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Organometallic Fluorides: Compounds Containing Carbon–Metal–Fluorine Fragments of d-Block Metals[†]

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I. Abbreviations

Cp	η^5-C_5H_5
Cp*	η^5-C_5Me_5
Cp′	general cyclopentadienyl ring
R_nCp	$C_5H_{5-n}R_n$ with $n = 1$, 2, or 3 and positions of groups on ring are given by 1, 3, and 5
R_nCp^*	$C_5Me_{5-n}R_n$ with $n = 1$ typically
M	transition metal
M′	main group metal
X	halide
E	chalcogen
tmpy·2HF	2,3,5-trimethylpyridine hydrofluoride
TAS-F	$[(Me_2N)_3S][Me_3SiF_2]$
[PPN]F	$[(Ph_3P)_2N]F$
acac	acetylacetonate
dmpe	bis(dimethyphosphino)ethane
dppe	bis(diphenylphosphino)ethane
bpy	bipyridine
tmen	tetramethylethylenediamine ($Me_2NCH_2CH_2$-NMe_2)
MAO	methylaluminoxane
EBTHI	(*S*,*S*)-ethylenebistetrahydroindene

II. Introduction and Scope of Review

For the purpose of this review the term *organometallic fluoride* is used strictly to describe compounds containing fluorine−metal and carbon−metal bonds with the same metal atom. What may appear to be a strict definition encompasses a remarkably large number of compounds. Given the necessity to restrict this review to organometallic fluorides of the transition metals, it is timed to appear in conjunction with two independent minor reviews of organometallic main group[1] and f-block fluorides.[2] In combination, the three articles provide a comprehensive overview of the entire field of organometallic fluoride chemistry up to mid-1997.

While no single review dealing specifically with organometallic fluorides of the transition metals has been published, related surveys have appeared. Doherty and Hoffman described the variety of low-valent organometallic fluorides with carbonyl, phosphine, and stibine ligands which were to be found in the literature up to the end of 1990.[3] The large number of subsequent publications dealing with low oxidation state organometallic fluorides are described here. Also included in this review are the 12 organometallic fluorides which were structurally characterized prior to 1991. This is a worthwhile exercise since one of the problems in the area of late transition metal fluorides has been the unambigiuos assignment of structure in the absence of X-ray crystal structure analysis. Beck and Sünkel reviewed metal complexes of weakly coordinating anions, paying special attention to organometallic complexes of weakly coordinating fluorinated anions such as BF_4^-, PF_6^-, AsF_6^-, and SbF_6^-.[4] Toward the end of 1988 there were four examples of structurally characterized compounds belonging to this class which are

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[†] Dedicated to Professor Achim Müller on the occasion of his 60th birthday.

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Eamonn Francis Murphy was born in New Ross, in the south east of Ireland, in 1965. He received his B.Sc. (Hons) in 1987 and Ph.D. (NUI) in 1993, both at St. Patrick's College Maynooth, Co. Kildare. His doctoral thesis, carried out under the direction of Dr. Malachy McCann, deals with the coordination chemistry of chiral binaphthyl phosphoric acid modified mono- and bimetallic complexes and their use in asymmetric catalysis. Funded by a EU Human Capital and Mobility Fellowship he traveled to Göttingen, Germany, in early 1994 to work in the area of early transition metal organometallic fluorides, with inspiration in this direction ably provided by Prof. Herbert W. Roesky. Following an enjoyable two and a half years in Germany, he returned to Ireland in Nov. 1996 to join the group of Prof. Julian R. H. Ross at the Center for Environmental Research, University of Limerick, where he is currently investigating the influence of metal halides in heterogeneous partial oxidation catalysis.

Ramaswamy Murugavel was born in Alagramam, India. He obtained his B.Sc. (Government Arts College in Villupuram, 1984) and M.Sc. (School of Chemistry, 1987) degrees from the University of Madras. He later received his Ph.D. degree in 1993 (under the direction of Professor S. S. Krishnamurthy) at the Indian Institute of Science, Bangalore, where he continued as a Research Associate until July 1994. He was awarded the Dr. J. C. Ghosh Medal for his Ph.D. work. In August 1994, he moved to Göttingen as an Alexander-von-Humboldt Research Fellow to carry out his research in Professor H. W. Roesky's group. He remained there as a Research Scientist until December 1997. Accepting a recent offer, he will be joining the Faculty of the Chemistry Department, Indian Institute of Technology—Bombay, in December 1997. His research interests are centered around the synthesis, structure, and bonding in organometallic chemistry. He is currently concentrating on the use of silanols and phosphonic acids as possible building blocks in low-temperature materials chemistry. He has authored/co-authored approximately 35 publications including a review article in this journal in 1996.

Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his Diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, Tokyo Institute of Technology, and Kyoto University and also frontiers lecturer at Texas A&M University at College Station, University of Texas at Austin and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, the Academy of Scientists "Leopoldina" in Halle, and the Academia Europaea in London. He served as the vice president of German Chemical Society during 1995, and presently he is the speaker of Wöhler Vereinigung für Anorganische Chemie. He has received many awards, e.g., the Dr.rer.nat.h.c. of Bielefeld, Brünn, and Bucharest Universities, Alfred-Stock-Memorial Award, and French Alexander-von-Humboldt award. More than 700 publications, articles, patents, and books document his research activity in the areas of inorganic chemistry and materials science.

included in this review. Subsequent publications describing new complexes having "weakly" coordinated fluorinated anions are described here. Osterberg and Richmond have reviewed the intriguing area of carbon−fluorine bond activation up to the end of 1993.[5] Reports of organometallic fluorides which are involved in C−F bond activation, which have appeared since the beginning of 1994 are included at the appropriate points in the text. It must be pointed out that in this review C−F bond activation is seen to be of value only as a synthetic route to organometallic fluorides. The limited number of organometallic fluorides derived from C−F bond activation which were structurally characterized prior to 1994 are included here. The early work of Witt and Roesky concentrated largely on sterically demanding perfluorinated substituents and to a lesser extent on metal fluorides with bulky ligands such as the cyclopentadienyl group.[6] The limited coverage of organometallic fluorides in this report allows us to incorporate most of the material in the tables included in the text here. It is hoped that this review will serve to unify the data already available from previous articles and present an overall perspective of the present-day status of organometallic fluoride chemistry.

Many recent advances in solid-state chemistry, coordination chemistry, main group element chemistry, and organometallic chemistry have relied on the physical and chemical properties of the most electronegative element, fluorine. A list of monographs and papers detailing inorganic, organic, and organometallic fluoride chemistry attests to the interdisciplinary nature of research in fluorine chemistry.[7]

The general outlay of the review is as follows. First a general overview of fluorinating reagents and procedures is given to initiate the novice fluorine chemist. This is followed by the main body of the text. Organotransition metal fluorides are reviewed

Table 1. Routes to Organometallic Fluorides

method	reagent	comment
metathesis	alkali fluorides	typically involves reaction of organometallic chloride with alkali fluoride
	ammonium fluorides	difficulty in preparing "dry" reagents has been a problem
	Me_3SnF	versatile reagent for the preparation of group 4−6 fluorides
	TAS-F/modified method	involves generation of cation followed by reaction with organic solvent-soluble fluorinating reagent such as TAS-F
protonation of metal alkyl/hydride	Olah's reagent tmpy·2HF	clean reaction with formation of fluoride accompanied by gas evolution, both are mild fluorinating reagents readily available in anhydrous form
oxidative fluorination	XeF_2/HF	successful for the preparation of late transition metal carbonyl/phosphine fluorides, has advantage that fluorination occurs at lower temperatures than protonation of clusters, fluorination accompanied by metal oxidation
C−F bond activation		restricted mainly to compounds of W(II) and Pt(II)coordinated by Schiff base ligands having fluorinated substituents
decomposition of weakly coordinated anions	$Cp_2Ti(AsF_6)_2$	usually affords fluoride in poor yield
conproportionation	metal fluoride + organometallic	insolubility of fluoride starting material can be a problem
modification	organometallic fluoride	modify an existing organometallic fluoride

by group number with comprehensive reference to the original literature. Within each group the metals are listed in decreasing oxidation state. For each subsection of sections IV−X, the topics have been arranged in the following sequence; synthesis, characterization, fluoro−chloro, fluoro−oxo, fluoro−nitro, fluoro−alkyl compounds, complexes of weakly coordinated fluorinated anions, and recent reports of C−F bond activation. Slight variations will necessarily be found for example where uses of the fluorides in synthesis and catalysis are included.

In the final section, conclusions regarding the reactivity patterns exhibited by organometallic fluorides in comparison with the heavier halides are made. Tables 12 and 13 represent an up to date summary of terminal and bridging M−F bond distance ranges, and also related bond distances in complexes of weakly coordinating anions. Organometallic fluorides have found novel applications in both synthesis and catalysis, and these are summarized in Table 14.

Ligands such as the bulky teflate group ($OTeF_5^-$), having electronegativity values comparable with that of fluorine, are considered pseudofluorides.[8,9] Pseudofluorides are now well-established as ligands in main group and high oxidation state transition metal chemistry and are not dealt with here. Carbon−fluorine−metal bridges are relatively uncommon in organometallic systems and are only briefly mentioned with some examples. A selective representation of such "organometallic fluorides" includes $Ru(SC_6F_4\text{-}\mu\text{-}F)(SC_6F_5)(PPhMe_2)$,[10] $\{2,4,6\text{-}(CF_3)_3C_6H_2\}Li$,[11] $[Cp^*ThMe][B(C_6F_5)_4]$,[12] $Cp(acac)Zr(\mu\text{-}Cp)B(C_6F_5)_3$,[13] and $Cp^*_2ZrOB(C_6F_5)_3$.[14] In these compounds one perfluoro group orients itself so that a fluorine approaches the metal. This contact is typically longer than any metal−fluorine bond distance. The associated C−F bond is lengthened (~0.05 Å) over the average of the remaining C−F bond distances. This is consistent with C−F−M bridge formation. Very often low-temperature ^{19}F NMR spectroscopy confirms the static structure established in the solid state.

III. Fluorinating Reagents and Procedures

A general guide to synthetic strategies for the preparation of organometallic fluorides with representative examples is given in Table 1. This table is in no way intended to be comprehensive, and those searching for a particular fluorinating procedure should consult the detailed tables listing organometallic fluorides, starting material, and fluorinating reagent which are presented throughout the text. A major factor contributing to the scarcity of organometallic fluoro compounds in the past has been the lack of convenient ways of introducing the ligand.[3] This problem has been ameliorated to a large extent by the introduction of several new fluorinating reagents (see Tables 2−11). While some fluorinating procedures have been discovered with a degree of serendipity, it is now possible to approach the preparation of new fluorides in a rational manner.

Many starting materials used in the preparation of organometallic fluorides are readily available and conveniently handled as the chloro or bromo derivatives. Consequently halide metathesis, using alkali metal fluorides (sodium and potassium mainly), has proven to be one of the most reliable routes to the title compounds. A common problem encountered with this method, however, involves separation of the fluorinating reagent from the product. Products obtained often contain significant amounts of the fluorinating reagent. This feature has been elegantly demonstrated in the reaction of Cp^*TiF_3 with sodium and potassium fluorides leading to adducts, $[\{(Cp^*TiF_3)_4F_2\}M']M'$ (M′ = Na, K), of crown ether-type (section V.A.2).[15] Thus use of excess fluorinating reagent is wisely avoided in this method. Within the class of halide metathesis reagents trimethyltin fluoride deserves special mention. Trimethyltin fluoride has proven to be a versatile fluorinating reagent particularly in the conversion of group 4−6[16] and also main group chlorides[17] to the corresponding fluorides (Scheme 1). Trimethyltin chloride generated during the metathesis is readily removed in vacuo and may be recycled using sodium or potassium fluoride. The insolubility of trimethyltin fluoride, in combination with the high volatility and solubility of trimethyltin chloride makes this an "ideal fluorinating system".[16] Halide metathesis proceeds equally well in the presence of oxygen-[16,18,19] and nitrogen[20]-containing ligands. In addition trimethyltin fluoride has proven effective in the fluorination of transition metal hydride [21] and alkyl derivatives.[22]

Scheme 1

$$\mathrm{Cp'_mMCl_n + n\,Me_3SnF \rightarrow Cp'_mMF_n + n\,Me_3SnCl}$$

$$\mathrm{Cp'_mMCl_n(OR) + n\,Me_3SnF \rightarrow Cp'_mMF_n(OR) + n\,Me_3SnCl}$$

$$\mathrm{Cp'_mMCl_n(NR_2) + n\,Me_3SnF \rightarrow Cp'_mMF_n(NR_2) + n\,Me_3SnCl}$$

$$\mathrm{Me_3SnCl + M'F \rightarrow Me_3SnF + M'Cl}$$

$$\mathrm{Cp'_mMR_n + n\,Me_3SnF \rightarrow Cp'_mMF_n + n\,Me_3SnR}$$

R = alkyl, M = Ti, Zr, Hf, Nb, Ta, W

Polar fluorine-containing reagents display a pronounced tendency to form strong hydrogen bonds. The tenacity with which fluoride reagents hold onto water and other protic compounds often makes the preparation of "clean" reagents difficult. For example, silver fluoride prepared from aqueous solution always contains some water, even when exhaustively heated and dried over phosphorus pentoxide.[23] Such fluorinating reagents invariably lead to transition metal complexes containing hydroxide or bifluoride instead of the desired fluoride.[24] The propensity of fluoride systems to etch glassware often heralds further complications. Use of Pyrex glass vessels can lead to contamination by fluoroboric acids.[23]

Chemists are continuously searching for highly nucleophilic sources of fluoride, often termed "naked fluoride". These procedures typically involve the synthesis of fluoride with elaborate counterions.[25] Amine hydrofluoride salts, such as tmpy·2HF[22] and Olah's reagent[26] are mild fluorine-transfer reagents and do not etch glassware. In the latter two cases anhydrous reagents are conveniently obtained via distillation or sublimation.

