Transition-Metal Fluoro Compounds Containing Carbonyl, Phosphine, Arsine, and Stibine Ligands

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I. Introduction

Many organotransition-metal compounds contain chloro, bromo, and iodo ligands. The reactivity of these species is dictated by the nature of the metal, the halide, and the ancillary ligands. Steric and electronic properties of these three components have been used extensively for homogeneous catalyst design.[1] Relatively unexplored, however, is the chemistry of organotransition-metal fluoro complexes, especially species containing low-valent metal centers. For example, a recent study of substitution of carbonyl ligands in $[Rh_5(CO)_{15}]^-$ by monoanions employed chloride, bromide, iodide, and thiocyanate, but not fluoride.[2] Similarly, the kinetics of carbonyl substitution by phosphines in $WX(NO)(CO)_4$ were examined for X = Cl, Br, and I, but not for F.[3] Several factors have contributed to the lack of study of organotransition-metal fluoro complexes. The principal one appears to be labeling of the combination of a low-valent metal center and a fluoride ion as inherently unstable by hard/soft acid/base rules, in spite of considerable experimental evidence suggesting the opposite when π-back-bonding ligands are also present.

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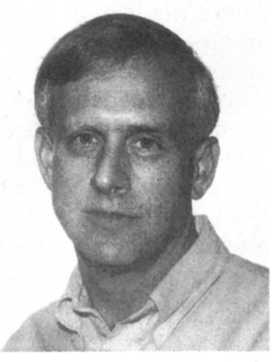

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The properties of the halogens which are important in considering their bonding to metal centers are listed

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TABLE I. Properties of the Halogens

halogen	ionic radius, Å[a]	covalent radius, Å[a]	electro-negativity[a]	cone angle[b]
F	1.36	0.709	3.98	92
Cl	1.81	0.994	3.16	102
Br	1.95	1.142	2.96	105
I	2.16	1.333	2.66	107

[a] From ref 4a. [b] From ref 4b.

in Table I.[4] The monoanion of fluorine, the most electronegative element in the periodic table, is small and only weakly polarizable, and is therefore considered a hard base in the Pearson system.[5] Chlorine is of lower electronegativity and the chloride ion larger and of intermediate polarizability. This trend continues for bromide and iodide. Overall, chloride and bromide are considered borderline bases and the large and easily polarized iodide ion, a soft base.

Many important organotransition-metal systems contain low-valent metal centers and considerable loosely held electron density, so these are weakly polarizing cations and are considered soft acids.[6] The Pearson rule-of-thumb predicts that in solution soft acids form more stable complexes with soft bases than with hard bases. That criterion implies on purely electronic grounds that halide preference in solution by low-valent organometallics should follow the trend $F^- < Cl^- < Br^- < I^-$. Reinforcing the expectation of relatively weak metal–fluoride bonding in organometallic systems are reports of rhodium(I) and iridium(I) compounds in which coordinated fluoride can be replaced by chloride, bromide, or iodide by using the sodium salt, or even the perchlorate ion (section IV).

Other factors contributing to lack of study of organometallic fluoro compounds arise principally from the dearth of convenient ways to introduce fluoro ligands. Most starting materials used for synthesizing organometallics are more readily available and more easily handled as chloro or bromo derivatives, particularly given the propensity of fluoride systems to etch glassware. The difficulties of working with elemental fluorine and hydrogen fluoride[7] are major deterrents to extending reactions readily performed with the heavier halogens and hydrogen halides to F_2 and HF. Furthermore, although the challenges of working with F_2, HF, and MF_x can be surmounted by available experimental apparatus, exerting control over the reactivity of these species remains an issue (see section II). The tenacity with which fluoride reagents hold onto water and other protic reagents due to strong hydrogen bonding[8] makes the preparation of clean fluoride reagents difficult.[9-11] This can lead to the isolation of transition-metal complexes containing hydroxide[12] or bifluoride[13] instead of the desired fluoride.

In spite of these many obstacles, there are, in fact, a number of organotransition-metal fluoro compounds scattered throughout the literature.[14] These include high-valent cyclopentadienyl fluoro derivatives,[15] metal carbonyl fluorides, and fluoro compounds containing one or more carbon-bound groups supported by ancillary phosphine ligands. The subject of this review is transition-metal fluoro compounds containing carbonyl, phosphine, arsine, and stibine ligands. This classification includes a great majority of known low-valent metal fluoro derivatives, as well as a variety of high-valent metal fluoro complexes. It should be noted that many of the compounds in this review do not fit the strict definition of organometallics because they do not contain metal–carbon bonds. Nonetheless, most are closely related to important organometallic systems (e.g., $RhF(PPh_3)_3$ vs $RhF(CO)(PPh_3)_2$).

More than two hundred compounds reported in the literature available through the end of 1990 are covered by the title subject. These are listed in Tables II–IX organized by d^n configuration, with the exception of the carbonyl fluorides, $MF_x(CO)_y$, which are discussed separately. Literature formulations are presented in the tables, except where convincing subsequent evidence has shown earlier descriptions to be incorrect. It should be noted that the level of certainty in characterization of metal fluoro compounds varies considerably. Perusal of the literature also reveals a general incompleteness of spectral data reported for metal fluoro complexes.

The characterization data unique to metal fluoro complexes, M–F bond lengths and ^{19}F NMR spectra, are summarized in Tables X and XI. For the compounds which have been the subject of X-ray crystallographic studies, terminal M–F distances can be seen to span a relatively broad range from 1.88 to 2.21 Å (Table X). ^{19}F NMR data have been reported for fewer than a quarter of the compounds described in this review. The ^{19}F chemical shifts for the fluoro ligands are presented in Table XI, along with associated ^{31}P chemical shifts and P–F coupling constants if reported. We have attempted to place the ^{19}F NMR data on a single scale with positive chemical shift values downfield relative to $CFCl_3$ at δ 0; similarly, we have converted the ^{31}P NMR data to a single chemical shift scale.[16] No attempt will be made here to draw conclusions from the varied data reported in the literature. In several instances, lack of observable ^{19}F NMR signals for metal fluoro complexes has been noted; however the origin of this phenomenon is not clear.

Because one of the major obstacles to the study of metal fluoro derivatives is their preparation, Tables II–IX list the starting material plus reagent combinations which yield these compounds. As can be seen from the compilations, the syntheses of many metal fluorides involve halide metathesis. Other common methods include addition of HF and oxidation of metal complexes by fluorinating agents including formyl fluoride, xenon difluoride, and sulfur tetrafluoride. Many of the reported fluorides are unexpected products of F^- abstraction from polyfluoro anions or organic ligands. Additionally, many of the compounds listed in Tables III–X are prepared from other metal fluorides found in these tables by simple ligand substitution or oxidative–addition reactions.

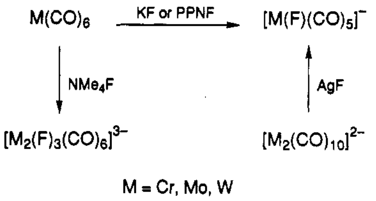
Although the number of fluoro derivatives included in the title subject is fairly large, many of the compounds have only a single literature citation, principally focused on preparation and identification. There are relatively few reports describing the chemical reactivity of these species. This is surprising because the combination of a soft low-valent transition-metal center and a hard fluoride ion suggests the potential for interesting chemistry as has been observed for other soft metal/hard ligand combinations.[17] Our interests in metal fluoro compounds are directed at developing a better understanding of their reactivity both for comparison

TABLE II. Metal Carbonyl Fluoro Compounds

	starting material	reagent(s)	refs
$[MF(CO)_5]^-$; M = Cr, Mo, W	$Cr(CO)_6$	KF, dibenzo-18-crown-6	29
	$Mo(CO)_6$	KF or $NaBF_4$	30
	$W(CO)_6$	KF, dibenzo-18-crown-6	31
	$M(CO)_6$; M = Cr, W	NEt_4F	31
	$M(CO)_6$; M = Cr, W	PPNF	32
	$[M_2(CO)_{10}]^{2-}$; M = Cr, W	AgF	32
$MoF_2(CO)_3$	$Mo(CO)_6$	XeF_2	25
$MF_2(CO)_4$; M = Mo, W	$MCl_2(CO)_4$; M = Mo, W	HF	51
$MoF_3(CO)_3$	$MoF_2(CO)_4$	XeF_2	51
$MoF_4(CO)_2$	$Mo(CO)_6$	MoF_6	50
$MoF_4(CO)_3$	$MoF_2(CO)_4$	XeF_2	51
$[M_2F_3(CO)_6]^{3-}$; M = Cr, Mo, W	$M(CO)_6$; M = Cr, Mo, W	NMe_4F	33
$MnF_3(CO)_3$	$MnBr(CO)_5$	AgF	45
	$Mn(OClO_3)(CO)_5$	NEt_4F	46
$[Mn_2F(CO)_9]^-$	$Mn_2(CO)_{10}$	KF, dibenzo-18-crown-6	52
$Mn_2F_2(CO)_8$	$MnBr(CO)_5$	AgF	45
$Mn_3(\mu\text{-}F)(\mu\text{-}OEt)_2(CO)_9$	$Mn_3(\mu\text{-}OEt)_3(CO)_9$	BF_3	53
$Mn_4(\mu\text{-}F)_x(\mu\text{-}OH)_{4-x}(CO)_{12}$; $x = 1, 2, 3$	$MnX(CO)_5$; X = Cl, Br	TlF or AgF	12
$ReF(CO)_3 = [Re(\mu\text{-}F)(CO)_3]_4$	$ReBr(CO)_5$	AgF	43, 44
$ReF(CO)_5$	$[Re_2F(CO)_{10}]^+$	MeCN	42
	$ReCl(CO)_5$	HF	35, 39
	$Re_2(CO)_{10}$	ReF_6 or XeF_2	35
$ReF_2(CO)_3$	$Re_2(CO)_{10}$	XeF_2	41
$ReF_3(CO)_3 = [Re(CO)_6][ReF_6]$	$[Re(CO)_5](\mu\text{-}F)(ReF_5)$	CO	26
	$Re_2(CO)_{10}$	XeF_2	26
$ReF_3(CO)_3$	$Re_2(CO)_{10}$	ReF_6	35, 36
	$ReF(CO)_5$	XeF_2	35
$[Re_2(\mu\text{-}F)(CO)_{10}]^+$	$ReMe(CO)_5$	$[CPh_3][PF_6]$ or HPF_6	42
$Re_2F_6(CO)_5 = [Re(CO)_5](\mu\text{-}F)(ReF_5)$	$Re_2(CO)_{10}$	ReF_6	37, 40
	$Re_2(CO)_{10}$	XeF_2	39
$Re_3F_{11}(CO)_6 = [Re(CO)_6][Re_2F_{11}]$	$Re_2(CO)_{10}$	ReF_6	26, 37, 38
$RuF_2(CO)_3 = [Re(\mu\text{-}F)F(CO)_3]_4$	$Ru_2F_7(CO)_2$	CO	47
	$Ru_3(CO)_{12}$	XeF_2	27
$RuF_3(CO)_3$	$Ru_3(CO)_{12}$	XeF_2 or F_2	27
$Ru_2F_7(CO)_2$	RuF_5	CO	28
$Ru_2F_7(CO)_6 = [RuF(CO)_3]_2(\mu\text{-}F)_4(RuF_4)_2$	RuF_5	CO	27
	$Ru_3(CO)_{12}$	XeF_2	27
$[Ru_5FC(CO)_{15}]^-$	$Ru_5C(CO)_{15}$	NEt_4F	54
$RhF_3(CO)_3$	RhF_4	CO	48
$IrF_2(CO)_2$	IrF_5	CO	49
$IrF_2(CO)_3$	IrF_5	CO	49

with that of the heavier halide derivatives[18-20] and for use of metal fluoride chemistry to advantage in synthetic schemes.[20-23] The purpose of this review is to provide a basis for ourselves and others to discuss and understand the chemistry of metal fluoro compounds and to extend these studies to other organometallic systems.

SCHEME I



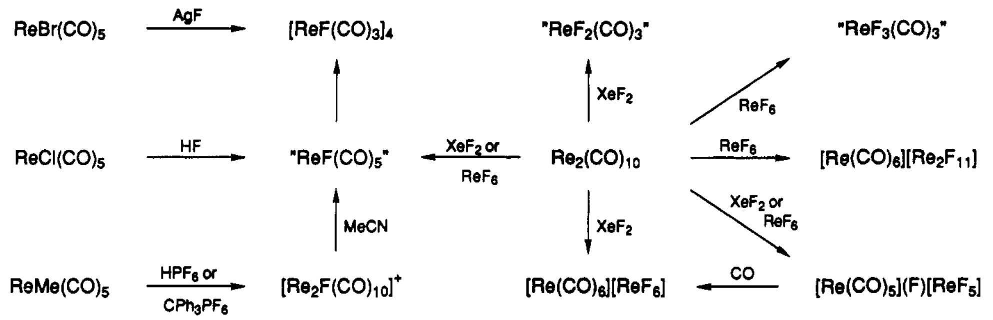
II. Metal Carbonyl Fluoro Compounds

The class of low-valent metal fluoro compounds first approached in any systematic way was that of metal carbonyl fluorides. Reported examples of these compounds are presented in Table II along with their methods of preparation; a subset has been reviewed by Bruce and Holloway and presented along with their scheme for predicting the stable building blocks of metal carbonyl fluorides.[24] The formulas given in Table II are empirical compositions as they appear in the literature and are based primarily on elemental analyses. In the absence of single-crystal X-ray structural determination, unambiguous assignment of structure to most $MF_x(CO)_y$ compounds is difficult: their infrared and mass spectra are frequently consistent with more than one formulation, and ^{19}F and ^{13}C NMR spectroscopy have not been applied to any of these systems. In some cases, the composition of products reported in early papers has been brought into question in more recent studies;[12,25-28] the formulations best supported by the evidence available in the literature are presented here.

A. Chromium, Molybdenum, and Tungsten

A relatively straightforward series of $MF_x(CO)_y$ compounds are the fluoropentacarbonyl anions of chromium, molybdenum, and tungsten, $[MF(CO)_5]^-$ (Scheme I).[29-32] These are prepared by reactions of the fluoride salts KF, NEt_4F, or (PPN)F with the parent hexacarbonyls (M = Cr, Mo, W)[29-32] or by addition of silver fluoride to the anionic dimers $[M_2(CO)_{10}]^{2-}$ (M = Cr, W).[32] In the latter reaction, silver fluoride apparently acts both as a source of the fluoro ligand and as an oxidizing agent. Note that the report of formation of dinuclear fluoro-bridged anions $[M_2F_3(CO)_6]^{3-}$ when NMe_4F is used[33] indicates that fluoride substitution in this system is not completely straightforward. Infrared spectroscopic studies for the series of compounds $PPN[WX(CO)_5]$ (X = F, Cl, Br, I) and $PPN[CrX(CO)_5]$ (X = F, I) reveal a surprising insensitivity of ν_{CO} to the

SCHEME II



identity of the halide ligand.[32] In contrast, ^{95}Mo NMR data for the series of molybdenum compounds [MoX(CO)$_5$]$^-$ show substantial changes in chemical shift with changes in X.[30] For these compounds, shielding of the molybdenum center increases in the order F (δ −943) < Cl (δ −1513) < Br (δ −1540) < I (δ −1660).[30] This is the so-called "normal halogen dependence" frequently observed for transition-metal NMR of open shell (e.g., d^4, d^6, and d^8) complexes.[34]

B. Manganese and Rhenium

Rhenium carbonyl fluorides are particularly illustrative of the complexities possible in $MF_x(CO)_y$ systems (Scheme II). A compound of formula $ReF_3(CO)_3$ isolated from the reaction of dirhenium decacarbonyl and xenon difluoride is best described as a salt, $[Re(CO)_6][ReF_6]$.[26] One product of the reaction of dirhenium decacarbonyl and rhenium hexafluoride is also formulated as $ReF_3(CO)_3$;[35,36] however, comparison of the infrared and X-ray powder diffraction data for this species and $[Re(CO)_6][ReF_6]$ indicates that they are not the same material;[26] furthermore, a different ionic compound, $[Re(CO)_6][Re_2F_{11}]$, has been isolated from the reaction of $Re_2(CO)_{10}$ with ReF_6 and structurally characterized.[26,37,38]

Further complicating interpretation of the rhenium system is the observation that small differences in reaction conditions can result in different products. For example, the reaction of $Re_2(CO)_{10}$ and 3–4 equiv of XeF_2 produces predominantly $[Re(CO)_6][ReF_6]$ when the CO pressure in the reaction vessel is allowed to build up to roughly 1 atm, exclusively $[Re(CO)_5](\mu\text{-}F)(ReF_5)$ when the CO is removed under vacuum during the course of the reaction, and a mixture of the two at intermediate CO pressures.[39] Additionally, $[Re(CO)_5](\mu\text{-}F)(ReF_5)$ can be isolated from the reaction of $Re_2(CO)_{10}$ and ReF_6,[37,40] and a compound of formula $ReF_2(CO)_3$ has been reported as the product of reaction of dirhenium decacarbonyl and xenon difluoride.[41]

Disparate results exist in the literature concerning $ReF(CO)_5$. This compound is reported to be produced by the reaction of $Re_2(CO)_{10}$ with XeF_2 or ReF_6,[35] by the addition of HF to $ReCl(CO)_5$,[35,39] and by the cleavage of $[Re_2(\mu\text{-}F)(CO)_{10}]^+$ by acetonitrile.[42] However, reaction of AgF and $ReBr(CO)_5$ yields a different compound, structurally characterized tetrameric $[Re(\mu\text{-}F)(CO)_3]_4$, proposed to form via facile decarbonylation of intermediate $ReF(CO)_5$ at ambient temperature.[43,44] Note that similar attempts to prepare manganese pentacarbonyl fluoride likewise result in formation of fluoro compounds which have lost CO ligands and are formulated as $[MnF(CO)_4]_2$ and $MnF_3(CO)_3$.[45,46]

C. Other Systems

As for the metal carbonyl fluorides described above, other $MF_x(CO)_y$ compounds in Table II are synthesized by three principal methods: carbonylation of metal fluorides,[27,28,47–49] oxidation of metal carbonyls by XeF_2 or MF_x,[25,27,50,51] and substitution of fluoride for coordinated carbon monoxide or halide.[12,51–54] Note that the first two routes require solvents which can withstand the highly oxidizing conditions present during the reaction and subsequent purification steps; CCl_2FCClF_2, anhydrous HF, and metal fluorides have been used. As described above, some of the structurally characterized compounds in Table II do not have both fluoro and carbonyl ligands attached to the same metal center; this may be true for other $MF_x(CO)_y$ compounds as well. Additionally, a tendency for fluoro ligands to bridge two or more metal centers can be noted. Clearly many of the simple empirical formulas taken from the literature are likely to represent more complex species including carbonyl fluoride salts, fluoro-bridged structures, and mixtures of products.

