metal system involves an $\eta^5 \rightarrow \eta^1$ rearrangement of the coordinated pyrrolyl ring in azaferrocene (*110*). The rearrangement only occurs for π-acid ligands.



The unstable 18-electron complex $[(\eta^5\text{-}C_5Me_5)_2ZrH_2(PF_3)]$ is also readily formed by direct addition (method G) of PF_3 to the formally 16-electron complex $[(\eta^5\text{-}C_5Me_5)_2ZrH_2]$. On the basis of its ^1H NMR spectrum the structure of the PF_3 adduct (**15**) appears to be analogous to $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ with PF_3 occupying the central equatorial position mutually cis to both hydride ligands (*27, 243, 244*). Complexes synthesized by all the above routes are listed in Table XII.



(**15**)

XIV. Transition Metal Carbonyl Complexes

Trifluorophosphine and carbon monoxide readily undergo ligand-exchange reactions in their transition metal complexes. The close similarity in bonding characteristics of the two ligands toward transition metals has been discussed extensively in several review articles (*72, 174, 272*) and the evidence will not be repeated here. Extensive vibrational spectroscopic studies have been made on mixed carbonyl–PF_3 metal complexes (*72, 174*) and force constant calculations have been carried out in some cases.

More recently, the volatility of metal–PF_3 complexes, metal carbonyls, and mixed PF_3–CO compounds has enabled UV photoelectron spectroscopic studies to be carried out (see Section V), and the data

suggest that PF_3 has a slightly greater overall electron-withdrawing effect than CO when attached to a transition metal.

Several ^{19}F and ^{31}P NMR studies of mixed PF_3–CO transition metal complexes have appeared and the fluxional nature of five-coordinated complexes such as $[Fe(PF_3)_{5-n}(CO)_n]$ and $[CoR_f(PF_3)_{4-n}(CO)_n]$ were among the first examples of this structural type to be studied in detail. So far, structural data are available only for $[Mo(PF_3)(CO)_5]$ from an electron diffraction study in the gas phase (*47*).

Synthetic routes to these complexes are summarized in Table XIII, which also lists the spectroscopic studies that have been made on this class of complexes. The action of PF_3 or CO usually under pressure with simultaneous UV irradiation on metal carbonyls or metal trifluorophosphine complexes, respectively, is of general applicability (method A). More recently, photolysis using a KrF laser has also been utilised, e.g.,

$$Cr(CO)_6 \xrightarrow[h\nu]{PF_3} Cr(PF_3)_n(CO)_{6-n}$$

$$Ni(PF_3)_4 \xrightarrow{CO} Ni(CO)_x(PF_3)_{4-x}$$

Often because of the close similarity in volatility and solubility of the mixed carbon–trifluorophosphine metal complexes the best separative method involves gas chromatography. Vapor pressures and enthalpy of sublimation data for the complexes $[M(PF_3)(CO)_5]$ (M = Cr, W) are comparable with the values for the corresponding hexacarbonyl complexes.

Intermolecular ligand-exchange reactions often occur extremely easily between metal–PF_3 complexes and the corresponding metal carbonyls (method B), for example, all possible $[Ni(CO)_x(PF_3)_{4-x}]$ complexes result on gently heating a mixture of $[Ni(PF_3)_4]$ and $[Ni(CO)_4]$.

A useful synthetic route to specific carbonyl–PF_3 transition metal complexes (method C) involves displacement of relatively weakly bound ligands such as ammonia, iodide ion, or unsaturated organic ligands (e.g., dienes, arenes) from suitable metal carbonyl complexes.

$$[Mo(CO)_5I]^- \xrightarrow{PF_3} Mo(CO)_5(PF_3)$$

$$Cr(CO)_4(C_7H_8) \xrightarrow{PF_3} Cr(CO)_4(PF_3)_2$$

The direct interaction between the metal, hydrogen, and mixtures of CO and PF_3 under pressure has been used successfully in the

TABLE XIII. TRANSITION METAL CARBONYL

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	δ_P[a]
$Cr(PF_3)_3(CO)_3$	(A) (B) (C)	White	34	—
$Cr(PF_3)_2(CO)_4$ (*cis*)	(A) (B) (C)	White	Liquid	−173.2
$Cr(PF_3)_2(CO)_4$ (*trans*)	(A) (B) (C)	White	Liquid	−179.8
$Cr(PF_3)(CO)_5$[f]	(A) (B) (C)	White	—	—
$MnH(PF_3)_4(CO)$[g]	(A)	Colorless	−56 to −52	—
$MnH(PF_3)_3(CO)_2$[g]	(A)	Colorless	−73 to −51	—
$MnH(PF_3)_2(CO)_3$[g]	(A)	Colorless	< −108	—
$MnH(PF_3)(CO)_4$[g]	(A)	Colorless	−56 to −24	—
$Mn_2(PF_3)_3(CO)_7$	(A) (F)	Yellow	38	—
$Mn_2(PF_3)_2(CO)_8$	(A) (F)	Yellow	45	—
$Mn_2(PF_3)_2(CO)_8$[h]	(A) (F)	Yellow	81	—
$Mn_2(PF_3)(CO)_9$	(A) (F)	Yellow	90	—
$Mn(PF_3)_3(CO)_2K$	(A)	—	—	—
$Mn(PF_3)_3(CO)_2I$	(A)	—	—	—
$Fe(PF_3)_4(CO)$[i]	(A) (B)	Yellow	—	—
$Fe(PF_3)_3(CO)_2$[i]	(A) (B)	Yellow	—	—
$Fe(PF_3)_2(CO)_3$[i]	(A) (B)	Yellow	—	—
$Fe(PF_3)(CO)_4$[i]	(A) (B)	Yellow	—	—
$CoH(PF_3)_3(CO)$	(A) (D)	Yellow	−67 (80.5/715)	—
$CoH(PF_3)_x(CO)_{4-x}$	(A) (E)	—	—	—
$Co(PF_3)_3(CO)K$	(A)	Colorless	205 dec.	—
$Ni(PF_3)_3(CO)$	(A) (B)	Colorless	−93 (0/88)	−137.2
$Ni(PF_3)_2(CO)_2$	(A) (B)	Colorless	−93 (0/56)	−136.8
$Ni(PF_3)(CO)_3$	(A) (B)	Colorless	(0/41)	−136.5
$Mo(PF_3)_5(CO)$[l]	(A) (B)	White	45	—
$Mo(PF_3)_4(CO)_2$ (*cis*)[l]	(A) (B) (C)	White	117	—
$Mo(PF_3)_4(CO)_2$ (*trans*)[l]	(A) (B)	White	94	—
$Mo(PF_3)_3(CO)_3$ (*cis*)[l]	(A) (B) (C)	White	64	—
$Mo(PF_3)_3(CO)_3$ (*trans*)[l]	(A) (B) (C) (G)	White	42	−150.6
$Mo(PF_3)_2(CO)_4$ (*cis*)[l]	(A) (B) (C)	White	27–28; 32	−148.0
$Mo(PF_3)_2(CO)_4$ (*trans*)[l]	(A) (B) (C)	White	10	—

COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

ϕ_F[b]	$^1J_{PF}$[c,d]	Remarks	Reference
—	—	MS (*267*), IR (*175, 176*), magnetic susceptibility (*175*)	*175, 176, 272, 349*
−0.2	1312[e]	MS (*267*)	*98, 228, 296*
1.1	1318	MS (*267*)	*165, 236, 267*
2.1	1315	MS (*267*), PES (*96, 367*), ESCA (*8*)	*8*
—	—	IR (*259*)	
—	—	IR (*259*)	
0.4, 3.5	1298, 1292	IR (*259*)	*259–261*
3.7, 2.6	1302, 1302		
5.2, 1.6	1310, 1307	IR (*259*), ^{1}H NMR (*260*)	
—	—	IR (*76, 127*)	
—	—	IR (*76, 127, 167, 297*)	
—	—	IR (*76, 127*)	*76, 127*
—	—	IR (*76, 127*)	*167, 170*
—	—	—	*185, 297*
—	—	—	
—	—[j,k]	MS (*267, 354*), IR (*70, 127, 239, 347, 354*), Raman (*36*), PES (*142, 267*), ^{13}C NMR(*239*)	*70, 176, 215*
—	—[j,k]	MS (*267, 354*), IR (*70, 127, 239, 347, 354*), PES (*142, 267*), ^{13}C NMR (*239*)	*34, 35, 269, 296*
5.6	1322[j,k]	MS (*267, 354*), IR (*70, 127, 239, 347, 354*), PES (*142, 267*) ^{13}C NMR (*239*)	*30, 127, 239, 240, 269, 327, 347, 354*
6.2	1329[j,k]	MS (*354*), IR (*70, 127, 239, 347, 354*), PES (*142*), ^{13}C NMR (*239*)	*36, 142, 267, 269*
—	—	IR (*204, 351*), magnetic susceptibility (*204*)	*180, 204, 351*
—	—	IR (*204, 351*)	*120, 180, 204, 351*
—	—	IR (*204*), magnetic susceptibility (*204*)	*204*
—	—	IR (*32, (33), 35, 44, 49, 85, 127, 233*), Raman (*35, 233*) Force constants (*30, 34, 43, 230*)	*30, 31, 32, 75*
18.9	1357	IR (*32, (33), 35, 44, 48, 49, 71, 85, 127*), Raman (*35*), Force Constants (*30, 34, 43, 230*)	*11, 43, 44, 48, 49 63, 71, 85,*
—	—	IR((*32, (33), 35, 44, 71, 85, 127*), Raman (*35*), Force Constants (*30, 34, 43, 230*)	*73, 230, 233, 249, 250, 296*
—	—	IR (*73, 121, 127*)	
—	—	IR (*73, 127*)	*35, 117, 215*
—	—[m]	IR (*73, 127*)	*34, 73, 117, 127*
1.2	1296[e,m]	IR (*12, 73, 85, 127, 176, 215, 332*), magnetic susceptibility (*11*)	*12, 85, 121*
3.0	1300[m]	IR (*12, 73, 127*)	*47, 98, 228, 332*
2.9	1305[e,m]	IR (*12, 73, 127*)	*11, 13, 130, 236, 258*
4.0	1320[m]	IR (*73, 127*)	*305, 322*

(*continued*)

TABLE XIII

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	δ_P[a]
$Mo(PF_3)(CO)_5$[l,n]	(A) (B) (C)	White	5[o]	—
$Ru(PF_3)_x(CO)_{5-x}$	(A)	Yellow	—	—
$[RhCl(PF_3)(CO)]_2$	(A) (B)	Red	40.5–41.5	—
$Rh_2Cl_2(PF_3)_3(CO)$	(A) (B)	Red	—	—
$[RhBr(PF_3)(CO)]_2$	(A) (B)	Red	—	—
$[RhI(PF_3)(CO)]_2$	(A) (B)	Red	—	—
$W(PF_3)_2(CO)_4$ (*cis*)	(A) (B) (C)	White	—	−122.0
$W(PF_3)_2(CO)_4$ (*trans*)	(A) (B)	White	—	—
$W(PF_3)(CO)_5$[p,q]	(A)	White	—	—
$ReH(PF_3)_n(CO)_{5-n}$	(A)	—	—	—
$ReBr(PF_3)_2(CO)_3$	(F)	White	40–41	—

[a] In ppm relative to $P(OMe)_3$.
[b] In ppm and CCl_3F.
[c] In Hz.
[d] In general, $^1J_{PF}$ listed = $^1J_{PF} + n^3J_{PF'}$ for $(PF_3)_{n+1}$ complexes.
[e] Accurate $^1J_{PF}$ values from full spectral analysis.
[f] $\Delta H_{subl.} = 85.5 \pm 2.9$ kj/mol (*45*).
[g] ^{55}Mn shifts (ppm relative to $LiMnO_4$) are 2888, complex (CO); 2813 (complex $(CO)_2$; 2742, complex $(CO)_3$; and 2673, complex $(CO)_4$ (*261*).
[h] Diaxial isomer.
[i] Alkene isomerization catalysts (*337*).

preparation of $[CoH(PF_3)_3(CO)]$ (method D), while certain σ-bonded silyl metal carbonyls react with phosphorus pentafluoride to afford the desired complexes (method E).

$$Co + H_2 + CO + PF_3 \longrightarrow CoH(PF_3)_3(CO)$$

$$Co(SiH_3)(CO)_4 \xrightarrow{PF_5} CoH(PF_3)_3(CO)$$

$Ni(PF_3)_4$ can act as a source of PF_3 in reactions with metal carbonyl complexes (method F), and fluorination of preformed carbonyl metal–PCl_3 complexes using potassium fluorosulfinate has also been described (method G).

$$ReBr(CO)_5 \xrightarrow{Ni(PF_3)_4} ReBr(PF_3)_2(CO)_3$$

$$Mo(PCl_3)_3(CO)_3 \xrightarrow{KSO_2F} Mo(PF_3)_3(CO)_3$$

(continued)

ϕ_F[b]	$^1J_{PF}$[c,d]	Remarks	Reference
4.7	1310[m]	IR (*73, 127, 332*), PES (*96, 367*), electron diffraction(*47*), ESCA(*8*)	*8, 117*
—	~1300	MS, IR (*350*)	*350*
17.0	1328	MS, IR (*18, 291*)	*18, 291*
—	—	MS, IR (*18, 291*)	*18, 291*
17.9	1343	—	*18, 291*
16.3	1358	—	*18, 291*
6.0	1281	—	*169, 228, 236, 332*
7.0	1286	—	
7.9	1245	IR (*169*), PES (*96, 367*)	
11.0, 5.5	1282, 1293[r]	MS, IR, ^{1}H NMR (*260*)	*260*
—		IR (*170*)	*170*

[j] ^{13}C NMR data available (*239*).
[k] Temperature-dependent spectra (*240*).
[l] Hot atom chemistry reported (*117*).
[m] $^1J_{MoP}$ data (*10, 258*).
[n] Mo–P (2.369 Å).
[o] Corrected later (*117*) to 175°C.
[p] $^1J_{WP}$ = 485 Hz (*169*).
[q] ΔH_{subl} = 77.4 ± 1.5 kj/mol (*45*).
[r] Data for $ReH(PF_3)(CO)_4$.

XV. Transition Metal Nitrosyl Complexes

PF_3-containing transition metal nitrosyl complexes such as $[Co(NO)(PF_3)_3]$ and $[Fe(NO)_2(PF_3)_2]$ were first prepared by Kruck and Lang (*206, 207*) by reduction of dimeric nitrosyl halide complexes with copper in the presence of PF_3 (method A).

$$[Fe(NO)_2Br]_2 \xrightarrow{Cu/PF_3} Fe(NO)_2(PF_3)_2$$

More recently these volatile complexes have also been made by metal vapor syntheses (method B) in which vapors of the metals were cocondensed with NO, PF_3, and boron trifluoride at liquid nitrogen temperature. The method also afforded $[Mn(NO)_3(PF_3)]$, however, it is important to point out that in the absence of BF_3 the condensate exploded violently on warming a little above −196°C (*257*).