The preparation of early and late transition metal fluorides pose very different challenges for the synthetic chemist. Doherty and Hoffman have described the variety of low-valent organometallic fluorides containing carbonyl ligands reported prior to 1991.[3] Facile displacement of weakly coordinating ligands by fluoride has proven to be a particularly promising route to the latter class of compound. In several systems net metathesis of fluoride for chloride is accomplished cleanly and in good yield via abstraction of chloride using AgOTf or $AgBF_4$, followed by addition of fluoride from organic solvent-soluble sources such as [PPN]F,[3] $[NR_4]F$,[25] or TAS-F.[3]

The challenges of working with elemental fluorine, hydrogen fluoride, and metal fluorides are readily surmounted by available experimental designs. Exerting control over the reactivity of fluorine is still a problem, however, in the preparation of organometallic fluorides.[3] Hydrogen fluoride, a common fluorinating reagent, also easily cleaves many carbon−metal bonds.[27] Another experimental approach uses oxidative addition of fluorine-containing reagents such as formyl fluoride,[28] xenon difluoride (section IX.A), and sulfur tetrafluoride.[29]

In the past, low solubilities of organometallic fluorides in most common solvents have rendered them of limited practical use. Solubility restrictions of early transition metal fluorides have been overcome to a large extent by incorporating bulky organic substituents as ligands leading to enhanced solubility properties. The propensity of fluorine to act as a bridging ligand is also reduced by the presence of bulky organic groups.[6] Readily available chlorinated solvents such as dichloromethane have proven satisfactory when reactions are carried out at room temperature. Long reaction times at elevated temperatures often lead to chloride formation.[30]

The choice of solvent for reactions of carbonyl clusters with fluorinating reagents is restricted. Typically the solvent must be able to withstand strongly oxidizing reaction conditions and simultaneously facilitate solubility of the reactants. Again a considerable number of reactions have been successfully conducted in dichloromethane. At low temperatures anhydrous HF/XeF_2 provides an exceptional solvent/fluorinating system. Anhydrous HF serves first as a suitable solvent[31] for clusters such as $Os_3(CO)_{12}$. Secondly it acts as a catalyst in the fluorination reaction with XeF_2.[32] In HF solutions, XeF_2 forms the adduct $F{-}Xe^+\ F{\cdots}H{-}F^-$ which has been described as an "aggressive" fluorinating reagent.[33] Fluorination occurs at much lower temperatures than the reaction of HF with the carbonyl cluster. At higher temperatures protonation of $Os_3(CO)_{12}$ in anhydrous HF leads to $[HOs_3(CO)_{12}]^+$.[34] Carbonyl clusters often exhibit complex reactivity patterns with XeF_2. The isolation of carbonyl fluoride products with higher carbonyl-to-metal ratios than in the starting material is one such complicating feature. During metal−metal bond cleavage carbonyl scrambling occurs around the metal centers. Such scrambling inevitably contributes to the large number of products isolated in reactions of metal carbonyls with XeF_2/HF (section IX.A).

Organometallic complexes containing a fluorine ligand are of special interest since M−F bonds play a key role in the cleavage and formation of C−F bonds, i.e., C−F bond activation. Current global concern to help halt the depletion of stratospheric ozone has led to the search for CFC alternatives. These will almost certainly be fluorocarbons. C−F bond activation is of fundamental importance in the functionalization of these fluorocarbons. Considerable progress toward this goal has been made utilizing transition metal complexes in the activation of C−F bonds in unsaturated and aromatic fluorocarbons. It is only recently that reports concerning saturated fluorocarbons appeared.[35] These reactions generally proceed in low yield and under rather harsh conditions. There have been a few reports of reactions of transition metal species involving C−F bond activation which proceed under mild conditions and in high yields[36] and of homogeneous metal-catalyzed C−F bond activation.[37]

One of the central objectives of organometallic chemistry is the preparation of transition metal complexes with open coordination sites or easily displaced ligands.[4,38] Such molecules facilitate the first step of any catalytic cycle which involves substrate coordination at the metal. The role of cocatalysts in group 4 metallocene-mediated catalysis is generally accepted to be facilitating the formation of electron deficient/coordinatively unsaturated cationic metallocene alkyl species which are the active catalysts. Methylaluminoxane (MAO), for instance, is one of the most effective cocatalysts in olefin polymerization.[39] Despite intensive research in this area MAO has not been fully characterized and has the undesirable habit of exhibiting variable composition.[40] In addressing this problem, several workers have attempted to prepare reactive cationic species with various "noncoordinating anions", including several fluorinated anions.[4,41] In many instances organometallic fluorides have been the unexpected products of fluoride abstraction in the decomposition of complexes of fluorinated anions.

IV. Group 3

Organometallic fluorides of the group 3 metals are restricted to three reports concerning organoscandium fluorides. Two of these deal with C−F bond activation mediated by permethylscandocene complexes and are included here for the sake of completeness.

Scandium trifluoride reacts with Cp_2Mg or CpNa to give mixtures of the very water-sensitive compounds Cp_2ScF (**1**) and Cp_3Sc in 1:2 or 1:1 ratios, respectively. Toluene-insoluble Cp_3Sc is readily separated from toluene soluble **1**. Compound **1** is trimeric in the solid state with a planar $(Sc-F)_3$ ring ($Sc-F_{av}$, 2.05 Å) (Figure 1). The ^{19}F NMR spectrum of **1** recorded at 200 K in toluene exhibits a sharp resonance at −66.8 ppm, which collapses to a broad envelope of weak intensity at room temperature. An equilibrium involving **1** and monomeric or other oligomeric species at ambient temperature best explains this behavior.[42]

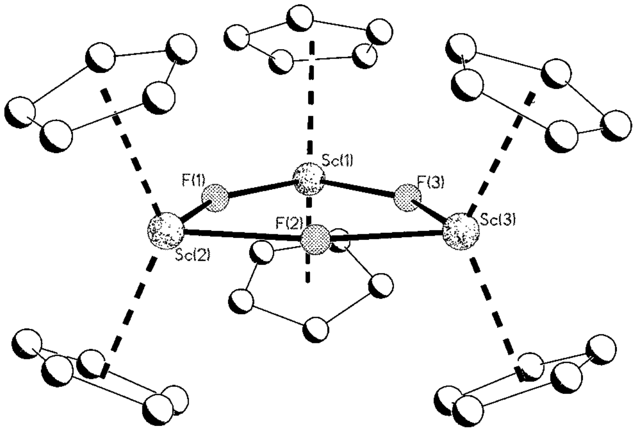


Figure 1. Structure of Cp_2ScF (**1**). (Reprinted from ref 42. Copyright 1985 American Chemical Society.)

More recently, C−F bond activation has been observed in reactions of permethylscandocene complexes with vinyl fluoride. An equimolar mixture of permethylscandocene fluoride Cp^*_2ScF (**2**) and Cp^*_2ScEt is obtained on reaction of vinyl fluoride with permethylscandocene hydride (eq 1). Alternatively, reaction of vinyl fluoride with Cp^*_2ScMe at 298 K leads to **2** and propene (eq 2).[43]

$$Cp^*_2ScH + FHC{=}CH_2 \rightarrow \underset{\mathbf{2}}{Cp^*_2ScF} + Cp^*_2ScEt \qquad (1)$$

$$Cp^*_2ScMe + FHC{=}CH_2 \rightarrow \underset{\mathbf{2}}{Cp^*_2ScF} + MeHC{=}CH_2 \qquad (2)$$

V. Group 4

Certainly one of the most extensively studied and readily prepared classes of organometallic fluorides is that of the group 4 metals. In the past, syntheses of group 4 fluorides were typically based on halogen exchange with alkali metal fluorides. Currently trimethyltin fluoride is proving to be an exceptionally versatile reagent for the preparation of group 4 in particular, and group 5 and 6 fluorides (Scheme 1).[16]

As group 4 metallocenes have received most attention in recent years they are documented first, followed by monocyclopentadienyl compounds. An artificial classification based on the number of cyclopentadienyl ligands is possible here since there are no non-cyclopentadienyl-substituted organotitanium, zirconium, or hafnium fluorides. Incorporation of the Cp* ligand has provided exceptionally stable and highly crystalline complexes in comparison with Cp analogues. Similarities in the chemistries of organozirconium and hafnium fluorides warrant their inclusion in a single section. Organotitanium(III) fluoride chemistry is currently a well-established field (section V.B). Titanium(II) fluorides have not been reported. Similarily, zirconium/hafnium(III) and -(II) fluorides are not known and metal(IV) compounds are dealt with exclusively in section V.C. As in the case of the corresponding chlorides, group 4 metallocene difluorides are generally air-stable and monocyclopentadienyl compounds unstable.

Given the greater tendency of fluorine to bridge metal centers, in comparison with the other halides, it is not possible to make direct structural comparisons of organometallic group 4 fluorides with related systems. For example Cp^*ZrCl_3 readily forms the bis-THF adduct $Cp^*ZrCl_3{\cdot}2THF$ and is dimeric in the solid state.[44] Cp^*ZrF_3 on the other hand is tetrameric in the solid and in solution and a THF adduct has not been reported.[16] $(MeCp)TiF_3$ forms a THF-bridged dimer,[16] Cp^*TiF_3, a dimer, and $(EtCp^*)TiF_3$, a tetramer.[45] Clearly a dependence on cyclopentadienyl ring subtitution introduces an even greater number of structural possibilities in these compounds.

Two reports regarding rather unusual compounds have appeared. $C_5H_4TiF_2$ has been postulated as a yellow, ether-insoluble, polymer containing cyclopentadienylene groups with η^5 and η^1 bonds to titanium[46] and a compound of composition $C_5H_5Br_4TiF_2$.[47] The authenticity of these compounds is doubtful.[48]

A. Titanium(IV)

1. Titanium(IV) Metallocenes

For convenient evaluation of the various synthetic routes to titanocene difluorides, a list of starting materials, fluorinating reagents, and product yields is presented in Table 2. Preparation of the first member of the family of dicyclopentadienyltitanium difluorides Cp_2TiF_2 (**3**) was reported in 1954. On heating a solution of Cp_2TiBr_2 in 12N HF, Wilkinson and Birmingham isolated **3** in 50% yield.[49] In the

Table 2. Titanocene Difluorides

no.	compound	starting material/reagent (% yield)	ref
3	Cp_2TiF_2	Cp_2TiCl_2/Me_3SnF (98)	16
		$Cp_2TiCl_2/AgBF_4$ (80)	52
		NaF (60)	55,56
		$BF_3 \cdot OEt_2$	69
		NH_4F (100)	50i
		Cp_2TiBr_2/12 N HF (50)	49
		$(Cp_2TiCl)_2O/HF$ (100)	50c
4	$(MeCp)_2TiF_2$	$(MeCp)_2TiCl_2/Me_3SnF$ (90)	51
		$(MeCp)_2TiCl_2/NH_4F_{(aq)}$ (95)	50i
		$(MeCp)_2TiCl_2/NaF_{(aq)}$ (52)	55,56
		$[(MeCp)_2TiCl]_2O/HF_{(aq)}$	50j
5	$(EtCp)_2TiF_2$	$(EtCp)_2TiCl_2/(NH_4)_2SiF_6$	60
		$(EtCp)_2Ti(OPh)_2/HF_{(aq)}$	50h
6	$(PrCp)_2TiF_2$	$(PrCp)_2TiCl_2/(NH_4)_2SiF_6$ $(PrCp)_2Ti(OPh)_2/HF_{(aq)}$	60
		$(PrCp)_2TiCl_2/BF_3 \cdot OEt_2$ (90)	50h
		$(PrCp)_2TiCl_2/NH_4F$ (90)	69
7	$(BuCp)_2TiF_2$	$(BuCp)_2TiCl_2/(NH_4)_2SiF_6$	60
8	$(allylCp)_2TiF_2$	$(allylCp)_2Ti(OPh)_2/HF_{(aq)}$	50k
9	$(3\text{-methylcyclopentyl})_2TiF_2$	$(3\text{-methylcyclopentyl})_2Ti(OPh)_2/HF_{(aq)}$	50l
10	$Cp^*_2TiF_2$	$Cp^*_2TiCl_2/Me_3SnF$ (70)	16
11	$(Me_3SiCp)_2TiF_2$	$(Me_3SiCp)_2TiCl_2/Me_3SnF$ (80)	51
		AgF (83)	50d
12	$[(Me_3Si)MeCp]_2TiF_2$	$[(Me_3Si)MeCp]_2TiCl_2/Me_3SnF$ (95)	51
		AgF (80)	50d
13	$[(Me_3Si)_2Cp]_2TiF_2$	$[(Me_3Si)_2Cp]_2TiCl_2/Me_3SnF$ (81)	51
		$AgBF_4$ (57), X-ray	41
14	$(MeCp)CpTiF_2$	$(MeCp)CpTiCl_2/(NH_4)_2SiF_6$	60
		$(MeCp)CpTiCl_2/BF_3 \cdot OEt_2$	50g
15	$(EtCp)CpTiF_2$	$(EtCp)CpTiCl_2/(NH_4)_2SiF_6$	60
16	$(PrCp)CpTiF_2$	$(PrCp)CpTiCl_2/(NH_4)_2SiF_6$	60
17	$(BuCp)CpTiF_2$	$(BuCp)CpTiCl_2/(NH_4)_2SiF_6$	60
18	$(n\text{-}C_5H_{11}Cp)CpTiF_2$	$(n\text{-}C_5H_{11}Cp)CpTiCl_2/(NH_4)_2SiF_6$	60
19	$[(Me_3Si)_2Cp]CpTiF_2$	$[(Me_3Si)_2Cp]CpTiCl_2/AgBF_4$ (57)	41
20	$[(Me_3Si)_2Cp](Me_3SiCp)TiF_2$	$[(Me_3Si)_2Cp](Me_3SiCp)TiCl_2/AgBF_4$ (57)	41
21	$[(Me_3Si)_3Cp]CpTiF_2$	$[(Me_3Si)_3Cp]CpTiCl_2/AgBF_4$ (57)	41
22	$[(Me_3Si)_3Cp](Me_3SiCp)TiF_2$	$[(Me_3Si)_3Cp](Me_3SiCp)TiCl_2/AgBF_4$ (57), X-ray	41
23	Cp^*CpTiF_2	$Cp^*CpTiCl_2$/NaF, MeOH	61
		NaF, H_2O	55
24	(S,S)-(EBTHI)TiF_2	(S,S)-(EBTHI)$TiCl_2$/CsF	65
25	$(Cp^*_2TiF)_2(\mu\text{-}OC_6H_4O)$	Cp^*_2TiF/OC_6H_4O	18
26	$[(Me_3SiCp)_2TiF]_2(\mu\text{-}OC_6H_4O)$	$(Me_3SiCp)_2TiF/OC_6H_4O$	18
27	$[(MeCp)TiF(NMes)]_2$	$(MeCp)_2TiF_2/[MeAl(NMes)]_4$ (30)	20
28	$Cp_2TiF(Me)$	Cp_2TiF_2/Cp_2TiMe_2	73
29	$Cp_2TiF(Ph)$	Cp_2TiF_2/Cp_2TiPh_2	73
31	$(MeCp)_2TiF[OS(O)Bu]$	$(MeCp)_2TiF(Bu)/SO_2$	74
32	$Cp^*_2TiF(CH{=}CH_2)$	$Cp^*_2TiCl(CH{=}CH_2)$/NaF	75
		$Cp^*_2TiF_2/Li(CH{=}CH_2)$	75
33	$Cp_2Ti(AsF_6)_2$	Cp_2TiF_2/AsF_5	77
		$Cp_2TiCl_2/AgAsF_6$	78
34	$Cp_2Ti(SbF_6)_2$	Cp_2TiF_2/SbF_5	77
		$Cp_2TiCl_2/AgSbF_6$	78
35	$Cp_2Ti(C_6F_5)F$	$Cp_2Ti(C_6F_5)_2$/heat	80
		$Cp_2Ti(C_6F_5)_2/HF_{(aq)}$	81