Excluded from Table II are highly reactive or unstable metal carbonyl fluoro derivatives which have been reported in the literature. For example, coordinatively unsaturated $MF_2(CO)$ (M = Cr, Mn, Ni, Cu) and $(MF_2)_2(CO)$ (M = Cr, Ni) have been generated and characterized by matrix isolation techniques, and $NiF_2(CO)$ has been the subject of a theoretical study.[55] Also studied by matrix isolation techniques is $MoFCp(CF_2)(CO)_3$, generated by the first example of α-F elimination upon stepwise ejection of two carbon monoxides from $MoCp(COCF_3)(CO)_3$.[56] Neutral and cationic chromium carbonyl fluorides, $CrF(CO)_5$ and $[CrF(CO)_5]^+$, are formed in solution by electrochemical oxidation of the anion $[CrF(CO)_5]^-$.[29] An anionic ruthenium carbonyl fluoride may be involved in CO hydrogenation catalyzed by $Ru_3(CO)_{12}$ plus KF, analogous to the species $[Ru(CO)_3I_3]^-$ observed spectroscopically when iodide is added; note that fluoride is the least efficient in the $Ru_3(CO)_{12}/X^-$ systems for production of oxygenates from synthesis gas.[57] In the gas phase, addition of F^- to $Fe(CO)_5$ produces $[FeF(CO)_3]^-$,[58] whereas addition of fluoride to $CoCp(CO)_2$ produces $[CoFCp(CO)]^-$ and $[CoFCp]^-$.[59] In contrast, neither Cl^- nor I^- adds to $CoCp(CO)_2$; this is proposed to reflect the much weaker gas-phase basicity of the heavier halides compared to F^-.[59]

III. Fluoro Complexes of d^{10} Metal Centers

Triarylphosphine copper(I) and silver(I) fluoro complexes have been reported (Table III). Reaction of

TABLE III. Fluoro Complexes of d^{10} Metal Centers

	starting material	reagent(s)	refs
$CuF(PPh_3)_3$	CuF_2	PPh_3	60–62
$AgF[P(p\text{-tol})_3]_n$; $n = 2, 3$	AgF	$P(p\text{-tol})_3$	63

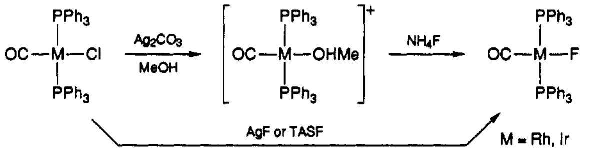
CuF_2 and PPh_3 in refluxing ethanol or methanol results in reduction of the copper(II) center and formation of $CuF(PPh_3)_3$.[60–62] An X-ray crystal structure reveals the expected tetrahedral arrangement of the four ligands about this d^{10} center in the solid state; however, solution conductivity measurements and ^{19}F NMR spectra for $CuF(PPh_3)_3$ suggest substantial ionic dissociation of this species in methanol.[60] In dichloromethane, a much lower solution conductivity and a complex temperature dependence of the ^{19}F and ^{31}P NMR spectra are interpreted as arising from two temperature-dependent processes, phosphine dissociation to yield $CuF(PPh_3)_2$ and partial dissociation of F^-.[60] Related three- and four-coordinate silver compounds, $AgF[P(p\text{-tol})_3]_2$ and $AgF[P(p\text{-tol})_3]_3$, are prepared by addition of phosphine to AgF.[63]

IV. Fluoro Complexes of d^8 Metal Centers

The many applications of d^8 systems in organometallic chemistry have inspired a variety of studies of rhodium(I), iridium(I), nickel(II), platinum(II), and, to a lesser extent, palladium(II) fluorides.

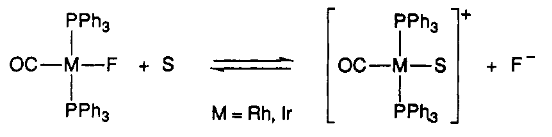
A. Rhodium(I) and Iridium(I)

Certaintly the most extensively studied and readily prepared of all organometallic fluorides are the rhodium and iridium Vaska's derivatives, $MF(CO)(PPh_3)_2$ (M = Rh, Ir) (eq 1). These compounds can be synthesized in high yield by reaction of $MCl(CO)(PPh_3)_2$ with silver carbonate and ammonium fluoride via the intermediacy of the methanol cation $[Ir(MeOH)(CO)(PPh_3)_2]^+$.[64,65] They can also be prepared by reaction of the acetonitrile cation and fluoride,[66–68] or from the chloride by using either silver fluoride[69–71] or $[S(NMe_2)_3][SiF_2Me_3]$ (TASF),[22] an excellent anhydrous and organic solvent soluble source of the fluoride ion.[72] Related tri-p-tolylphosphine,[22,73] alkyldiphenylphosphine,[74] triphenylarsine,[75,76] and triphenylstibine[75] carbonyl fluoro derivatives have also been reported.



$$OC-\overset{PPh_3}{\underset{PPh_3}{M}}-Cl \xrightarrow[MeOH]{Ag_2CO_3} \left[OC-\overset{PPh_3}{\underset{PPh_3}{M}}-OHMe\right]^+ \xrightarrow{NH_4F} OC-\overset{PPh_3}{\underset{PPh_3}{M}}-F \qquad (1)$$

Solution conductivity measurements indicate that $RhF(CO)(PPh_3)_2$ and $IrF(CO)(PPh_3)_2$ behave as weak electrolytes in methanol[64,65] or tetrahydrofuran,[22] but not in acetone or nitrobenzene in which they are nonconductors.[64,65] This suggests that the solvolytic equilibrium in eq 2 is important in some media.



$$OC-\overset{PPh_3}{\underset{PPh_3}{M}}-F + S \underset{M = Rh,\ Ir}{\rightleftharpoons} \left[OC-\overset{PPh_3}{\underset{PPh_3}{M}}-S\right]^+ + F^- \qquad (2)$$

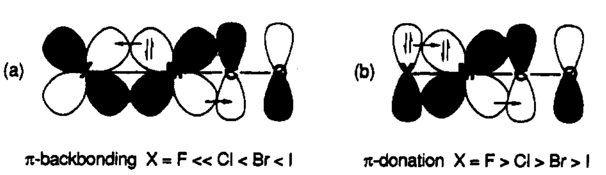


Figure 1. Halides can be considered to (a) compete with CO for π-backbonding to M and (b) enhance π-backbonding to CO via π-donation to M.

In the rhodium system, anion preference of $[Rh(CO)(PPh_3)_2]^+$ has been shown to follow the trend $X^- = F^- > Cl^- > Br^- > I^-$ in dichloromethane solution (eq 3),[18,19] opposite that predicted by hard/soft acid/base rules.[5] Earlier observation of similar trends for $[MX_2(CO)_2]^-$ and $MX(CO)(PPh_3)_2$, where X = Cl, Br, or I, led Forster to suggest that "in rigorously aprotic solvents, fluoro derivatives may frequently be found to be the most stable halocarbonyl species."[77] The position of the equilibrium in eq 3 is shifted markedly to the right by the presence of small amounts of compounds such as water and methanol, presumably because of the considerable affinity of uncomplexed fluoride for these species due to strong hydrogen bonding to their hydroxyl groups.[19] Vaska has exploited this property of the fluorides to prepare a wide range of $MY(CO)(PPh_3)_2$ products (e.g., Y = Cl, Br, I, CN, NCS, NCO, N_3, OH, OPh, O_2CH, O_2CMe, O_2CPh, ONO_2, $OClO_3$) by anion metathesis in methanol solvent.[64,65]

$$OC-\overset{PPh_3}{\underset{PPh_3}{Rh}}-F + X^- \rightleftharpoons OC-\overset{PPh_3}{\underset{PPh_3}{Rh}}-X + F^- \qquad (3)$$

Physicochemical studies of the series of rhodium(I) and iridium(I) Vaska's halides have been reported, including electronic, infrared, and NMR spectroscopies, Mössbauer and XPS data,[78,79] and electrochemistry. These data almost always display significant differences between the fluoro complex and the heavier halo derivatives, which are frequently quite similar to each other. The patterns which emerge with variation of halide have been interpreted in terms of the interplay of the σ-donor and π-acceptor characteristics of the halide ligands. Surprisingly, the possible influence of the π-donor ability of the halides (which is expected to follow the order $F^- > Cl^- > Br^- > I^-$) on the spectral properties of these compounds is not discussed in the literature. Figure 1 illustrates metal–halide π-bonding interactions in *trans*-halocarbonylmetal complexes such as the Vaska's halides.

The electronic absorption spectra of $MX(CO)(PPh_3)_2$ in benzene show λ_{max} for the $d_{z^2} \rightarrow b_1\pi$ transition[80,81] increasing in the order X = F < Cl < Br < I (Table XII).[80] This has been discussed in terms of greater stabilization of the $b_1\pi$ level with increasing π-acceptor strength of X,[80] which is considered to follow the order F ≪ Cl < Br < I on the basis of the availability of low-lying empty d_π orbitals on the halide.[64,80] An alternative explanation invokes greater destabilization of d_{z^2} with increasing σ-donor ability in the order F < Cl < Br < I, paralleling decreasing electronegativity and increasing polarizability.[80]

The carbonyl stretching frequencies of $MX(CO)(PPh_3)_2$ in various solvents are found to follow the order X = F < Cl ≤ Br ≤ I (Table XII),[20,64,69,70,82] consistent with increasing π-acceptor strength of the halides along this series.[64] These IR data have been used to explain the observed trend in halide affinity for $[Rh(CO)(PPh_3)_2]^+$, with fluoride most preferred, on the basis of minimizing competition between the halide and the trans carbon monoxide for electron density in the filled rhodium d_π orbitals (Figure 1).[19] Analogous trends in ν_{CO} with variation of X are observed for $RhX(CO)L_2$, (L = $AsPh_3$, $SbPh_3$)[75] and $IrX(CO)(PEtPh_2)_2$.[74] However, ν_{CO} values do not follow a readily interpretable pattern with variation of L.[74] This indicates that carbonyl stretching frequencies are not necessarily a simple measure of the σ-donor or π-acceptor capabilities of ligands attached to the metal in the $MX(CO)L_2$ system.

^{19}F and ^{31}P NMR data for $MF(CO)(PPh_3)_2$ have been reported by several different groups (Tables XI).[71,78,83-87] Comparisons of ^{31}P NMR chemical shifts for the rhodium halides, $RhX(CO)(PPh_3)_2$, show no discernible trend.[83,84] However, variation in the magnitude of the ^{103}Rh–^{31}P coupling constants in the order F (–135.5 Hz) > Cl (–126.9 Hz) > Br (–125.0 Hz) > I (–123.5 Hz) has been interpreted as indicating increased effective electronegativity of the rhodium center with increased electronegativity of X.[83] ^{103}Rh NMR data for this series of compounds have also been reported and indicate that shielding of the metal center increases in the order F (δ 5711) < Cl (δ 5488) < Br (δ 5436) < I (δ 5324),[83] the normal halogen dependence.[34] Chemical shift differences in metal NMR are dominated by variations in the paramagnetic contribution to shielding (σ_p) which depend on the distance of the metal d electrons from the nucleus (r) and the average energy of excited states of appropriate symmetry (ΔE) as shown in eqs 4 and 5.[34,88]

$$\sigma = \sigma_d + \sigma_p \tag{4}$$

$$\sigma_p = -2/3(e\hbar/mc)^2\langle 1/r^3\rangle(1/\Delta E) \tag{5}$$

It has been noted[84] that the trend observed for δ (^{103}Rh) in the rhodium Vaska's halides is opposite that expected based on the $1/\Delta E$ term: because $RhF(CO)(PPh_3)_2$ has the smallest λ_{max} values,[80] it should have the most shielded rhodium center. However, the variation in δ (^{103}Rh) is consistent with increasing d electron distance from the metal nucleus and increasing M–X bond covalency on going from fluoride to iodide.

Overall, the spectral data for $MX(CO)L_2$ are most consistent with the surprising interpretation that the fluoro complex has the most electron-rich metal center. This is further supported by electrochemical experiments which show the peak potentials for irreversible reduction of $MX(CO)(PPh_3)_2$ (M = Rh, Ir) follow the order F < Cl < Br < I (Table XII);[89] that is, the fluoro complexes are the most difficult to reduce. These observations are opposite expectations based on electronegativity arguments and suggest that differences in metal–halide π-bonding dominate in the electronic structure of their rhodium(I) and iridium(I) compounds, with fluoride the poorest π-acceptor and best π-donor. By using this interpretation, the surprising halide preference and spectral trends for $MX(CO)(PPh_3)_2$ are readily explained.

A variety of reactivity studies of the rhodium(I) and iridium(I) Vaska's halides has been reported, included detailed kinetics of the oxidative addition of small molecules to iridium(I). The second-order rate constants (M^{-1} s^{-1}) for oxidative addition of methyl iodide to $IrX(CO)(PPh_3)_2$ (eq 6) follow the trend X = F (2.2×10^{-2}) > Cl (1.0×10^{-2}) > Br (6.0×10^{-3}) > I (4.8×10^{-3}).[90] In contrast, the opposite trend is observed for

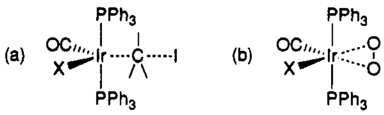
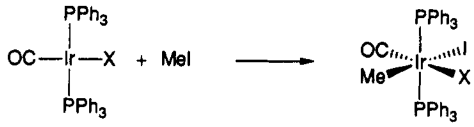
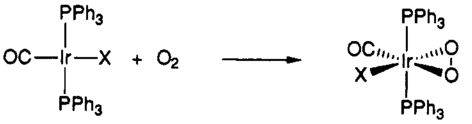


Figure 2. Proposed transition states for oxidative addition of (a) methyl iodide and (b) dioxygen to iridium Vaska's halides.



(6)

addition of several other addenda to iridium halides. For example, second-order rate constants (M^{-1} s^{-1}) for uptake of O_2 by $IrX(CO)(PPh_3)_2$ follow the order X = F (1.48×10^{-2}) < Cl (1.01×10^{-1}) < Br (2.06×10^{-1}) < I (7.23×10^{-1}) (eq 7).[91,92] The same order of reactivity



(7)

is also observed for $IrX(CO)(PMePh_2)_2$ and $IrX(CO)(PEtPh_2)_2$.[74] Rates of addition of both MeI and O_2 to $IrX(CO)L_2$ increase with increasing basicity of L.[74,90] The rate trend X = Cl < Br < I is observed for addition of organoazides to $RhX(CO)(PPh_3)_2$[93] and for addition of dihydrogen,[94] chloroacetylenes,[95] and organoazides[96] to the heavier halides of $IrX(CO)(PPh_3)_2$.