Other useful methods involve displacement of CO by PF_3 from mixed-metal carbonyl nitrosyl complexes (method C), passing CO_2 through a

TABLE XIV

TRANSITION METAL NITROSYL COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Mn(PF_3)(NO)_3$	(B)	Green	-120 ± 2	—	—	*206, 257*
$Mn(PF_3)(NO)(CO)_3$	(C)	—	—	6.5	1337	*353*
$Mn(PF_3)_2(NO)(CO)_2$	(C)	—	—	—	1319	*353*
$Mn(PF_3)_3(NO)(CO)$	(C)	—	—	—	—	*353*
$Fe(PF_3)_2(NO)_2$	(A) (B)	Red	−72 (dec. 118), 97/227	9.4	1360	*69, 174, 206, 207*
$Fe(PF_3)_3(NO)H$	(G)	Orange	−86, 80/720	—	—	*207*
$Fe(PF_3)_3(NO)K$	(G)	Yellow	—	—	—	*207*
$Fe(PF_3)(PF_2OC_2H_5)(NO)_2$	(F)	Red	-78, $80/10^{-3}$	—	—	*223*
$[Fe(PF_3)(PF_2O)(NO)_2]Ba$	(F)	—	—	—	—	*233*
$Co(PF_3)_3(NO)$	(A) (B) (D)	Orange-red	−92, 81/732	9.9	1375	*69, 174, 206, 207, 257*
$Co(PF_3)_x(CO)_{3-x}(NO)$	(C)	Red				
$Co(PF_3)_2(PF_2OC_2H_5)(NO)$			—	—	—	*69, 77*
$[Co(PF_3)_2(PF_2O)NO][Pr^i_2NH]$	(F)	Red	-78, $70/10^{-3}$	—	—	*223*
$[Co(PF_3)_2(PF_2O)(NO)]_2Ba$	(F)	Ochre	—	—	—	*223*
$Rh(PF_3)_3(NO)$[d,e]	(C) (D) (E)	Orange	−87	3.8	1416	*46, 80, 174, 277, 293*

[a] In ppm relative to CCl_3F.

[b] In Hz.

[c] $^1J_{PF} + J_{PF'}$ in $(PF_3)_2$ complexes and $^1J_{PF}$ in (PF_3) complexes.

[d] Rh—P bond length = 2.245 Å (*46*).

[e] A full NMR analysis has been carried out (*277*).

trifluorophosphine metallate salt in the presence of nitrite (method D), and displacement of η^3-allylic ligands (which are 3*e* donors) coordinated to metals via treatment with NO or NOCl (method E).

$$Mn(NO)(CO)_4 \xrightarrow{PF_3} Mn(NO)(CO)_3(PF_3)$$

$$KM(PF_3)_4 \xrightarrow{CO_2/NO_2^-} M(NO)(PF_3)_3 \quad (M = Co, Rh)$$

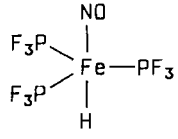
$$Rh(\eta^3\text{-}C_3H_5)(PF_3)_3 \xrightarrow{NO} Rh(NO)(PF_3)_3$$

Since the P—F bonds are labile in these complexes some mixed trifluorophosphine–fluorophosphite nitrosyl complexes have been prepared by reactions with either diisopropyl–water mixtures or barium hydroxide (method F) to give the $(PF_2O)^-$ compounds which can be alkylated.

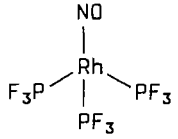
$$Fe(NO)_2(PF_3)_2 \xrightarrow{Ba(OH)_2} [Fe(NO)_2(PF_3)(PF_2O)]^{2-} \xrightarrow{R_3O^+} Fe(NO)_2(PF_3)(PF_2OR)$$

Treatment of $[Fe(NO)_2(PF_3)_2]$ with potassium amalgam and PF_3 (method G) gives the salt $K[Fe(NO)(PF_3)_3]$, which on acidification gives the hydride complex $[FeH(NO)(PF_3)_3]$.

The molecular structure of $[FeH(NO)(PF_3)_3]$ (**16**) has been proposed to be based on a trigonal bipyramid with the H and NO ligands occupying axial positions and the PF_3 groups likely to be distorted toward the small hydride. The molecular structure of $[Rh(NO)(PF_3)_3]$ (**17**) has been determined in the gas phase by an electron diffraction study (*46*) and has the expected C_{3v} symmetry with an Rh–P distance of 2.245(5) Å. Nitrosyl complexes containing PF_3 are listed in Table XIV.



(**16**)



(**17**)

XVI. Transition Metal Complexes Containing Other Ligands with Nitrogen, Phosphorus, or Arsenic Donor Atoms

A very large number of trifluorophosphine–metal complexes of this type are known, as evidenced by the number of entries in Table XV. The most widely used synthetic methods are displacement of PF_3 from a

TABLE XV

METAL TRIFLUOROPHOSPHINE COMPLEXES CONTAINING OTHER LIGANDS HAVING N, P, OR AS DONOR LIGANDS

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Ti(CO)_2(PF_3)(dmpe)_2$[d]	(B)	Red	—	—	—	*365*
$Fe(PF_3)_4(PF_2OEt)$	(D)	Bright-yellow	−45 (121/760)	1.0	1260	*191*
$[Fe(PF_3)_4PF_2O]_2Ba$	(D)	Bright-yellow	—	1.5	1265	*191*
$Fe(PF_3)_2(PMe_3)_3$	(A)	Yellow	—	—	—	*265, 303*
$Fe(PF_3)_2[P(OMe)_3]_3$	(A) (B)	Colorless	—	—	1213	*131, 265*
$Fe(PF_3)(dppe)_2$	(B)	Orange	225–230	—	—	*164*
$Fe(PF_3)(dppe)_2$	(B) (I)	—	—	—	—	*6, 345*
$Fe(PF_3)(dmpe)_2$	(B) (I)	—	—	12.6	—	*164*
$CoH(PF_3)_3(PH_3)$	(A) (B)	Pale-yellow	25	9.8	1117	*60*
$CoH(PF_3)_3(PPh_3)$	(A) (B)	Yellow	175–176 subl.	8.0	1231	*57, 58, 209*
$CoH(PF_3)_3(AsPh_3)$	(A)	Yellow	83 (dec. 120)	—	—	*209*
$CoH(PF_3)_3(SbPh_3)$	(A)	Yellow	62 (dec. 100)	—	—	*209*
$CoH(PF_3)_2(PPh_3)_2$	(B)	Yellow	200 dec.	6.2	1265	*58*
$Co(PF_3)_2(PPh_3)_2K$	(A)	—	—	—	—	*202*
$CoI(PF_3)_2(PPh_3)_2$	(A)	Dark-brown	144 dec.	—	—	*202*
$CoH(PF_3)(PPh_3)_3$	(B)	Yellow	147–149 dec.	0.8	1239	*58*
$CoH(PF_3)_3P(CF_3)_2OCH_2CH_2Cl$	(A)	Colorless	—	—	—	*79*
$Ni(PF_3)_3(PH_3)$	(A) (C)	Colorless	−22	19.8	—	*341, 346*
$Ni(PF_3)_2(PH_3)_2$	(C)	Colorless	Liquid	—	—	*341*
$Ni(PF_3)_3(C_6H_{11}NC)$	(A)	Pale-yellow	—	—	—	*166*
$Ni(PF_3)_3$(pyridine)[e]	(A)	Yellow	—	—	—	*181*
$Ni(PF_3)_3(PPh_3)$	(A)	Colorless	123–125	—	—	*181*
$Ni(PF_3)_3(AsPh_3)$	(A)	Colorless	111	—	—	*177*
$Ni(PF_3)_3(SbPh_3)$	(A)	Colorless	96–97	—	—	*177*
$Ni(PF_3)_3(PF_2OEt)$	(D)	Colorless	−67 (110/760)	17.5	1340	*191*

$Ni(PF_3)_3(PF_2NEt_2)$	(D)	Colorless	(67.2–68.2/12)	17.5	1266	*190, 192*
$Ni(PF_3)_3(PF_2NH_2)$	(D)	Colorless	Liquid	—	—	*213*
$Ni(PF_3)_3(PF_2NHPr^n)$	(D)	Colorless	(56.5/12)	18.5	1295	*190, 192*
$Ni(PF_3)_3(PF_2NHBu^n)$	(D)	Colorless	(68.5/12)	17.0	—	*212*
$Ni(PF_3)_3(PF_2NHMe)$	(D)	Colorless	(48/12)	—	—	*212*
$Ni(PF_3)_3[PFNH(CH_2)_2NH]$	(D)	Colorless	—	18.0	1287	*190, 192*
$Ni(PF_3)_2[PF_2NH(CH_2)_2]$	(D)	Colorless solid	$(92–93/10^{-2})$	17.6	1254	*190, 192*
$Ni(PF_3)_3[PF_2N(SiMe_3)_2]$	(D)	Colorless	$(49/10^{-3})$	—	—	*213*
$Ni(PF_3)_3(PF_2NHSiMe_3)$	(D)	Colorless	$(60–70/10^{-3})$	—	—	*213*
$Ni(PF_3)_3(PF_2NMeSiMe_3)$	(D)	Colorless	$(36/10^{-1})$	—	—	*212*
$Ni(PF_3)_3(PF_2NEtSiMe_3)$	(D)	Colorless	$(27/10^{-1})$	—	—	*212*
$Ni(PF_3)_3(PF_2NBuSiMe_3)$	(D)	Colorless	$(40/10^{-1})$	16.5	—	*212*
$Ni(PF_3)_3(PF_2NPhSiMe_3)$	(D)	Colorless	$(63.5/10^{-3})$	—	—	*212*
$Ni(PF_3)_3(PF_2N_2H_3)$	(D)	Colorless	31	—	—	*130*
$[Ni(PF_3)_3PF_2O]^-$	(D)	Colorless	—	—	—	*190*
$Ni(PF_3)_2(PPh_3)_2$	(A)	Yellow	213	—	—	*177, 178, 181*
$Ni(PF_3)_2(AsPh_3)_2$	(A)	Colorless	157 dec.	—	—	*181*
$Ni(PF_3)_2(SbPh_3)_2$	(A)	Colorless	177	—	—	*181*
$Ni(PF_3)_2$(*o*-phen)	(A)	Red	225 dec.	—	—	*181*
$Ni(PF_3)_2$(dipyridyl)	(A)	Orange-red	120 dec.	—	—	*181*
$Ni(PF_3)_2[(PPh_2)_2C_2H_4]$	(A)	Yellow	203–205	—	—	*175*
$Ni(PF_3)_2(PF_2NEt_2)_2$	(D)	Colorless	(76–77/0.5)	17.4	1295	*189, 190, 192*
$Ni(PF_3)_2(PF_2NH_2)_2$	(D)	Colorless	(46.5/0.8)	9.1	1259	*190, 192*
$Ni(PF_3)_2(PF_2NPr^n{}_2)_2$	(D)	Colorless	—	18.4	1298	*189, 190, 192*
$Ni(PF_3)_2(PF_2NBu^n{}_2)_2$	(D)	Colorless	—	17.4	1292	*190, 192*
$Ni(PF_3)_2(PF_2NHMe)_2$	(D)	Colorless	$(28/10^{-3})$	—	—	*212*
$Ni(PF_2)_2[PF_2N(SiMe_3)_2]_2$	(D)	Pale-yellow	60 dec.	—	—	*213*
$Ni(PF_3)_2(PClPh_2)[PF_2N(PPh_2)]_2$	(A) (D)	Yellow	(108–110 dec.)	—	—	*213*
$Ni(PF_3)[P(OPh)_3]_3$	(A)	Colorless	89	—	—	*178*
$Ni(PF_3)(PPh_2Cl)_3$	(A)	Colorless	114 dec.	—	—	*181*
$Ni(PF_3)(PF_2NEt_2)_3$	(D)	Colorless	Oil	17.9	1349	*190, 192*
$Ni(PF_3)(PF_2NC_5H_{10})_3$	(D)	Colorless	45	17.1	1292	*189, 190, 192*
$Ni(PF_3)(PF_2NHBu^t)_3$	(D)	Colorless	—	—	—	*190*

(*continued*)

TABLE XV (*continued*)

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Ni(PF_3)(PF_2NMeSiMe_3)_3$	(D)	Colorless	−10	—	—	*212*
$Ni(PF_3)(PF_2NHMe)_3$	(D)	Colorless	$(68/10^{-3})$	—	—	*212*
$Ni(PF_3)_3(PF_2Ph)$	(D)	Colorless	$38/10^{-1}$	15.9	1330	*211*
$Ni(PF_3)_3(PFPh_2)$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)_2(PF_2Et)_2$	(D)	Colorless	$35/10^{-3}$	16.7	1330	*211*
$Ni(PF_3)_3(PFEt_2)$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)_2(PF_2Et)(PFEt_2)$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)(PF_2Et)_3$	(D)	Colorless	—	15.6	1320	*211*
$Ni(PF_3)_3(PF_2Bu)$	(D)	Colorless	$26/10^{-1}$	—	—	*211*
$Ni(PF_3)_2(PF_2Bu)_2$	(D)	Colorless	$42/10^{-3}$	—	—	*211*
$Ni(PF_3)_2(PF_2Me)_2$	(D)	Colorless	$14/10^{-1}$	—	—	*211*
$Ni(PF_3)_3(PFMe_2)$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)(PF_2Bu)_3$	(D)	Colorless		—	—	*211*
$Ni(PF_3)_2(PFBu_2)(PF_2Bu)$	(D)	Colorless	$90/10^{-3}$	—	—	*211*
$Ni(PF_3)_3(PBu_3)$	(D)	Colorless		—	—	*211*
$Ni(PF_3)(PF_2Me)_3$	(D)	Colorless		—	—	*211*
$Ni(PF_3)_2(PFMe_2)(PF_2Me)$	(D)	Colorless	$26/10^{-1}$	—	—	*211*
$Ni(PF_3)_3(PMe_3)$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)_3(PF_2C_6H_{11})$	(D)	Colorless	$34/10^{-1}$	—	—	*211*
$Ni(PF_3)_3[P(C_3H_5)_3]$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)_2(PF_2C_3H_5)[PF(C_3H_5)_2]$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)(PF_2C_3H_5)_3$	(D)	Colorless	—	—	—	*211*
$Ni(PF_3)_3(PEt_3)$	(D)	Colorless		—	—	*211*
$Ni(PF_3)_2(PF_2Et)(PFEt_2)$	(D)	Colorless	$46/10^{-3}$	—	—	*211*
$Ni(PF_3)(PF_2Et)_3$	(D)	Colorless		—	—	*211*
$Ni(PF_3)_3(PCl_3)$	(A)	—	—	−19.4	—	*312*
$Ni(PF_3)_2(PCl_3)_2$	(A)	—	—	−22.1	—	*312*
$Ni(PF_3)(PCl_3)_3$	(A)	—	—	−24.3	1359	*312*