intervening time a plethora of alternative preparative procedures has appeared.[50] Me_3SnF has proven to be an effective fluorinating reagent for the preparation of titanocene difluorides (eq 3).[16] Subtle solvent

$$Cp'_2TiCl_2 \quad + \quad 2\ Me_3SnF \quad \rightarrow \quad Cp'_2TiF_2 \quad + \quad 2\ Me_3SnCl \qquad (3)$$

dependent features of this fluorinating procedure have been highlighted.[51] In the preparation of **3** with $AgBF_4$ use of a slight excess of reagent enhances both yield and product purity.[52]

Compound **3** is more soluble in water than the other halides and may be purified by recrystallization from 3N HF or by sublimation in vacuo at 383 K. Low-frequency IR, Raman[53,54] and ^1H, ^{19}F, and ^{13}C NMR[55,56] spectra of **3** have been recorded. Ti−F stretching vibrations for **3** appear at 565 and 540 cm^{-1} while other metal−halide stretching frequencies are typically below 400 cm^{-1}.[53,54] Substitution of the cyclopentadienyl ring protons with methyl or trimethylsilyl groups has minimal effect on the position of the Ti−F IR absorptions.[51] $^{19}F-^1H$ coupling gives rise to a triplet in the ^1H NMR spectrum of **3**. Zirconocene and hafnocene difluorides do not exhibit similar interactions due to increased metal−Cp ring distances.[55,56] He I and He II photoelectron spectra have been reported for **3**.[57] Compound **3** has been screened for biological use.[58]

Effects of cyclopentadienyl ring substitution on metallocene reactivity[59] have given impetus to the development and study of substituted titanocene difluorides **4**−**23**. Various mixed-ring systems $(R_nCp)CpTiF_2$ and $(R_nCp)_2TiF_2$ (n = 1, 2) have been prepared (eq 4) and are listed in Table 2.[60] Incorporation

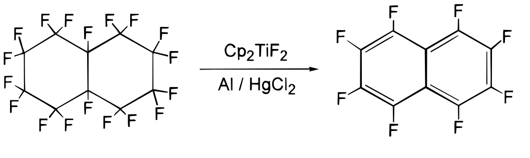
$$(RCp)CpTiCl_2 + (NH_4)_2SiF_6 \rightarrow (RCp)CpTiF_2 + 2\,NH_4Cl + SiF_4 \qquad (4)$$

of bulky lipophilic trimethylsilyl substituents on the cyclopentadienyl ring has been employed, albeit unsuccessfully, in an effort to stabilize cationic species having tetrafluoroborate anions. Steric effects of the bulky groups enhance the kinetic stability of cationic complexes with tetrafluoroborate counterions, although not sufficiently to prevent slow decomposition to the titanocene difluorides. Decomposition involving fluoride abstraction leads to the respective titanocene difluorides in moderate yields. Curiously, titanocene dichlorides with three or more trimethylsilyl substituents are sufficiently crowded to prevent reaction with NaF. More highly substituted titanocenes $[(Me_3Si)_3Cp][(Me_3Si)_2Cp]TiF_2$ were not isolated using $AgBF_4$. Dynamic NMR techniques have been used to estimate the rotational barrier of the cyclopentadienyl rings in **13** to be 8.9 kcal/mol.[41]

Solid-state structures of $[(Me_3Si)_2Cp]_2TiF_2$ (**13**) and $[(Me_3Si)_3Cp](Me_3SiCp)TiF_2$ (**20**) ($Ti-F_{av}$, 1.83 Å for **13** and **20**) and the related zirconocene difluoride **83** show the preferred cyclopentadienyl geometry to be that in which bulky groups adopt the sterically least demanding orientation. In **13**, **20**, and **85** the smaller fluoride leads to diminished steric interactions in comparison with the related dichloride systems.[41]

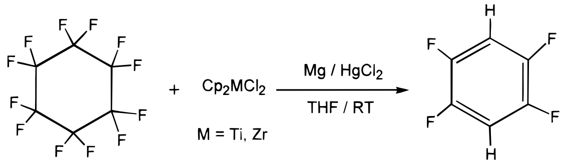
In general replacement of Cp by Cp* in mono- and dicylopentadienyl complexes of transition metals results in significant changes in chemical reactivity, stability, and sensitivity to moisture. Gassman and co-workers have shown that depending on the degree of ring substitution, ^{49}Ti NMR chemical shift values for **3**, $CpCp^*TiF_2$ (**23**), and $Cp^*_2TiF_2$ (**10**) show an inverse relationship to the $Ti(^2P_{1/2})$ binding energies of the same compounds as measured by ESCA. A comparable systematic decrease in binding energies occurs on complete methyl substitution of titanocene dichlorides and dibromides. Substitution of one Cp* for Cp in **3** results in a downfield shift in the ^{49}Ti NMR resonance of ~148 ppm. Substitution of two Cp* for Cp groups results in a downfield shift of ~312 ppm and has an electronic effect approaching that of a one-electron reduction of the complexed metal.[61,62]

Recently, Richmond and co-workers have shown that group 4 metallocenes mediate electron transfer from readily available terminal reductants such as aluminum and magnesium metals. Treatment of perfluorodecalin at room temperature with Cp_2TiF_2 (**3**) in the presence of excess aluminum results in catalytic production of perfluoronaphthalene (eq 5).



(5)

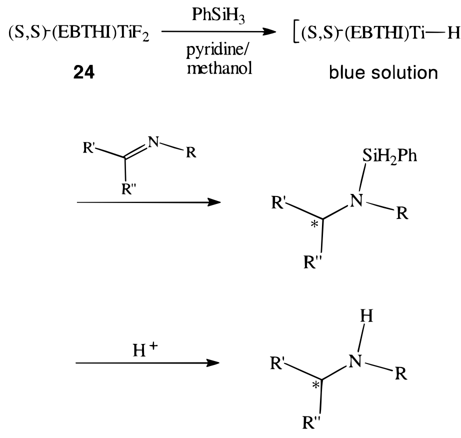
This process has been extended to other ring systems such as perfluoro(tetradecahydrophenanthrene). Similarly Cp_2ZrCl_2 and Cp_2ZrF_2 in the presence of Mg/$HgCl_2$ are equally effective for this transformation. A mild stepwise hydrogenation of aromatic carbon–fluorine bonds occurs on stirring Cp_2MCl_2 (M = Ti, Zr) and perfluorocyclohexane in the presence of activated magnesium accompanied by formation of 1,2,4,5-tetrafluorobenzene (eq 6). Richmond also demonstrated that low-valent zirconocene and titanocene reagents stoichiometrically effect intermolecular C–F activation of saturated perfluorocarbons.[63] Interestingly, it has been found that aluminum- and magnesium-mediated reductions of Cp'_2TiF_2 and $Cp'TiF_3$ compounds lead to fluorine-bridged di- and bimetallic titanium(III) systems (section V.B.2). These fluorine-bridged compounds may well be catalyst precursors or the active catalysts in the above processes.



(6)

Buchwald and co-workers have made ingenious use of organotitanium fluorides in a new highly enantioselective method for the catalytic hydrosilylation of imines. This method features an unprecedented catalyst activation step, involving metal reduction and conversion of a Ti–F bond to a Ti–H bond. Buchwald demonstrated that the addition of phenylsilane to a yellow solution of **3** affords a dark blue solution which is catalytically active for the hydrosilylation of imines (Scheme 2).[64] By using a similar procedure hydrosilylation of prochiral imines, with (*S*,*S*)-(EBTHI)TiF_2 (**24**)[65] (EBTHI, ethylenebis(η^5-tetrahydroindenyl)) as precatalyst, gives conversion of imines to amines under mild conditions. This procedure operates with remarkably high substrate: catalyst ratios and a broad range of substrates. The high Si–F bond energy is considered to be the driving force for Ti–F bond cleavage.[64] On formation of the active catalyst the reaction probably proceeds by a catalytic cycle similar to that for the titanocene-catalyzed hydrogenation of imines.[66]

Scheme 2



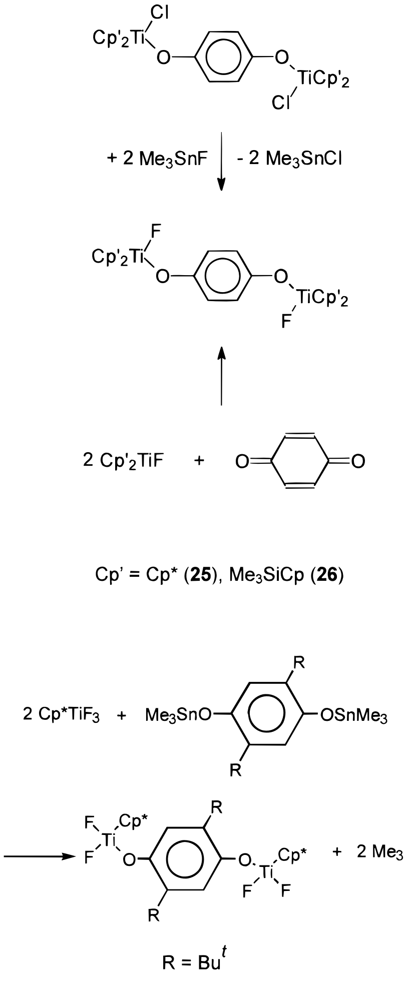
Surprisingly, $CpTiCl_3$ is the main product isolated from the reaction of Cp_2TiCl_2 with ClF. Trace amounts of $CpTiCl_2F$ are also detected in the mass spectrum of the product. No evidence for Cp_2TiF_2 or Cp_2TiFCl formation is found. It was suggested that

Cl_2 produced by fluorine−chlorine exchange reacts readily with Cp_2TiFCl to form $CpTiCl_3$.[67] Reactions of Cp_2TiCl_2 with 1 equiv of Me_3SnF[68] or $AgBF_4$[52] in toluene or acetonitrile yield mixtures of the dichloride Cp_2TiCl_2, difluoride Cp_2TiF_2 (**3**), and the mixed fluoro−chloro titanocene Cp_2TiFCl as major product. A ^1H NMR study of an equimolar mixture of Cp_2TiCl_2 and Cp_2TiF_2 shows that an equilibrium distribution is established (eq 7). Similar observations have been reported for the related $Cp_2TiBrCl$ system.[69] This is in contrast to the relative ease with which fluoro−chloro zirconocenes and hafnocenes are prepared using these reagents.[70] Interestingly, the reaction of Cp_2TiCl_2 with cobaltocenium fluoride affords Cp_2TiFCl and **3** in a stepwise fashion in quantitative spectroscopic yields.[71]

$$Cp_2TiCl_2 + Cp_2TiF_2 \rightleftharpoons 2\ Cp_2TiClF \qquad (7)$$

Hydroquinone-bridged dinuclear fluorides **25** and **26** may be prepared by three routes: (i) halide metathesis of the corresponding chloride with Me_3SnF, (ii) oxidative reaction of an organotitanium(III) compound with a benzoquinone, and (iii) straightforward reaction of the cyclopentadienyltitanium(IV) fluoride with a substituted *O,O′*-bis(trimethylstannyl)-1,4-hydroquinone (Scheme 3). Formation of mono-bridged products is independent of the steric requirements of the quinonide ring substituents (R). Compounds **25** and **26** are probably isostructural with the corresponding chlorides.[18] The light-yellow oxo−fluoride compound $(Cp_2TiF)_2O$ was mentioned briefly (mp 493 K). In general compounds of the formula $(Cp_2TiX)_2O$ (X = F, Cl, Br, I) are not sufficiently soluble to permit complete characterization.[72]