The opposing trends for oxidative addition of methyl iodide vs dioxygen to iridium(I) have been discussed in terms of the different transition states (Figure 2) associated with these two different reactions.[90] A five-coordinate transition state (Figure 2a) has been proposed to describe nucleophilic attack of iridium on methyl iodide. Competition between the electrophilic methyl carbon and the halide for the σ-bonding p_x and p_y orbitals in this proposed trigonal-bipyramidal structure will affect the energy of the transition state, hence the rate of reaction: strong σ-bonding of iridium to X = I, the best σ-donor of the halides, is suggested to lead to poor Ir–Me σ-overlap, consequent destabilization of the transition state, and a slower rate of reaction. The observed trend is also consistent with the idea that for the halide series the iridium center is most electron rich, therefore most nucleophilic, in the fluoro complex.

Addition of dioxygen to iridium is proposed to proceed through a six-coordinate transition state (Figure 2b). For the series of halides $IrX(CO)(PPh_3)_2$, this is a reversible process (eq 7) and activation parameters for both the forward and reverse reactions have been measured.[91] The entropies of activation ($\Delta S^{\ddagger}$) for O_2 addition are identical in sign and close in magnitude with the entropies (ΔS°) for the forward reaction, suggesting a late transition state which strongly resembles the O_2 adduct.[92] For such a transition state, stability and hence rate of reaction should parallel the stability of the iridium(III) products. This is indeed the case; the equilibrium constants (M^{-1}) for eq 7 in-

TABLE IV. Fluoro Complexes of d^8 Metal Centers

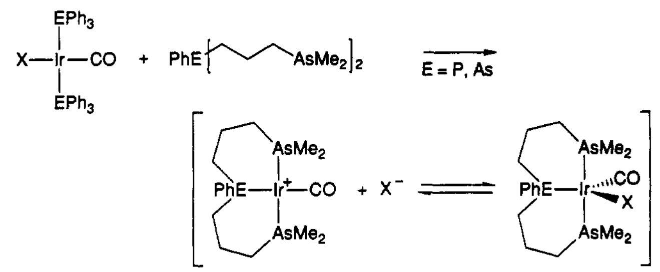
	starting material	reagent(s)	refs
$RhF(CO)(PPh_3)_2$	$RhCl(CO)(PPh_3)_2$	(i) NH_4F; (ii) Ag_2CO_3	64,65
	$RhCl(CO)(PPh_3)_2$	AgF	69,70,71
	$RhCl(CO)(PPh_3)_2$	TASF	22
	$RhF(PPh_3)_3$	CO	102
	$RhF(C_2F_4)(PPh_3)_2$	CO	87
$RhF(CO)[P(p\text{-tol})_3]_2$	$RhCl(CO)[P(p\text{-tol})_3]_2$	(i) NH_4F; (ii) Ag_2CO_3	73
$RhF(CO)L_2$; L = $AsPh_3$, $SbPh_3$	$RhCl(CO)L_2$	AgF	75
$RhF(CO)(TCNE)(AsPh_3)_2$	$RhF(CO)(AsPh_3)_2$	TCNE	75
$RhF(CO)(SO_2)L_2$; L = PPh_3, $AsPh_3$	$RhF(CO)L_2$	SO_2	69,75
$RhF(C_2F_4)(PPh_3)_2$	$RhCl(C_2F_4)(PPh_3)_2$	(i) $AgBF_4$; (ii) TASF	87
	$[RhF(C_2H_4)(C_2F_4)]_4$	PPh_3	87
$RhF(PPh_3)_3$	$[RhF(C_8H_{14})_2]_n$	PPh_3	102
$RhF(PCy_3)_2$	$[RhF(C_8H_{14})_2]_n$	PCy_3	85
$[RhF(C_8H_{14})(PCy_3)]_n$	$[RhF(C_8H_{14})_2]_n$	PCy_3	85
$RhFL(PCy_3)_2$; L = CO, C_2H_4, PhCCPh	$RhF(PCy_3)_2$	L	85
$[Rh(\mu\text{-F})L]_2$; L = dippe, dippp	$[Rh(\mu\text{-H})L]_2$	C_2F_4	86
$IrF(CO)(PPh_3)_2$	$IrCl(CO)(PPh_3)_2$	(i) NH_4F; (ii) Ag_2CO_3	64,65
	$IrCl(CO)(PPh_3)_2$	AgF	71
	$IrCl(CO)(PPh_3)_2$	TASF	22
	$[Ir(NCMe)(CO)(PPh_3)_2][ClO_4]$	NH_4F or HF, NEt_3	66,67,68
$IrF(CO)[P(p\text{-tol})_3]_2$	$IrCl(CO)[P(p\text{-tol})_3]_2$	TASF	22
$IrF(CO)L_2$; L = $PMePh_2$, $PEtPh_2$	$IrF(CO)(AsPh_3)_2$	L	74
$IrF(CO)(AsPh_3)_2$	$[Ir(NCMe)(CO)(AsPh_3)_2]^+$	HF, NEt_3	76
$IrF(CO)[PPh(CH_2CH_2AsMe_2)_2]$	$IrF(CO)L_2$; L = PPh_3, $AsPh_3$	$PPh(CH_2CH_2AsMe_2)_2$	101
$IrF(CO)(RCCR)(PPh_3)_2$; R = CF_3, COOMe	$IrF(CO)(PPh_3)_2$	$RC{\equiv}CR$	97,104
$IrF(CO)(C_2F_4)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	C_2F_4	104
$IrF(CO)L(PPh_3)_2$; L = TCNE, $CH_2{=}CHCN$, $MeCH{=}CHCN$, $CNCH{=}CHCN$	$IrF(CO)(PPh_3)_2$	L	68,97,103,104
$IrF(CO)(SO_2)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	SO_2	68,97
$IrF(N_2)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	$N_3CO(C_4H_4O)$	100
$IrF(AsPh_3)_3$	$IrCl(CO)(AsPh_3)_2$	(i) NH_4F; (ii) Ag_2CO_3	76
$NiF(C_6F_5)(PEt_3)_2$	$Ni(cod)(PEt_3)_2$	C_6F_6	106
$NiF(COPh)(PEt_3)_2$	$Ni(cod)(PEt_3)_2$	PhCOF	106
NiF_2L_2; L = PBu_3, PPh_3, PCy_3; L_2 = dppe	NiF_2	L	108
$Ni_2F(OMe)Me_2(PMe_3)_2$	$Ni_2(OMe)_2Me_2(PMe_3)_2$	MeCOF	109
$Ni_2F(NMe_2)Me_2(PMe_3)_2$	$Ni_2F_2Me_2(PMe_3)_2$	Me_2NSiMe_3	109
$Ni_2FClMe_2(PMe_3)_2$	$Ni_2Cl_2Me_2(PMe_3)_2$	$Ni_2F_2(Me)_2(PMe_3)_2$	109
$Ni_2F_2Me_2(PMe_3)_2$	$Ni_2F(OMe)Me_2(PMe_3)_2$	MeCOF	109
$PdFH(PPh_3)_2$	$Pd(PPh_3)_4$	HCOF	110
$[PdF(PEt_3)_3][BF_4]$	$[PdCl(PEt_3)_3][BF_4]$	AgF	71,118
$[Pd_2F_2(PPh_3)_4]F_2$	$Pd(PPh_3)_4$	HF	111
$PtFH(PPh_3)_2$	$Pt(PPh_3)_4$	HCOF	110
$PtFMe(PEt_3)_2$	$PtClMe(PEt_3)_2$	AgF	21
$PtFPh(PEt_3)_2$	$PtClPh(PEt_3)_2$	AgF	13
$PtF[CH(CF_3)_2](PPh_3)_2$	$Pt(PhCH{=}CHPh)(PPh_3)_2$	$N_2C(CF_3)_2$	114,115
$PtFCl(PPh_3)_2$	$PtClX(PPh_3)_2$; X = Cl, H	HF	111
	$PtClH(PPh_3)_2$	(i) $FCH{=}CF_2$; (ii) acetone, CCl_4	119
$PtFBr(PPh_3)_2$	$PtBr_2(PPh_3)_2$	HF	111
$[PtFL_3][BF_4]$; L = PEt_3, PMe_2Ph, PPh_3; L_3 = $(PEt_3)_2(PPh_3)$	$[PtClL_3][BF_4]$	AgF	71,111,117,118
$[PtF(PEt_3)_2L][ClO_4]$; L = PPh_3, $P(OPh)_3$	$[PtCl(PEt_3)_2L]ClO_4$	AgF	71
$[PtFL_3][HF_2]$; L = $PMePh_2$, PPh_3	PtL_4	HF	111
$[PtF(PPh_3)_3]X$; X = BF_4, BPh_4	$[PtF(PPh_3)_3][HF_2]$	$LiBF_4$ or $NaBPh_4$	111
$PtF_2(PPh_3)_2$	$Pt(PPh_3)_3$	XeF_2	116
$[Pt_2F_2(PPh_3)_4][ClO_4]_2$	$[PtF(PPh_3)_3][HF_2]$	$LiClO_4$	111

crease in the same order as the rates of the forward reaction: F (2.9×10^2) < Cl (7.3×10^3) < Br (6.2×10^4) < I (8.6×10^5) (see section V).[91] Linear correlations between the enthalpy of the forward reaction (ΔH°) and the electronegativity of X[91,92,97] and between the free energy of activation ($\Delta G^\ddagger$) and the lowest electronic excitation energy[92] have been noted, although not fully rationalized.

Two examples of the use of $MF(CO)(PPh_3)_2$ as homogeneous catalysts have been reported. The iridium compound is a good catalyst for the reaction of silanes and alcohols to yield dihydrogen and siloxides.[98] Comparison of the activity of $RhX(CO)(PPh_3)_2$ in the hydroformylation of formaldehyde shows that the yield of glycolaldehyde decreases in the order Cl > Br > I > F, whereas the yield of methanol, the byproduct resulting from competing hydrogenation of formaldehyde, follows roughly the opposite order.[99]

In addition to Vaska's rhodium and iridium fluorides, other d^8 fluoro derivatives of these metals have been reported (Table IV). A dinitrogen iridium Vaska's fluoride analogue, $IrF(N_2)(PPh_3)_2$, has been prepared by reaction of $IrF(CO)(PPh_3)_2$ and furoyl azide.[100] The dinitrogen stretching frequencies in the compounds $IrX(N_2)(PPh_3)_2$ follow a trend analogous to that of ν_{CO} in the carbonyl derivatives; ν_{NN} increases in the order F (2088 cm^{-1}) < Cl (2103 cm^{-1}) < Br (2109 cm^{-1}) < I (2113 cm^{-1}).[100] The reaction of $IrF(CO)L_2$ (L = PPh_3, $AsPh_3$) and a chelating diarsinophosphine ligand yields a compound of formula $IrF(CO)[PPh(CH_2CH_2CH_2AsMe_2)_2]$; the latter is nonconducting in nitromethane solution and is therefore proposed to be a five-coordinate iridium(I) fluoride (Scheme III).[101] In contrast, the heavier halides are reported to produce

SCHEME III



mixtures of five-coordinate $IrX(CO)[PPh(CH_2CH_2CH_2AsMe_2)_2]$ and the four-coordinate iridium(I) cations as their halide salts $[Ir(CO)(PPh[CH_2CH_2CH_2AsMe_2]_2)]X$ (Scheme III).[101] When the analogous chelating diarsinoarsine ligand, $AsPh(CH_2CH_2CH_2AsMe_2)_2$, is used, only salts are observed for all of the halides (Scheme III).[101] Surprisingly, reaction of $IrCl(CO)(AsPh_3)_2$ with Ag^+ and then F^- in methanol does not produce $IrF(CO)(AsPh_3)_2$, which is prepared by addition of fluoride to the acetonitrile cation $[Ir(NCMe)(CO)(AsPh_3)_2]^+$, but rather yields the tris(triphenylarsine) compound, $IrF(AsPh_3)_3$.[76]

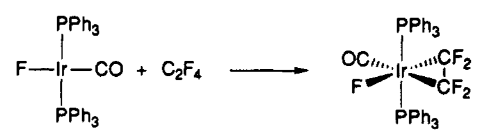
A rhodium(I) olefin complex $[RhF(C_8H_{14})_2]_n$, synthesized by the action of AgF on the chloride, can be used as the starting material for phosphine-substituted rhodium(I) fluorides such as $RhF(PPh_3)_3$, $[RhF(C_8H_{14})(PCy_3)]_n$, and $RhF(PCy_3)_2$.[85,102] ^{31}P NMR data for $RhF(PCy_3)_2$ indicate that it has a monomeric structure; comparison of its extremely large phosphorus–fluorine coupling constant (J_{PF} = 165 Hz) with those of square-planar $MF(CO)L_2$ (J_{PF} = 20–30 Hz) further suggests that $RhF(PCy_3)_2$ is a three-coordinate complex with FRhP angles greater that 90°.[85] In contrast, rhodium(I) fluoro compounds containing chelating diphosphine ligands dippe ($^iPr_2PCH_2CH_2P^iPr_2$) and dippp ($^iPr_2PCH_2CH_2CH_2P^iPr_2$) which were the unexpected products of the reactions of $Rh_2H_2L_2$ (L = dippe, dippp) and tetrafluoroethylene are clearly shown to be fluoro-bridged dimers $Rh_2F_2L_2$ (L = dippe, dippp) by ^{31}P NMR spectroscopy.[86]

Supporting the idea of a three-coordinate structure for $RhF(PCy_3)_2$, facile addition of ligands occurs producing carbonyl, ethylene, and diphenylacetylene complexes, $RhFL(PCy_3)_2$.[85] All these rhodium(I) fluoro compounds have labile F^- ligands readily displaced by a variety of coordinating anions when metathesis is performed in a two-layer benzene/water mixture.[85] However, although chloro, bromo, or iodo derivatives can be prepared in this manner by using NaX as the source of the halide, where comparisons have been made, the fluoro derivatives have been found to be significantly more thermally stable than their heavier halide analogues.[85,102] This again demonstrates that the affinity of fluoride for hydrogen bonding to hydroxyl groups markedly influences the reactivity of metal fluoro compounds. In two cases, comparison of the reactivity of $RhF(PCy_3)_2$ with that of the heavier halide derivatives $RhX(PCy_3)_2$ shows striking differences. Coordination of N_2 to form $RhX(N_2)(PCy_3)_2$ occurs rapidly for X = I (15 min) and Br (3 h) and slowly for X = Cl (4–5 days), but not at all for X = F.[85] Reaction of O_2 and $RhX(PCy_3)_2$ produces the dioxygen adducts of the heavier halides, but yields $POCy_3$ in the case of X = F.[85]

A recent paper describes rhodium(I) tetrafluoroethylene fluoro complexes.[87] Reaction of $[RhCl(C_2H_4)(C_2F_4)]_2$ with $AgBF_4$ followed by TASF yields the analogous fluoride, shown to have a tetrameric structure, $[RhF(C_2H_4)(C_2F_4)]_4$.[87] This compound reacts with triphenylphosphine to produce $RhF(C_2F_4)(PPh_3)_2$ which can alternatively be prepared from $RhCl(C_2F_4)(PPh_3)_2$ by reaction with $AgBF_4$ followed by TASF; CO readily displaces C_2F_4 from the fluoro complex to produce rhodium Vaska's fluoride, $RhF(CO)(PPh_3)_2$ (eq 8).[87] In

$$\underset{PPh_3}{\overset{PPh_3}{F{-}Rh{-}C_2F_4}} + CO \longrightarrow \underset{PPh_3}{\overset{PPh_3}{F{-}Rh{-}CO}} + C_2F_4 \qquad (8)$$

the case of iridium, a tetrafluoroethylene adduct of Vaska's fluoride, $IrF(CO)(C_2F_4)(PPh_3)_2$, can be isolated (eq 9).[103,104] This compound is significantly more stable



(9)

than the corresponding chloride, $IrCl(CO)(C_2F_4)(PPh_3)_2$, which loses C_2F_4 on recrystallization.[103,104]

Related cyanoolefin and SO_2 adducts of $IrF(CO)(PPh_3)_2$[68,97,103,104] and $RhF(CO)(AsPh_3)_2$[75] have been reported; additionally, $RhF(CO)(SO_2)(PPh_3)_2$[69] and adducts of $IrF(CO)(PPh_3)_2$ with hexafluoro-2-butyne or dimethyl acetylenedicarboxylate have been prepared.[103,104] Though formally described in many reports as five-coordinate adducts containing rhodium(I) and iridium(I) centers, all of these compounds contain η^2-coordinated electron-withdrawing ligands; on the basis of their CO stretching frequencies compared with $MF(O_2)(CO)(PPh_3)_2$, they can be considered as d^6 iridium(III) octahedral complexes[97,105] (section V).