$Ni(PF_3)_3(PBr_3)$	(A)	—	—	−20.8	1286	*312*
$Ni(PF_3)_2(PBr_3)_2$	(A)	—	—	−23.8	1292	*312*
$Mo(PF_3)_2(bipy)_2$	(B)	Red-black	—	—	965[f]	*83*
$Mo(CO)_2(PF_3)_2PhP(Me_2pz)_2$	(G)	—	—	—	~1300	*298*
$ReCl(PF_3)(N_2)(PPh_3)_2$	(B)	Orange	—	—	—	*64*
$Ru(PF_3)_4(PPh_3)$	(I)	Colorless	Oil	−1.1	1234	*2, 4, 279*
$Ru(PF_3)_3(PPh_3)_2$	(I)	Colorless	170 (dec.)	4.3	1288	*2, 4*
$RuClL^R(PF_3)(PEt_3)_2$[g]	(G)	Colorless	180–190 (dec.)	—	1301	*152*
$RuClL^R(PF_3)(PPh_3)_2$	(G)	Colorless	140–150	—	1304	*151, 152*
$[RuClL^R(PF_3)]BF_4$	(B)	Pink	214	—	—	*151, 152*
$RuCl_2(PF_3)(L^R)_4$	(B)	White-pink	130	—	—	*150*
$Ru_2Cl_4(PF_3)(PPh_3)_4$	(B)	Deep-red	166	—	—	*134, 137*
$Ru_2Cl_4(PF_3)_2(PPh_3)_3$	(B)	Orange-yellow	191–192	—	1290[h]	*134, 136, 137*
$Ru_2Cl_4(PF_3)(CO)(PPh_3)_3$	(B)	Yellow	184	—	—	*134*
$RuCl_2(PF_3)(DMA)(PPh_3)_2$	(B)	Yellow	—	—	—	*134*
$RuCl_2(PF_3)_2(PPh_3)_2$[i]	(B) (E) (H)	Pale-yellow	191–193 (dec.)	12.4	1285	*3, 134, 136, 140, 148*
$RuBr_2(PF_3)_2(PPh_3)_2$	(B)	Orange	141 (dec.)	12.4	1291	*134*
$RuCl_2(CO)(PF_3)(PPh_3)_2$	(B)	Colorless	225	12.6	1305	*137*
$RuCl_2(DMF)(PF_3)(PPh_3)_2$	(B)	Yellow	170	4.7	1257	*136*
$Ru(O_2CCF_3)_2(PF_3)(PPh_3)_2$	(D)	—	203–205	8.6	1283	*3*
$Ru(O_2CCF_3)[PF_2(OCCF_3)](PF_3)(PPh_3)_2$	(D)	—	200	5.9	1276	*3*
$Ru_2Cl_3(CF_3COCHOCCF_3)(PF_3)(PPh_3)_4$	(A)	Pink	184 (dec.)	—	—	*137*
$RuH_2(PF_3)_2(PPh_3)_2$	(B)	Colorless	169–170	6.8	1291	*135*
$RuH_2(PF_3)(PPh_3)_3$	(B)	Colorless	171	4.8	1285	*135*
$RuHCl(PF_3)_2(PPh_3)_2$	(B)	Colorless	164	13.2, 4.2	1350, 1244	*3*
$RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2$	(H)	—	170	13.4, 1.8	1351, 1254	*3*
$RuH_2(PF_3)(PF_2NMe_2)(PPh_3)_3$	(B)	Colorless	175.6	6.2	1300	*135*
$[RuH(PF_3)(CH_3CN)(ttp)]BF_4$[j]	(B)	White	130 (dec.)	—	1323	*229*
$OsH_2(PF_3)(PPh_3)_3$	(B)	Colorless	198	7.4	1300	*135*
$OsH_2(PF_3)_2(PPh_3)_2$	(B)	Colorless	185–187	8.3	1296	*135*

(*continued*)

TABLE XV (*continued*)

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$OsHCl(PF_3)_2(PPh_3)_2$	(H)	Colorless	207–209	7.4, 10.3	1346, 1254	*3*
$OsCl_2(PF_3)(PMe_2Ph)_3$	(H)	Colorless	228	13.1	1208	*3*
$OsCl_2(PF_3)_2(PMe_2Ph)_2$[k]	(B)	Colorless	—	18.8	1230	*3*
$OsCl_2(PF_3)_2(PMe_2Ph)_2$[l]	(B)	Yellow	149	32.9	1453	*3*
$OsCl_2(PF_3)(PMe_2Ph)_3$	(B)	Yellow	171	25.4	1267	*3*
$OsCl_2(PF_3)_2(PPh_3)_2$	(H)	Colorless	>230	18.4	1234	*136*
$Pd(PF_3)_2(PPh_3)_2$	(A)	Colorless	156–158 (dec.)	—	—	*177*
$Pd(PF_3)(CO)(PPh_3)_2$	(A)	Colorless	—	—	—	*177*
$[IrH(PF_3)(dppe)_2](BF_4)_2$	(G)	White	174 (dec.)	14.8	1338	*154*
$IrCl(PF_3)(PPh_3)_2$	(B) (I)	Yellow	134	—	—	*25, 348*
$IrCl(PF_3)$(diphos)	(B)	White	270 (dec.)	—	—	*356*
$Pt(PF_3)_3(PPh_3)$	(A)	Colorless	121	—	—	*177*
$Pt(PF_3)_3(C_6H_{11}NC)$	(A)	Off-white	—	—	—	*166*
$Pt(PF_3)_2(PPh_3)_2$	(A)	Colorless	202 (dec.)	—	—	*177*
$Pt(PF_3)[MeC(CH_2PPh_2)_3]$	(B)	—	—	—	1321	*65*
$PtCl_2(PF_3)(PEt_3)$[m]	(B)	White	—	—	—	*143, 153, 242*
$PtCl_2(PF_3)(PCl_3)$	(A)	—	—	—	—	*312*
$RhH(PF_3)(PPh_3)_3$[n]	(B)	Yellow	—	—	1333[o]	*147, 160, 290*
$RhH(PF_3)_2(PPh_3)_2$	(B)	White	—	—	—	*290*
$RhCl(PF_3)(PPh_3)_2$	(B) (E)	Yellow	144–148	15.2	1286	*18, 80, 81, 182*
$RhCl(PF_3)(AsPh_3)_2$	(B) (E)	Yellow	165–170	15.2	1271	*18*
$RhCl(PF_3)(PPh_3)(AsPh_3)$	(B)	Yellow	130–136 (dec.)	13.9	1281	*18*
$RhCl(PF_3)[P(NMe_2)_3]_2$	(B)	Yellow	—	15.6	1279	*18*
$RhBr(PF_3)(PPh_3)_2$	(E)	Yellow	70 (dec.)	17.7	1248	*18*
$RhCl(PF_3)[\{C_6H_5(PPh_2)(NMe_2)\}]$	(B)	Yellow	200	—	—	*304*

$[RhCl(PF_3)(Azb)]_2$[p]	(B) (E)	Dark-red	—	19.3	1333	*281*
$Rh_2Cl_2(PF_3)(CO)(Azb)_2$[p]	(B)	Red	—	20.3	1346	*281*
$RhCl_3(PF_3)(PPh_3)_2$	(B) (F)	Yellow	152–154	30.9	1349	*18, 133, 138*
$RhCl_3(PF_3)(AsPh_3)_2$	(B)	Yellow	—	—	—	*18*
$RhHCl_2(PF_3)(PPh_3)_2$	(B)	Yellow	—	—	—	*18*
$RhHBrCl(PF_3)(PPh_3)_2$	(B)	Yellow	—	—	—	*18*
$RhCl(SO_2)(PF_3)(PPh_3)$	(B)	Yellow	—	—	—	*18*
$RhCl(SO_2)(PF_3)(AsPh_3)$	(B)	Yellow	—	—	—	*18*
$[RhCl(PF_3)(PPh_3)]_2$	(E)	Yellow	180–183 (dec.)	—	—	*18*
$RhCl(PF_3)_2$(benzo-[c]-cinnoline)	(E)	Yellow	140–145	19.2, 20.2	1304, 1324	*283*
$RhCl(PF_3)_2$(R-dim)[q]	(E)	—	—	Several	1300	*300*

[a] In ppm relative to CCl_3F.

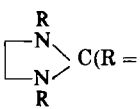
[b] In Hz.

[c] Some spectra are second order and in general $^1J_{PF}$ quoted equals $^1J_{PF} + n^3J_{PF'}$ for $(PF_3)_{n+1}$ complexes.

[d] X-Ray structure.

[e] The related $Cr(PF_3)_5$(pyridine) complex has been briefly reported (*338*).

[f] Value likely to be in error.

[g] L^R = carbene ligand  C(R = Me).

[h] Spectra complex, isomers present.

[i] X-Ray crystal structure (*148*) (Ru—PF_3 = 2180, 2160 Å; Ru—PPh_3 = 2.471, 2.456 Å).

[j] ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$.

[k] *cis*-Isomer.

[l] *trans*-Isomer.

[m] X-Ray crystal structure (*153*) (Pt—PF_3 = 2.141 Å; Pt—PEt_3 = 2.272 Å).

[n] X-Ray crystal structure (*147*) (Rh—PF_3 = 2.155 Å; Rh—PPh_3 = 2.34 Å).

[o] $^2J_{PRh}$ = 254 Hz (PF_3). ^{19}F NMR spectrum temperature dependent.

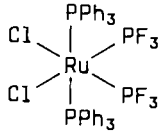
[p] AzbH = azobenzene.

[q] R-dim = RNCHCHNR (R = ^{t}Bu)

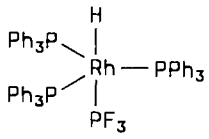
metal trifluorophosphine complex under the influence of the added ligand (method A); alternatively, the reverse reaction can be utilized (method B), since PF_3 invariably displaces most other coordinated ligands. A reducing agent may also be added. Some typical examples are listed below (dppe = $Ph_2PCH_2CH_2PPh_2$).

$$Ni(PF_3)_4 \xrightarrow{PPh_3} Ni(PF_3)_3(PPh_3)$$
$$CoH(PF_3)_4 \xrightarrow{SbPh_3} CoH(PF_3)_3(SbPh_3)$$
$$RuH_4(PPh_3)_3 \xrightarrow{PF_3} RuH_2(PF_3)(PPh_3)_3$$
$$Fe(dppe)_2(C_2H_4) \xrightarrow{PF_3} Fe(PF_3)(dppe)_2$$
$$OsCl_3(PR_3)_3 \xrightarrow[Zn]{PF_3} OsCl_2(PF_3)(PR_3)_3$$

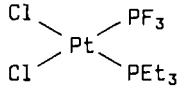
Single-crystal X-ray crystallographic studies have been carried out to establish the molecular structures of complexes **18**–**20**. However, in these and many other such complexes, the characteristic patterns of lines in the ^{31}P NMR spectrum resulting from spin–spin coupling between the various types of phosphorus and/or metal nuclei can often be diagnostic for a particular structure.



(18)



(19)



(20)

As expected in these mixed phosphine—trifluorophosphine complexes, the metal–phosphorus bond lengths to PF_3 are usually significantly shorter than to the PR_3 ligands (e.g., in **18**, Ru–PF_3 = 2.180 Å, 2.160 Å; Ru–PPh_3 = 2.471 Å, 2.456 Å; in **19**, Rh–PF_3 = 2.155 Å, Rh–PPh_3 = 2.34 Å; and in **20**, Pt–PF_3 = 2.141 Å; Pt–PEt_3 = 2.272 Å).

Of special interest is the recently described red zero-valent titanium complex $[Ti(CO)_2(PF_3)(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) which is a PF_3 derivative of the nonexistent titanium carbonyl complex $[Ti(CO)_7]$ (*365*). A single-crystal X-ray crystallographic study has established the structure shown in Fig. 21 in which the geometry around the metal is approximately a capped trigonal prism.

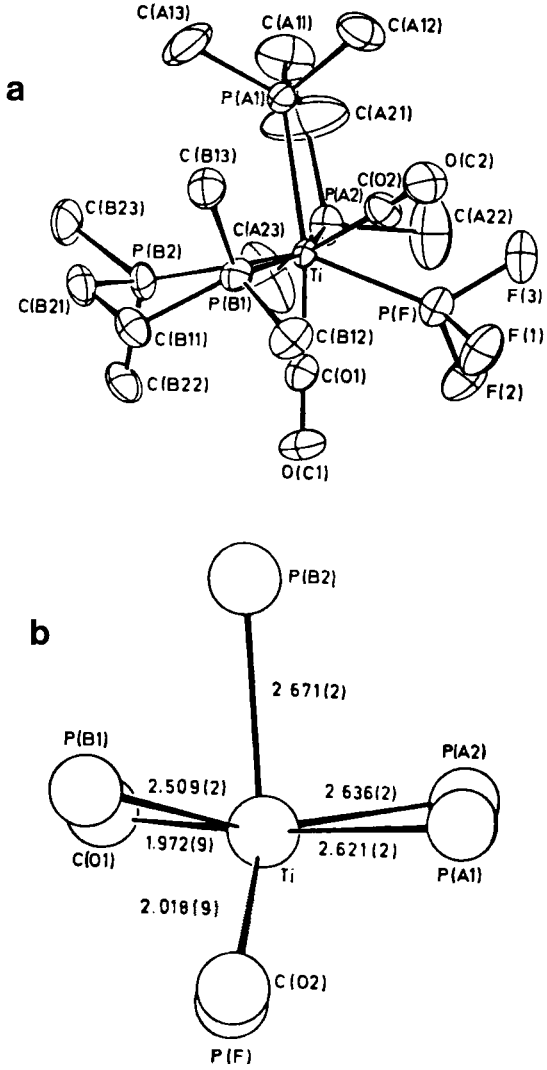
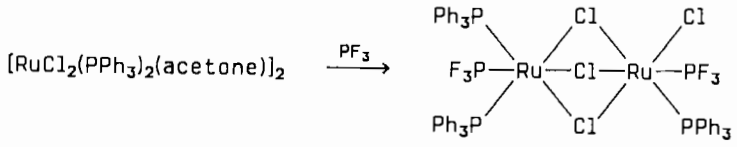


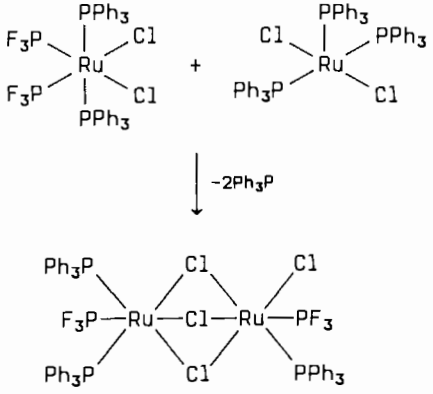
FIG. 21. (a) Structure of $Ti(CO)_2(PF_3)(dmpe)_2$. (b) Inner coordination sphere. [Reproduced from reference (*365*) with permission.]