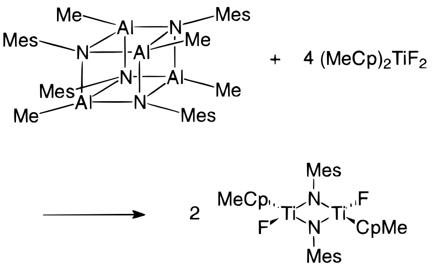
Scheme 3



Cp' = Cp* (**25**), Me_3SiCp (**26**)

R = Bu^t

Iminoalanes have been used as imino group-transfer reagents. The high affinity of aluminum for fluorine makes this a potentially ideal procedure. Transamination of $(MeCp)_2TiF_2$ (**4**) with $[MeAl(NMes)]_4$ affords $[(MeCp)TiF(NMes)]_2$ (**27**) in 30% yield (eq 8). A mixture of products is obtained from the corresponding Cp^*TiF_3 reaction.[20]



(8)

27

Dismutation reactions of Cp_2TiF_2 and Cp_2TiR_2 (R = Me, Ph) yield Cp_2TiFR (R = Me (**28**), Ph (**29**)). Kinetic and NMR studies of these reactions have been carried out and show that variation in rate with R group is small. Decomposition of Cp_2TiR_2 competes with the ligand exchange process.[73] Two patents describe the insertion of SO_2 into the Ti−C σ bond of $(MeCp)_2TiF(Bu)$ (**30**) to give the sulfinate compound $(MeCp)_2TiF[OS(O)(Bu)]$ (**31**).[74] Vinylidenetitanocene $Cp^*_2TiF(CH{=}CH_2)$ (**32**) has been prepared in good yield by halide metathesis (eq 9) and via reaction of **10** with vinyllithium (eq 10). In the solid state **32** shows $Ti{-}C(sp^2)$ bond distances similar to related alkenyltitanium compounds (2.10 Å) and has a Ti−F terminal distance of 1.85 Å.[75]

$$Cp^*_2TiCl(CH{=}CH_2) + NaF \rightarrow \underset{\mathbf{32}}{Cp^*_2TiF(CH{=}CH_2)} + NaCl \qquad (9)$$

$$\underset{\mathbf{10}}{Cp^*_2TiF_2} + Li(CH{=}CH_2) \rightarrow \underset{\mathbf{32}}{Cp^*_2TiF(CH{=}CH_2)} + LiF \qquad (10)$$

Lewis acid adducts of Cp_2TiF_2 of the type $Cp_2Ti(F{\cdot}L)_2$ (L = BF_3, PF_5) are unstable and do not exist in the solid state. On the basis of conductivity measurements they may be associated in dichloromethane solution.[76] $Cp_2Ti(EF_6)_2$ (E = As (**33**), Sb (**34**)) compounds have been prepared (eqs 11 and 12).[77,78]

$$Cp_2TiF_2 + 2\ EF_5 \rightarrow Cp_2Ti(EF_6)_2 \qquad (11)$$

$$Cp_2TiCl_2 + 2\ AgEF_6 \rightarrow Cp_2Ti(EF_6)_2 + 2\ AgCl \qquad (12)$$

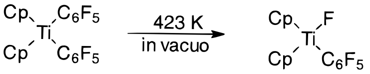
E = As (**33**), Sb (**34**)

Compounds **33** and **34** are isostructural.[79] The increase in Ti−F bond distance for **33** is reflected in a lowering of the ν_{Ti-F} vibration by ~30 cm^{-1}. Compounds **33** and **34** appear to be thermodynamically unstable with respect to decomposition processes involving formation of transition metal−

fluorine bonds. Compound **33** reacts with acetonitrile, but not with CF_3CN, to yield the cationic titanocene derivative $[Cp_2Ti(MeCN)_3][AsF_6]_2$ quantitatively (eq 13). In this case the Cp_2Ti^{2+} fragment attains an 18-electron configuration by coordinating three acetonitriles.[77]

$$Cp_2Ti(AsF_6)_2 + 3\,MeCN \rightarrow [Cp_2Ti(MeCN)_3][AsF_6]_2 \quad (13)$$

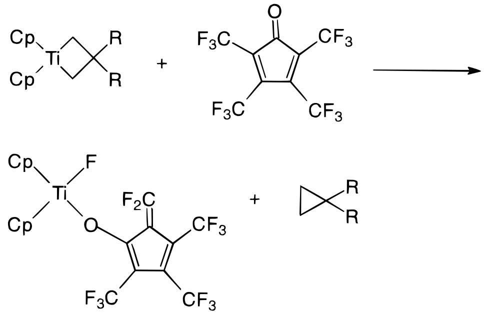
Thermal decomposition (~423 K) of $Cp_2Ti(C_6F_5)_2$ affords $Cp_2Ti(C_6F_5)F$ (**35**) in low yield (eq 14).[80]



(14)

35

Alternatively **35** is prepared from $Cp_2Ti(C_6F_5)_2$ on treatment with HF.[81] Compound **35** melts at 513 K and is purified by sublimation in vacuo. Later, Burk et al. showed that tetrakis(trifluoromethyl)cyclopentadienone undergoes rapid reaction at 253 K with bis(cyclopentadienyl)titanacyclobutanes to give the organotitanium dienone–fluoride product **36** in 80% yield (eq 15). This is in contrast with the expected methylene transfer to the dienone. A mechanism involving activation of an sp^3 C–F bond via an intermediate titanocene–dienone complex has been postulated for this transformation. The structure of **36** has been confirmed by X-ray crystallography (Ti–F, 1.84 Å).[82]



(15)

36

2. Titanium(IV) Monocyclopentadienyl

A list of monocyclopentadienyltitanium(IV) fluorides and fluoride derivatives is presented in Table 3. $CpTiF_3$ (**37**) is prepared from the corresponding trichloride using Me_3SnF[16] or alternatively from $CpTi(OEt)_3$ via metathesis with MeC(O)F (eqs 16 and 17).[28] In the latter case, scrambling reactions of **37**

$$CpTiCl_3 + 3\,Me_3SnF \rightarrow \underset{\mathbf{37}}{CpTiF_3} + 3\,Me_3SnCl \quad (16)$$

$$CpTi(OEt)_3 + 3\,MeC(O)F \rightarrow \underset{\mathbf{37}}{CpTiF_3} + 3\,MeCO_2Et \quad (17)$$

with the starting material led to partially fluorinated species $CpTiF(OEt)_2$ and $CpTiF_2(OEt)$.[28] Arsenic

Table 3. Monocyclopentadienyltitanium Fluorides

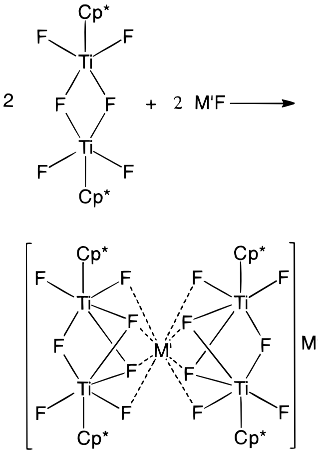
no.	compound	starting material/reagent (yield %)	ref
37	$CpTiF_3$	$CpTiCl_3/Me_3SnF$ (95)	16
		$CpTi(OEt)_3/MeCOF$ (77)	28
38	$(MeCp)TiF_3$	$(MeCp)TiCl_3/Me_3SnF$ (90), X-ray	16
39	$(Me_3SiCp)TiF_3$	$(Me_3SiCp)TiCl_3/Me_3SnF$ (81)	51
40	$[(Me_3Si)MeCp]TiF_3$	$[(Me_3Si)MeCp]TiCl_3/Me_3SnF$ (80)	51
41	$[(Me_3Si)_2Cp]TiF_3$	$[(Me_3Si)_2Cp]TiCl_3/Me_3SnF$ (90)	51
42	$Cp*TiF_3{\cdot}2AsF_3$	$Cp*TiCl_3/AsF_3$, X-ray	45
43	$Cp*TiF_3$	$Cp*TiCl_3/Me_3SnF$ (92)	16
		42/vacuum	45
44	$(EtCp*)TiF_3$	$(EtCp*)TiCl_3/Me_3SnF$ (92)	45
45	$[\{(Cp*TiF_3)_4F_2\}Na]Na$	$Cp*TiF_3/NaF$	15
46	$[\{(Cp*TiF_3)_4F_2\}K]K$	$Cp*TiF_3/KF$	15
47	$(Cp*TiF_3)_4CaF_2$	$Cp*TiF_3/Me_3SnF + CaCl_2$	86
48	$(EtCp*TiF_3)_4CaF_2$	$EtCp*TiF_3/Me_3SnF + CaCl_2$	86
49	$Cp*TiFCl_2$	$Cp*TiMeCl_2/Me_3SnF$	22
50	$[Cp*Ti(\mu\text{-}O)F]_4$	$[Cp*Ti(\mu\text{-}O)Cl]_3/Me_3SnF$ (87)	16
		$Cp*TiF_3/O(SnBu_3)_2$ (91)	88
		$Cp*TiF_3/NH_2NH_2{\cdot}H_2O$	68
		$Cp*_2TiF/O_2$ air, X-ray	68
51	$[Cp*Ti(\mu\text{-}O)\{F(AlMe_3)\}]_4$	$[Cp*Ti(\mu\text{-}O)F]_4/AlMe_3$	90
52	$[Cp*TiF_2(\mu\text{-}O_2CCF_3)]_2$	$Cp*TiF_3/Me_3SiOCOCF_3$, X-ray	91
53	$[Cp*TiF_2(\mu\text{-}O_2CC_6F_5)]_2$	$Cp*TiF_3/Me_3SiOCOC_6F_5$, X-ray	91
54	$[CpTiF_2(\mu\text{-}O_2CCF_3)]_2$	$CpTiF_3/Me_3SiOCOCF_3$	91
55	$[Cp*TiF(O_2CCF_3)(\mu\text{-}O_2CCF_3)]_2$	$Cp*TiF_3/Me_3SiOCOCF_3$	91
56	$[Cp*TiF_2\{O{=}C(OEt)C(Ph){=}C(OEt)\text{-}O\}]_2$	$Cp*TiF_3/O{=}C(OEt)C(Ph){=}C(OEt)OLi$ (62), X-ray	45
57	$[Cp*TiF_2]_2[\mu\text{-}O(C_6H_2Bu^t_2\text{-}2,5)O]$	$Cp*TiF_3/(C_6H_2Bu^t_2\text{-}2,5)(OSnMe_3)_2$	18
58	$[Cp*TiF(OSiBu^t_2O)]_2$	$[Cp*TiCl_2(OSiBu^t_2OH)]/Me_3SnF$ (37), X-ray	19
59	$[(EtCp*)TiF(OSiBu^t_2O)]_2$	$[(EtCp*)TiCl_2(OSiBu^t_2OH)]/Me_3SnF$	19
60	$[(MeCp)TiF(OSiBu^t_2O)]_2$	$[(MeCp)TiCl(OSiBu^t_2O)]_2/Me_3SnF$ (81), X-ray	19
61	$[(MeCp)TiF(NPh)]_2$	$[(MeCp)TiCl(NPh)]_2/Me_3SnF$, py	20
62	$[(Me_3SiCp)TiF(NBu^t)]_2$	$[(Me_3SiCp)TiCl(NBu^t)]_2/Me_3SnF$, py	20
63	$[(EtCp*)TiF(NSnMe_3)]_2$	$(EtCp*)TiF_3/N(SnMe_3)_3$ X-ray	20
64	$[(MeCp)TiF(NSnMe_3)]_2$	$(MeCp)TiF_3/N(SnMe_3)_3$	20
65	$[(MeCp)TiF(NMes)]_2$	$(MeCp)_2TiF_2/(MeAlNMes)_4$	20
66	$Cp*TiF_2(NPPh_3)$	$Cp*TiF_3/Me_3SiNPPh_3$ (87), X-ray	45
67	$(Cp*TiF_2NPPh_2)_2C_2H_2$	$Cp*TiF_3/(Me_3SiNPPh_2)_2C_2H_2$ (77), X-ray	45
68	$Cp*TiF_2[(NSiMe_3)_2CC_6H_4OMe]$	$Cp*TiF_3/[(Me_3Si)_2N]_2CC_6H_4OMe$ (79), X-ray	45

trifluoride has also been used to convert Cp*TiCl$_3$ to the corresponding trifluoride Cp*TiF$_3$·2AsF$_3$ (**42**). Metathesis with AsF$_3$, gives the AsF$_3$ adduct **42** from which AsF$_3$ solvate is removed in vacuo, affording Cp*TiF$_3$ (**43**). (EtCp*)TiF$_3$ (**44**) has been obtained similarly.[45]

(MeCp)TiF$_3$ (**38**) forms a symmetrically bridged dimer (Ti−F$_{av}$, 2.03 Å) with one THF molecule coordinated through oxygen to both titanium atoms. Four remaining terminal fluorines (Ti−F$_{av}$, 1.82 Å) complete a distorted octahedral environment about titanium.[16] The AsF$_3$ adduct **42** is dimeric in the solid state with an equidistant Ti$_2$F$_2$ four-membered ring and a distorted trigonal-pyramidal geometry at titanium. The absence of any Ti−AsF$_3$ interaction in **42** shows a Lewis acidity that is much reduced over that of the parent halide. As a consequence of the greater steric requirements of the EtCp* group, **44** is tetrameric in the solid state with two five- and two six-coordinated titanium centers. Bridging (Ti−F, 2.00 and 2.02 Å **42**, 1.99−2.06 Å **44**) and terminal Ti−F bond distances (Ti−F$_{av}$, 1.83 Å **42** and **44**) are not significantly different for the two complexes. The appearance of singlets in the ^{19}F NMR spectra of **38**, **42**, and **44** indicate that the compounds are monomeric in solution.[45]