B. Nickel(II), Palladium(II), and Platinum(II)

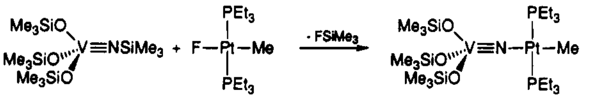
Several square-planar group 10 metal fluoro complexes have appeared in the literature (Table IV). Intermolecular oxidative additions of C–F bonds to the nickel(0) complex $Ni(cod)(PEt_3)_2$ are reported to yield $NiF(C_6F_5)(PEt_3)_2$ from hexafluorobenzene and $NiF(COPh)(PEt_3)_2$ from benzoyl fluoride.[106] Similarly, formation of $NiFBr(C_6F_4\text{-}4\text{-}PPh_3)(PPh_3)$ via C–F addition to an unspecified intermediate is proposed to explain the product $[P(4\text{-}C_6F_4H)Ph_3]Br$ obtained upon hydrolysis of the solid produced by fusion of a mixture of $NiBr_2$, C_6F_5Br, and PPh_3.[107] Nickel(II) difluoro bis(phosphine) complexes are the proposed products of reaction of excess L and NiF_2.[108] Dinuclear fluoro-bridged nickel(II) derivatives $Ni_2(\mu\text{-}F)(\mu\text{-}X)Me_2(PMe_3)_2$ have been prepared for X = OMe or F by replacement of fluoride for methoxide in $Ni_2(\mu\text{-}OMe)_2Me_2(PMe_3)_2$ by using acetyl fluoride, for X = Cl by reaction of $Ni_2(\mu\text{-}F)_2Me_2(PMe_3)_2$ and $Ni_2(\mu\text{-}Cl)_2Me_2(PMe_3)_2$, and for X = NMe_2 by addition of Me_2NSiMe_3 to $Ni_2(\mu\text{-}F)_2Me_2(PMe_3)_2$.[109]

Palladium(II) and platinum(II) phosphine fluoro complexes can be prepared by oxidation of metal(0) compounds. Reactions of $M(PPh_3)_4$ and formyl fluoride yield $MFH(PPh_3)_2$ (M = Pd, Pt), which can be viewed as HF adducts of these metals.[110] Interestingly, hydrido fluoro complexes are not found to be the products of reactions of ML_4 and HF. Instead, addition of HF to $Pd(PPh_3)_4$ is reported to yield $[Pd_2F_2(PPh_3)_4]F_2$,[111] and addition of HF to PtL_4, which was originally reported to yield PtF_2L_2,[112,113] has been shown to produce $[PtFL_3][HF_2]$.[111] The platinum(II) fluoride, $PtF[CH(CF_3)_2](PPh_3)_2$, is among the products isolated from the reaction of $Pt(PhCH{=}CHPh)(PPh_3)_2$ and $N_2C(CF_3)_2$; the cis isomer has been structurally characterized by X-ray crystallography.[114,115] Preliminary evidence suggests that a platinum(II) difluoride, $PtF_2(PPh_3)_2$, can be cleanly prepared by addition of XeF_2 to $Pt(C_2H_4)(PPh_3)_2$.[116] Because XeF_2 is readily consumed by PPh_3, $Pt(PPh_3)_4$ is not a practical starting material for this reaction; an excess of the expensive fluorinating reagent must be used and problems arise in purification of the metal-containing product due to difficulties in separating it from the PF_2Ph_3 byproduct.[116]

Halide metathesis can also be used to prepare palladium(II) and platinum(II) phosphine fluorides. Addition of silver fluoride to $[MClL_3]X$ produces $[MFL_3]X$, where X is a tetrafluoroborate or perchlorate ion.[71,111,117,118] One member of this group of compounds, $[PtF(PEt_3)_3][BF_4]$, has been structurally characterized.[117] Simple exchange of the counterion occurs readily upon reaction of the related $[PtF(PPh_3)_3][HF_2]$ with $LiBF_4$ or $NaBPh_4$; however, addition of $LiClO_4$ to this bifluoride salt results in loss of phosphine and formation of a dimeric compound, $[Pt_2F_2(PPh_3)_4][ClO_4]_2$.[111] NMR studies of a series of these $[MXL_3]^+$ compounds where X = F or Cl shows a correlation between low values of $^1J_{PtF}$ and weak Pt–F bonding and, based on values of $^1J_{PtP}$ for the phosphine ligand trans to X, suggest that the trans influence of fluoride is slightly greater than that of chloride.[71]

Neutral platinum(II) fluoro complexes, $PtFX(PPh_3)_2$ where X = Cl or Br, have been prepared by reaction of anhydrous HF and $PtX_2(PPh_3)_2$ or $PtClH(PPh_3)_2$;[111] $PtFCl(PPh_3)_2$ is also isolated as a byproduct in the reaction of the hydride and trifluoroethylene.[119] $PtFPh(PPh_3)_2$ is produced, albeit in low yields, from the reaction of $PtClPh(PPh_3)_2$ with silver fluoride in methanol;[13] an analogous preparation of $PtFMe(PPh_3)_2$ has been described.[21]

Some intriguing chemistry of the latter complex has been reported: upon reaction with $V(NSiMe_3)(OSiMe_3)_3$, quantitative elimination of $FSiMe_3$ and formation of a nitride-bridged complex occurs (eq 10).[21]



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Analogous condensation reactions yield rhodium(I) and iridium(I) nitride-bridged complexes $(R_3SiO)_3V(\mu\text{-}N)M(CO)(PPh_3)_2$; for a range of anionic X ligands in $MX(CO)(PPh_3)_2$, only the fluoro, methoxy, and acetato derivatives from sufficiently strong Si–X bonds to drive the reaction.[22] Related syntheses of vanadium–rhenium[20] and diiridium[23] nitride-bridged complexes suggest that this condensation reaction represents a good general route to main group atom bridged transition-metal compounds and illustrate the utility of metal fluorides in synthetic schemes. Note, however, that not all $MF(SiR_3)$ species eliminate $FSiR_3$ under ambient conditions; examples of such d^6 complexes have been isolated and characterized (see section V).

V. Fluoro Complexes of d^6 Metal Centers

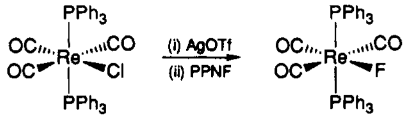
The stability and variety of six-coordinate d^6 organometallic complexes suggest that a range of d^6 transition-metal carbonyl and phosphine fluorides should be possible; indeed examples of such 18-electron organometallic fluorides are known for almost all of the group 6–9 transition metals (Table V). In these compounds, the fluoro ligand is frequently found trans to a strong π-acceptor, such as nitrosyl or carbonyl, as is observed for the d^8 organometallic fluorides.

A. Chromium(0), Molybdenum(0), and Tungsten(0)

The trans geometry is noted for $CrF(NO)(dppe)_2$, prepared by reduction of the corresponding chromium(I) cation; this chromium(0) complex has the shortest M–F distance yet determined by X-ray crystallography.[120] Analogous molybdenum(0) and tungsten(0) nitrosyl fluorides are prepared in good yield by substitution of NO for the diazenido ligand in $MF(NNH)(dppe)_2$;[121] $MoF(NO)(dppe)_2$ is also isolated in low yield from the reaction of $MoH_4(dppe)_2$ and $(NO)PF_6$.[122] Related carbonyl-substituted tungsten complexes $WF(NO)(CO)_2L_2$ have been prepared for L = $P(O^iPr)_3$ by reaction of $[W(NO)(CO)_3[P(O^iPr)_3]_2][PF_6]$ and either KF or NaH[123] and for L = PPh_3 by displacement of the weakly coordinating perchlorate ion in $W(OClO_3)(NO)(CO)_2(PPh_3)_2$ using NBu_4F.[124] The L = PPh_3 compound is proposed to possess a trans,trans structure on the basis of spectroscopic data and comparison with the heavier halide derivatives, $WX(NO)(CO)_2(PPh_3)_2$.[124] This geometry places the halide ligand cis to the carbonyls and trans to the nitrosyl, resulting in almost no change in ν_{CO} with variation of the halide, but large variation in ν_{NO} (1606 cm^{-1} for X = F, 1624 cm^{-1} for X = Cl, 1613 cm^{-1} for X = Br, 1618 cm^{-1} for X = I) which does not appear to follow any simple trend.[124] Small amounts of $WF(NO)(CO)_2(PPh_3)_2$ and the difluoro complex $WF_2(NO)_2(PPh_3)_2$ are observed upon decomposition of solutions of $[W(NO)(CO)_3(PPh_3)_2][PF_6]$, prepared from $W(CO)_4(PPh_3)_2$ plus $(NO)PF_6$; similarly, reaction of $(NO)PF_6$ and $Mo(CO)_4(PPh_3)_2$ produces $MoF_2(NO)_2(PPh_3)_2$.[124]

B. Manganese(I) and Rhenium(I)

One example of a manganese(I) phosphine fluoro complex, $MnF(CO)_3(PPh_3)_2$, has been reported as a byproduct isolated in the preparation of $[Mn(CO)_5(PPh_3)][BF_4]$.[125] The related rhenium(I) fluoride, $ReF(CO)_3(PPh_3)_2$, is readily prepared by substitution of F^- for a weakly coordinated ligand by using PPNF (eq 11).[20] $ReF(CO)_3(PPh_3)_2$ is significantly more labile



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with respect to substitution of both the fluoro and carbonyl ligands than its chloro analogue.[20] In this regard it is interesting to note that while the pentacarbonyl complexes $MX(CO)_5$ of the heavier halides are

TABLE V. Fluoro Complexes of d^6 Metal Centers

	starting material	reagent(s)	refs
$CrF(NO)(dppe)_2$	$[CrF(NO)(dppe)_2][BF_4]$	$NaBH_4$	120
$MoF(NO)(dppe)_2$	$MoF(NNH)(dppe)_2$	NO	121
	$MoH_4(dppe)_2$	$(NO)PF_6$	122
$MoF_2(NO)_2(PPh_3)_2$	$Mo(CO)_4(PPh_3)_2$	$(NO)PF_6$	124
$WFBr(NO)_2(PPh_3)_2$	$WBr(NO)(CO)_2(PPh_3)_2$	$(NO)PF_6$	124
$WF(NO)(CO)_2[P(O^iPr)_3]_2$	$[W(NO)(CO)_3[P(O^iPr)_3]_2][PF_6]$	KF or NaH	123
$WF(NO)(CO)_2(PPh_3)_2$	$W(OClO_3)(NO)(CO)_2(PPh_3)_2$	NBu_4F	124
$WF(NO)(dppe)_2$	$WF(NNH)(dppe)_2$	NO	121
$WF_2(NO)_2(PPh_3)_2$	$[W(NO)(CO)_3(PPh_3)_2][PF_6]$	decomposition	124
$MnF(CO)_3(PPh_3)_2$	$Mn_2(CO)_8(PPh_3)_2$	(i) Na/Hg; (ii) HBF_4	125
$ReF(CO)_3L_2$; L = PPh_3;	$ReCl(CO)_3(PPh_3)_2$	(i) AgOTf; (ii) (PPN)F	20
L = $SbPh_3$; L_2 = tmeda, bipy, dppe	$ReBr(CO)_3L_2$	$AgHF_2$	44,126
$ReFCp(NO)(CO)$	$Re(FBF_3)Cp(NO)(CO)$	TASF	129
$[ReF(NO)(CO)(tacn)]F$	$[ReMe(NO)(CO)(tacn)][BF_4]$	HF	130
$[ReF(NO)(CO)(PPh_3)_3][BF_4]$	$ReH_2(NO)(PPh_3)_3$	HBF_4, CO	127
$[ReF(NO)(CO)(PPh_3)_3][ClO_4]$	$[ReF(NO)(CO)(PPh_3)_3][BF_4]$	$NaClO_4$	127
$ReFH(NO)(CO)(PPh_3)_2$	$[ReF(NO)(CO)(PPh_3)_3][BF_4]$	$NaBH_4$	127
	$ReFH(NO)(PPh_3)_3$	CO	128
$ReFH(NO)(CN\text{-}p\text{-}tol)(PPh_3)_2$	$ReFH(NO)(PPh_3)_3$	*p*-tolNC	128
$ReFH(NO)(PPh_3)_3$	$[ReH(MeOH)(NO)(PPh_3)_3][ClO_4]$	$KF{\cdot}2H_2O$	128
$ReF(OMe)(NO)(CO)(PPh_3)_2$	$[ReF(NO)(CO)(PPh_3)_2][BF_4]$	NaOMe	127
$ReF_2(NO)(CO)(PPh_3)_2$	$[ReF(NO)(CO)(PPh_3)_2][BF_4]$	KF	127
$FeFCp(CO)_2$	$Fe(SiMe_2CH{=}CH_2)Cp(CO)_2$	HF or HBF_4	131
$FeFCp(CO)(PPh_3)$	$FeFCp(CO)_2$	$RhCl(PPh_3)_3$	133
$[FeF(CNMe)(dppe)_2][BF_4]$	$[FeH(CNMe)(dppe)_2][BF_4]$	oxidation	139
$[Fe_2F(SMe)_2(CO)_4(PMe_3)_2][PF_6]$	$Fe_2(SMe)_2(CO)_4(PMe_3)_2$	$AgPF_6$	140
$RuFCp(CO)(PCy_3)$	$RuClCp(CO)(PCy_3)$	(i) AgOTf; (ii) (PPN)F	137
$RuFCpL_2$; L = PPh_3;	$RuClCp(PPh_3)_2$	(i) NH_4F; (ii) Ag_2CO_3	134
L = $AsPh_3$, $SbPh_3$; L_2 = $(PPh_3)(AsPh_3)$	$RuHCpL_2$	HF	136
$[RuF(CO)L_2]X$; L = dppm, X = BF_4, PF_6; L = dppe, X = BF_4	$RuCl_2L_2$	AgX,CO	138
$[Ru_2F_3(PMe_2Ph)_6]^+$	$[RuH(cod)(PMe_2Ph)_3][PF_6]$	HF	141
$OsF(CO)_2(N{=}NPh)(PPh_3)_2$	$[Os(NNPh)(CO)_2(PPh_3)_2][PF_6]$	NEt_4F	142
$RhFCl(COPh)(PPh_3)_2$	$RhCl(PPh_3)_3$	PhCOF	143
$FhFX_2(CO)(PPh_3)_2$; X = Cl;	$RhCl(CO)(PPh_3)_2$	SF_5Cl	148
X = Cl, Br, I, SCN	$RhF(CO)(PPh_3)_2$	X_2	149
$IrFHX(CO)L_2$; X = Cl, L = PMe_3 PPh_3;	$IrCl(CO)L_2$	HCOF	110
X = Cl, Br, I, L = PPh_3	$IrX(CO)(PPh_3)_2$	HF	145
$IrFH(SiR_3)(CO)(PPh_3)_2$; SiR_3 = $SiPh_3$, $SiMeCl_2$, $Si(OEt)_3$, SiF_3	$IrF(CO)(PPh_3)_2$	$HSiR_3$	150
$IrFH_2(CN\text{-}p\text{-}tol)(AsPh_3)_2$	$IrH_3(CN\text{-}p\text{-}tol)(AsPh_3)_2$	HF	156
$IrFClMe(CO)(PPh_3)_2$	$IrCl(OTf)Me(CO)(PPh_3)_2$	NEt_4F	151
$IrFIMe(CO)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	MeI	90
$IrF(O_2)(CO)L_2$; L = $PMePh_2$, $PEtPh_2$, PPh_3	$IrF(CO)L_2$	O_2	66,68,74,91,97
$IrF(1,2\text{-}O_2C_6Cl_4)(CO)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	$1,2\text{-}O_2C_6Cl_4$	97
$IrFCl_2(CO)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	SF_5Cl	148
$IrFI_2(CO)(PPh_3)_2$	$IrF(CO)(PPh_3)_2$	I_2	66,97
$IrFCl(SO_2C_{10}H_7)(CO)(PPh_3)_2$	$IrCl(CO)(PPh_3)_2$	$FSO_2C_{10}H_7$	144
$IrFX(SF_3)(CO)(PEt_3)_2$; X = Cl, Br, I	$IrX(CO)(PEt_3)_2$	SF_4	147
$[IrFCl(SF_2)(CO)(PEt_3)_2][BF_4]$	$IrFCl(SF_3)(CO)(PEt_3)_2$	BF_3	147
$[Ir(COF)(CO)_2(PEt_3)_2]X$; X = BF_4, PF_6	$[Ir(CO)_3(PEt_3)_2]X$	XeF_2	146
$[IrF[(C_4(COOMe)_4](\overline{COCH_2CH_2CH_2})(PPh_3)_2$	not reported	not reported	157
$[IrF(\eta^2\text{-}NH{=}NC_6H_3\text{-}2\text{-}Br)(CO)(PPh_3)_2]^+$	$IrF(CO)(PPh_3)_3$	$(2\text{-}BrC_6H_4N_2)BF_4$	154
$[IrF(\eta^2\text{-}NH{=}NC_6H_3X)(CO)(PPh_3)_2]^+$; X = 2-F, 4-F, 2-$CF_3$, 4-Me, 2-$NO_2$	$IrH(CO)(PPh_3)_3$	$(XC_6H_4N_2)BF_4$, air	155
$IrF(\eta^2\text{-}NNC_6H_3\text{-}2\text{-}Br)(CO)(PPh_3)_2$	$[IrF(\eta^2\text{-}NH{=}NC_6H_3\text{-}2\text{-}Br)(CO)(PPh_3)_2]^+$	NEt_3 or NaOH or NaOAc	154
$PtF_2Cl_2(PPh_3)_2$	$Pt(PhCH{=}CHPh)(PPh_3)_2$	$CF_3CCl{=}CCl_2$	158
$PtF_2Cl_2(PPh_3)_2$	$Pt(PhCH{=}CHPh)(PPh_3)_2$	$CF_3CCl{=}CCl_2$	158
	$PtCl(SF_5)(PPh_3)_2$	CH_2Cl_2 or acetone	148

readily prepared,[107,108] the analogous fluoro complexes still remain elusive (see section II), perhaps due to related ligand lability. The fluoro complexes $ReF(CO)_3L_2$ where L = $SbPh_3$ or L_2 = tmeda, bipy, or dppe are prepared in good yield from the rhenium bromide plus silver bifluoride.[44,126]