In certain cases treatment of monomeric complexes with PF_3 can lead to more complicated products, for example, displacement of acetone and PPh_3 from $[RuCl_2(PPh_3)_2(acetone)]_2$ leads to the triply chloro-bridged diruthenium complex **21** (*134, 136, 137*).



(21)

Similar behavior is observed in controlled reactions of PF_3 with $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PF_3)(PPh_3)_2(DMA)](DMA = CH_3CONMe_2)$. The dimeric product is also obtained when $[RuCl_2(PPh_3)_3]$ and [*cis*-$RuCl_2(PF_3)_2(PPh_3)_2$] are refluxed together in an unusual ligand-exchange reaction.



The technique of metal vapor synthesis (method C) is obviously restricted to volatile ligands and has only been utilized so far in the synthesis of $[Ni(PF_3)_2(PH_3)_2]$ and $[Ni(PF_3)_3(PH_3)]$.

Kruck and co-workers have used cleavage reactions of the phosphorus–fluorine bonds of coordinated PF_3 ligands to synthesize a wide variety of complexes of the type $[M(PF_3)_n(PF_2X)_m]$ (X = NHR, NR_2, OR, etc.) (method D), e.g., (*190, 192*),

$$Ni(PF_3)_4 \longrightarrow Ni(PF_3)_3(PF_2NR_2)$$
$$\longrightarrow Ni(PF_3)_2(PF_2NR_2)_2$$
$$\longrightarrow Ni(PF_3)(PF_2NR_2)_3$$
$$Fe(PF_3)_5 \longrightarrow Fe(PF_3)_4(PF_2OR)$$

More recently, the fluorine atoms in $[Ni(PF_3)_4]$ have been partially substituted by organic groups using RLi or RMgCl (*211*).

$$Ni(PF_3)_4 \xrightarrow{RLi} Ni(PF_3)_{4-n}(PF_2R)_n \quad (n = 1\text{–}3)$$
$$\longrightarrow Ni(PF_3)_3(PFR_2)$$
$$\longrightarrow Ni(PF_3)_2(PF_2R)(PFR_2)$$
$$\longrightarrow Ni(PF_3)_3(PR_3)$$

Metal–halogeno bridge cleavage reactions by PF_3 or other phosphines have also been useful in certain cases (method E), e.g.,

$$[PtCl_2(PR_3)]_2 \xrightarrow{PF_3} PtCl_2(PF_3)(PR_3)$$
$$[RhCl(PF_3)_2]_2 \xrightarrow{PPh_3} RhCl(PF_3)(PR_3)_2$$

Although normally PF_3 stabilizes low oxidation states of transition metals it has been possible in some cases to directly oxidize a low-valent complex with chlorine (method F).

$$RhCl(PF_3)(PPh_3)_2 \xrightarrow{Cl_2} RhCl_3(PF_3)(PPh_3)_2$$

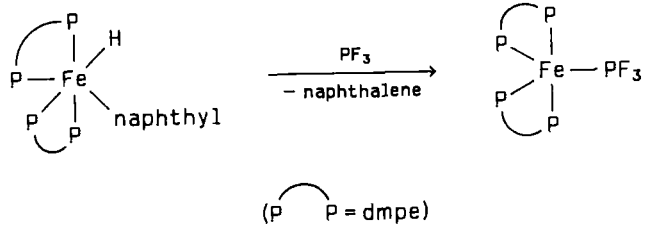
The structure of the Rh(III) product has been established by a detailed study of its ^{31}P NMR spectrum.

Addition of PF_3 to a coordinatively unsaturated complex has been used (method G), and mixed PF_3–ligand hydrides can be converted to the corresponding hydrochloride or dichloride systems by treatment with HX (usually HCl or HBF_4) and Et_4NCl (method H).

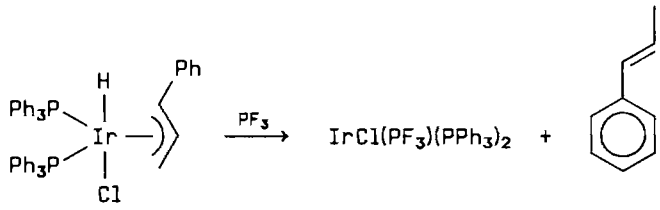
An interesting synthesis of zero-valent ruthenium phosphine–trifluorophosphine complexes has been reported (*2, 4*) (method I) via reductive elimination of acetic acid from the ruthenium(II) hydrido acetato complex $[RuH(CO_2Me)(PPh_3)_3]$.

$$RuH(CO_2Me)(PPh_3)_3 \xrightarrow[-CH_3CO_2H]{PF_3} Ru(PF_3)_3(PPh_3)_2 \xrightarrow{PF_3} Ru(PF_3)_4(PPh_3)$$

A related reaction is that of the naphthyl hydrido derivative of iron(II), which forms the corresponding zero-valent PF_3 iron complex (*164*):



Also noteworthy is the interaction of PF_3 with the stable iridium(III) allyl hydride $[IrClH(\eta^3\text{-}C_3H_4Ph)(PPh_3)_2]$ to eliminate β-Me-styrene and generate $[IrCl(PF_3)(PPh_3)_2]$ *(348)*.



These reactions underline the tendency for PF_3 to stabilize low oxidation states of metals.

XVII. Transition Metal Alkyl and Alkenyl Complexes

Relatively few examples of σ-bonded η^1-alkyl or alkenyl metal trifluorophosphine complexes of formula $[MR_x(PF_3)_y$ are known (see Table XVI).

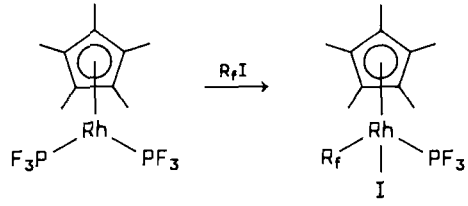
Alkyltetrakis(trifluorophosphine)cobalt complexes can be prepared from the anion $[Co(PF_3)_4]^-$ only with strong alkylating agents because of the low nucleophilicity of the anion (method A). Thus, treatment of $[Co(PF_3)_4]^-$ with an oxonium salt yields $[Me_3O]$ $[Co(PF_3)_4]$, which on heating gives the desired product.

$$Co(PF_3)_4^- \longrightarrow [Me_3O][Co(PF_3)_4] \xrightarrow[-Me_2O]{100^\circ C} Co(PF_3)_4Me$$

An alternative route utilizes the reaction between the appropriate hydrido–metal PF_3 complex with diazomethane at low temperatures, followed by pyrolysis of the resulting salt (method B).

$$CoH(PF_3)_4 + CH_2N_2 \xrightarrow{Et_2O} [Et_2OMe][Co(PF_3)_4] \longrightarrow Co(PF_3)_4Me + Co(PF_3)_4Et$$

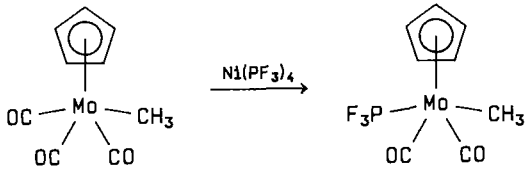
Good yields of certain rhodium(III) perfluoroalkyl derivatives have been obtained in oxidative addition reactions of perfluoroalkyl iodides (R_fI) with rhodium(I) trifluorophosphine complexes (method C).



Substitution of CO in the perfluoroalkyl metal carbonyl derivative provides a synthetic route to perfluoroalkyl mixed-carbonyl trifluorophosphine metal complexes (method D).

$$Co(CO)_4CF_3 \xrightarrow{PF_3} Co(CO)_{4-x}(PF_3)_xCF_3$$

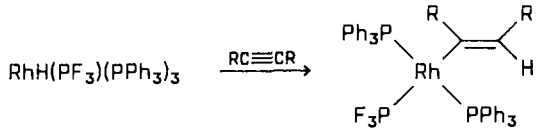
Alternatively, $[Ni(PF_3)_4]$ has proved effective as the source of PF_3 in some reactions (method E).



Fluoroolefins have been inserted into the metal–hydrogen bond of a metal hydride (method F).

$$MnH(CO)_4(PF_3) \xrightarrow{C_2F_4} Mn(CO)_4(PF_3)(C_2F_4H)$$

Likewise, alkynes undergo similar reactions to produce alkenyl complexes, however, both single- and double-insertion reactions can occur (Scheme 12). A surprising feature of the double-insertion



(R = CO_2Me, CF_3)

SCHEME 12

reaction is that the same product is obtained by insertion into either an Rh—C or a C—H bond (see Scheme 13) (*160*). Finally, a synthetic route

TABLE XVI

TRANSITION METAL ALKYL DERIVATIVES CONTAINING TRIFLUOROPHOSPHINE

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	J_{PF}[b,c]	Reference
$Mn(PF_3)(CO)_4CF_3$	(D)	—	—	—	—	*259*
$Mn(PF_3)(CO)_4COCF_3$	(D)	—	—	—	—	*259*
$Mn(PF_3)(CO)_4C_2F_4H$	(D) (F)	—	—	—	—	*259*
$Co(PF_3)_4CH_3$	(A) (B)	Yellow	104.4/760	—	—	*222*
$Co(PF_3)_4C_2H_5$	(A) (B)	Yellow	25/0.5 (dec. >40)	—	—	*222*
$Co(PF_3)_4C_7H_7$	(A)	Yellow	dec. 130	—	—	*222*
$Co(PF_3)(CO)_3CF_3$	(D)	—	Liquid	47.8[d]	1371	*351, 352, 355*
$Co(PF_3)_2(CO)_2CF_3$	(D)	—	Liquid	47.1[d]	1337	*351, 352, 355*
$Co(PF_3)_3(CO)CF_3$	(D)	—	Liquid	47.3[d]	1395	*351, 352, 355*
$Co(PF_3)_4CF_3$	(D)	—	Liquid	50.1[d]	1319	*351, 352, 355*
$Co(PF_3)(CO)_3C_2F_5$	(D)	—	Liquid	49.7[d]	1371	*351, 352, 355*
$Co(PF_3)_2(CO)_2C_2F_5$	(D)	—	Liquid	49.0[d]	1348	*351, 352, 355*
$Co(PF_3)_3(CO)C_2F_5$	(D)	—	Liquid	49.7[d]	1342	*351, 352, 355*
$Co(PF_3)_4C_2F_5$	(D)	—	Liquid	51.4[d]	1329	*351, 352, 355*
$Co(PF_3)(CO)_3C_3F_7$	(D)	—	Liquid	49.6[d]	1373	*351, 352, 355*
$Co(PF_3)_2(CO)_2C_3F_7$	(D)	—	Liquid	49.0[d]	1348	*351, 352, 355*
$Rh(PF_3)\{\eta^5\text{-}C_5(CH_3)_5\}CF_3I$	(C)	Orange-brown	dec. >200	24.7	1392	*170, 171*

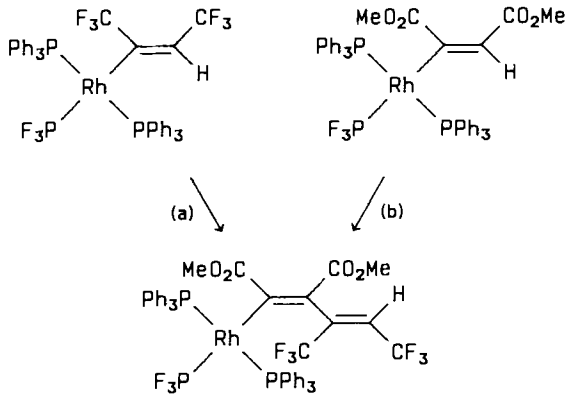
$Rh(PF_3)\{\eta^5\text{-}C_5(CH_3)_5\}C_2F_5I$	(C)	Red-brown	230–231	22.5	1383	*170, 171*
$Rh(PF_3)\{\eta^5\text{-}C_5(CH_3)_5\}C_3F_7I$	(C)	Deep-red	147–149	21.2	1389	*170, 171*
$Rh(PF_3)\{\eta^5\text{-}C_5(CH_3)_5\}C_7F_{15}I$	(C)	Orange	86–88	22.2	1379	*170*
$Rh(PF_3)(PPh_3)_2(CF_3C{=}CHCF_3)$	(F)	Yellow	137–142	18.3	1308	*160*
$Rh(PF_3)(PPh_3)_2(CO_2MeC{=}CH{-}CO_2Me)$	(F)	Yellow	—	19.6	1307	*160*
$Rh(PF_3)(PPh_3)_2[(CO_2MeC{=}C{-}CO_2Me)CF_3C{=}CHCF_3]$	(F)	Yellow	90 (dec.)	18.8	1310	*160*
$Mo(PF_3)(\eta\text{-}C_5H_5)(CO)_2CH_3$	(E)	Yellow	—	—	—	*170*
$W(PF_3)(\eta\text{-}C_5H_5)(CO)_2CH_3$	(E)	Yellow	119–121	—	—	*170*
$W(\eta^5\text{-}C_5H_5)(CO)(PF_3)(PMe_3)CH(CO_2H)C_6H_4Me$	(G)	Orange	—	—	—	*107*

[a] In ppm relative to CCl_3F.

[b] In Hz.

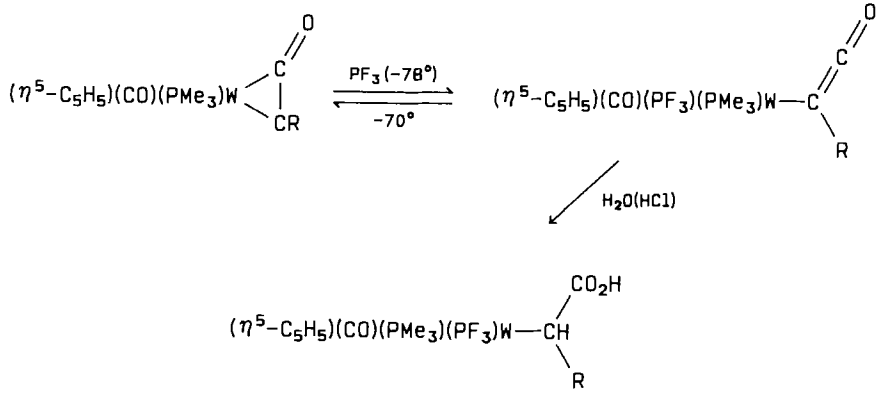
[c] $^1J_{PF}$ is correct for *mono* PF_3 complexes, equals $^1J_{PF} + n^3J_{PF}$, for $(PF_3)_{n+1}$ complexes.

[d] In ppm relative to $PhCF_3$ (*355*).