The IR spectra of CpTiX$_3$ compounds, including CpTiF$_3$, CpTiF$_2$(OEt), and CpTiF(OEt)$_2$, have been recorded and the ν_{Cp-Ti} band assigned.[83] Thermal deposition of **37** and other CpTi complexes on borosilicate glass heated above the decomposition point leads to titanium carbide coatings.[84] Interaction of CpMn(CO)(dppe) with **37** has been studied with the use of IR, UV, and ESR spectroscopy and conductivity measurements. No direct structural proposal was made but oxidation of manganese is assumed on the basis of the IR shift ($\Delta\nu_{CO} = 97$ cm^{-1}) of the carbonyl group to a higher wavenumber.[85]

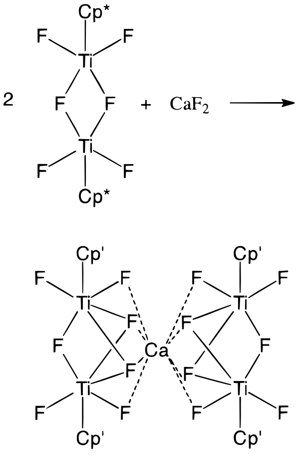
Formation of host−guest-type compounds occurs on treatment of Cp*TiF$_3$ (**43**) with sodium and potassium fluorides to give **45** and **46**, respectively (eq 18).[15] Selective ion exchange of the external sodium cation in **45** with Ph$_4$P$^+$ is facile. No reaction occurs with lithium and calcium fluoride which is probably a consequence of their high lattice energies and poor solubilities in organic solvents. Addition of cesium fluoride to solutions of **43** leads to an insoluble polymeric product.[15] Interestingly, when calcium fluoride is generated *in situ* in the presence of **43** and **44**, soluble neutral compounds **47** and **48** are formed respectively (eqs 19 and 20).[86] Compounds **47** and **48** are diamagnetic as opposed to similar paramagnetic compounds obtained via metal reduction (section V.B.2). These organometallic fluoride systems represent the first examples of molecular recognition by nucleophilic host molecules which are formed in a template-controlled manner.[15]



(18)

M' = Na (**45**), K (**46**)

$$2\ Me_3SnF + CaCl_2 \longrightarrow CaF_2 + 2\ Me_3SnCl \quad (19)$$



(20)

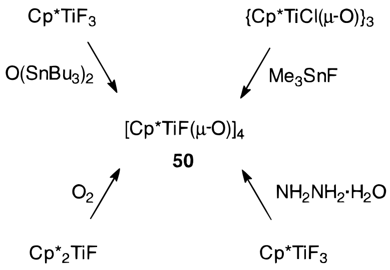
Cp' = Cp* (**47**), EtCp* (**48**)

Me$_3$SnF displays an unusual preference in the fluorination of Cp*TiMeCl$_2$. Methyl−fluoride exchange predominates over halide metathesis to give the mixed fluoro−chloro compound Cp*TiFCl$_2$ (**49**) (eq 21).[22] In contrast to the related reactions of Cp*ZrF$_3$ with Me$_3$SiX (X = Cl, Br), attempts to prepare mixed fluoro−halo compounds Cp*TiF$_n$X$_{3-n}$ (n = 1, 2) from the trifluoride Cp*TiF$_3$ and appropriate Me$_3$SiX reagent were not successful.[87]

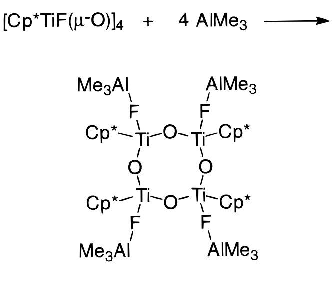
$$Cp^*TiMeCl_2 + Me_3SnF \longrightarrow \underset{\mathbf{49}}{Cp^*TiFCl_2} + Me_4Sn \quad (21)$$

Cp*TiF$_3$ (**43**) has a high affinity for oxygen and oxygen-containing ligands. Various organometallic fluorine−oxygen systems including oxides, carboxylates, and siloxanes have been investigated. The first example of a group 4 organometallic oxo fluoride, [Cp*TiF(μ-O)]$_4$ (**50**), was isolated on reaction of Cp*TiF$_3$ and O(SnBu$_3$)$_2$ (Scheme 4). In the solid, **50** displays an almost planar eight-membered ring with

Scheme 4



four Cp*TiF units bridged by four μ_2-oxygen atoms. Four terminal fluorine atoms (Ti–F_{av}, 1.85 Å) complete the coordination at titanium. Given the propensity of fluorine and oxygen to act as bridging ligands, **50** provides a unique comparison of the preferential bridging tendencies of oxygen and fluorine in the same molecule.[88] Ring expansion is observed on reaction of [Cp*TiCl(μ-O)]$_3$ with Me_3SnF to give **50**.[16] Hydrolysis of Cp*TiF$_3$ (**43**) has proven very sensitive to the method of water delivery. Hydrolysis of **43** with a stoichiometric amount of water gives an intractable product mixture.[88] Hydrazine hydrate as the hydrolyzing reagent affords **50** as the major product.[68] The aqueous chemistry of the related CpTiCl$_3$ has been the subject of a recent review article.[89] Interestingly, aerial oxidation of a dark-green toluene solution of Cp*$_2$TiF (**69**) affords **50** in good yield.[68] Reaction of **50** with trimethylaluminum provides intriguing insight into the interactions of group 4 and 13 compounds (eq 22). Instead of oxygen or fluorine abstraction from **50**, trimethylaluminum forms a thermally unstable almost-linear Ti–F–Al-bridged adduct **51**.[90] This reaction is interesting in that it is potentially a one-pot synthesis of a cationic organotitanium fluoride and an organoaluminum oxygen-containing compound; a combination reminiscent of metallocene/MAO concoctions used in olefin polymerizations.[39]



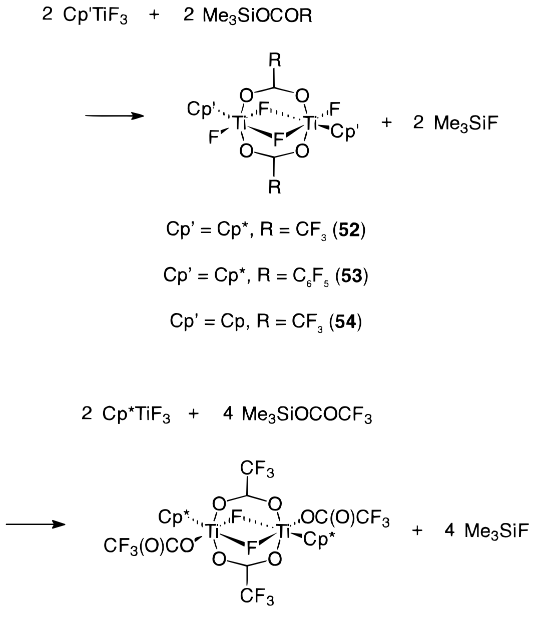
51

(22)

Investigations of the Lewis acidity of Cp*TiF$_3$ (**43**) toward a variety of bidentate ligands have been made. Dimeric cyclopentadienyltitanium carboxylate fluorides **52**–**55** provide the first examples of carboxylate-bridged organotitanium halides. Cyclopentadienyltitanium fluorides react with the trimethylsilyl esters of fluorinated acids to give compounds **52**–**54** with generation of Me_3SiF (Scheme 5). Compounds **52** and **53** are isostructural, as is **54** on the basis of the similarity of ^{19}F NMR spectra. Compounds **52** and **53** have unsymmetrical four-membered Ti_2F_2 rings (Ti–F_{av}, 1.99 and 2.08 Å) with two *trans* terminal fluorines (Ti–F_{av}, 1.83 Å). In addition the Ti_2F_2 rings are bridged by two perfluorocarboxylate groups. Monofluoro diacetate **55** is obtained similarily (Scheme 5). Characteristic ν_{sym} and ν_{asym} absorptions for bridging and monodentate carboxylate groups are found in the IR spectrum of **55**.[91]

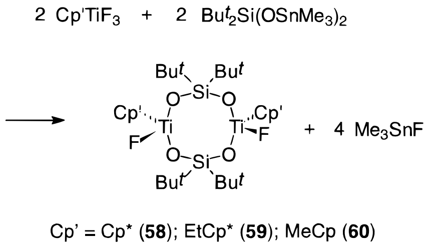
Reaction of lithium diethyl phenylmalonate with Cp*TiF$_3$ (**43**) furnishes the hexacoordinated titanium complex [Cp*TiF$_2${O=C(OEt)C(Ph)=C(OEt)O}]$_2$ (**56**). Replacement of one fluorine atom by the chelating 1,3-diketonate leads to an increase in metal coordination number demonstrating the high Lewis acidity of the titanium center in **43** (Ti–F_{ter}, 1.83 Å, Ti–F_b, 1.94 and 2.17 Å).[45] Hydroquinine bridged [Cp*TiF$_2$]$_2$[O($C_6H_2Bu^t_2$-2,5)O] (**57**) is formed on reaction of Cp*TiF$_3$ with *O,O′*-bis(trimethylstannyl)-substituted 1,4-hydroquinone (Scheme 3).[18] The very poor acceptor ability of CpTiX$_3$ (X = Cl, Br) for a wide range of potentially bidentate ligands has been previously noted.[92]

Scheme 5



55

Scheme 6



$$[\mathrm{Cp'TiCl(OSiBu^t_2O)}]_2 + 2\ \mathrm{Me_3SnF} \rightarrow [\mathrm{Cp'TiF(OSiBu^t_2O)}]_2 + 2\ \mathrm{Me_3SnCl}$$

Cp′ = Cp* (**58**); Cp′ = EtCp* (**59**)

Direct reaction of various substituted Cp′TiF$_3$ with $Bu^t_2Si(OSnMe_3)_2$ leads to eight-membered titanium siloxane ring compounds **58**–**60** (Scheme 6). In contrast to the corresponding reactions of Cp′TiCl$_3$ no dependence on cyclopentadienyl ring substitution is detected here. Direct fluorination of acyclic titanium siloxanes (RCp*)TiCl$_2$($OSiBu^t_2O$) (R = Me, Et) with Me_3SnF also affords **58** and **59**, respectively. Compound **60** is prepared similarily from (MeCp)-TiCl$_2$($OSiBu^t_2O$). Structural studies of the *trans* isomers of **58** and **59** (Ti–F_{av} 1.82 Å, Ti–O range, 1.79–1.83 Å) show the eight-membered $Ti_2O_4Si_2$ rings adopt chair-type conformations in both compounds. ^1H NMR studies indicate that in solution a *trans*:*cis* ratio greater than one exists for **58**–**60**. It is likely that this slight bias for the *trans* isomer is responsible for the preferential crystallization in the two cases studied. Interestingly, titanocene difluoride fails to react with $Bu_2Si(OSnMe_3)_2$.[19] Studies of the chemistry of related polymetalloorganosiloxanes have attracted much attention recently, mainly as a result of the similarity to highly active catalytic systems.[93]

Isoelectronic imidoorganotitanium fluorides are available via two routes. In the presence of pyridine, imido-substituted organometallic chlorides readily undergo chlorine–fluorine metathesis with trimethyltin fluoride to give compounds **61** and **62** (eq 23).

$$[(\mathrm{RCp})\mathrm{TiCl}(\mathrm{NR'})]_n + n\,\mathrm{Me_3SnF} \rightarrow [(\mathrm{RCp})\mathrm{TiF}(\mathrm{NR'})]_n + n\,\mathrm{Me_3SnCl} \qquad (23)$$

$\mathrm{R = Me,\ R' = Ph},\ n = 2$ (**61**)

$\mathrm{R = Me_3Si,\ R' = Bu^t},\ n = 1$ (**62**)

Generation of a mononuclear pyridine reaction intermediate CpTiCl(NR)·py is probable since in the absence of pyridine the exchange reaction does not proceed. Alternatively imidoorganotitanium fluorides have been obtained from the reaction of cyclopentadienyltitanium trifluorides and trialkylstannyl substituted amines. Treatment of the trifluorides $Cp'TiF_3$ with $N(SnMe_3)_3$ affords imido compounds **63** and **64** (eq 24). Compound **63** forms a N-bridged dimer in which the ligands adopt a *cis* geometry with respect to the Ti_2N_2 ring. Typical Ti–N (1.90–1.91 Å) and Ti–F (mean 1.84 Å) bond distances are found for **63**. Investigations of the transamination of Cp^*TiF_3 with $[MeAl(NMes)]_4$ have been reported. Despite the high affinity of aluminum for fluorine this reaction is sluggish, even at 350 K, and yields product mixtures.[20]

$$\mathrm{Cp'TiF_3} + \mathrm{N(SnMe_3)_3} \rightarrow [\mathrm{Cp'TiF(NSnMe_3)}]_2 \qquad (24)$$

Cp' = EtCp* (**63**); Cp' = MeCp (**64**)

Reactions of Cp^*TiF_3 with $Ph_3PNSiMe_3$ and $(C_2H_2)(Ph_3PNSiMe_3)_2$ lead to $Cp^*TiF_2(NPPh_3)$ (**66**) and $(Cp^*TiF_2NPPh_2)_2(C_2H_2)$ (**67**), respectively, with concurrent generation of Me_3SiF. Compound **66** is monomeric in the solid state ($Ti-F_{av}$, 1.81 Å), whereas in **67** the diphosphine bridging two Cp^*TiF_2 groups gives a dimeric structure (Ti–F, 1.87 and 1.92 Å). The short Ti–N (1.81 Å for **66** and **67**) and P–N (1.57 Å for **66** and 1.56 Å for **67**) bond distances in both compounds indicate a resonance form of the type $Ti^-{=}N^+{=}P$ prevails. The increased electron density at titanium is consistent with the upfield shift of ^{19}F signals for **66** and **67**. Lithium benzamidinate reacts with Cp^*TiF_3 to give dimeric $Cp^*TiF_2[(Me_3SiN)_2C\text{-}C_6H_4(OMe)\text{-}4]$ (**68**) (bridging $Ti-F_{av}$, 1.86 Å).[45]

Preparation (eq 25), stability, and decomposition patterns of $CpTi(EF_6)_3$ (E = As, Sb) have been investigated. While these compounds appear to be stable in frozen SO_2 (77 K), they decompose slowly in solution at 223 K and within minutes at room temperature. ^1H NMR studies indicate rapid fluorine exchange and dissociation processes in solution. HF and TiF_4 have been detected as decomposition products on removal of SO_2. Unlike the corresponding titanocenes both compounds are thermodynamically and kinetically unstable.[94]

$$\mathrm{CpTiCl_3} + 3\,\mathrm{AgEF_6} \rightarrow \mathrm{CpTi(EF_6)_3} + 3\,\mathrm{AgCl} \qquad (25)$$

E = As, Sb

B. Titanium(III)

A list of organotitanium(III) fluoride compounds is compiled in Table 4. Organotitanium(III) fluorides are prepared via two routes: (i) fluorination of suitable titanium(III) precursors (section V.B.1) and (ii) reduction of available organotitanium(IV) fluorides (section V.B.2). The latter approach has provided novel clusters with unusual metal–fluorine coordination environments.