Several rhenium(I) fluoro complexes containing nitrosyl ligands have been reported, including the difluoride $ReF_2(NO)(CO)(PPh_3)_2$[127] and hydrido compounds such as $ReFH(NO)(CO)(PPh_3)_2$.[127,128] The cyclopentadienyl derivative ReFCp(NO)(CO) can be synthesized by displacement of the tetrafluoroborate ion from $Re(FBF_3)Cp(NO)(CO)$ by using TASF.[129] The cationic rhenium(I) triaza derivative [ReF(NO)(CO)(tacn)]F and its heavier halide analogues [ReX(NO)(CO)(tacn)]X are all prepared simply by addition of aqueous HX to a cationic rhenium methyl complex $[ReMe(NO)(CO)(tacn)][BF_4]$.[130] Comparison of IR spectra for the series shows that ν_{CO} and ν_{NO} decrease respectively in the order F (1970, 1720 cm^{-1}) > Cl (1950, 1710 cm^{-1}) > Br (1940, 1700 cm^{-1}) > I (1935, 1700 cm^{-1}),[130] consistent with σ-donor ability in the order F < Cl < Br < I, paralleling decreasing electronegativity and increasing polarizability. This spectroscopic trend is opposite that observed for the Vaska's derivatives (section IV) and can be understood by considering that the tripodal tacn ligand requires coordination of the halide cis to CO and NO, decreasing the importance of

π-bonding effects relative to those in the square-planar systems with trans CO and X ligands.

C. Iron(II), Ruthenium(II), and Osmium(II)

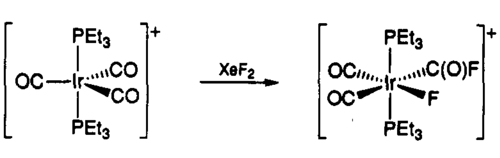
An iron(II) cyclopentadienyl fluoro complex $FeFCp(CO)_2$ is isolated in good yield from the reaction of a vinylsilyl derivative, $Fe(SiMe_2CH{=}CH_2)Cp(CO)_2$, and HF or HBF_4;[131] however, this fluoride is not readily prepared by simple halide metathesis[132] despite the stability and ubiquity of the $[FeCp(CO)_2]$ fragment. The related $FeFCp(CO)(PPh_3)$ has been very briefly mentioned.[133] The ruthenium complex $RuFCp(PPh_3)_2$ is the reported product of reaction of the chloride and NH_4F plus Ag_2CO_3 in methanol.[134] The ^1H NMR spectrum for this fluoride shows the cyclopentadienyl protons at δ 4.56, substantially shifted from the chloride at δ 4.01, with no observed coupling to the ^{19}F atom, whose resonance itself is not observed.[134] Lack of ^{19}F NMR signals is a phenomenon not uncommonly noted for metal fluoro complexes.[135] Related arsine and stibine cyclopentadienyl ruthenium(II) fluorides, $RuFCp(SbPh_3)_2$, $RuFCp(AsPh_3)_2$, and $RuFCp(AsPh_3)(PPh_3)$, have been reported.[136] Preparation of a carbonyl-substituted derivative, $RuFCp(CO)(PCy_3)$, is possible via reaction of the chloride with silver triflate and then (PPN)F.[137]

Bis(chelating phosphine) fluoro complexes of ruthenium, $[RuF(CO)L_2]X$ where L = dppm or dppe, have been reported and possess cationic octahedral ruthenium(II) centers in which the fluoro ligand is trans to CO.[138] Electrochemical oxidation of $[FeH(CNMe)(dppe)_2][BF_4]$ in THF/$[NBu_4][BF_4]$ allows the electrosynthesis of a related iron(II) isonitrile complex, $[FeF(CNMe)(dppe)_2][BF_4]$.[139] Chemical oxidation of an iron(I) dimer $Fe_2(SMe)_2(CO)_4(PMe_3)_2$ by $AgPF_6$ produces $[Fe_2F(SMe)_2(CO)_4(PMe_3)_2][PF_6]$, which is proposed to have one fluoro and two methylthiolato bridges.[140] A related trifluoro-bridged diruthenium cation $[Ru_2F_3(PMe_2Ph)_6]^+$ has also been reported.[141] One example of an organometallic osmium fluoro complex, $OsF(CO)_2(NNPh)(PPh_3)_2$ prepared by addition of NEt_4F to $[Os(NNPh)(CO)_2(PPh_3)_2][PF_6]$, has been described.[142]

D. Rhodium(III), Iridium(III), and Platinum(IV)

A variety of d^6 rhodium(III) and iridium(III) fluorides has been prepared, principally by oxidation of d^8 starting materials. An attempt to prepare $Ph^{18}F$ via $RhCl(PPh_3)_3$-promoted decarbonylation of the labeled benzoyl fluoride produced $Rh^{18}FCl(COPh)(PPh_3)_2$.[143] Similarly, $IrFCl(SO_2C_{10}H_7)(CO)(PPh_3)_2$ is obtained from the attempted desulfonation of naphthalenesulfonyl fluoride by Vaska's chloride.[144] In contrast to these reactions, formyl fluoride is decarbonylated by $IrCl(CO)L_2$, producing HF adducts $IrFHCl(CO)L_2$.[110] The triphenylphosphine-substituted adducts $IrFHX(CO)(PPh_3)_2$ where X = Cl or Br have also been prepared by addition of HF to the d^8 halides.[145]

Novel fluoro complexes have been prepared via addition of hypervalent main-group fluorides to rhodium(I) and iridium(I). For example, XeF_2 formally adds two fluorines across an iridium–carbonyl bond of $[Ir(CO)_3(PEt_3)_2]^+$, generating the unusual fluoroformyl ligand in the product $[IrF(COF)(CO)_2(PEt_3)_2]^+$ (eq 12).[146] Oxidative addition of an S–F bond of SF_4 to $IrX(CO)(PEt_3)_2$ (X = Cl, Br, I) affords $IrFX(SF_3)(CO)(PEt_3)_2$, in which the fluoride is trans to carbon monoxide (eq 13).[147] ^{19}F and ^{31}P NMR studies show that the three fluorines attached to the sulfur atom are inequivalent at low temperatures, resulting in inequivalent PEt_3 ligands; at higher temperatures, this molecule undergoes an as yet unidentified fluxional process involving the fluorines of the SF_3 ligand.[147] In a somewhat different pattern, reactions of SF_5Cl with $MCl(CO)(PPh_3)_2$ produce the d^6 dichlorofluoro complexes $MFCl_2(CO)(PPh_3)_2$ (M = Rh, Ir).[148] Such $MFX_2(CO)(PPh_3)_2$ compounds can be more generally prepared by addition of X_2 to the d^8 fluorides.[66,97,149]



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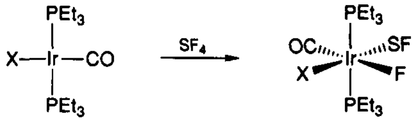


(13)

Oxidative additions of a variety of other small molecules to $IrF(CO)(PPh_3)_2$ produce iridium(III) fluorides. Substituted silanes yield $IrFH(SiR_3)(CO)(PPh_3)_2$ derivatives;[150] tetrachloro-*o*-quinone produces a catecholate complex $IrF(1,2\text{-}O_2C_6Cl_4)(CO)(PPh_3)_2$;[97] and methyl iodide yields $IrFIMe(CO)(PPh_3)_2$.[90] The analogous methyl chloride complex, $IrFClMe(CO)(PPh_3)_2$, has been prepared by substitution of fluoride for triflate.[151] The iridium(I) fluoro complexes $IrF(CO)L_2$ where L = PPh_3, $PMePh_2$, or $PEtPh_2$ reversibly add O_2 to form $IrF(O_2)(CO)L_2$.[66,68,74,91,92,97] For the heavier halide $IrX(O_2)(CO)(PPh_3)_2$ complexes, X-ray crystallographic studies show the O–O distance increases in the order Cl (1.30 Å)[152] < Br (1.36 Å)[91] < I (1.51 Å),[153] indicating that the iridium(III) center is most electron-releasing for X = I and less so for X = Br or Cl. Note that the electron richness at the metal centers in d^6 complexes is found to follow the order F < Cl < Br < I in several cases, paralleling decreasing electronegativity and increasing polarizability, hence increasing σ-donor ability. This trend is opposite that observed for the iridium(I) Vaska's derivatives (section IV) and can be understood by considering the cis arrangement of X and CO in the roughly octahedral $IrX(O_2)(CO)(PPh_3)_2$ which decreases the importance of π-bonding effects relative to those in the square-planar $IrX(CO)(PPh_3)_2$ systems. As discussed in section IV, a variety of adducts of $MF(CO)(PPh_3)_2$ with electron-withdrawing ligands such as TCNE, MeOOCC≡CCOOMe, and SO_2 have been reported and can be considered as iridium(III) oxidative addition products.

Ortho-metallated aryldiazene iridium(III) fluoro cations $[IrF(\mu^2\text{-}NH{=}NC_6H_3R)(CO)(PPh_3)_2]^+$ are the ultimate products obtained from the oxidative addition of aryldiazonium tetrafluoroborates to $IrF(CO)(PPh_3)_2$[154] or $IrH(CO)(PPh_3)_3$;[155] in the latter case, the iridium center abstracts fluoride from the BF_4^- counterion.[155] Deprotonation of the diazene ligand yielding a diazenato fluoro complex has been reported in one case.[154] Reaction of the trihydridoiridium(III) isonitrile complex $IrH_3(CN\text{-}p\text{-}tol)(AsPh_3)_2$ with HF results in

TABLE VI. Fluoro Complexes of d^4 Metal Centers

	starting material	reagent(s)	refs
$[VFCp(CO)_3][PEt_4/Na]$	$[VICp(CO)_3][PEt_4]$	NaF	180
$[MoF(HCCPh)(dppe)_2[BF_4]$	$MoH_4(dppe)_2$	HBF_4, $PhC\equiv CH$	169
$[MoF(CO)_2(dppe)_2][PF_6]$	$Mo(CO)_2(dppe)_2$	$(NO)PF_6$, CH_2Cl_2	44,172,173
	$[Mo_2F(CO)_4(dppe)_4][PF_6]_3$	NEt_4F	172
$[MoF(CO)_2(dppe)_2]X$; X = BPh_4, ClO_4	$[MoF(CO)_2(dppe)_2][PF_6]$	$NaBPh_4$ or $LiClO_4$	172
$[MoF(CO)_2(S_2CNEt_2)_2][NEt_4]$	$Mo(CO)_2(S_2CNEt_2)_2$	NEt_4F	160
$[MoF(CO)_2(S_2CNC_4H_4)_2][NEt_4]$	$Mo(CO)_3(S_2CNC_4H_4)_2$	NEt_4F	161
$MoF(NNH)(dppe)_2$	$[MoF(NNH_2)(dppe)_2][BF_4]$	K_2CO_3 or NEt_3 or NaOMe	121, 174
$MoF(NNCMe{=}CHCOMe)(dppe)_2$	$[MoF(NN{=}CMeCH_2COMe)(dppe)_2][BF_4]$	NaOMe	175
$MoFBr(NHO)(dppe)_2$[a]	$MoF(NO)(dppe)_2$	PhCOBr	122
$[MoF(NHO)(dppe)_2]X$; X = BF_4, PF_6	$MoF(NO)(dppe)_2$	HX	122
$[MoF(NHO)(dppe)_2][PF_6]$	$[Mo(NO)(dppe)_2]_2$	HPF_6	122
	$MoH_4(dppe)_2$	NOP_6	122
$[MoF(NHO)(dppe)_2]I_3$	$[MoF(NHO)(dppe)_2][PF_6]$	I_2	122
$MoF_2(dppe)_2$	$MoH_4(dppe)_2$	HBF_4	169
$[Mo_2F(CO)_4(dppe)_4][PF_6]_3$	$Mo(CO)_2(dppe)_2$	$(NO)PF_6$, $MeNO_2$	172
$[WF(CHCH_2Ph)(dppe)_2][BF_4]$	$WH_2(C\equiv CPh)_2(dppe)_2$	HBF_4	170
$[WF(CO)_2(S_2CNR_2)_2][NEt_4]$; R = Me, Et	$W(CO)_2(S_2CNR_2)_2$	NEt_4F	160
$[WF(CO)_2(S_2CNC_4H_4)_2][NEt_4]$	$W(CO)_3(S_2CNC_4H_4)_2$	NEt_4F	161
$[WF(CO)_2(bipy)L][BF_4]$; L = dppm, dppe	$[W(CO)_2(bipy)_2][BF_4]_2$	L	171
$[WF(CO)_3(tacn)][PF_6]$	$W(CO)_3(tacn)$	(i) HF, air; (ii) $NaPF_6$	163
$[WF(CO)_3(Me_3tacn)][PF_6]$	$W(CO)_3(Me_3tacn)$	(i) HF, air; (ii) $NaPF_6$	164
$WF(CO)_3(\eta^3\text{-}NR_2C_6H_4\text{-}2\text{-}N{=}CHC_6F_4)$; R = H, Me	$W(CO)_3(NCEt)_3$	$1,2\text{-}NR_2C_6H_4N{=}CHC_6F_5$	165
$WF(CO)_3(\eta^3\text{-}NMe_2CH_2CH_2N{=}CHC_6F_4)$	$W(CO)_3(NCEt)_3$	$1,2\text{-}NR_2CH_2CH_2N{=}CHC_6F_5$	166
$WF(CO)_3(\eta^3\text{-}NMe_2CH_2CH_2N{=}CHC_6H_4)$	$WCl(CO)_3(\eta^3\text{-}NMe_2CH_2CH_2N{=}CHC_6H_4)$	$KF{\cdot}2H_2O$	166
$WF(CO)_3(\eta^3\text{-}NHRCH_2CH_2N{=}CHC_6H_4)$; R = H, Ph	not reported	not reported	167,168
$WF(NNH)(dppe)_2$	$[WF(NNH_2)(dppe)_2][BF_4]$	K_2CO_3 or NEt_3	121
$WF(NNCMe{=}CHCOMe)(dppe)_2$	$[WF(NN{=}CMeCH_2COMe)(dppe)_2[BF_4]$	NaOMe	175
$WF[NNCX{=}C(CN)Y](dppe)_2$; X = H, Y = CN, COOEt; X = Cl, Y = CN	$[WF(NNH_2)(dppe)_2][BF_4]$	$ClCX{=}C(CN)Y$, NEt_3	178
$WF[NNC_6H_3\text{-}2,4\text{-}(NO_2)_2](dppe)_2$	$[WF(NNH_2)(dppe)_2][BF_4]$	$FC_6H_3\text{-}2,4\text{-}(NO_2)_2$, K_2CO_3	179
$[WF(dppe)_2]_2(\mu\text{-}NNCH_2CH_2NN)$	$[WF(NN{=}CH_2)(dppe)_2][BF_4]$	reduction	176,177
$[TcF_2(diars)_2]^+$	TcO_4^-	HF, diars	182

[a] Addition of HBr present in PhCOBr.

replacement of one of the hydrides by fluoride to yield $IrFH_2(CN\text{-}p\text{-}tol)(AsPh_3)_2$.[156] Fluoro- and chloroiridium(III) metallacyclecarbene derivatives, $IrX[C_4(COOMe)_4](\overline{COCH_2CH_2CH_2})(PPh_3)_2$, have recently been reported.[157]

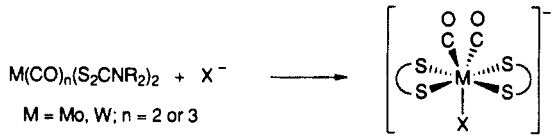
A high-valent platinum fluoride $PtF_2Cl_2(PPh_3)_2$ is the reported product of two processes: the reaction of trichloro-3,3,3-trifluoropropene with $Pt(PhCH{=}CHPh)(PPh_3)_2$[158] and the decomposition of $PtCl(SF_5)(PPh_3)_2$ in dichloromethane or acetone.[148] It is interesting that this platinum(IV) compound and the ruthenium(II) complexes $RuFCpL_2$ described earlier constitute the only reported examples of d^6 organometallic fluorides containing phosphine, arsine, or stibine ligands which do not also contain at least one strong π-acceptor ligand. Although not included in the specific purview of this review, $PtFMe_2(\eta^3\text{-}NMe_2CH_2CH_2\text{-}2\text{-}N{=}CHC_6F_4)$ constitutes an additional example of a platinum(IV) fluoride, again without a strong π-acceptor ligand.[159]

VI. Fluoro Complexes of d^4 Metal Centers

A variety of molybdenum(II) and tungsten(II) fluoro compounds containing carbonyl and phosphine ligands has been reported. They are listed in Table VI along with one vanadium(I) carbonyl fluoride and one technetium(III) arsine fluoro complex.