(a) = $MeO_2CC{\equiv}CCO_2Me$ (b) = $CF_3C{\equiv}CCF_3$

SCHEME 13. (a) = $MeO_2CC{\equiv}CCO_2Me$; (b) = $CF_3C{\equiv}CCF_3$.



SCHEME 14

to a σ-alkyl complex involving a PF_3-containing thermolabile η^1-ketene complex (method G) has been reported (Scheme 14) (*107*).

XVIII. Transition Metal Complexes Containing σ-Bonded Group IV Elements Other Than Carbon

Synthetic routes to the class of compounds listed in Table XVII include UV photochemical displacement of PF_3 from a metal PF_3 complex with MCl_3 anions (M = group IV element) (method A).

TABLE XVII

TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES CONTAINING σ-BONDED GROUP IV ELEMENTS

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Mn(PF_3)_x(CO)_{5-x}SiMe_3$	(D)	Pale-yellow	−52.4 to −51.8	16.2	1316	*29, 314*
$[Mn(PF_3)_2(\eta^5\text{-}C_5H_5)GeCl_3]^-$[d]	(A)	Gold	144	9.2	1250	*184*
$[Mn(PF_3)_2(\eta^5\text{-}C_5H_5)SnCl_3]^-$[e]	(A)	Gold-yellow	210	11.9	1230	*184*
$[Fe(PF_3)_3SnCl_3]^{2-}$[e]	(A)	Orange	75	−1.5	1235	*184*
$[Fe(PF_3)(NO)_2GeCl_3]^-$[d]	(A)	Red-brown	dec. >78	—	—	*184*
$[Co(PF_3)_2(NO)SnCl_3]^-$[d]	(A)	Red	45	—	—	*214*
$Co(PF_3)_x(CO)_{4-x}SiH_2CH_3$	(E)	—	—	—	—	*29, 120, 314*
$Co(PF_3)_x(CO)_{4-x}SiCl_3$	(E)	—	—	—	—	*29, 120, 314*
$[Ni(PF_3)_3SnCl_3]^-$[d]	(A)	Colorless	115–117	15.8	1295	*184*
$Ru(CO)_3(PF_3)(SiCl_3)_2$	(D)	White	—	—	—	*301*
$Ru(CO)_2(PF_3)_2(SiCl_3)_2$	(D)	White	—	—	—	*301*
$Rh(PF_3)_4Si(OEt)_3$	(C)	White	−20	—	—	*17*
$Rh(PF_3)_4SiCl_3$	(C)	Yellow	20–22.5	—	—	*17*
$Rh(PF_3)_4SiPh_3$	(C)	White	105 dec.	5.6	1355	*17*
$Rh(PF_3)_4GePh_3$	(C)	White	105–108 dec.	—	—	*17*
$Rh(PF_3)_4SnPh_3$	(B)(C)	White	100 dec.	—	—	*17*
$Ir(PF_3)_4SiPh_3$	(C)	White	98–101	—	—	*17*
$Ir(PF_3)_4SnPh_3$	(B)(C)	White	113–114	—	—	*17*
$Ir(PF_3)_4PbPh_3$	(C)	White	117–118	—	—	*17*
$IrHCl(Si(OEt)_3)(PF_3)(PPh_3)_2$	(F)	White	—	—	—	*41*
$[Mo(PF_3)_5SnCl_3]^-$[e]	(A)	Pink	173	−5.7	1230	*184*

[a] In ppm relative to CCl_3F.

[b] In Hz.

[c] $^1J_{PF}$ quoted in $^1J_{PF} + n^3J_{PF'}$ for $(PF_3)_{n+1}$ complexes.

[d] $[AsPh_4]^+$ salt.

[e] $[Et_4N]^+$ salt.

$$Fe(PF_3)_5 \xrightarrow{SnCl_3^-} [Fe(PF_3)_3(SnCl_3)]^{2-}$$
$$Mn\text{-}\eta^5\text{-}(C_5H_5)(PF_3)_3 \xrightarrow{GeCl_3^-} [Mn\text{-}\eta^5\text{-}(C_5H_5)(PF_3)_2GeCl_3]^-$$

The products are usually isolated as their $[Ph_4As]^+$ or $[Et_4N]^+$ salts.

Alternatively, treatment of trifluorophosphine metallates with R_3MCl (method B) or via metal–metal bond cleavage reactions of dinuclear PF_3 metal complexes with a group IV metal hydride R_3MH (method C) have been useful synthetic methods, e.g.,

$$KRh(PF_3)_4 + Ph_3SiCl \longrightarrow Rh(PF_3)_4SiPh_3 + KCl$$
$$Rh_2(PF_3)_8 \xrightarrow{Ph_3SnH} Rh(PF_3)_4SnPh_3$$

Carbonyl precursors of the type $[R_3MM'(CO)_5]$ (M = group IV metal; M′ = transition metal) react readily with PF_3 either thermally or under the influence of UV irradiation (method D), and PF_5 has also been utilized in the case of silyl-substituted metal carbonyl complexes (method E).

$$Ru(CO)_4(SiCl_3)_2 \xrightarrow{PF_3} Ru(CO)_3(PF_3)(SiCl_3)_2$$
$$Co(CO)_4(SiCl_3) \xrightarrow{PF_3} Co(CO)_3(PF_3)(SiCl_3)$$

An interesting extension of this type of reaction involves the photosubstitution of the surface-confined cobalt tetracarbonyl system $[S]\geqslant SiCo(CO)_4$ (where [S] represents a high surface-area silica) and the technique of Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS) has been applied for the first time (*172*) to study photoreactions of a species on the surface.

$$[S]\geqslant SiCo(CO)_4 + PF_3 \xrightarrow{h\nu} [S]\geqslant SiCo(CO)_3(PF_3)$$

Small ligands like PF_3 can be added to the five-coordinate iridium(III) complex $[IrHX(SiR_3)L_2]$ (method F) to give six-coordinate complexes in which the PF_3 group has predominantly entered trans to the silyl group.

XIX. Transition Metal PF_3 Complexes Containing Other Anionic or Cationic Ligands

The small number of complexes of this type (listed in Table XVIII) have been obtained via the reaction of a trifluorophosphine metallate

TABLE XVIII

TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES CONTAINING OTHER ANIONIC OR CATIONIC LIGANDS

Complex	Method of preparation	Color	M.P. (°C), B.P. (°C/mmHg)	ϕ_F[a]	$^1J_{PF}$[b,c]	Reference
$Mn(CO)_3(PF_3)(B_3H_8)$	(F)	Yellow-orange	—	—	—	*116*
$[Cu(PF_3)][AsF_6]$	(D)	Colorless	—	—	—	*101*
$[Ag(PF_3)][HF_2]$	(D)	—	—	—	—	*101*
$Rh_2(PF_3)_2(CH_3CO_2)_4$[d]	(G)	—	—	—	—	*66*
$[Rh(PF_3)_2(CH_3CO_2)]_2$	(B)	Red-brown	126–128	17.2	1308	*285*
$[Rh(PF_3)_2(CF_3CO_2)]_2$	(B) (C)	Magenta	123–125	18.1	1306	*285*
$Rh(PF_3)_2(acac)$[e]	(B) (E)	Orange	75–77	20.5	1322[g]	*17, 278*
$Rh(PF_3)_2(facac)$[f]	(B)	Red	—	—	—	*278*
$Rh(PF_3)_4(AuPPh_3)$	(A)	White	158–159	—	—	*17*
$Ir(PF_3)_2(acac)$	(E)	Orange	—	26.4	1205	*17*
$Ir(PF_3)(C_8H_{14})(acac)$	(E)	Yellow	—	—	—	*17*
$Ir(PF_3)_4(AuPPh_3)$	(A)	White	161–162	—	—	*17*
$Hg_2(PF_3)(AsF_6)_2$	(D)	White	—	47.7	1555	*99, 100*
$Hg_2(PF_3)_2(AsF_6)_2$	(D)	—	—	—	—	*99, 100*

[a] In ppm relative to CCl_3F.

[b] In Hz.

[c] $^1J_{PF}$ listed = $^1J_{PF} + nJ_{PF'}$, for $(PF_3)_{n+1}$ complexes.

[d] Rh—PF_3 = 2.42(l) Å (X-ray).

[e] acac = $CH_3COCHCOCH_3$.

[f] facac = $CF_3COCHCOCF_3$.

[g] Accurate value for $^1J_{PF}$; $^3J_{PF'}$ = 4 Hz.

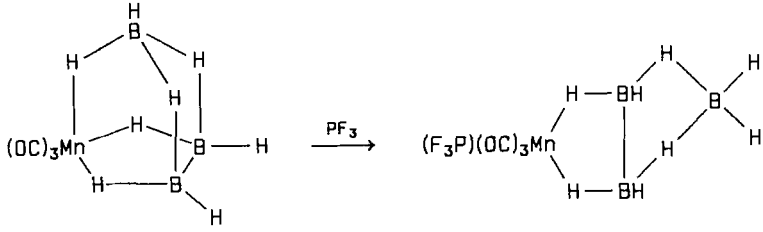
with an appropriate halide (method A), e.g.,

$$M(PF_3)_4^- + AuCl(PPh_3) \longrightarrow M(PF_3)_4AuPPh_3 + Cl^-$$
$$(M = Rh, Ir)$$

by treatment of halogeno-trifluorophosphine complexes with thallium or silver salts of other anions (e.g., acac, facac, trifluoroacetate) (method B), from η^3-allyl trifluorophosphine complexes by treatment with acids (method C), via direct interaction between PF_3 and transition metal salts containing complex ions in liquid SO_2 or liquid HF (method D), and by ligand displacement by PF_3 from suitable salts (method E).

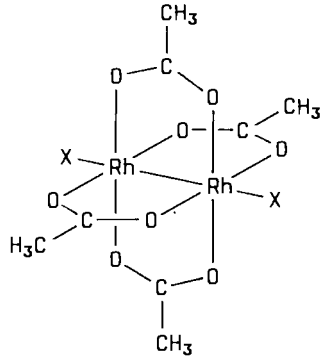
$$[RhCl(PF_3)_2]_2 \xrightarrow{CF_3CO_2Ag} [Rh(CO_2CF_3)(PF_3)_2]_2$$
$$Rh(C_3H_5)(PF_3)_3 \xrightarrow{CF_3CO_2H} [Rh(CO_2CF_3)(PF_3)_2]_2$$
$$Cu(AsF_6) \xrightarrow[liq\,SO_2]{PF_3} [CuPF_3][AsF_6]$$
$$Rh(diene)(acac) \xrightarrow{PF_3} Rh(PF_3)_2(acac)$$

A rather interesting synthetic method for a PF_3 manganese complex containing the unusual octahydrotriborate anion ($B_3H_8^-$) involves a change in the denticity of the coordinated anion on addition of PF_3 (Scheme 15) (method F).



SCHEME 15

An important paper describes the formation of the metal–metal bonded dirhodium tetracarboxylate trifluorophosphine complex $[Rh_2(OCOCH_3)_4(PF_3)_2]$ made directly from the dirhodium tetraacetate complex by direct addition of PF_3 to the formally metal–metal triple bond. The structure was determined by a single-crystal X-ray study, and has been compared with other $[Rh_2(OAc)_4X_2]$ systems (X = py, Et_2NH, CO, and $P(OR)_3$).



(22)

(X = PF_3) (Rh—Rh = 2.430(3) Å)

The Rh—Rh distance is much shorter than the 2.7 Å expected for a single Rh—Rh bond, thus suggesting that an Rh—Rh triple bond exists. However, this is inconsistent with spectroscopic data. The situation is best considered as involving extensive mixing of metal and bridging ligand orbitals, but could also be due in part to interactions arising from mixing of higher energy empty orbitals into the ground state MOs for the complex. As a consequence of these interactions, the formal bond order is not a useful indication of the metal–metal interactions in these systems.

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REFERENCES

1. Al-Ohaly, A. R., and Nixon, J. F., *J. Organomet. Chem.* **202,** 297 (1980).
2. Al-Ohaly, A. R., Head, R. A., and Nixon, J. F., *J. Organomet. Chem.* **156,** C43 (1978).
3. Al-Ohaly, A. R., Head, R. A., and Nixon, J. F., *J. Chem. Soc., (Dalton)* Trans., p. 889 (1978).
4. Al-Ohaly, A. R., Head, R. A., and Nixon, J. F., *J. Organomet. Chem.* **205,** 99 (1981).
5. Almenningen, A., Anderson, B., and Astrup, E. E., *Acta Chem. Scand.* **24,** 1579 (1970).
6. Antle, P. E., and Tolman, C. A., *J. Organomet. Chem.* **159,** 5 (1978).