1. Halide Metathesis

Teuben has demonstrated the utility of Cp^*_2TiCl as a synthon in the preparation of other Cp^*_2TiX complexes using chloride metathesis.[95] Halide metatheses with Me_3SnF[16] and $BF_3\cdot OEt_2$[96] provide the most convenient routes to Cp'_2TiF species **69**–**72**. Reactions of the borohydride Cp_2TiBH_4 with borontrihalides (BX_3, X = Cl, Br) afford the corresponding

Table 4. Titanium(III) Fluorides

no.	compound	starting material/reagent (% yield)	ref
69	Cp^*_2TiF	Cp^*_2TiCl/Me_3SnF (88)	16
		$Cp^*_2TiCl/BF_3\cdot OEt_2$	96
		$Cp^*_2TiF_2$/[K-graphite] (63), X-ray	96
70	Cp_2TiF	Cp_2TiCl/Me_3SnF (90)	16
		Cp_2TiF_2/[Na/Hg] (95)	96
71	$(MeCp)_2TiF$	$(MeCp)_2TiCl/Me_3SnF$ (89)	16
		$(MeCp)_2TiF_2$/[Na/Hg] (92)	96
72	$(Me_3SiCp)_2TiF$	$(Me_3SiCp)_2TiCl/Me_3SnF$	16
73	$Cp_2Ti(\mu\text{-}F_2BF_2)$	$Cp_2Ti(BH_4)/BF_3\cdot OEt_2$	97
74	$[\{(CpTi)(\mu\text{-}F)\}_2(\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)]$	Cp_2TiF_2/K	21
75	$(Cp_2TiF)_3(TiF_3)$	$Cp_2TiF_2/Cp_2Ti(CO)_2$	110
77	$(Cp_2TiF)_3(AlF_3)$	Cp_2TiF_2/Al	110
78	$[(MeCp)_2TiF]_3(AlF_3)$	$(MeCp)_2TiF_2$/Al	110
79	$[(MeCp)_2TiF]_3(GaF_3)$	$(MeCp)_2TiF_2$/Ga	111
80	$(Cp^*TiF_2)_6(NaF)_7\cdot 2.5THF$	Cp^*TiF_3/[Na/Hg] (65), X-ray	112
81	$(Cp^*TiF_2)_{12}(TiF_3)_2(NaF)_{18}\cdot 6THF$	Cp^*TiF_3/[Na/Hg] and dmpe, X-ray	113
82	$(Cp^*TiF_2)_4(MgF_2)_2\cdot 3THF$	$Cp^*TiF_3/[Mg/HgCl_2]$ (75), X-ray	112
83	$(Cp^*TiF_2)_6(CaF_2)\cdot 2THF$	Cp^*TiF_3/[Ca/Hg] (62), X-ray	113
84	$[(Me_3SiCp)TiF_2]_5(AlF_3)\cdot THF$	$(Me_3SiCp)TiF_3/[Al/HgCl_2]$ (59), X-ray	111

Cp_2TiX compounds (eq 26). Reaction with $BF_3{\cdot}OEt_2$ gives the light-blue borofluoride $Cp_2Ti(\mu\text{-}F_2BF_2)$ (**73**) (eq 27).[97] On the basis of ESR measurements a distorted tetrahedral geometry with bidentate BF_4^- has been deduced for **73**.[98]

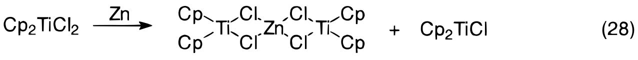
$$3\,Cp_2TiBH_4 + BX_3 \rightarrow 3\,Cp_2TiX + 2\,(BH_3)_2 \qquad (26)$$

$$(X = Cl, Br)$$

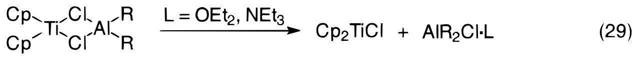
$$3\,Cp_2TiBH_4 + 4\,BF_3{\cdot}OEt_2 \rightarrow 3\,Cp_2TiF_2BF_2 + 2\,(BH_3)_2 + 4\,OEt_2 \qquad (27)$$

73

Reductions of dicyclopentadienyltitanium(IV) compounds (not including fluorides) using metals (Na, Zn, Mg, and Al), Grignard reagents, $LiAlH_4$, and aluminum alkyls to give low valent cyclopentadienyltitanium derivatives have been reported.[99] A number of these procedures are complicated by complex formation between the reduced titanium(III) species and the reduction byproduct.[100] For instance, zinc-mediated reduction of Cp_2TiCl_2 in THF affords Cp_2TiCl. The poor yield of Cp_2TiCl in this instance is a consequence of the competing formation of the dimetallic complex $[(Cp_2TiCl_2)_2Zn]$ (eq 28).[101] Complexation of aluminum with triethylamine or diethyl ether allows isolation of the titanocene(III) chloride Cp_2TiCl in good yield (eq 29).[102]



(28)



(29)

Magnetic susceptibility measurements for Cp_2TiF (**70**) suggest Ti−Ti exchange interactions are present and that these interactions increase in the series F < Cl < Br.[103] A strong band at 470 cm^{-1} in the IR spectrum of **70** has been assigned to a bridging Ti−F stretching frequency.[104] Compound **70** shows a decreased sensitivity to oxygen compared with the other halide derivatives and is soluble in deoxygenated water, THF, and benzene. Dissolution of **70** in organic solvents generally tends to be slower.[103] Aerial oxidation of a dark-green toluene solution of Cp^*_2TiF (**69**) gives $[Cp^*TiF(\mu\text{-}O)]_4$ (**50**) as the major product.[68]

$(MeCp)_2TiF$ (**71**) forms a fluorine-bridged dimer in the solid state. In **71** the fluorine atoms are symmetrically arranged (Ti−F$_{av}$, 2.09 Å) with distorted tetrahedral titanium geometries.[16] X-ray structural analysis of the more sterically demanding Cp*-substituted compound Cp^*_2TiF (**69**) reveals two crystallographically independent but virtually identical molecules in the asymmetric unit with Ti−F$_{av}$ bond lengths of 1.86 Å. Unlike Cp_2TiX systems in which the d^1 electrons are coupled, Cp^*_2TiX systems are monomeric and paramagnetic.[96] The Cp'_2Ti structural units of **69** and **71** are similar to those for related Cp'_2TiX systems.[105]

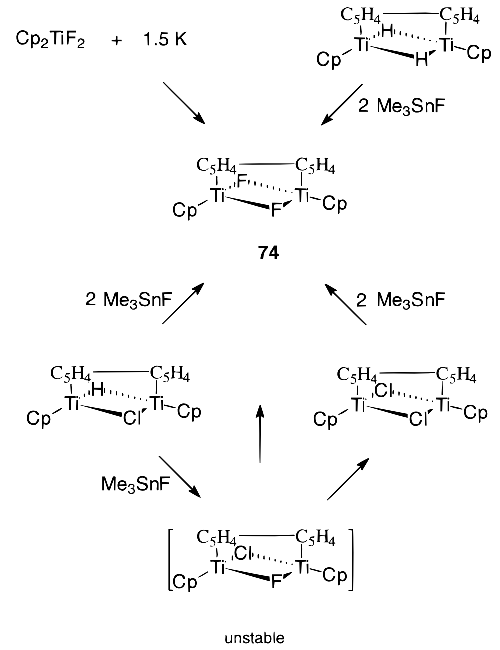
Electronic and EPR spectroscopy have been used to rank ligands (X) of d^1 bent metallocene compounds (Cp'_2TiX) in terms of π-donating ability. The ligand π-donor series follows the order $N(Me)H \approx NH_2 \approx OMe > OPh \approx F > N(Me)Ph > Cl > Br > I > H$.[96] This trend has been observed among the halides in previous analyses of bonding in bent metallocenes. Strong overlap between the p orbitals of the halide and d orbitals of the bent metallocene fragment is responsible for this ordering.[106]

2. Reduction of Titanium(IV) Fluorides

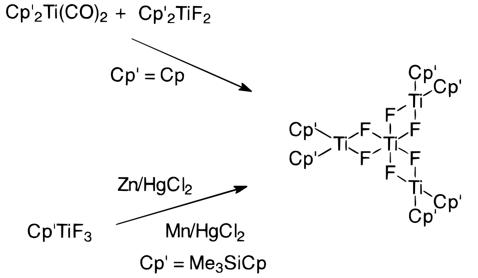
The second route to organotitanium(III) fluorides involves reduction of suitable organotitanium(IV) fluoride precursors. An inherent disadvantage of this approach is that the reducing agent cannot be regenerated as readily as common fluorinating reagents used in metathesis, e.g., regeneration of Me_3SnCl to Me_3SnF.[16] Polarographic reduction of Cp_2TiF_2 (**3**), in both protic and aprotic solvents, proceeds via successive addition of electrons to titanium. This reaction is complicated by hydrolysis and complexation, and no product was isolated.[107]

Reduction of Cp_2TiF_2 with potassium metal leads to the dinuclear η^5,η^5-fulvalene complex $[\{CpTi(\mu\text{-}F)\}_2(\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)]$ (**74**). Oxidative coupling of two cyclopentadienyl rings affords the fulvalene molecule which acts as a bridging ligand in the product. Compound **74** is also obtained on treatment of the dichloride and dihydride compounds $[\{CpTi(\mu\text{-}X)\}_2(\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)]$ (X = Cl, H) with two equivalents of Me_3SnF (Scheme 7). Attempts to isolate the mixed fluoro−hydride $[(CpTi)_2(\mu\text{-}H)(\mu\text{-}F)](\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)]$ from the related chloro−hydride lead instead to a mixture of **74** and the dichloride $[\{CpTi(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)]$. The two titaniums in **74** are bridged by a twisted fulvalene ligand (dihedral angle 15.3°) and two fluorines (Ti−F$_{av}$, 2.05 Å) with no Ti−Ti interaction (Ti−Ti, 3.17 Å).[21] Cp^*_2TiF (**69**) is obtained on reduction of the difluoride $Cp^*_2TiF_2$ with potassium graphite[108] in hexane.[96] Reduction of Cp_2TiF_2 with activated aluminum gives a blue compound which decomposes at 520 K (10^{-4} mmHg) accompanied by sublimation of crystalline Cp_2TiF (**70**).[109]

Scheme 7

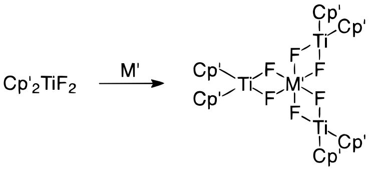


Conproportionation of $Cp_2Ti(CO)_2$ with Cp_2TiF_2 gives a mixture of compounds **70**, **75**, and an unidentified insoluble brown solid. Reduction of $(Me_3SiCp)TiF_3$ with activated zinc or manganese leads to **76** (eq 30). A central distorted octahedral TiF_6 moiety is the main structural feature of **75** and **76**. Addition of AgF to **75** affords metallocene difluoride **3**. Although loss of Cp′ from metallocene is well known, this reaction represents an unprecedented migration of Cp′ leading to a metallocene moiety. Direct synthesis of **75** from **3** using activated titanium as reducing agent is not possible. Aluminum- and gallium-mediated reductions of Cp'_2TiF_2 yield compounds **77**−**79** which are isostructural with **75** (eq 31). Three four-membered Ti_2F_2 rings in **75** and three $M'F_2Ti$ rings in **78** and **79** exhibit unsymmetrical metal−fluorine distances and surround the central metals in a “propeller-like” fashion with no direct metal−metal interactions. Indium appears to be too weak a reducing agent to effect the $Ti^{IV}-Ti^{III}$ reduction. Formation of metal−fluorine bonds, Al−F and Ga−F bonds in **77**−**79**, appears to be a strong thermodynamic driving force for these reactions. In related zinc and manganese reductions no corresponding Zn−F or Mn−F bond formation is observed.[110,111] It seems likely in the light of this work that the unidentified precursor of **70** is also a dimetallic complex of formulation $(Cp'_2TiF)_3AlF_3$.