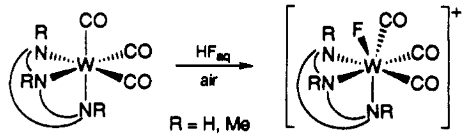
A. Molybdenum(II) and Tungsten(II)

Addition of F^- to the netural d^4 carbonyl compounds $M(CO)_n(S_2CNR_2)_2$ (M = Mo, W; n = 2 or 3) results in formation of seven-coordinate 18-electron anionic fluoro derivatives $[MF(CO)_2(S_2CNR_2)_2]^-$.[160,161] Analogous reactions of Cl^-, Br^-, and I^- and these carbonyls have also been examined (eq 14). When S_2CNR_2 is pyrrole-N-carbodithioate, the seven-coordinate adducts are stable solids for X = F, Cl, and Br.[161] However, when S_2CNR_2 is the diethyldithiocarbamate ligand, a more electron-releasing ligand than pyrrole-N-carbodithioate, the structurally characterized fluoride $[MoF(CO)_2(S_2CNEt_2)_2][NEt_4]$ is the only isolable member of the series;[160,161] for X = Cl or Br, equilibrium formation of $[MoX(CO)_2(S_2CNEt_2)_2]^-$ from $Mo(CO)_2(S_2CNEt_2)_2$ and the halide ion is observed in dichloromethane solution[162] and no adduct is found for X = I.[160] NMR, infrared, and electronic absorption spectra for these series of halide compounds have been reported;[160,161] however, no simple correlation of the spectral data with the nature of the halide ligand is found.



(14)

Seven-coordinate tungsten(II) fluoro complexes containing triazacyclononane ligands, $[WF(CO)_3(tacn)]^+$ and $[WF(CO)_3(Me_3tacn)]^+$, are prepared from the corresponding neutral tungsten(0) compounds by air oxidation in the presence of aqueous HF (eq 15).[163,164]



(15)

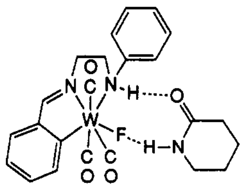


Figure 3. Hydrogen-bonding of δ-valerolactam to a tungsten(II) fluoro complex.

Comparison of the infrared spectra for the series of halide compounds $[WX(CO)_3(Me_3tacn)]^+$ shows an increase in each of the three strong ν_{CO} bands in the order X = F (1985, 1895, 1855 cm^{-1}) < Cl (1990, 1910, 1865 cm^{-1}) < Br (2000, 1930, 1895 cm^{-1}) < I (2101, 1950, 1895 cm^{-1}).[164] The origins of this trend, which is opposite to that observed for the analogous molybdenum complexes $[MoX(CO)_3(Me_3tacn)]^+$ (X = Cl, Br, I), are not understood,[164] and no simple trend is observed in the IR spectra of $[WX(CO)_3(tacn)]^+$ (X = F, Br, I).[163]

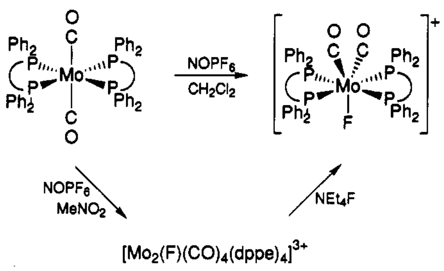
Related seven-coordinate tungsten(II) tricarbonyl fluoro compounds containing chelating unsymmetrical Schiff base ligands have been prepared either by oxidative addition of ligand C–F bonds to tungsten(0) compounds[165] or by metathesis of fluoride for chloride[166] and have been the subject of ^{183}W NMR[167] and X-ray structural[165,166] studies. Surprisingly, the presence of water fails to shift the fluoride/chloride competition equilibrium in this system as is observed for Rh(I) (Section IV); the tungsten(II) chloro complex reacts quantitatively with $KF \cdot 2H_2O$ to yield the fluoro analogue. The possible use of these compounds as transition-metal-based reagents for molecular recognition, due to their ability to bind organic substrates via, in part, hydrogen-bonding with the metal fluoride (Figure 3), has been discussed.[168]

Several of the compounds listed in Table VI are the products of fluoride abstraction from BF_4^- or PF_6^- ions. These are often quite complex reactions, combining F^- abstraction with protonation, ligand addition, or redox chemistry. For example, the addition of $HBF_4 \cdot OEt_2$ to $MoH_4(dppe)_2$ in the presence of phenylacetylene yields the structurally characterized cationic fluoro complex $[MoF(HCCPh)(dppe)_2]^+$.[169] A tungsten carbene fluoro complex $[WF(CHCH_2Ph)(dppe)_2][BF_4]$ is produced by reaction of a tungsten diacetylide dihydride $WH_2(C{\equiv}CPh)_2(dppe)_2$ with HBF_4.[170] In these cases, the fluoride ion comes from an added reagent, HBF_4. Alternatively, the fluoride ion may come from the counterion in a stable starting metal complex, as in the reaction of *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$ and L = dppm or dppe to produce $[WF(CO)_2(bipy)L][BF_4]$.[171]

The molybdenum(0) compound $Mo(CO)_2(dppe)_2$ reacts with $(NO)PF_6$, a powerful oxidant, to yield molybdenum(II) products with terminal or bridging fluoro ligands, depending on the solvent (Scheme IV).[44,172] Subsequent addition of fluoride to the fluoro-bridged complex results in complete conversion to $[MoF(CO)_2(dppe)_2][PF_6]$,[172] which has been structurally characterized.[173]

Reaction of $(NO)PF_6$ and $MoH_4(dppe)_2$ afforded two products in which net reduction of the metal center has occurred: the molybdenum(0) compound $MoF(NO)(dppe)_2$ (section V) and $(MoF(NHO)(dppe)_2]^+$, a rare example of a compound containing a nitroxyl ligand.[122] The latter compound is also produced by the reaction of $[Mo(NO)(dppe)_2]_2$ and HPF_6.[122] More straightforward formation of the nitroxyl fluoro compound is observed upon protonation of the nitrosyl ligand of $MoF(NO)(dppe)_2$.[122] The fluoride ion in $[MoF(NHO)(dppe)_2]^+$ is readily displaced by chloride, bromide, or iodide upon reaction with an alkali metal halide salt in acetone.[122]

SCHEME IV



Diazenido complexes of molybdenum(II) and tungsten(II) with supporting dppe and fluoro ligands have been prepared from cationic hydrazido or diazoalkane fluoro complexes as part of studies focused on the chemistry of nitrogen-containing ligands relevant to nitrogen fixation. For example, deprotonation of $[MF(NNH_2)(dppe)_2]^+$ (M = Mo, W) (section VII) by potassium carbonate, triethylamine, or sodium methoxide yields $MF(NNH)(dppe)_2$.[121,174] Analogous reactions of $[MF(NN{=}CMeCH_2COMe)(dppe)_2]^+$ (M = Mo, W) (section VII) and sodium methoxide produce $MF(NNCMe{=}CHCOMe)(dppe)_2$.[175] One-electron reduction of the diazomethane complex $[WF(NN{=}CH_2)(dppe)_2]^+$ (section VII) results in formation of $[WF(dppe)_2]_2(\mu\text{-}NNCH_2CH_2NN)$, presumably via coupling of two $[WF(NNCH_2)(dppe)_2]^{\bullet}$ units to produce the carbon–carbon bond.[176,177] Reactions of $[WF(NNH_2)(dppe)_2]^+$ with chlorinated (poly)cyanoalkanes[178] or 2,4-dinitrofluorobenzene[179] in the presence of triethylamine yield neutral diazenido fluoro complexes, $WF(NNR)(dppe)_2$.

B. Other Systems

The vanadium(I) ion, $[VFCp(CO)_3]^-$, prepared by metathesis of fluoride for iodide, has been examined as part of a study on the influence of halide ligands on metal shielding in low-valent vanadium complexes.[180] For the series of d^4 compounds $[VXCp(CO)_3]^-$, the ^{51}V NMR spectral data show a normal halogen dependence[34] of the metal shielding, F (δ +417) < Cl (δ −515) < Br (δ −578) < I (δ −742).[180] In contrast, the related d^4 molybdenum anions, $[MoX(CO)_2(S_2CNEt_2)_2]^-$, exhibit an inverse halogen dependence of the metal shielding by ^{95}Mo NMR spectroscopy for X = F (δ +125) and Cl (δ +315).[181]

The technetium cation $[TcF_2(diars)_2]^+$ has been prepared as one of a series of halide complexes, $[^{99m}TcX_2(diars)_2]^+$, for evaluation and comparison as myocardial imaging agents.[182] This compound is generated in saline solutions from a mixture of pertechnetate, hydrofluoric acid, ethanol, and the diars ligand.[182]

VII. Fluoro Complexes of d^2 Metal Centers

Fluoro complexes containing phosphine ligands attached to d^2 metal centers, molybdenum(IV), tung-

TABLE VII. Fluoro Complexes of d² Metal Centers

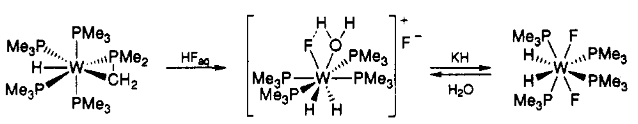
	starting material	reagent(s)	refs
$MoF(N)(dppe)_2$	$[MoF(NH)(dppe)_2][BF_4]$	reduction	189
$[MoF(NH)(dppe)_2][BF_4]$	$MoN(N_3)(dppe)_2$	(i) HF; (ii) HBF_4	186
	$MoH_4(dppe)_2$	HBF_4, N_3^-	169
$[MoF(O)(dppe)_2][BF_4]$	$MoH_4(dppe)_2$	HBF_4, H_2O or SO_2	169
$[MoF(S)(dppe)_2][BF_4]$	$MoH_4(dppe)_2$	HBF_4, H_2S or SO_2	169
$[MoF(NNH_2)(dppe)_2][BF_4]$	$Mo(N_2)_2(dppe)_2$	HBF_4	194,195
	$MoF(NNH)(dppe)_2$	HBF_4	121
	$MoH_4(dppe)_2$	HBF_4, N_2	169
$[MoF(NNH_2)(dppe)_2][BF_6]$	$Mo(N_2)_2(dppe)_2$	$(NO)PF_6$, MeOH	122
$[MoF(NNH_2)(triphos)(PPh_3)][BF_4]$	$Mo(N_2)_2(triphos)(PPh_3)$	HBF_4 or $[PHPh_3][BF_4]$	190–193
$[MoF(NN{=}CHR)(dppe)_2][BF_4]$; R = H, Me, Et, Ph, CH_2Ph, $CH{=}CHCH_3$, $CH{=}CHPh$	$[MoF(NNH_2)(dppe)_2][BF_4]$	RCHO	196,200
$[MoF(NN{=}CHC_6H_4\text{-}4\text{-}X)(dppe)_2][BF_4]$; X = OMe, Cl	$Mo(N_2)_2(dppe)_2$	(i) HBF_4; (ii) $4\text{-}XC_6H_4CHO$	201
$[MoF(NN){=}CR_2)(dppe)_2][BF_4]$; $CR_2 = CMe_2$, $\overline{C(CH_2CH_2CH_2CH_2C}H_2)$, $CMeCH_2COMe$	$[MoF(NNH_2)(dppe)_2][BF_4]$	R_2CO	196,200
$[MoF(SCH_2CH_2PPh_2)_2(OEt_2)][BF_4]$	$[Mo(OH)_2(SCH_2CH_2PPh_2)_2][BF_4]_2$	MeOH, Et_2O	208
$MoF_4(PPh_3)_2$	$MoF_4(CO)_2$	PPh_3	50
$[Mo_2(\mu\text{-}F)_3H_4(PMePh_2)_6][BF_4]$	$MoH_4(PMePh_2)_4$	HBF_4	185
$[Mo_2(\mu\text{-}F)_3H_4(PMePh_2)_6]X$; X = BPh_4, PF_6	$[Mo_2(\mu\text{-}F)_3H_4(PMePh_2)_6][BF_4]$	$NaBPh_4$ or $NaPF_6$	185
$[WFH_2(H_2O)(PMe_3)_4]F$	$WH(CH_2PMe_2)(PMe_3)_4$	HF	183,184
	$WF_2H_2(PMe_3)_4$	H_2O	183,184
$[WFH_2(H_2O)(PMe_3)_4][PF_6]$	$WH(CH_2PMe_2)(PMe_3)_4$	HPF_6	183,184
$WF(CCH_2COOMe)(dppe)_2$	$WH_2(C{\equiv}CCOOMe)_2(dppe)_2$	HBF_4	170
$WF(CCH_2Ph)(CO)_2(dppe)$	$[W(CCH_2Ph)(CO)_2(dppe)][BF_4]$	NEt_4F	205
$[WF(NH)(dppe)_2][BF_4]^a$	$[W(NH)(N_3)(dppe)_2]Cl$	(i) LiOMe; (ii) HF	187
$[WF(NNH_2)(dppe)_2][BF_4]$	$W(N_2)_2(dppe)_2$	HBF_4	195,196
	$WF(NNH)(dppe)_2$	HBF_4	121
	$[WF[NNHCH{=}C(CN)_2](dppe)_2][BF_4]$	reduction	204
$[WF(NNH_2)(dppe)_2][PF_6]$	$[W(OH)(NNH_2)(dppe)_2][PF_6]$	$HFeCo_3(CO)_{12}$	197
$[WF(NNH_2)(PMe_2Ph)_4][BF_4]^a$	$W(N_2)_2(PMe_2Ph)_4$	HF	199
$[WF[NNHCH{=}C(CN)_2](dppe)_2][BF_4]$	$WF[NNCH{=}C(CN)_2](dppe)_2$	HBF_4	204
$[WF[NNHC_6H_3\text{-}2,4\text{-}(NO_2)_2](dppe)_2]X$	$WF[NNC_6H_3\text{-}2,4\text{-}(NO_2)_2](dppe)_2$	HCl or CF_3COOH	179
$[WF(NN{=}CH_2)(dppe)_2][BF_4]$	not reported	not reported	176
$[WF(NN{=}CHR)(dppe)_2][BF_4]$; R = Et, Ph, $C_6H_4\text{-}2\text{-}OH$, $C_{10}H_6\text{-}2\text{-}OH$	$[WF(NNH_2)(dppe)_2][BF_4]$	RCHO	196,202
$[WF(NN{=}CHC_6H_4\text{-}4\text{-}X)(dppe)_2][BF_4]$; X = H, Me, NMe_2, OMe, Cl, NO_2	$W(N_2)_2(dppe)_2$	(i) HBF_4; (ii) $4\text{-}XC_6H_4CHO$	201
$[WF(NN{=}CMeCH_2COMe)(dppe)_2][BF_4]$	$[WF(NNH_2)(dppe)_2][BF_4]$	$MeCOCH_2COMe$	175,196
$[WF(NN{=}CMeCH_2COMe)(dppe)_2]Cl$	$WF(NNCMeCHCOMe)(dppe)_2$	HCl	175
$[WF(N\overline{NCOCH_2CH_2C}O](dppe)_2][BF_4]$	$[WF(NNH_2)(dppe)_2][BF_4]$	$ClCOCH_2CH_2COCl$	203
$WF_2H_2(PMe_3)_4$	$[WFH_2(H_2O)(PMe_3)_4]F$	KH	183,184
	$WH(CH_2PMe_2)(PMe_3)_3$	(i) HBF_4; (ii) KH	183,184
$[W_2F_2(dppe)_4(\mu\text{-}NNHCH_2CH_2NHN)]Br_2$	$[WF(NNCH_2)(dppe)][BF_4]$	(i) reduction; (ii) HBr	176
$[ReF(CCH_2{}^tBu)(dppe)_2][BF_4]$	$ReCl(C{=}CH^tBu)(dppe)_2$	HBF_4	206
$[ReFMe_2(NHPh)(PMe_3)_2][BF_4]$	$Re(NPh)Me_3(PMe_3)_2$	HBF_4	207
$[ReFH(O)[PPh(CH_2CH_2CH_2PCy_2)_2][SbF_6]$	$[ReH_6[PPh(CH_2CH_2CH_2PCy_2)_2][SbF_6]$	1:2 acetone/benzene	210
$[ReF_3(O)(PPh_3)]_n$	$KReO_4$	HF, PPh_3	209

[a] BF_4^- from action of HF on borosilicate glass.

sten(IV), and rhenium(V), are listed in Table VII. As might be expected for the combination of a relatively high-valent metal center and a strong π-acid, d² fluoro compounds possessing carbonyl ligands are rare; only one such example appears in Table VII, a tungsten alkylidyne fluoride compound. Additionally, there are two reported examples of formally d² metal fluoro compounds containing only carbonyl ligands, $MoF_4(CO)_2$[50] and $MoF_4(CO)_3$[51] (section II), however, these species are incompletely characterized.