7. Avanzio, S. C., Chen, H. W., Donahue, C. J., and Jolly, W. L., *Inorg. Chem.* **19,** 2201 (1980).
8. Avancino, S. C., Bakke, A. A., Chen, H. W., Donahue, C. J., Jolly, W. L., Lee, T. H., and Ricco, A. J., *Inorg. Chem.* **19,** 1931 (1980).
9. Babichev, A. P., Klimov, V. D., Kushlyanikii, O. A., Legasov, V. A., Lebedev, A. V., Nastyukha, A. I., and Khorashev, S. S., *Dokl, Acad. Nauk. SSSR* **259,** 109 (1981).
10. Bailey, T. J., Clark, R. J., and Levy, G. C., *Inorg. Chem.* **21,** 2085 (1982).
11. Barlow, C. G., and Nixon, J. F., *Inorg. Nucl. Chem. Lett.* **2,** 323 (1966).
12. Barlow, C. G., Nixon, J. F., and Webster, M., *J. Chem. Soc. A*, p. 2216 (1968).
13. Barlow, C. G., Nixon, J. F., and Swain, J. R., *J. Chem. Soc. A*, p. 1082 (1969).
14. Bassett, P. J., Higginson, B. R., Lloyd, D. R., Lynaugh, N., and Roberts, P. J., *J. Chem. Soc., Dalton Trans.*, p. 2316 (1974).
15. Benazeth, S., Loutellier, A., and Bigorgne, M., *J. Organomet. Chem.* **24,** 479 (1970).
16. Benfield, F. W. S., Green, M. L. H., Ogden, J. S., and Young, D., *J. Chem. Soc., Chem. Commun.*, p. 866 (1973).
17. Bennett, M. A., and Patmore, D. J., *Inorg. Chem.* **10,** 2387 (1971).
18. Bennett, M. A., and Turney, T. W., *Aust. J. Chem.* **26,** 2321 (1973).
19. Bennett, M. A., Johnson, R. N., and Turney, T. W., *Inorg. Chem.* **15,** 2938 (1976).
20. Bennett, M. A., Johnson, R. N., and Turney, T. W., *Inorg. Chem.* **15,** 90 (1976).
21. Bennett, M. A., Johnson, R. N., Robertson, G. B., Turney, T. W., and Whimp, P. O., *Inorg. Chem.* **15,** 97 (1976).
22. Bennett, M. A., Johnson, R. N., and Turney, T. W., *Inorg. Chem.* **15,** 107 (1976).
23. Bennett, M. A., Johnson, R. N., and Turney, T. W., *Inorg. Chem.* **15,** 111 (1976).
24. Bennett, M. A., Hann, E. J., and Johnson, R. N., *J. Organomet. Chem.* **124,** 189 (1977).
25. Bennett, M. A., and Milner, D. L., *J. Am. Chem. Soc.* **91,** 6983 (1969).
26. Bennett, M. A., Johnson, R. N., Robertson, G. B., Turney, T. W., and Whimp, P. O., *J. Am. Chem. Soc.* **94,** 6540 (1972).
27. Bercaw, J. E., *Adv. Chem. Ser.* **167,** 136 (1978).
28. Berry, A. D., *Organometallics* **2,** 895 (1983).
29. Berry, A. D., and MacDiarmid, A. G., *Inorg. Nucl. Chem. Lett.* **5,** 601 (1969).
30. Besnainov, S., and Labarbe, P., *J. Chim. Phys.* **67,** 512 (1970).
31. Bigorgne, M., *Bull. Soc. Chim. Fr.*, p. 1986 (1960).
32. Bigorgne, M., *J. Inorg. Nucl. Chem.* **26,** 107 (1964).
33. Bigorgne, M., *J. Organomet. Chem.* **2,** 68 (1964).
34. Bigorgne, M., and Bernard, J., *Rev. Chim. Miner.* **3,** 831 (1966).
35. Bigorgne, M., and Bouquet, G., *C.R. Hebd. Seances Acad. Sci., Ser. C* **264,** 1485 (1967).
36. Bigorgne, M., and Tripathi, J. B. P., *J. Mol. Struct.* **10,** 449 (1971).
37. Blackborow, R. J., Eady, C. R., Grevels, F. W., Koerner Von Gustorf, E. A., Scrivanti, A., Wolfbeis, O. S., Benn, R., Brauer, D. J., Kruger, C., Roberts, P. J., and Tsay, Y. H., *J. Chem. Soc., Dalton Trans*, p. 661 (1981).
38. Blackborow, J. R., Eady, C. R., Koerner Von Gustorf, E. A., Scrivanti, A., and Wolfbeis, O., *J. Organomet. Chem.* **108,** C32 (1976).
39. Blackborow, J. R., Grubbs, R., Miyashita, A., and Scrivanti, A., *J. Organomet. Chem.* **120,** C49 (1976).
40. Blackborow, J. R., Grubbs, R. H., Miyashita, A., Scrivanti, A., and Koerner Von Gustorf, E. A., *J. Organomet. Chem.* **122,** C6 (1976).
41. Blackburn, S. N., Haszeldine, R. N., Parish, R. V., and Setchfield, J. H., *J. Chem. Res. (S)*, p. 170 (1980); *J. Chem. Res. (M)*, p. 2442 (1980).
42. Bönnemann, H., *Angew. Chem., Int. Ed. English* **9,** 736 (1970).
43. Bouquet, G., and Bigorgne, M., *Spectrochim. Acta, Part A* **27,** 139 (1971).

44. Bouquet, G., Loutellier, A., and Bigorgne, M., *J. Mol. Struct.* **1,** 211 (1968).
45. Boxhoorn, G., Jesse, A. C., Ernsting, J. M., and Oskam, A., *Thermochim. Acta* **27,** 261 (1978).
46. Bridges, D. M., Rankin, D. W. H., Clement, D. A., and Nixon, J. F., *Acta Crystallogr., Sect. B* **28,** 1130 (1972).
47. Bridges, D. M., Holywell, G. C., Rankin, D. W. H., and Freeman, J. M., *J. Organomet. Chem.* **32,** 87 (1971).
48. Burg, A. B., and Street, G. B., *Inorg. Chem.* **5,** 1532 (1966).
49. Burg, A. B., and Street, G. B., *J. Am. Chem. Soc.* **85,** 3522 (1963).
50. Burns, R. C., and O'Donnell, T. A., *J. Inorg. Nucl. Chem.* **42,** 1613 (1980).
51. Burns, R. C., and O'Donnell, T. A., *J. Inorg. Nucl. Chem.* **42,** 1285 (1980).
52. Busch, M. A., and Clark, R. J., *Inorg. Chem.* **14,** 219 (1975).
53. Busch, M. A., and Clark, R. J., *Inorg. Chem.* **14,** 226 (1975).
54. Cable, R. A., Green, M., Mackenzie, R. E., Timms, P. L., and Turney, T. W., *J. Chem. Soc., Chem. Commun.*, p. 270 (1976).
55. Cairns, M. A., and Nixon, J. F., *J. Organomet. Chem.* **87,** 109 (1975).
56. Cairns, M. A., and Nixon, J. F., *J. Organomet. Chem.* **51,** C27 (1973); *J. Chem. Soc., Dalton Trans.*, p. 2001 (1974).
57. Cairns, M. A., and Nixon, J. F., *J. Organomet. Chem.* **64,** C19 (1974).
58. Cairns, M. A., and Nixon, J. F., *J. Organomet. Chem.* **74,** 263 (1974).
59. Cairns, M. A., Nixon, J. F., and Wilkins, B., *J. Chem. Soc., Chem. Commun.*, p. 86 (1973).
60. Campbell, J. M., and Stone, F. G. A., *Angew. Chem., Int. Ed. English* **8,** 140 (1967).
61. Cassoux, P., Savariault, J.-M., Laurent, J. P., and Commenges, G., *J. Chim. Phys.* **67,** 258 (1970).
62. Chatt, J., *J. Chem. Soc.*, p. 3340 (1949).
63. Chatt, J., and Williams, A. A., *J. Chem. Soc.*, p. 3061 (1951).
64. Chatt, J., Dilworth, J. R., and Leigh, G. J., *J. Chem. Soc., Dalton Trans.*, p. 612 (1973).
65. Chatt, J., Mason, R., and Meek, D. W., *J. Am. Chem. Soc.* **97,** 3826 (1979).
66. Christoph, G. G., and Koh, Y. B., *J. Am. Chem. Soc.* **101,** 1422 (1979).
67. Ciullo, G., Sgmellotti, A., Tarantelli, F., De Alti, G., and Decleva, P., *Gazz. Chim. Ital.* **110,** 305 (1980).
68. Clark, R. J., *New Aspects Chem. Met. Carbonyls Deriv. Int. Symp. Proc. 1st, 1968,* **A5** (1968).
69. Clark, R. J., *Inorg. Chem.* **6,** 299 (1967).
70. Clark, R. J., *Inorg. Chem.* **3,** 1395 (1964).
71. Clark, R. J., and Brimm, E. O., *Inorg. Chem.* **4,** 651 (1965).
72. Clark, R. J., and Busch, M. A., *Acc. Chem. Res.* **6,** 246 (1973), and references therein.
73. Clark, R. J., and Hoberman, P. I., *Inorg. Chem.* **4,** 1771 (1965).
74. Clark, R. J., Abraham, M., and Busch, M. A., *J. Organomet. Chem.* **35,** C33 (1972).
75. Clark, R. J., Hoberman, P. I., and Brimm, E. O., *J. Inorg. Nucl. Chem.* **27,** 2109 (1965).
76. Clark, R. J., Hargaden, J. P., Haas, H., and Sheline, R. K., *Inorg. Chem.* **7,** 673 (1968).
77. Clark, R. J., and Morgan, K. A., *Inorg. Chim. Acta* **2,** 93 (1968).
78. Clark, R. J., Swartz, G. L., and George, H. A., *Fundam. Res. Homogeneous Catal.* **3,** 835 (1979).
79. Clegg, W., and Morton, S., *J. Chem. Soc., Dalton Trans.*, p. 1452 (1978).
80. Clement, D. A., Nixon, J. F., and Sexton, M. D., *J. Chem. Soc., Chem. Commun.*, p. 1509 (1969).
81. Clement, D. A., and Nixon, J. F., *J. Chem. Soc., Dalton Trans.*, p. 2553 (1972).
82. Clement, D. A., Nixon, J. F., and Wilkins, B., *J. Organomet. Chem.* **37,** C43 (1972).

83. Connor, J. A., and Overton, C., *J. Chem. Soc., Dalton Trans.*, p. 2397 (1982).
84. Corderman, R. R., and Beauchamp, J. L., *Inorg. Chem.* **17,** 1585 (1978); *ibid* **16,** 3159 (1977).
85. Cotton, F. A., *Inorg. Chem.* **3,** 702 (1964).
86. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." Wiley, New York, 1980.
87. Crocker, C., and Goggin, P. L., *J. Chem. Res.* (*S*), p. 36 (1981); *J. Chem. Res.* (*M*), p. 701 (1981).
88. Crocker, C., Goggin, P. L., and Goodfellow, R. J., *J. Chem. Res.* (*S*), p. 37 (1981); *J. Chem. Res.* (*M*), p. 720 (1981).
89. Crocker, C., and Goodfellow, R. J., *J. Chem. Res.* (*S*), p. 38 (1981); *J. Chem. Res.* (*M*), p. 742 (1981).
90. Crocker, C., Goggin, P. L., and Goodfellow, R. J., *J. Chem. Soc., Chem. Commun.*, p. 1056 (1978).
91. Crocker, C., Goggin, P. L., and Goodfellow, R. J., *J. Chem. Soc., Dalton Trans.*, p. 2494 (1976).
92. Cyvin, S. J., *J. Mol. Struct.* **30,** 311 (1971).
93. Cyvin, S. J., *Z. Anorg. Allg. Chem.* **403,** 193 (1974).
94. Cyvin, S. J., and Lyham, L., *J. Mol. Struct.* **25,** 151 (1975).
95. Cyvin, S. J., and Müller, A., *Acta Chem. Scand.* **25,** 1149 (1971).
96. Daamen, H., Boxhoorn, G., and Oskam, A., *Inorg. Chim. Acta* **28,** 2631 (1978).
97. Dabard, R., Jaouen, G., Simonneaux, G., Cais, M., Kohn, D. H., Lapid, A., and Tartarsky, D., *J. Organomet. Chem.* **184,** 91 (1980).
98. Dalton, J., Paul, I., Smith, J. G., and Stone, F. G. A., *J. Chem. Soc.* (*A*), p. 1195 (1968).
99. Dean, P. A. W., and Ibbott, D. G., *Inorg. Nucl. Chem. Lett.* **11,** 119 (1975).
100. Dean, P. A. W., and Ibbott, D. G., *Can. J. Chem.* **54,** 177 (1976).
101. Desjardins, C. D., Edwards, D. B., and Passmore, J., *Can. J. Chem.* **57,** 2714 (1979).
102. Desobry, V., and Kundig, E. P., *Helv. Chim. Acta* **64,** 1288 (1981).
103. Dickson, R. S., Oppenheim, A. P., and Pain, G. N., *J. Organomet. Chem.* **224,** 377 (1982).
104. Doiran, C. E., and McMahon, T. B., *Inorg. Chem.* **19,** 3037 (1980).
105. Dougherty, R. C., Krevalis, M. A., and Clark, R. J., *J. Am. Chem. Soc.* **101,** 2642 (1979).
106. Doyen, G., *Surf. Sci.* **122,** 505 (1982).
107. Eberl, K., Wolfgruber, M., Sieber, W., and Kreissl, F. R., *J. Organomet. Chem.* **236,** 171 (1982).
108. Edwards, H. G. M., and Woodward, L. A., *Spectrochim. Acta Part A* **26,** 897 (1970).
109. Edwards, B. H., Rogers, R. D., Sikora, D. J., Atwood, J. L., and Rausch, M. D., *J. Am. Chem. Soc.* **105,** 416 (1983).
110. Efraty, A., and Jubran, N., *Inorg. Chim. Acta* **44,** L191 (1980).
111. Ernst, R. D., Liu, J.-Z., and Wilson, D. R., *J. Organomet. Chem.* **250,** 257 (1983).
112. Ertl, G., Küppers, J., Nitschké, F., and Weiss, M., *Chem. Phys. Lett.* **52,** 309 (1977).
113. Ferrari, R. P., Vaglio, G. A., Gambino, O., Valle, M., and Cetini, G., *J. Chem. Soc., Dalton Trans.*, p. 1998 (1972).
114. Fjare, K. L., and Ellis, J. E., Organometallics **1,** 1373 (1982).
115. Frenz, B. A., and Ibers, J. A., *Inorg. Chem.* **9,** 2403 (1970).
116. Gaines, D. F., and Hildebrandt, S. J., *Inorg. Chem.* **17,** 794 (1978).
117. Gedris, T. E., Clark, R. J., and Catral-Navarreté, J., *J. Inorg. Nucl. Chem.* **43,** 431 (1981).
118. Gerlach, D. H., Peet, W. G., and Muetterties, E. L., *J. Am. Chem. Soc.* **94,** 4545 (1972).

119. Goggin, P. L., Goodfellow, R. J., Haddock, S. R., Taylor, B. F., and Marshall, I. R. H., *J. Chem. Soc., Dalton Trans.*, p. 459 (1976).

120. Gondal, S. K., MacDiarmid, A. G., Saalfield, F. E., and McDowell, M. V., *Inorg. Nucl. Chem. Lett.* **5,** 351 (1969).

121. Graham, W. A. G., *Inorg. Chem.* **7,** 315 (1968).

122. Green, J. C., King, D. I., and Eland, J. H. D., *J. Chem. Soc., Chem. Commun.*, p. 1121 (1970).

123. Guest, M. F., Hillier, I. H., and Saunders, V. R., *J. Chem. Soc., Faraday Trans. 2*, p. 867 (1972).

124. Huheey, J. E., "Inorganic Chemistry." Harper, New York, 1983.

125. Koerner Von Gustorf, E. A., Jaenicke, O., Wolfbeis, G., and Eady, C. R., *Angew, Chem., Int. Ed. Engl.* **14,** 278 (1975).