(30)

Cp′ = Cp (**75**), Me_3SiCp (**76**)



(31)

Cp′ = Cp, M′ = Al (**77**)

Cp′ = MeCp; M′ = Al (**78**), M′ = Ga (**79**)

Reduction of Cp^*TiF_3 using group 1, 2, and 13 metals has led to the structural characterization of compounds which demonstrate a wide range of metal fluoride environments. A similar construction principle is evident in all of these clusters. Typically the cluster core is occupied by an inorganic fluoride fragment, while the periphery is covered by organic ligands. A summary of the products isolated from the reductions of organotitanium(IV) trifluorides is given in Scheme 8.

Scheme 8

$$6\ Cp^*TiF_3 + Na/Hg \rightarrow (Cp^*TiF_2)_6(NaF)_7 \cdot 2.5THF$$

80

$$14\ Cp^*TiF_3 + Na/Hg \rightarrow (Cp^*TiF_2)_{12}(TiF_3)_2(NaF)_{18} \cdot 6THF$$

81

$$4\ Cp^*TiF_3 + Mg/Hg \rightarrow (Cp^*TiF_2)_4(MgF_2)_2 \cdot 3THF$$

82

$$6\ Cp^*TiF_3 + Ca/Hg \rightarrow (Cp^*TiF_2)_6(CaF_2) \cdot 2THF$$

83

$$15\ (Me_3SiCp)TiF_3 + 5\ Al \rightarrow 3\ [(Me_3SiCp)TiF_2]_5(AlF_3) \cdot THF$$

84

The sodium−amalgam reduction of Cp^*TiF_3 demonstrates very clearly how changing a single reaction parameter can affect the nature of the product obtained. Reactions of Cp^*TiF_3, in the absence and presence of dppe, proceed with a solution color change from red to dark-green but without the expected precipitation of sodium fluoride (Scheme 8). Recrystallization of the green products $(Cp^*TiF_2)_6(NaF)_7 \cdot 2.5THF$ (**80**) (Figure 2) and $(Cp^*TiF_2)_{12}(TiF_3)_2(NaF)_{18} \cdot 6THF$ (**81**) made X-ray structural characterization possible. The descriptive aggregate formulas used in Scheme 8 show that **80** may be viewed as consisting of six Cp^*TiF_2 groups enclosing seven sodium fluoride molecules with a molecular NaF structure formed within the aggregate. In **81**, 12 Cp^*TiF_2 groups almost completely wrap a central inorganic core consisting of two TiF_3 and 18 NaF units. Dppe added to stabilize a Ti(III) reaction intermediate is not present in the product **81**, but does seem to play an important directing influence in the dimensions of the cluster. In **80** and **81**, the organic layer of Cp* groups and solvent molecules covering the inorganic core gives acceptable solubility properties in organic solvents. The central inorganic structural unit of **80** is shown in Figure 2. A wide range of different sodium coordination environments

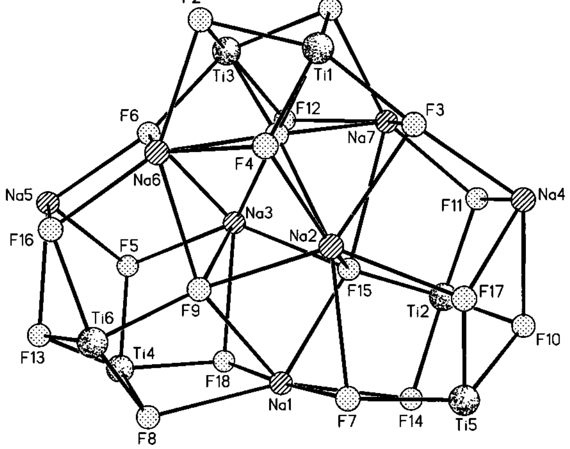


Figure 2. Structure of $(Cp^*TiF_2)_6(NaF)_7 \cdot 2.5THF$ (**80**). The organic substituents and solvent molecules have been omitted for clarity. (Reprinted with permission from ref 112. Copyright 1994 VCH Publishers.)

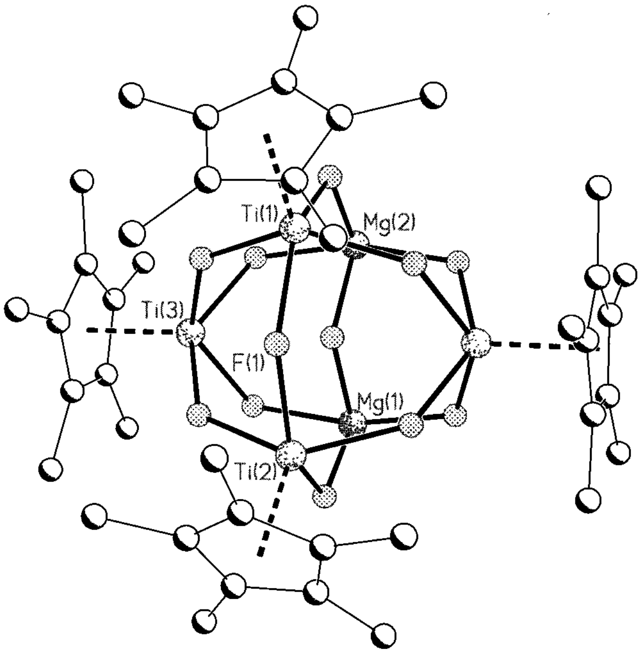


Figure 3. Structure of $(Cp^*TiF_2)_4(MgF_2)_2\cdot3THF$ (**82**). (Reprinted with permission from ref 112. Copyright 1994 VCH Publishers.)

are present in these compounds. In **80** and **81** sodium is five- and six-coordinated surrounded by fluorines and solvent molecules. In **80**, Na2 and Na3 are seven-coordinated.[112,113] Although the variation in Na−F distances is large, the average of the independent Na−F distances for **80** (2.35 Å) and **81** (2.32 Å) are close to that found for crystalline sodium fluoride (2.31 Å).[114]

Magnesium- and calcium-mediated reductions of Cp^*TiF_3 lead to similar coordination patterns in $(Cp^*TiF_2)_4(MgF_2)_2\cdot3THF$ (**82**)[112] and $(Cp^*TiF_2)_6(CaF_2)\cdot2THF$ (**83**)[113] (Scheme 8). In **82** four titanium, two magnesium and 12 fluorines form a cagelike framework which has a single μ_2-bridging fluorine projecting into it (Figure 3). Only the Mg−F(4) distances are similar to those in magnesium fluoride (2.05 Å),[115] while the remaining Mg−F distances (mean, 1.91 Å) are considerably shorter. As in the rutile lattice of magnesium fluoride the two magnesium atoms in **82** are six-coordinated with two coordination sites of each magnesium occupied by oxygens of three THF molecules. The structure of **82** provides a rare example of a THF molecule bridging two alkaline earth metal centers. Calcium fluoride was similarily prepared *in situ* (Scheme 8) with formation of the aggregate **83** (Figure 4). Two $Cp^*{}_3Ti_3F_7\cdot THF$ moieties encapsulate one calcium cation so that the calcium is eight-coordinated with four long (mean, 2.53 Å) and four short (mean, 2.26 Å) Ca−F distances. The structural features of calcium fluoride in **83** are dissimilar to those found in fluorite.[116]

Reduction of $CpTiX_3$ (X = Cl, Br, I) with zinc dust at room temperature in THF affords $CpTiX_2$ compounds. These readily undergo thermal decomposition with loss of THF to yield $CpTiX_2$. Reduction of Cp^*TiF_3 with zinc or aluminum was not possible because of the relatively high reduction potential of the Cp*-substituted fluoride complex. Redox potentials at the metal center decrease as a function of the cyclopentadienyl ligands in the order Cp* > Cp > Me_3SiCp. Reaction of $(Me_3SiCp)TiF_3$ with mercuric chloride-activated aluminum yields $[(Me_3SiCp)TiF_2]_5(AlF_3)\cdot THF$ (**84**) (Scheme 8). Compound **84** provides a unique example of an octahedral mixed-metal $AlTi_5$ arrangement formed around a single interstitial fluorine F(13) (Figure 5).[117]

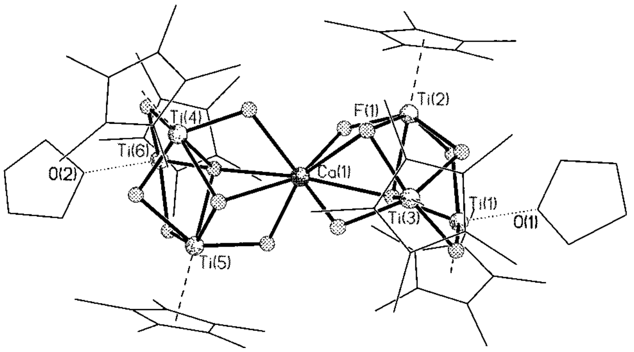


Figure 4. Structure of $(Cp^*TiF_2)_6CaF_2\cdot2THF$ (**83**). (Reprinted with permission from ref 113. Copyright 1995 VCH Publishers.)

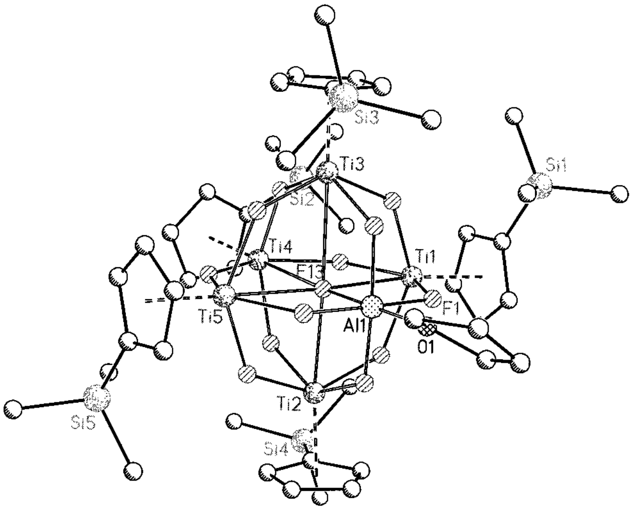


Figure 5. Structure of $(Cp^*TiF_2)_5AlF_3\cdot THF$ (**84**). (Reprinted with permission from ref 111. Copyright 1997 Elsevier.)

Clusters **77**−**84** can be viewed as soluble precursors of highly active/nucleophilic forms of groups 1, 2, and 13 metal fluorides (NaF, MgF_2, CaF_2, AlF_3, GaF_3). The diamagnetic green titanium(II) species $[CpTiCl]_4$ is generated on reduction of $CpTiCl_3$ with lithium nitride.[118] Halide metathesis of this compound to generate CpTiF has not been reported. Patents describe the syntheses of compounds having the empirical formulas (MeCp)TiF and (π-indenyl)-TiF.[119]

C. Zirconium and Hafnium

1. Zirconocene and Hafnocene Metallocenes

Ziconocene and hafnocene fluorides are listed in Table 5. Metallocenes Cp_2ZrF_2 (**85**) and Cp_2HfF_2 (**86**) are obtained in almost quantitative yield from the corresponding metallocene dichlorides using Me_3SnF (eq 32).[16,51] Zirconocene and hafnocene difluorides

$$Cp_2MCl_2 + 2\,Me_3SnF \rightarrow Cp_2MF_2 + 2\,Me_3SnCl \qquad (32)$$

Table 5. Zirconocene and Hafnocene Fluorides

no.	compound	starting material/reagent (yield %)	ref
85	Cp_2ZrF_2	Cp_2ZrCl_2/Me_3SnF (73)	51
		$AgBF_4$ (78)	52
		$Cp_2Zr(OBu^t)_2/BF_3{\cdot}OEt_2$ (52),	120
		$Cp_2ZrMe_2/HBF_4{\cdot}OEt_2$	50f
		$Cp_2Zr(NMe_2)_2/BF_3{\cdot}OEt_2$ (39)	120
		Cp_2ZrX_2/C_6F_5CN (65)	120
86	Cp_2HfF_2	$Cp_2Hf(NMe_2)_2/BF_3{\cdot}OEt_2$ (66)	120
		$Cp_2Hf(NMe_2)_2/C_6F_5CN$ (61)	120
87	$(MeCp)_2ZrF_2$	$(MeCp)_2ZrCl_2/Me_3SnF$ (91), X-ray	16
88	$[(Me_3Si)MeCp]_2ZrF_2$	$[(Me_3Si)MeCp]_2ZrCl_2/Me_3SnF$	16
89	$[(Me_3Si)_2Cp]_2ZrF_2$	$[(Me_3Si)_2Cp]_2ZrCl_2/Me_3SnF$	16
		$[(Me_3Si)_2Cp]_2Zr(NMe_2)_2/BF_3{\cdot}OEt_2$ (81)	120
		$[(Me_3Si)_2Cp]_2Zr(CO)_2/AgBF_4$	120
90	$Cp^*{}_2ZrF_2$	$Cp^*{}_2ZrCl_2/Me_3SnF$	16
91	$Cp^*{}_2HfF_2$	$Cp^*{}_2HfCl_2/Me_3SnF$ (92)	16
92	$(Me_4C_5CH_2\text{-})_2ZrF_2$	$(Me_4C_5CH_2\text{-})_2ZrCl_2/NaF$	50e
93	$Cp_2ZrCl(F)$	$(Cp_2ZrCl)_2O/HF$	125
94	$Cp^*{}_2ZrCl(F)$	$Cp^*{}_2ZrCl_2/HF$	124
95	$(EtCp^*)_2ZrCl(F)$	$(EtCp^*)_2ZrCl_2/Me_3SnF$ (83), X-ray	70
96	$Cp^*{}_2HfCl(F)$	$Cp^*{}_2HfCl_2/Me_3SnF$ (75)	70