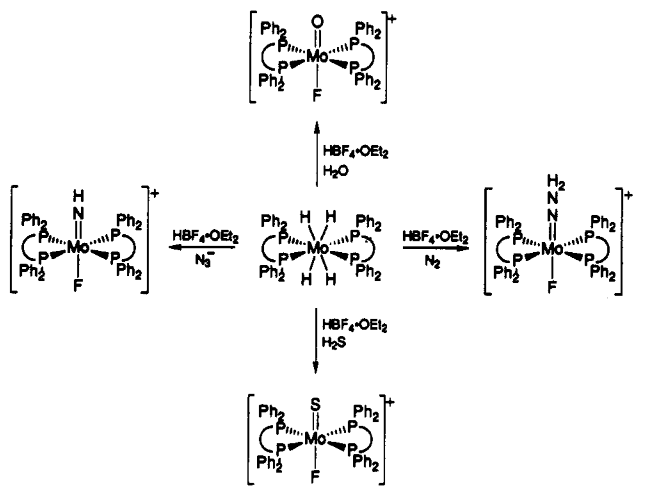
Reaction of metal hydrido derivatives and HF, HPF_6, or HBF_4 can yield fluoro compounds. For example, the tungsten(II) compound $WH(CH_2PMe_2)(PMe_3)_4$ reacts with aqueous HF or HPF_6 to yield $[WFH_2(H_2O)(PMe_3)_4]^+$ with F^- or PF_6^- as the counterion.[183,184] The fluoride salt $[WFH_2(H_2O)(PMe_3)_4]F$, which has been structurally characterized by X-ray crystallography, undergoes reaction with potassium hydride to yield a neutral difluoro dihydrido complex, $WF_2H_2(PMe_3)_4$, which can readily revert to the aquo cation upon addition of H_2O (Scheme V).[183,184] In methanol-d_4, $[WFH_2(H_2O)(PMe_3)_4]F$ shows two distinct ^{19}F NMR resonances consistent with its formulation as a fluoride salt of a monofluoro cation; however, its ^{19}F NMR spectrum in THF-d_8 shows only a single peak at the same chemical shift as that of $WF_2H_2(PMe_3)_4$, suggesting facile interconversion of these two species.[184]

SCHEME V



The molybdenum(IV) hydrido phosphine complex $MoH_4(PMePh_2)_4$ reacts with methanolic HBF_4 to form a structurally characterized bimetallic trifluoro-bridged complex, $[Mo_2(\mu\text{-}F)_3H_4(PMePh_2)_6]^+$, which retains two hydrido ligands per metal.[185] In contrast, reaction of $MoH_4(dppe)_2$ and $HBF_4{\cdot}OEt_2$ in the presence of various small molecules results in loss of all four hydrido ligands to yield complexes of formula $[MoFY(dppe)_2]^+$ where Y is a dianionic oxo, imido, sulfido, or hydrazido ligand

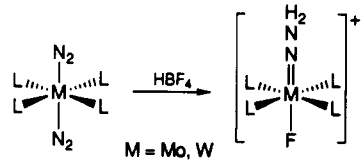
SCHEME VI



(Scheme VI).[169] The imido fluoro complex [MoF(NH)(dppe)$_2$]$^+$ has previously been prepared by reaction of MoN(N$_3$)(dppe)$_2$ and aqueous HF, followed by addition of HBF$_4$.[186] The analogous tungsten imido fluoride, [WF(NH)(dppe)$_2$]$^+$, has been isolated from the reaction of [W(NH)(N$_3$)(dppe)$_2$]$^+$ with lithium methoxide followed by addition of aqueous HF.[187]

Reaction of [MoF(NH)(dppe)$_2$]$^+$ or the related chloro, bromo, iodo, and methoxy derivatives and base ultimately yields ammonia. In the case of the halide ligands, these reactions are reported to proceed through initial deprotonation of the imido group, followed by loss of halide to yield a common intermediate, [Mo(N)(dppe)$_2$]$^+$.[186] The acidity of the imido group in *trans*-[MoX(NH)(dppe)$_2$]$^+$ is found to decrease in the order X = I, Br, Cl > F > OMe;[186] an analogous acidity trend is observed for [WX(NH)(dppe)$_2$]$^+$.[188] In the molybdenum system, this effect is attributed to increasing π-bonding between the X ligand and the metal along the series due both to the inability of fluoride and methoxide to accept π-electron density from the metal center compared with the heavier halides and to the π-electron-donating capability of the fluoro and methoxy ligands;[186] it is also consistent with the irreversible reduction potentials of these compounds which indicate that the ease of reduction follows the order I (−2.00 V) > Br (−2.02 V) > Cl (−2.09 V) > F (−2.51 V) > OMe (−2.62 V).[189] Subsequent loss of halide from the proposed intermediate MoX(N)(dppe)$_2$ occurs rapidly in methanol solution for the chloro, bromo, and iodo derivatives, but slowly enough from the fluoro derivative MoF(N)(dppe)$_2$ to allow spectroscopic detection,[186] suggesting that fluoride forms the strongest bond to molybdenum(IV) in this system. MoF(N)(dppe)$_2$ has also been observed as the major product of the electrochemical reduction of [MoF(NH)(dppe)$_2$]$^+$.[189]

Molybdenum and tungsten hydrazido cations containing fluoro ligands are prepared by the reactions of neutral molybdenum(0) or tungsten(0) dinitrogen complexes and tetrafluoroboric acid, either as an aqueous solution or in the anhydrous forms HBF$_4$·OEt$_2$ or [PHPh$_3$][BF$_4$] (eq 16).[190–196] The acidities of [MoX(NNH$_2$)(dppe)$_2$]$^+$ for X = F, Br have been compared and fit the trend described above for the imido complexes, with the hydrazido ligand of the fluoro derivative more acidic than that of the bromo.[174] The hydrazido fluoro complexes, [MF(NNH$_2$)(dppe)$_2$]$^+$, can



(16)

also be obtained for M = Mo, W upon protonation of the corresponding diazenido complexes[121] (section VI) or for M = Mo in low yield on reaction of HBF$_4$·OEt$_2$ and MoH$_4$(dppe)$_2$ under an N$_2$ atmosphere;[169] [MoF(NNH$_2$)(dppe)$_2$]$^+$ has been structurally characterized with BF$_4^-$ as its counterion.[194] The PF$_6^-$ salt of this cation is the major, though unexpected, product isolated from the reaction of Mo(N$_2$)$_2$(dppe)$_2$ and NOPF$_6$.[122] Similarly, [WF(NNH$_2$)(dppe)$_2$][PF$_6$] is the unexpected product of the reaction of [W(OH)(NNH$_2$)(dppe)$_2$][PF$_6$] and HFeCo$_2$(CO)$_{12}$.[197]

Mo(N$_2$)$_2$(triphos)(PPh$_3$) reacts with HBF$_4$ to produce [MoF(NNH$_2$)(triphos)(PPh$_3$)]$^+$, in contrast to its reactions with HX (X = Cl, Br, I) and H$_2$SO$_4$ to yield ammonia and free dinitrogen;[190–193] the isolation of the fluoro hydrazido complex has been attributed to lack of lability of the coordinated fluoride in this species compared with the other halides.[191,198] The identity of the phosphine ligands can also affect the course of the protonation reaction; addition of anhydrous HBF$_4$ to M(N$_2$)$_2$(PMe$_2$Ph)$_4$ (M = Mo, W) produces ammonia without the detectable intermediacy of a hydrazido complex.[195] Note, however, that the tungsten hydrazido complex, [WF(NNH$_2$)(PMe$_2$Ph)$_4$]$^+$, can be isolated from the reaction of W(N$_2$)$_2$(PMe$_2$Ph)$_4$ and methanolic HF.[199]

In studies focused principally on chemistry of the nitrogen-containing ligand, molybdenum and tungsten diazoalkane fluoro complexes have been prepared by reactions of hydrazido ligands with aldehydes[196,200–202] ketones,[175,196,200] and succinyl dichloride[203] and by protonation of diazenido complexes (section VI).[175,176,179,204] The structures of two of these diazenido fluoro complexes, [WF(NN=CMeCH$_2$COMe)(dppe)$_2$][BF$_4$] and [WF[N$\overline{\mathrm{NCOCH_2CH_2C}}$O](dppe)$_2$][BF$_4$], have been determined by X-ray crystallography.[196,203] Reduction of [WF[NNHCH=C(CN)$_2$](dppe)$_2$]$^+$ under N$_2$ results in regeneration of the hydrazido complex, [WF(NNH$_2$)(dppe)$_2$]$^+$, accompanied by release of 5-amino-4-cyanopyrazole.[204]

Tungsten and rhenium alkylidyne complexes can be prepared which formally contain d^2 metal centers but are closely related to octahedral d^6 compounds with strong π-acid ligands. Addition of F$^-$ to the cationic alkylidyne compound [W(CCH$_2$Ph)(CO)$_2$(dppe)]$^+$ yields WF(CCH$_2$Ph)(CO)$_2$(dppe);[205] WF(CCH$_2$COOMe)(dppe)$_2$ is prepared by reaction of WH$_2$(C≡CCOOMe)$_2$(dppe)$_2$ and HBF$_4$.[170] Protonation of the vinylidene complex ReCl(C=CH^{t}Bu)(dppe)$_2$ by HBF$_4$ yields [ReF(CCH$_2$^{t}Bu)(dppe)$_2$][BF$_4$].[206] A rhenium(V) amido fluoro compound [ReFMe$_2$(NHPh)(PMe$_3$)$_2$][BF$_4$] is isolated upon reaction of Re(NPh)Me$_3$(PMe$_3$)$_2$ and aqueous HBF$_4$.[207]

Three of the compounds listed in Table VII have been characterized only by elemental analysis. Unstable [MoF(OEt$_2$)(SCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$] is reported as the product of decomposition upon attempted recrystallization of a compound formulated as [Mo(OH)$_2$(SCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$]$_2$, prepared by reaction of a

TABLE VIII. Fluoro Complexes of d^0 Metal Centers

	starting material	reagent(s)	refs
NbF_5(diars)	NbF_5	diars	213
$[TaF_4(PBu_3)_2][TaF_6]$	TaF_5	PBu_3	214
$WFCl(O)(CH^tBu)(PEt_3)_2$	$WCl_2(O)(CH^tBu)(PEt_3)_2$	$TlBF_4$, PEt_3	215
$[WFH(NNH_2)(dppe)_2][BF_4]_2$	not reported	not reported	216
WF_6L; L = PMe_3, PEt_3, $AsMe_3$	WF_6	L	211,212

TABLE IX. Odd Electron Metal Fluoro Complexes

	starting material	reagent(s)	refs
$TiF(TPP)(PBu_3)$	TiF(TPP)	PBu_3	217
CrF_3L; L = triphos, $P(CH_2CH_2PPh_2)_3$, $CMe(CH_2AsMe_2)_3$	$CrCl_3(thf)_3$	(i) AgF; (ii) L	218
$[CrF(NO)(dppe)_2][BF_4]$	$[Cr(NO)(NCMe)_5][BF_4]_2$	dppe	120
$[CrF(NO)(dppe)_2][PF_6]$	$[Cr(NO)(CN^tBu)_5][PF_6]_2$	dppe	219
$Mo_2F_2(OR)_4(PMe_3)_2$; OR = O^iPr, O^tBu	$Mo_4F_2(O^iPr)_{10}$ or $Mo_4(\mu\text{-}F)_4(O^tBu)_8$	PMe_3	222,223
$MoF(CO)_2(dppe)_2$	$Mo(CO)_2(dppe)_2$	F^-, oxidation	29
$CoF_2(PMe_2Ph)_3$	CoF_2	PMe_2Ph	221

molybdenum(VI) dioxo compound, $Mo(O_2)(SCH_2CH_2PPh_2)_2$, and HBF_4.[206] A molybdenum fluoro compound, $MoF_4(PPh_3)_2$, is the reported product of the reaction of $MoF_4(CO)_2$ and triphenylphosphine.[51] Attempts to synthesize the fluoro analogue of $ReCl_3(O)(PPh_3)_2$ from potassium perrhenate, triphenylphosphine, and HF in refluxing ethanol have produced a material formulated as a fluoro-bridged polymer $[ReF_3(O)(PPh_3)]_n$.[209]

A related rhenium oxo fluoro complex, $[ReFH(O)[PPh(CH_2CH_2CH_2PCy_2)_2][SbF_6]$, has recently been reported to form upon reflux of $[ReH_6[PPh(CH_2CH_2CH_2PCy_2)_2][SbF_6]$ in a 1:2 acetone/benzene solution.[210]

VIII. Fluoro Complexes of d^0 Metal Centers

Fluoro compounds of niobium, tantalum, and tungsten in their maximum oxidation states containing phosphine or arsine ligands can be prepared (Table VIII). Tungsten hexafluoride reacts with L = PMe_3,[211] PEt_3,[212] and $AsMe_3$[212] to produce seven-coordinate complexes of formula $WF_6(L)$ which have been characterized by ^{19}F NMR spectroscopy. Each compound shows a single resonance in its ^{19}F NMR spectrum, indicating that a fluxional process equilibrates the six fluoro ligands.[211,212] Phosphorus–fluorine coupling and ^{183}W satellites are resolved only for the PMe_3 adduct, which is fluxional down to −85 °C.[211] The PEt_3 and $AsMe_3$ complexes have been shown to undergo respective slow and fast exchange with free ligand.[212] Niobium pentafluoride is reported to react with diars to form an analogous seven-coordinate complex, NbF_5(diars).[213] In contrast, reaction of TaF_5 and 1 equiv of tributylphosphine affords a salt, $[TaF_4(PBu_3)_2][TaF_6]$, identified by ^{19}F NMR spectroscopy.[214]

High-valent metal complexes can readily abstract F^- from counterions such as BF_4^- or PF_6^- to produce fluoro derivatives. One d^0 fluoro phosphine compound, $WFCl(O)(CH^tBu)(PEt_3)_2$, has been prepared by this method upon reaction of $TlBF_4$ or $AgPF_6$ and $WCl_2(O)(CH^tBu)(PEt_3)_2$.[215] Spectral data, but not details of preparation, for an additional tungsten(VI) phosphine fluoride, $[WFH(NNH_2)(depe)_2][BF_4]_2$, have been reported.[216]

IX. Odd-Electron Metal Fluoro Complexes

Only a limited number of odd-electron fluoro compounds containing carbonyl, phosphine, or arsine ligands have been described (Table IX). This is consistent with the general emphasis organometallic chemistry has placed on diamagnetic compounds due to the power of NMR spectroscopy as a tool for characterizing organic fragments in these species.