126. Koerner Von Gustorf, E. A., Jaenicke, O., and Polansky, O. C., *Angew. Chem., Int. Ed. Engl.* **11,** 532 (1972).

127. Haas, H., and Sheline, R. K., *J. Chem. Phys.* **47,** 2996 (1967).

128. Hagen, A. P., and Elphingstone, E. A., *J. Inorg. Nucl. Chem.* **35,** 3719 (1973).

129. Hao, N., McGlinchey, M. J., Sayer, B. G., and Schrobilgen, G. J., *J. Magn. Reson.* **46,** 158 (1982).

130. Harris, R. K., Woplin, J. R., and Schmutzler, R., *Ber. Bunsenges. Phys. Chem.* **75,** 134 (1971).

131. Harris, T. V., Rathke, J. W., and Muetterties, E. L., *J. Am. Chem. Soc.* **100,** 6966 (1978).

132. Havel, J. J., Ph.D. Thesis, Pennsylvania State University, University Park (1972).

133. Head, R. A., and Nixon, J. F., *J. Chem. Soc., Chem. Commun.*, p. 62 (1976).

134. Head, R. A., and Nixon, J. F., *J. Chem. Soc., Chem. Commun.*, p. 135 (1975).

135. Head, R. A., and Nixon, J. F., *J. Chem. Soc., Dalton Trans.*, p. 885 (1978).

136. Head, R. A., and Nixon, J. F., *J. Chem. Soc., Dalton Trans.*, p. 895 (1978).

137. Head, R. A., and Nixon, J. F., *J. Chem. Soc., Dalton Trans.*, p. 901 (1978).

138. Head, R. A., and Nixon, J. F., *J. Chem. Soc., Dalton Trans.*, p. 909 (1978).

139. Head, R. A., Nixon, J. F., Sharp, G. J., and Clark, R. J., *J. Chem. Soc., Dalton Trans.*, p. 2054 (1975).

140. Head, R. A., Nixon, J. F., Swain, J. R., and Woodard, C. M., *J. Organomet. Chem.* **76,** 393 (1974).

141. Head, R. A., Nixon, J. F., and Clark, R. J., *J. Organomet. Chem.* **135,** 209 (1977).

142. Head, R. A., Nixon, J. F., Westwood, N. P. C., and Clark, R. J., *J. Organomet. Chem.* **145,** 75 (1978).

143. Heaton, B. T., D. Phil. Thesis, University of Sussex (1967).

144. Hillier, I. H., and Saunders, V. R., *Trans. Faraday Soc.* **66,** 2401 (1970).

145. Hillier, I. H., Saunders, V. R., Ware, M. J., Bassett, P. J., Lloyd, D. R., and Lynaugh, N., *J. Chem. Soc., Chem. Commun.*, p. 1316 (1970).

146. Hillier, I. H., Higginson, B. R., Lloyd, D. R., Lynaugh, N., and Roberts, P. J., *J. Chem. Soc., Dalton Trans.*, p. 2316 (1974).

147. Hitchcock, P. B., Nixon, J. F., and Swain, J. A., *Acta Crystallogr., Sect. B* **29,** 154 (1973).

148. Hitchcock, P. B., Nixon, J. F., and Sinclair, J., *J. Organomet. Chem.* **86,** C34 (1975).

149. Hitchcock, P. B., Morton, S., and Nixon, J. F., *J. Chem. Soc., Chem. Commun.*, p. 603 (1984). *J. Chem. Soc., Dalton Trans.*, p. 1295 (1985).

150. Hitchcock, P. B., Lappert, M. F., and Pye, P. L., *J. Chem. Soc., Chem. Commun.*, p. 644 (1976).

151. Hitchcock, P. B., Lappert, M. F., and Pye, P. L., *J. Chem. Soc., Dalton Trans.*, p. 826 (1978).

152. Hitchcock, P. B., Lappert, M. F., Pye, P. L., and Thomas, S., *J. Chem. Soc., Dalton Trans.*, p. 1929 (1979).
153. Hitchcock, P. B., Jacobson, B., and Pidcock, A., *J. Chem. Soc., Dalton Trans.*, p. 2043 (1977).
154. Hopkinson, M. J., and Nixon, J. F., *J. Organomet. Chem.* **148,** 201 (1978).
155. Hosseini, H. E., and Nixon, J. F., *J. Organomet. Chem.* **97,** C24 (1975).
156. Hosseini, H. E., and Nixon, J. F., *J. Organomet. Chem.* **150,** 129 (1978).
157. Hosseini, H. E., and Nixon, J. F., *J. Organomet. Chem.* **192,** C9 (1980).
158. Hosseini, H. E., and Nixon, J. F., *J. Less-Common Met.* **61,** 107 (1978).
159. Hosseini, H. E., Nixon, J. F., and Pinkerton, A. A., unpublished results.
160. Hosseini, H. E., Nixon, J. F., and Poland, J. S., *J. Organomet. Chem.* **164,** 107 (1979).
161. Howell, B. A., and Trahanovsky, W. S., *J. Am. Chem. Soc.* **97,** 2136 (1975).
162. Itoh, H., and Ertl, G., *Z. Naturforsch. A* **37,** 346 (1982).
163. Itoh, H., and Kunz, B. A., *Chem. Phys. Lett.* **64,** 576 (1979).
164. Ittel, S. D., Tolman, C. A., Krusic, P. J., English, A. D., and Jesson, J. P., *Inorg. Chem.* **17,** 3432 (1978).
165. Johnson, T. R., Lynden-Bell, R. M., and Nixon, J. F., *J. Organomet. Chem.* **21,** P15 (1970).
166. Johnston, R. D., Basolo, F., and Pearson, R. G., *Inorg. Chem.* **10,** 247 (1971).
167. Kasenally, A. S., Nyholm, R. S., Parker, D. J., Stiddard, M. H. B., Hodder, D. R. J., and Powell, H. M., *Chem. Ind. (London)*, p. 2097 (1965).
168. Kemmitt, R. D. W., Peacock, R. D., and Wilson, P. L., *J. Chem. Soc., Chem. Commun.*, p. 772 (1968).
169. Keiter, R. L., and Verkade, J. G., *Inorg. Chem.* **8,** 2115 (1969).
170. King, R. B., and Efraty, A., *J. Am. Chem. Soc.* **94,** 3768 (1972).
171. King, R. B., and Efraty, A., *J. Organomet. Chem.* **36,** 371 (1972).
172. Kinney, J. B., Staley, R. H., Reichel, C. L., and Wrighton, M. S., *J. Am. Chem. Soc.* **103,** 4273 (1981).
173. Kouba, J. K., Muetterties, E. L., Thompson, M. R., and Day, V. W., *Organometallics* **2,** 1065 (1983).
174. Kruck, T., *Angew. Chem., Int. Ed. Engl.* **6,** 53 (1967), and references therein.
175. Kruck, T., *Chem. Ber.* **97,** 2018 (1964).
176. Kruck, T., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **19,** 165 (1964).
177. Kruck, T., and Baur, K., *Z. Anorg. Allg. Chem.* **364,** 192 (1969).
178. Kruck, T., and Baur, K., *Chem. Ber.* **98,** 3070 (1965).
179. Kruck, T., and Baur, K., *Angew. Chem., Int. Ed. Engl.* **4,** 521 (1965).
180. Kruck, T., Baur, K., and Lang, W., *Chem. Ber.* **101,** 138 (1968).
181. Kruck, T., Baur, K., Glinka, K., and Stadler, M., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **23,** 1147 (1968).
182. Kruck, T., Derner, N., and Lang, W., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **21,** 1020 (1966).
183. Kruck, T., Diedershagen, H., and Engelmann, A., *Z. Anorg. Allg. Chem.* **397,** 31 (1973).
184. Kruck, T., Ehlert, K., and Molls, W., *Z. Anorg. Allg. Chem.* **422,** 59 (1976).
185. Kruck, T., and Engelmann, A., *Angew. Chem., Int. Ed. Engl.* **5,** 836 (1966).
186. Kruck, T., Engelmann, A., and Lang, W., *Chem. Ber.* **99,** 2473 (1966).
187. Kruck, T., and Hempel, H. U., *Angew. Chem., Int. Ed. Engl.* **10,** 408 (1971).
188. Kruck, T., Hieber, W., and Lang, W., *Angew. Chem., Int. Ed. Engl.* **5,** 247 (1966).
189. Kruck, T., Höfler, M., Jung, H., and Blume, H., *Angew. Chem., Int. Ed. Engl.* **8,** 522 (1969).
190. Kruck, T., Höfler, M., and Blume, H., *Chem. Ber.* **107,** 2145 (1974).

191. Kruck, T., Hofler, M., Baur, K., Junkes, P., and Glinka, K., *Chem. Ber.* **101,** 3827 (1968).
192. Kruck, T., Jung, H., Höfler, M., and Blume, H., *Chem. Ber.* **107,** 2156 (1974).
193. Kruck, T., and Knoll, L., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **28,** 34 (1973).
194. Kruck, T., and Knoll, L., *Chem. Ber.* **106,** 3578 (1973).
195. Kruck, T., and Knoll, L., *Chem. Ber.* **105,** 3765 (1972).
196. Kruck, T., and Knoll, L., *Chem. Ber* **105,** 3783 (1972).
197. Kruck, T., Knoll, L., and Laufenberg, J., *Chem. Ber.* **106,** 697 (1973).
198. Kruck, T., and Kobelt, R., *Chem. Ber.* **105,** 3765 (1972).
199. Kruck, T., and Kobelt, R., *Chem. Ber.* **105,** 3772 (1972).
200. Kruck, T., Kobelt, R., and Prasch, A., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **27,** 344 (1972).
201. Kruck, T., and Krause, V., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **27,** 302 (1972).
202. Kruck, T., and Lang, W., *Z. Anorg. Allg. Chem.* **343,** 181 (1966).
203. Kruck, T., and Lang, W., *Angew. Chem., Int. Ed. Engl.* **4,** 870 (1965).
204. Kruck, T., and Lang, W., *Chem. Ber.* **98,** 3060 (1965).
205. Kruck, T., and Lang, W., *Angew. Chem., Int. Ed. Engl.* **6,** 454 (1967).
206. Kruck, T., and Lang, W., *Angew. Chem., Int. Ed. Engl.* **3,** 700 (1964).
207. Kruck, T., and Lang, W., *Chem. Ber.* **99,** 3794 (1968).
208. Kruck, T., Lang, W., and Derner, N., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **20,** 705 (1965).
209. Kruck, T., Lang, N., Derner, N., and Stadler, M., *Chem. Ber.* **101,** 3816 (1968).
210. Kruck, T., Lang, W., and Engelmann, A., *Angew. Chem., Int. Ed. Engl.* **4,** 148 (1965).
211. Kruck, T., and Mäueler, G., *Z. Anorg. Allg. Chem.* **475,** 156 (1981).
212. Kruck, T., Mäueler, G., and Schmidgen, G., *Z. Anorg. Allg. Chem.* **412,** 239 (1975).
213. Kruck, T., Mäueler, G., and Schmidgen, G., *Chem. Ber.* **107,** 2421 (1974).
214. Kruck, T., and Molls, W., *Z. Anorg. Allg. Chem.* **411,** 54 (1975).
215. Kruck, T., and Prasch, A., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **19,** 669 (1964).
216. Kruck, T., and Hempel, H. U., *Angew. Chem., Int. Ed. Engl.* **13,** 201 (1974).
217. Kruck, T., and Prasch, A., *Z. Anorg. Allg. Chem.* **371,** 1 (1969).
218. Kruck, T., and Prasch, A., *Z. Anorg. Allg. Chem.* **356,** 118 (1968).
219. Kruck, T., and Prasch, A., *Angew. Chem., Int. Ed. Engl.* **3,** 754 (1964).
220. Kruck, T., Sylvester, G., and Kunau, I. P., *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **28,** 38 (1973).
221. Kruck, T., Sylvester, G., and Kunau, I. P., *Angew. Chem., Int. Ed. Engl.* **10,** 725 (1971).
222. Kruck, T., Sylvester, G., and Kunau, I. P., *Z. Anorg. Allg. Chem.* **396,** 165 (1973).
223. Kruck, T., Waldmann, J., Hofler, M., Birkenhager, G., and Odenbrett, C., *Z. Anorg. Allg. Chem.* **402,** 16 (1973).
224. Kruger, C., and Tsay, Y.-H., Abstr. A6, *1st Eur. Crystallogr. Meet., Bordeaux* (1973).
225. Kundig, E. P., and Timms, P. L., *J. Chem. Soc., Chem. Commun.*, p. 912 (1973).
226. Kundig, E. P., and Timms, P. L., *J. Chem. Soc., Dalton Trans.*, p. 991 (1980).
227. Küppers, J., Nitschké, F., Wandelt, K., and Ertl, G., *Ned. Tijdschr. Vacuumtech.* **16,** 131 (1978).
228. Lee, K. M., and Hester, R. E., *J. Organomet. Chem.* **57,** 169 (1973).
229. Letts, J. B., Mazanec, T. J., and Meek, D. W., *Organometallics* **2,** 695 (1983).
230. Loutellier, A., and Bigorgne, M., *J. Chim. Phys. Phys.-Chim. Biol.* **67,** 79 (1970).
231. Loutellier, A., and Bigorgne, M., *J. Chim. Phys. Phys.-Chim. Biol.* **67,** 99 (1970).
232. Loutellier, A., and Bigorgne, M., *J. Chim. Phys. Phys.-Chim. Biol.* **67,** 107 (1970).
233. Loutellier, A., and Bigorgne, M., *Bull. Soc. Chim. Fr.*, p. 3186 (1965).
234. Lucken, E. A. C., Noack, K., and Williams, D. F., *J. Chem. Soc. A*, p. 148 (1967).

235. Lynden-Bell, R. M., Nixon, J. F., and Schmutzler, R., *J. Chem. Soc. A*, p. 565 (1970).
236. Lynden-Bell, R. M., Nixon, J. F., Roberts, J., Swain, J. R., and McFarlane, W., *Inorg. Nucl. Chem. Lett.* **7,** 1187 (1971).
237. MacKenzie, R. E., and Timms, P. L., *J. Chem. Soc. Chem. Commun.*, p. 650 (1974).
238. Mague, J. T., and Wilkinson, G., *Inorg. Chem.* **7,** 542 (1968).
239. Mahnke, H., Clark, R. J., Rosanske, R., and Sheline, R. K., *J. Chem. Phys.* **60,** 2997 (1974).
240. Mahnke, H., Clark, R. J., and Sheline, R. K., *J. Chem. Phys.* **66,** 4822 (1977).
241. Maier, J. P., and Turner, D. W., *J. Chem. Soc., Faraday Trans.* **2,** p. 711 (1972).
242. Manojlovic-Muir, L., Muir, K. W., and Solomon, T., *J. Organomet. Chem.* **142,** 265 (1977).
243. Manriquez, J. M., McAllister, D. R., Sanner, R. D., and Bercaw, J. E., *J. Am. Chem. Soc.* **98,** 6733 (1976).
244. Manriquez, J. M., McAllister, D. R., Sanner, R. D., and Bercaw, J. E., *J. Am. Chem. Soc.* **100,** 2716 (1978).
245. Manriquez, J. M., McAllister, D. R., Rosenberg, E., Skiller, A. M., Williamson, K. L., Chan, S. I., and Bercaw, J. E., *J. Am. Chem. Soc.* **100,** 3078 (1978).
246. Marriott, J. C., Salthouse, J. A., Ware, M. J., and Freeman, J. M., *J. Chem. Soc., Chem. Commun.*, p. 595 (1970).
247. Marynick, D. S., *J. Am. Chem. Soc.* **106,** 4064 (1984).
248. Mason, R., and Meek, D. W., *Angew. Chem., Int. Ed. Engl.* **17,** 183 (1978).
249. Mathieu, R., Lenzi, M., and Poilblanc, R., *C.R. Hebd. Seances Acad. Sci. Ser. C* **266,** 806 (1968).
250. Mathieu, R., Lenzi, M., and Poilblanc, R., *Inorg. Chem.* **9,** 2030 (1970).
251. Meakin, P., Muetterties, E. L., and Jesson, J. P., *J. Am. Chem. Soc.* **94,** 5271 (1972).
252. Meakin, P., Jesson, J. P., Tebbe, F. N., and Muetterties, E. L., *J. Am. Chem. Soc.* **93,** 1797 (1971).
253. Meakin, P., Muetterties, E. L., and Jesson, J. P., *J. Am Chem. Soc.* **95,** 75 (1973).
254. Meriwether, L. S., and Leto, J. R., *J. Am. Chem. Soc.* **83,** 3192 (1961).
255. Micoud, M. H., Savariault, J. M., and Cassoux, P., *Bull. Soc. Chim. Fr.*, p. 3774 (1972).
256. Middleton, W., Ph.D. Thesis, University of Bristol, Bristol, England (1974).
257. Middleton, R., Hull, J. R., Simpson, J. R., Tomlinson, C. H., and Timms, P. L., *J. Chem. Soc., Dalton Trans.*, p. 120 (1973).
258. Milbrath, D. S., Verkade, J. G., and Clark, R. J., *Inorg. Nucl. Chem. Lett.* **12,** 921 (1976).
259. Miles, W. J., Jr., and Clark, R. J., *Inorg. Chem.* **7,** 1801 (1968).
260. Miles, W. J., Jr., and Clark, R. J., *J. Organomet. Chem.* **131,** 93 (1977).
261. Miles, W. J., Jr., Garrett, B. B., and Clark, R. J., *Inorg. Chem.* **8,** 2817 (1969).
262. Minniti, D., and Timms, P. L., *J. Organomet. Chem.* **258,** C12 (1983).
263. Moissan, H., *Bull. Soc. Chim. Fr.*, p. 454 (1891).
264. Montmayor, R. G., and Parry, R. W., *Inorg. Chem.* **18,** 1470 (1979).
265. Muetterties, E. L., and Rathke, J. W., *J. Chem. Soc., Chem. Commun.*, p. 850 (1974).
266. Müller, J., and Fenderl, K., *Chem. Ber.* **104,** 2207 (1971).
267. Müller, J., Fernderl, K., and Mertschenk, B., *Chem. Ber.* **104,** 700 (1971).
268. Müller, J., and Goll, W., *J. Organomet. Chem.* **69,** C23 (1974).
269. Nathanson, G., Gitlin, B., Rosan, A. M., and Yardley, J. T., *J. Chem. Phys.* **74,** 361 (1981).
270. Naumann, F., and Rehder, D., *J. Organomet. Chem.* **204,** 411 (1981).
271. Nitschké, F., Ertl, G., and Küppers, J., *J. Chem. Phys.* **74,** 5911 (1981).

272. Nixon, J. F., *Adv. Inorg. Chem. Radiochem.* **13,** 364 (1970), and references therein.
273. Nixon, J. F., *Endeavour* **32,** 19 (1973), and references therein.
274. Nixon, J. F., *J. Chem. Soc., Chem. Commun.*, p. 34 (1966).
275. Nixon, J. F., *J. Chem. Soc. A*, p. 1136 (1967).
276. Nixon, J. F., *J. Chem. Soc., Dalton Trans.*, p. 2226 (1973).
277. Nixon, J. F., *J. Fluorine Chem.* **3,** 179 (1973).
278. Nixon, J. F., "Nmr Spectra of Nuclei Other Than Protons" (T. Axenrod and G. A. Webb, eds.), Wiley, New York, 1974. Ch. 25.
279. Nixon, J. F., unpublished results.
280. Nixon, J. F., Clement, D. A., and Poland, J. S., *J. Organomet. Chem.* **76,** 117 (1974).
281. Nixon, J. F., and Kooti, M., *J. Organomet. Chem.* **63,** 415 (1973)
282. Nixon, J. F., and Kooti, M., *J. Organomet. Chem.* **104,** 231 (1976).
283. Nixon, J. F., and Kooti, M., *J. Organomet. Chem.* **149,** 71 (1978).
284. Nixon, J. F., and Pinkerton, A. A., *J. Organomet. Chem.* **37,** C47 (1972).
285. Nixon, J. F., Poland, J. S., and Wilkins, B., *J. Organomet. Chem.* **92,** 393 (1975).
286. Nixon, J. F., and Sexton, M. D., *J. Chem. Soc. A*, p. 1089 (1969).
287. Nixon, J. F., and Sexton, M. D., *Inorg. Nucl. Chem. Lett.* **4,** 275 (1968).
288. Nixon, J. F., Suffolk, R. J., Taylor, M. J., Norman, J. G., Jr., Hoskins, D. E., and Gmur, F. J., *Inorg. Chem.* **19,** 810 (1980).
289. Nixon, J. F., Suffolk, R. J., Taylor, M. J., Green, J. C., and Seddon, E. A., *Inorg. Chim. Acta* **47,** 147 (1981).
290. Nixon, J. F., and Swain, J. R., *J. Organomet. Chem.* **72,** C15 (1974).
291. Nixon, J. F., and Swain, J. R., *J. Chem. Soc., Dalton Trans.*, p. 1044 (1972).
292. Nixon, J. F., and Swain, J. R., *Platinum Met. Rev.* **19,** 22 (1975).
293. Nixon, J. F., and Wilkins, B., *J. Organomet. Chem.* **80,** 129 (1974).
294. Nixon, J. F., and Wilkins, B., *J. Organomet. Chem.* **87,** 341 (1975).
295. Nixon, J. F., Wilkins, B., and Clement, D. A., *J. Chem. Soc., Dalton Trans.*, p. 1993 (1974).
296. Ogilvie, F., Clark, R. J., and Verkade, J. G., *Inorg. Chem.* **8,** 1904 (1969).
297. Parker, D. J., and Stiddard, M. H. B., *J. Chem. Soc. A*, p. 695 (1966).
298. Peterson, L. K., Davis, H. B., Leung, F. Y., and Hoyano, J. K., *Inorg. Chim. Acta* **48,** 259 (1981).
299. Pidcock, A., "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands" (C. A. McAuliffe, ed.). MacMillan, New York, 1973.
300. der Poel, H. V., Van Koten, G., and Vrieze, K., *Inorg. Chim. Acta* **51,** 241 (1981).
301. Pomeroy, R. K., and Wijesekera, K. S., *Inorg. Chem.* **19,** 3729 (1980).
302. Prusakov, V. N., Petrov, Y. V., Terent'ev, A. A., and Simonev, N. F., *Radiokhimiya* **23,** 319 (1981).
303. Rathke, J. W., and Muetterties, E. L., *J. Am. Chem. Soc.* **97,** 3272 (1975).
304. Rauchfuss, T. B., and Roundhill, D. M., *J. Am. Chem. Soc.* **96,** 3098 (1974).
305. Reddy, G. S., and Schmutzler, R., *Inorg. Chem.* **6,** 823 (1967).
306. Rehder, D., *J. Magn. Reson.* **38,** 419 (1980).
307. Rehder, D., Bechtold, H. C., and Paulsen, K., *J. Magn. Reson.* **40,** 305 (1980).
308. Rehder, D., Bechtold, H. C., Kececi, A., Schmidt, H., and Siewing, M., *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **37,** 631 (1982).
309. Rehder, D., Dorn, W. L., and Schmidt, J., *Transition Met. Chem. (Weinheim Ger.)* **1,** 233 (1976).
310. Ritz, C. L., and Bartell, L. S., *J. Mol. Struct.* **31,** 73 (1976).
311. Ritz, C. L., Ph.D. Dissertation, University of Michigan, Ann Arbor (1974), *Diss. Abstr. B* **35,** 3271 (1975).

312. Rycroft, D. S., Sharp, D. W. A., and Wright, J. G., *Inorg. Nucl. Chem. Lett.* **14,** 451 (1978).
313. Saalfield, F. E., McDowell, M. V., Gondal, S. K., and MacDiarmid, A. G., *J. Am. Chem. Soc.* **90,** 3684 (1968).
314. Saalfield, F. E., McDowell, M. V., De Coreo, J. J., Berry, A. D., and MacDiarmid, A. G., *Inorg. Chem.* **12,** 48 (1973).
315. Saillard, J. Y., Lissilous, R., and Grandjean, D., *J. Organomet. Chem.* **210,** 365 (1981).
316. Saillard, J. Y., Grandjean, D., Le Beuze, A., and Simonneaux, G., *J. Organomet. Chem.* **204,** 197 (1981).
317. Savariault, J. M., Cassoux, P., and Gallais, F., *C.R. Hebd. Seances Acad. Sci. Ser. C* **271,** 477 (1970).
318. Savariault, J. M., Cassoux, P., and Gallais, F., *C. R. Hebd. Seances Acad. Sci. Ser. C* **277,** 759 (1973).
319. Savariault, J. M., and Labarre, J. F., *Theor. Chim. Acta* **42,** 207 (1976).
320. Savariault, J. M., Serafini, A., Pelissier, M., and Cassoux, P., *Theor. Chim. Acta* **42,** 155 (1976).
321. Schmidt, H., and Rehder, D., *Transition Met. Chem.* **5,** 214 (1980).
322. Schmutzler, R., *Adv. Chem. Ser.* **37,** 150 (1963).
323. Schmutzler, R., *Adv. Fluorine Chem.* **5,** 31 (1965).
324. Seel, F., Ballreich, K., and Schmutzler, R., *Chem. Ber.* **94,** 1173 (1961).
325. Severson, S. J., Cymbaluk, T. H., Ernst, R. D., Higaski, J. M., and Parry, R. W., *Inorg. Chem.* **22,** 3833 (1983).
326. Sheldrick, W. S., personal communication.
327. Sheline, R. K., and Mahnke, H., *New Synth. Methods* **3,** 219 (1975).
328. Sikora, D. J., Rausch, M. D., Rogers, R. D., and Atwood, J. L., *J. Am. Chem. Soc.* **101,** 5079 (1979).
329. Sikora, D. J., Rausch, M. D., Rogers, R. D., and Atwood, J. L., *J. Am. Chem. Soc.* **103,** 982 (1981).
330. Skell, P. S., Williams-Smith, D. L., and McGlinckey, M. J., *J. Am. Chem. Soc.* **95,** 3337 (1973).
331. Staplin, D. C., and Parry, R. W., *Inorg. Chem.* **18,** 1473 (1979).
332. Stelzer, O., and Unger, E., *Chem. Ber.* **108,** 1246 (1975).
333. Stroheimer, W., and Müller, F. J., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **22,** 451 (1967).
334. Street, G. B., and Burg, A., *Inorg. Nucl. Chem. Lett.* **1,** 47 (1965).
335. Sullivan, R. E., and Kiser, R. W., *J. Chem. Soc., Chem. Commun.*, p. 1425 (1968).
336. Svatos, G. F., and Flagg, E. E., *Inorg. Chem.* **4,** 422 (1965).
337. Swartz, G. L., and Clark, R. J., *Inorg. Chem.* **19,** 3191 (1980).
338. Timms, P. L., *Angew. Chem. Int. Edn.* **14,** 273 (1975).
339. Timms, P. L., *Adv. Inorg. Chem. Radiochem.* **14,** 121 (1972).
340. Timms, P. L., *J. Chem. Soc., Chem. Commun.*, p. 1033 (1969).
341. Timms, P. L., *J. Chem. Soc. A*, p. 2526 (1970).
342. Timms, P. L., personal communication (1978).
343. Timms, P. L., and Turney, T. W., *J. Chem. Soc., Dalton Trans.*, p. 2021 (1976).
344. Tolman, C. A., *J. Am. Chem. Soc.* **92,** 2956 (1970).
345. Tolman, C. A., Ittel, S. D., English, A. D., and Jesson, J. P., *J. Am. Chem. Soc.* **100,** 4080 (1978).
346. Trabelsi, M., Loutellier, A., and Bigorgne, M., *J. Organomet. Chem.* **56,** 369 (1973).
347. Tripathi, J. B. P., and Bigorgne, M., *J. Organomet. Chem.* **9,** 307 (1967).
348. Tulip, T. H., and Ibers, J. A., *J. Am. Chem. Soc.* **101,** 4201 (1979).

349. Tumas, W., Gitlin, B., Rosan, A. M., and Yardley, J. T., *J. Am. Chem. Soc.* **104,** 55 (1982).
350. Udovich, C. A., and Clark, R. J., *J. Organomet. Chem.* **36,** 355 (1972).
351. Udovich, C. A., and Clark, R. J., *Inorg. Chem.* **8,** 938 (1969).
352. Udovich, C. A., and Clark, R. J., *J. Am. Chem. Soc.* **91,** 526 (1969).
353. Udovich, C. A., and Clark, R. J., *J. Organomet. Chem.* **25,** 199 (1970).
354. Udovich, C. A., Clark, R. J., and Haas, H., *Inorg. Chem.* **8,** 1066 (1969).
355. Udovich, C. A., Krevalis, M. A., and Clark, R. J., *Inorg. Chem.* **15,** 900 (1976).
356. Vaska, L., and Catone, D. L., *J. Am. Chem. Soc.* **88,** 5324 (1966).
357. Warren, J. D., and Clark, R. J., *Inorg. Chem.* **9,** 373 (1970).
358. Warren, J. D., Busch, M. A., and Clark, R. J., *Inorg. Chem.* **11,** 452 (1972).
359. White, J. W., and Wright, C. J., *J. Chem. Soc., Faraday Trans. 2* **68,** 1423 (1972).
360. Whitmer, J. C., and Cyvin, S. J., *J. Mol. Struct.* **38,** 277 (1977).
361. Wilkinson, G., *J. Am Chem. Soc.* **73,** 5501 (1951).
362. Williams-Smith, D. L., Wolf, L. R., and Skell, P. S., *J. Am. Chem. Soc.* **94,** 4042 (1972).
363. Woodward, L. A., and Hall, J. R., *Nature (London)* **181,** 831 (1958).
364. Woodward, L. A., and Hall, J. R., *Spectrochim. Acta* **16,** 654 (1960).
365. Wreford, S. S., Fischer, M. B., Lee, S., James, E. J., and Nyburg, S. C., *J. Chem. Soc., Chem. Commun.*, p. 458 (1981).
366. Xiao, S. X., Trogler, W. C., Ellis, D. E., and Berkovitch-Yellin, Z., *J. Am. Chem. Soc.* **105,** 7033 (1983).
367. Yarbrough, L. W., and Hall, M. B., *Inorg. Chem.* **17,** 2269 (1978).
368. Ziegler, T., and Rauk, A., *Inorg. Chem.* **18,** 1755 (1979).