TABLE X. Structural Studies of Metal Fluoro Complexes

	$MF_{terminal}$, Å	ref
$CrF(NO)(dppe)_2$	1.880 (5)	120
$[MoF(NNH_2)(dppe)_2][BF_4]$	1.992 (8)	194
$[MoF(OtBu)_2(PMe_3)]_2$	1.983 (6)	222
$[MoF(HCCPh)(dppe)_2][BF_4]$	1.981 (4)	169
$[MoF(CO)_2(dppe)_2][PF_6]$	2.035 (6)	173
$[MoF(CO)_2(S_2CNEt_2)_2][NEt_4]$	2.055 (3)	160
$[WFH_2(H_2O)(PMe_3)_4]F$	2.08 (1)	183
$[WF(NN{=}CMeCH_2COMe)(dppe)_2][BF_4]$	2.019 (14)	196
$[WF[NNCOCH_2CH_2CO](dppe)_2][BF_4]$	not reported	203
$WF(CO)_3(\eta^3\text{-}NH_2C_6H_4\text{-}2\text{-}N{=}CHC_6F_4)$	2.032 (4)	165
$WF(CO)_3(\eta^3\text{-}NMe_2C_6H_4\text{-}2\text{-}N{=}CHC_6F_4)$	2.037 (2)	166
$[ReF(CCH_2{}^tBu)(dppe)_2][BF_4]$	2.134 (4)	206
$[ReF(NO)(CO)(PPh_3)_3][ClO_4]$	1.973 (13)	127
$ReF(CO)_3$(tmeda)	2.039 (4)	126
$[IrF(COF)(CO)_2(PEt_3)_2][BF_4]$	1.998 (3)	146
$[IrF(\eta^2\text{-}NH{=}NC_6H_3\text{-}4\text{-}F)(CO)(PPh_3)_2][BF_3OH]$	2.08 (1)	155
$[IrF(\eta^2\text{-}NH{=}NC_6H_3\text{-}2\text{-}CF_3)(CO)(PPh_3)_2][BF_4]$	2.21 (4)	155
$PtF[CH(CF_3)_2](PPh_3)_2$	2.03 (1)	115
$[PtF(PEt_3)_3][BF_4]$	2.043 (7)	117
$CuF(PPh_3)_3$	2.026 (2)	60

		$MF_{terminal}$, Å	MF_{bridge}, Å	MFM, deg	ref
$[Mo_2(\mu_2\text{-}F)_3H_4(PMePh_2)_6][BF_4]$			2.161 (27)[a]	97.7 (6)[a]	185
$Mn_3(\mu_2\text{-}F)(\mu_3\text{-}OEt)_2(CO)_9$			1.95 (3)[a]	93 (1)	53
$[Mn(CO)_3]_4(\mu_3\text{-}F)_2(\mu_3\text{-}OH)_2$			2.052 (3)[b]	102.4 (1)[b]	12
$[Re(CO)_5](\mu_2\text{-}F)[ReF_5]$	Re(I)		2.17 (4)[a]	140.4 (19)[a]	40
	Re(V)	1.84 (6)[a]	1.97 (3)[a]	140.4 (19)[a]	
$[Re(CO)_3]_4(\mu_3\text{-}F)_4$			2.200 (5)[a]	103.8 (11)[a]	43
$[RuF(CO)_3]_4(\mu_2\text{-}F)_4$		1.99 (7)[a]	2.04 (7)[a]	145[a]	47

[a] Average of two or more crystallographically independent values. [b] Average of MnF/MnO and MnFMn/MnOMn due to disordered structure.

One d^1 complex has been reported; $TiF(PBu_3)(TPP)$ has been prepared by addition of tributylphosphine to TiF(TPP) and characterized by ESR and UV–visible spectroscopy.[217] Paramagnetic d^3 compounds, CrF_3L, where L = triphos ($P(CH_2CH_2PPh_2)_3$) or $CMe(CH_2AsMe_2)_3$, have been synthesized by treatment of $CrCl_3(THF)_3$ with silver fluoride followed by addition of tridentate phosphine or arsine ligands and characterized by a variety of physicochemical techniques.[218] Examples of d^5 phosphine fluorides have been reported; reactions of the chromium(I) salts $[Cr(NO)(NCMe)_4][BF_4]_2$ and $[Cr(NO)(CN^tBu)_5][PF_6]_2$ with dppe result in displacement of the nitrile and isonitrile

TABLE XI. Selected NMR Data for Metal Fluoro Complexes

compd	solvent	$\delta(^{19}F)^a$	$\delta(^{19}F)^b$	$\delta(^{31}P)^a$	$\delta(^{31}P)^b$	J_{PF}	ref
$[TaF_4(PBu_3)_2]^+$	CH_2Cl_2	389.0^c	+64			70	214
$[MoF(CO)_2(dppe)_2]^+$	CD_2Cl_2	189.5^d	−266			28	172
	$CDCl_3$			-47.5^e	+48	27	172
$[MoF(NNH_2)(dppe)_2]^+$	MeOH or CH_2Cl_2	-160.1^f	−160	-94.7^g	+46	32	121,192
	not reported	88.1^i	−152			30	194
$[MoF(NN{=}CHEt)(dppe)_2]^+$	CD_2Cl_2	50.3^i	−114			30	196,200
$[Mo_2F(CO)_4(dppe)_4]^{3+}$	$CDCl_3$	62.4^d	−139	-56.5^e	+56		172
$Mo_2F_2(O^iPr)_4(PMe_3)_2$	toluene-d_8	-99.2^f	−99	-10.0^h	−10	116 (^2J), 35 (^3J)	223
$Mo_2F_2(O^tBu)_4(PMe_3)_2$	toluene-d_8	-93.5^f	−94	-10.3^h	−10	119 (^2J), 43 (^3J)	222
$[Mo_2(\mu\text{-}F)_3H_4(PMePh_2)_6]^+$	$CDCl_3$	-228^f	−228	50.8^h	+51	35	185
$WF(CCH_2COOMe)(dppe)_2$	CD_2Cl_2	-141.0^f	−141			35	170
$[WF(CHCH_2Ph)(dppe)_2]^+$	CD_2Cl_2	-97.3^f	−97			34	170
$WF(CO)_3(\eta^3\text{-}NH_2C_6H_4\text{-}2\text{-}N{=}CHC_6F_4)$	acetone-d_6	-226.0^f	−226				165
$WF[NNCH{=}C(CN)_2](dppe)_2$	not reported	157.7^j	−158?				178
$WF[NNCH{=}C(CN)(COOEt)](dppe)_2$	not reported	176.3^j	−176?				178
$WF[NNC_6H_3\text{-}2,4\text{-}(NO_2)_2](dppe)_2$	CD_2Cl_2	-173.9^f	−174	-34.5^h	−35	40	179
$[WF(NNH_2)(dppe)_2]^+$	MeOH or CH_2Cl_2	-172.2^f	−172	-105.2^g	+36	41	121,192
$[WF[NNHC_6H_3\text{-}2,4\text{-}(NO_2)_2](dppe)_2]^+$	CD_2Cl_2	-131.0^f	−131	-30.6^h	−30	42	179
$[WFH_2(H_2O)(PMe_3)_4]^+$	CD_3CN	-239.5^k	−181	$-73.8, -81.7^l$	−76, −84	50, 64	184
	CD_3OD	-243.6^k	−185	$-13.0, -16.0^l$	−15, −18		184
$WFCl(O)(CH^tBu)(PEt_3)_2$	C_6D_6	226^m	−226	23.1^h	+23	49	215
$WF_2H_2(PMe_3)_4$	C_6D_6	-231.4^k	−203	$-12.5, -15.5^l$	−15, −18	86, 51	184
$WF_6(PMe_3)$	CH_3CN	-135.5^m	+135			73	211
	SO_2	-137.4^m	+137			73	211
$WF_6(PEt_3)$	SO_2	148.5^f	+149				212
$WF_6(AsMe_3)$	SO_2	148.7^f	+149				212
$[ReFMe_2(NHPh)(PMe_3)_2]^+$	acetone-d_6	-167.6^f	−168	-26.7^h	−27	57	207
$[FeF(CNMe)(dppe)_2]$	CD_2Cl_2	-554.4^j	−554?			22	139
$[RuF(CO)(dppe)_2]^+$	$MeNO_2$	-400^f	−400	-42.7^h	−43	17	138
$RhF(CO)(PPh_3)_2$	CD_2Cl_2	-169.4^f	−170	24.9^h	+25		87
	$CDCl_3$	-270^j	−270?	25.2^h	+25	21	83
	$CHCl_3$	271^m	−271	115.1^n	+26	22	71
	$CHCl_3$			-23.3^e	+23		84
$RhF(C_2F_4)(PPh_3)_2$	DMSO-d_6	-152^f	−152				87
	CD_3CN	-158^f	−158				87
	acetone-d_6	-169.5^f	−170				87
	CD_2Cl_2			35.6^h	+36		87
$IrF(CO)(PPh_3)_2$	$CHCl_3$	254^m	−254			30	71
	C_6H_6			-24.4^e	+24	20	78
$IrFCl(SF_3)(CO)(PEt_3)_2$	CD_2Cl_2	-336.9^o	−337?	$7.6, 0.3^o$	+8, 0?	31, 36	147
$IrFBr(SF_3)(CO)(PEt_3)_2$	CD_2Cl_2	-344.1^o	−344?	$3.6, -3.6^o$	+4, −4?	32, 37	147
$IrFI(SF_3)(CO)(PEt_3)_2$	CD_2Cl_2	-356.2^o	−356?	$-1.7, -8.7^o$	−2, −9?	33, 38	147
$[IrFCl(SF_2)(CO)(PEt_3)_2]^+$	CD_2Cl_2	-360.9^o	−361?	8.1^o	+8?	33	147
$[IrF(COF)(CO)_2(PEt_3)_2]^+$	not reported	-394.6^j	−395?	2.9^h	+3	32	146
$Ni_2F(OMe)Me_2(PMe_3)_2$	toluene-d_8	422^m	−422	7.2^p	+7?	55	109
$Ni_2F(NMe_2)Me_2(PMe_3)_2$	toluene-d_8	467^m	−467	11.1^p	+11?	63	109
$Ni_2FClMe_2(PMe_3)_2$	toluene-d_8	394^m	−394	6.4^p	+6?	151	109
$Ni_2F_2Me_2(PMe_3)_2$	toluene-d_8	378^m	−378	5.3^p	+5?	49, 156	109
$[PdF(PEt_3)_3]^+$	$CHCl_3$	255^m	−255			29, 160	71
$[PtF(PEt_3)_3]^+$	acetone	252^m	−252	$115.8, 141.6^n$	+25, −1	32, 140	71
$[PtF(PMe_2Ph)_3]^+$	acetone	257^m	−257			34, 150	71
$[PtF(PPh_3)_3]^+$	acetone	232^m	−232	$114.7, 138.2^n$	+26, +3	39, 139	71
$[PtF(PEt_3)_2(PPh_3)]^+$	$CHCl_3$ or acetone	260^m	−260	$119.3, 141.0^n$	+22, 0	30, 158	71
$[PtF(PEt_3)_2[P(OPh)_3]]^+$	$CHCl_3$ or acetone	266^m	−266	$110.0, 82.9^n$	+31, +58	30, 246	71
$CuF(PPh_3)_3$	CD_3OD	9.6^m	−10	7.0^q	+13	70	60

[a] Signals for fluoro ligands and phosphine ligands as reported with positive chemical shifts upfield or downfield of reference substance ($\delta = 0$) as indicated in notes below. [b] ^{19}F and ^{31}P NMR data converted to single scales with positive chemical shifts downfield relative to $CFCl_3$ ($\delta = 0$) and downfield relative to external 85% H_3PO_4 ($\delta = 0$), respectively; question marks indicate best guess based on information available in literature citations. [c] Upfield, F_2. [d] Upfield, CF_3COOH. [e] Upfield, 85% H_3PO_4. [f] Downfield, $CFCl_3$. [g] Downfield, $P(OMe)_3$. [h] Downfield, 85% H_3PO_4. [i] Upfield, $C_6H_5CF_3$. [j] Direction of chemical shifts not indicated, $CFCl_3$. [k] Downfield, $(CF_3)_2CO$. [l] Downfield, $P(O)(OMe)_3$. [m] Upfield, $CFCl_3$. [n] Upfield, $P(OMe)_3$. [o] Reference not reported. [p] Direction of chemical shifts not indicated, 85% H_3PO_4. [q] Upfield, PPh_3.

ligands by the chelating phosphine and abstraction of F^- from the counterion to produce a common cation $[CrF(NO)(dppe)_2]^+$ in low yield.[120,219] The related neutral chromium(I) carbonyl fluoride, $CrF(CO)_5$, has been generated by electrochemical oxidation of $[CrF(CO)_5]^-$ (section II).[29] In the same report, $MoF(CO)_2(dppe)_2$ is described as the product of controlled-potential electrolysis of $Mo(CO)_2(dppe)_2$ in the presence of F^-.[29,220] Only one d^7 fluoro complex has been reported; $CoF_2(PMe_2Ph)_3$ is prepared by addition of dimethylphenylphosphine to CoF_2.[221] A trigonal-bipyramidal structure has been proposed based on the ESR spectrum of this compound. In contrast to the unreactive chloro and bromo analogues, $CoF_2(PMe_2Ph)_3$ undergoes adduct formation with dioxygen at low temperatures.[221]

In addition to the paramagnetic odd-electron compounds described above, diamagnetic molybdenum(III)–molybdenum(III) triply bonded complexes of formula $Mo_2F_2(OR)_4(PMe_3)_2$ (OR = O^{t}Bu, O^{i}Pr) have been prepared by addition of trimethylphosphine to $Mo_4F_4(O^tBu)_8$ or $Mo_4F_2(O^iPr)_{10}$.[222,223] Spectral charac-

TABLE XII. Spectral and Electrochemical Data for $MX(CO)(PPh_3)_2$

	ν_{CO}, cm^{-1} [a]		λ_{max}, nm [b]		$E_{1/2}$, V [c]	
halogen	M = Rh	M = Ir	M = Rh	M = Ir	M = Rh	M = Ir
F	1971	1957	358	427	−2.34	−2.55
Cl	1980	1965	367	439	−2.05	−2.22
Br	1980	1966	369	443	−2.00	−2.07
I	1981	1967	372	451	−1.88	−1.96

[a] From ref 64. [b] From ref 80. [c] From ref 89.

terization of both compounds has been reported, and a crystal structure of the *tert*-butoxide dimer shows all ligands terminally attached to the two molybdenum atoms.[222,223] These are the first examples of compounds containing fluoro ligands attached to a Mo≡Mo unit.[223]

X. Comments and Conclusions

This review describes the considerable variety of transition-metal fluoro compounds containing carbonyl, phosphine, arsine, and stibine ligands reported in the literature. Included are a number of stable low-valent organometallic fluorides, a class of compounds frequently assumed to be inaccessible on the basis of hard/soft acid/base predictions. A wide range of metal/ligand environments can support fluoro ligands. In fact, fluoro complexes are more stable in many instances than the corresponding heavier halogen analogues. Tables II–IX provide a comprehensive survey of the methods used to prepare metal fluoro complexes. Although a number of these syntheses appear to involve a large measure of serendipity, rational routes for the introduction of fluoro ligands are available. Particularly promising is the facile displacement of weakly coordinating ligands by fluoride; in several systems, net metathesis of fluoride for chloride is accomplished cleanly and in good yield via abstraction of Cl^- by AgOTf or $AgBF_4$ followed by addition of a fluoride reagent soluble in organic solvents (e.g., TASF or (PPN)F).

From the compounds and chemistry described in this review, several features emerge concerning the reactivity of the transition-metal fluoro compounds containing carbonyl, phosphine, arsine, and stilbine ligands. The combination of soft low-valent transition-metal centers and hard fluoride ions can produce unusual compounds with new reactivity patterns (e.g., $RhF(PCy_3)_2$). Fluoride appears to promote ligand-substitution lability at metal centers; this effect, combined with the stability of metal fluorine bonds, suggests promise for the use of organometallic fluoro compounds as catalysts and reagents in aprotic media. Fluoro ligands can also be useful sites for reaction chemistry; the propensity of F^- to form hydrogen bonds to hydroxylic compounds and the extremely strong Si–F bond can be used in synthetic schemes to prepare transition-metal compounds not accessible from chloro, bromo, or iodo starting materials. Overall, the fluoride ion clearly has a useful place in the repertoire of ligands available for the modification of organometallic compounds; its introduction into organometallic systems (e.g., clusters) can be expected to lead to new and interesting chemistry.

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XII. Abbreviations

bipy	2,2′-bipyridine
tmeda	*N,N,N′,N′*-tetramethylethylenediamine
tacn	1,4,7-triazacyclononane
Me_3-tacn	*N,N′,N″*-trimethyl-1,4,7-triazacyclononane
dmpe	1,2-bis(dimethylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dippe	1,2-bis(diisopropylphosphino)ethane
dippp	1,2-bis(diisopropylphosphino)propane
triphos	bis[(diphenylphosphino)ethyl]phenylphosphine
diars	1,2-bis(dimethylarsino)benzene
C_8H_{14}	η^2-cyclooctene
cod	η^4-1,5-cyclooctadiene
Cp	η^5-cyclopentadienyl
OTf	trifluoromethanesulfonate (triflate)
TPP	tetraphenylporphyrin
TCNE	tetracyanoethylene
PPN	bis(triphenylphosphine)iminium
TASF	tris(dimethylamino)sulfonium difluorotrimethylsilicate

XIII. References and Notes

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