are also prepared by chloride/fluoride, by chloride/NMe_2 followed by NMe_2/fluoride exchange, and by oxidative addition as in the reaction of $[(Me_3Si)_2Cp]_2Zr(CO)_2$ and $AgBF_4$.[120] The exothermic reaction shown in eq 33 resembles other ligand-exchange reactions such as that found in the Me_3SnNMe_2/BF_3 system.[121]

$$\mathrm{Cp_2MY_2 + 2\,BF_3{\cdot}OEt_2 \rightarrow Cp_2MF_2 + YBF_2{\cdot}OEt_2} \qquad (33)$$

$$\mathrm{Y = NMe_2,\ OBu^{\mathit{t}}}$$

$$\mathrm{M = Zr\ (\mathbf{85}),\ Hf\ (\mathbf{86})}$$

Curiously, nucleophilic substitution of perfluorobenzonitrile by metallocene diamides (eq 34) is favored over competing nitrile insertion into the metal−nitrogen bond. $Cp_2Zr(NMe_2)_2$, unlike $Me_2Sn(NMe_2)_2$, fails to react with hexafluorobenzene.[121] Synthetic routes to titanocene difluoride are not universally applicable to the preparation of **85** and **86**. Reactions of zirconocene and hafnocene dichlorides with sodium fluoride do not give **85** and **86** under the conditions used for Cp_2TiF_2.[122] Chloride−fluoride metatheses of the bulky trimethylsilyl-substituted zirconocenes **88** and **89** proceed perceptibly slower than for the parent compound Cp_2ZrCl_2.[120]

$$\mathrm{Cp_2M(NMe_2)_2 + 2\,C_6F_5CN \rightarrow Cp_2MF_2 + 2\ \mathit{p}\text{-}C_6F_4(NMe_2)CN} \qquad (34)$$

$$\mathrm{M = Zr\ (\mathbf{85}),\ Hf\ (\mathbf{86})}$$

Generally NMR spectra of Cp'_2MF_2 (M = Zr, Hf) analogues are similar and differ from those of the corresponding titanium compounds. Low-frequency IR and Raman spectra of **85** and **86** have been recorded.[53] The band at 563 cm^{-1} in the IR spectrum of $[(Me_3Si)_2Cp]_2ZrF_2$ (**88**) (Nujol mull) has been definitively assigned to $\nu_{asym}(Zr{-}F_2)$.[120] The corresponding vibration in **85** is at 528 cm^{-1}. Compounds **85** and **86** are purified by sublimation in vacuo at 300 K.[51]

Cp_2ZrF_2 (**85**)[123] (Zr−F, 1.98 Å) and $[(Me_3Si)_2Cp]_2ZrF_2$ (**89**)[120] are monomeric in the solid state with distorted tetrahedral arrangements of cyclopentadienyl groups and fluoride ligands around central zirconium atoms. A comparison of structural features for **85** and **89** shows the changes upon introduction of four bulky trimethylsilyl groups. An increase in F−Zr−F angle of 4.5° and Cp−Zr−Cp angle of 3.6° is observed on going from **85** to **89**. These changes are accompanied by a dramatic increase of 0.23 Å in Zr−F bond length and 0.01 Å in Zr−Cp(centroid) distance. Within the series Cp_2ZrX_2 and $(Me_3SiCp)_2ZrX_2$ (X = halide) the structural effect of changing the halide ligand is minimal.

In 1985, Minacheva outlined the preparation of $Cp^*{}_2ZrCl(F)$ (**93**) from the dichloride $Cp^*{}_2ZrCl_2$ using hydrogen fluoride. No characterization other than elemental analysis was presented.[124] $(Cp_2ZrCl)_2O$ reportedly reacts with HF to give $Cp_2ZrCl(F)$ (**94**) (eq 35).[125] Authentic examples of zirconium and hafnium mixed fluoro−chloro compounds **95** and **96** have been prepared from the dichlorides using 1 equiv of trimethyltin fluoride (eq 36).[70]

$$\mathrm{(Cp_2ZrCl)_2O + HF_{aq} \longrightarrow \underset{\mathbf{94}}{Cp_2ZrFCl}} \qquad (35)$$

$$\mathrm{Cp'_2MCl_2 + Me_3SnF \rightarrow Cp'_2MCl(F) + Me_3SnCl} \qquad (36)$$

$$\mathrm{M = Zr,\ Cp' = EtCp^*\ (\mathbf{95})}$$

$$\mathrm{M = Hf,\ Cp' = Cp^*\ \ (\mathbf{96})}$$

Mixed oxo−fluoro compounds **97**−**103** have been prepared by various routes (eqs 37−39). These compounds have been characterized by IR, mass, and ^{13}C NMR spectroscopy. Reactions with hydrogen fluoride and dibenzoylmethane proceed with partial elimination of CpH affording monocyclopentadienyl complexes **98**, **100**, **102**, and **103**.[126] $Cp^*{}_2ZrF_2$ (**90**) reacts with 1 or 2 equiv of $Me_3SiOCOCF_3$ to give the fluoro−acetate and diacetate complexes **104** and **105**, respectively (eq 40). Compound **105** is monomeric probably due to the presence of two bulky Cp* groups.[127] Methylzirconocene difluoride $(MeCp)_2ZrF_2$ (**87**) reacts with $Bu^t{}_2Si(OSnMe_3)_2$, in the presence of triethylamine, to give acyclic $(MeCp)_2ZrFOSiBu^t{}_2(OSnMe_3)$ (**106**). No reaction occurs on mixing

$$\mathrm{Cp_4M + HF_{(aq)} \rightarrow (Cp_2MF)_2O + CpMF_2(OH){\cdot}H_2O} \qquad (37)$$

$$\mathrm{M = Zr\ (\mathbf{97}) \qquad M = Zr\ (\mathbf{98})}$$

$$\mathrm{M = Hf\ (\mathbf{99}) \qquad M = Hf\ (\mathbf{100})}$$

$$\mathrm{(Cp_2ZrF)X + (OCPh)_2CH_2 \rightarrow \underset{\mathbf{101}}{Cp_2ZrF\{(OCPh)_2CH\}} + \underset{\mathbf{102}}{CpZrF\{(OCPh)_2CH\}_2}} \qquad (38)$$

$$\mathrm{(Cp_2HfF)_2O + 2\,(OCPh)_2CH_2 \rightarrow \underset{\mathbf{103}}{2\ CpHfF[(OCPh)_2CH]_2}} \qquad (39)$$

$$\mathrm{Cp'_2ZrF_2 + n\ Me_3SiOCOCF_3 \rightarrow Cp'_2ZrF_{2-n}(OCOCF_3)_n + n\ Me_3SiF} \qquad (40)$$

$$\mathrm{n = 1\ (\mathbf{104}),\ 2\ (\mathbf{105})}$$

titanocene difluoride (or dichloride) with $Bu^t{}_2Si(OSnMe_3)_2$. The reduced reactivity of the titanocene has been ascribed to steric restraints imposed by the decreased atomic size of titanium.[19]

Scrambling reactions between Cp_2ZrF_2 and Cp_2ZrMe_2 afford pure $Cp_2ZrF(Me)$ (**107**) in 90% yield (eq 41). Rate constants for this reaction have been determined and the reaction calculated to be second order. Methyl–fluoride exchange is fast and phenyl–fluoride exchange is extremely slow. In comparison with related titanocene systems the variation of rate with ligand is relatively large.[128] Symmetrization reactions of $Cp^*{}_2ZrF_2$ and $Cp^*{}_2ZrH_2$ at 420 K for 14 days under a hydrogen atmosphere afford $Cp^*{}_2ZrFH$ (**110**).[129] Ethylene insertion into the zirconium–hydrogen bond of **110** leads to $Cp^*{}_2ZrF(CH_2CH_3)$ (**113**). CO insertion into **110** at elevated temperatures leads to *cis*-$(Cp_2{}^*ZrF)_2(\mu\text{-}OCHCHO)$ (**114**). The alkyl precursors **109** and **111** are generated in high yields and the kinetics of their hydrogenolysis reactions have been studied (eq 42).[130] $CpM(CO)_2$ (M = Co, Rh) undergo oxidative hydrogen migration on reaction with **110** to form M^{III}carbene complexes (M = Co) **115** and (M = Rh) **116** in good yields (eq 43).[131]

$$Cp_2ZrF_2 \;+\; Cp_2ZrR_2 \;\rightarrow\; 2\,Cp_2ZrFR \qquad (41)$$

R = Me (**107**), Ph (**108**)

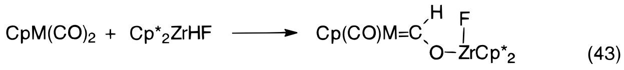
$$Cp'_2ZrF_2 \;+\; LiCH_2Bu^t \;\longrightarrow$$

$$Cp'_2ZrF(CH_2Bu^t) \;+\; LiF \;\xrightarrow{H_2}\; Cp'_2ZrFH \;+\; CH_3Bu^t$$

109 **110** Cp' = Cp*

111 **112** $Cp'_2 = \{Me_4C_5CH_2\text{-}\}_2$

(42)



$$CpM(CO)_2 + Cp^*{}_2ZrHF \longrightarrow Cp(CO)M{=}C(H)\text{–}O\text{–}Zr(F)Cp^*{}_2 \qquad (43)$$

110 M = Co (**115**), Rh (**116**)

A zirconium–fluorine analogue of the well-known Tebbe reagent $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$[132] is not known. Reaction of **90** with trimethylaluminum yields $Cp^*{}_2ZrMe_2$, quantitatively (eq 44). In the analogous hafnium reaction $Cp^*{}_2HfMe_2$ is isolated in only 50% yield.[133]

$$Cp^*{}_2MF_2 \;+\; 2\,AlMe_3 \;\rightarrow\; Cp^*{}_2MMe_2 \;+\; 2\,Me_2AlF \qquad (44)$$

M = Zr, Hf

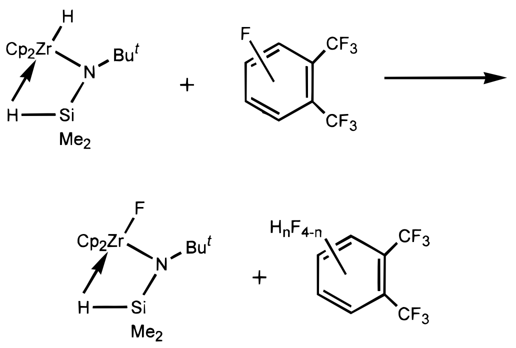
Salts of $Cp_2ZrR(L)^+$ cations incorporating BF_4^-, PF_6^-, or related anions are almost invariably unstable with respect to fluoride transfer. Transfer of fluoride initially yields neutral $Cp_2ZrF(R)$, suggesting that $Cp_2Zr(R)^+$ is a stronger Lewis acid for fluoride than BF_3 or PF_5. The salt $[Cp_2Zr(Me)(MeCN)][PF_6]$ is stable in the solid state but decomposes instantaneously in THF or dichloromethane solution to Cp_2ZrMeF (**107**) via fluoride abstraction from PF_6^- (eq 45). Compound **85** is observed as a secondary product formed by further methyl–fluoride exchange.[134] Slow decomposition of the cationic complex $[(Me_2Cp)_2ZrMe][MeB(C_6F_5)_3]$ to $[\{(Me_2Cp)_2ZrMe\}_2(\mu\text{-}F)][MeB(C_6F_5)_3]$ (**117**) occurs at 298 K in C_6D_6. A reaction mechanism involving transfer of an aryl ring to form $(Me_2Cp)_2ZrMe(C_6F_5)$, followed by intramolecular *o*-fluoride elimination to give **117** is possible. Alternatively, direct fluoride abstraction from the $[MeB(C_6F_5)_3]^-$ anion by the zirconium cation may be invoked. Previous examples supporting both mechanisms are known. Compound **117** consists of discrete cations and anions in the crystal. In **117** the two $(Me_2Cp)_2ZrMe$ fragments are almost identical with a near linear Zr–F–Zr configuration (Zr(1)–F–Zr(2) = 173.3°; Zr(1)–F, 2.11 Å and Zr(2)–F, 2.12 Å).[135] An organo zirconium cationic intermediate detected in the reaction of $[(Me_3Si)_2Cp]_2Zr(CO)_2$ and $AgBF_4$, decayed slowly at ambient temperature to give $[(Me_3Si)_2Cp]_2ZrF_2$ (**89**) among other products.[120]

$$[Cp_2Zr(Me)(MeCN)][PF_6] \;\rightarrow\; Cp_2ZrF(Me) \;+\; PF_5 \;\rightarrow\; Cp_2ZrF_2 \qquad (45)$$

107 **85**

Dienone-mediated oxidation chemistry observed for titanocene compounds (eq 15) has proven to be general for group 4 metals. Reaction of Cp_2ZrPh_2 with tetrakis(fluoromethyl)cyclopentadienone affords biphenyl and the zirconium analogue of **36**. Tetrakis(fluoromethyl)cyclopentadienone is an ideal reagent for the study of one-electron oxidation processes since the intermediates may be isolated as soluble adducts of the dienone.[82] Fluoride abstraction by $Cp^*{}_2ZrCl_2$ from $Cd(CF_3)_2{\cdot}DME$ at low temperature affords $Cp^*{}_2ZrF_2$ (**90**). No details of this transformation were given; however, α-fluoride elimination from a $Cp^*{}_2Zr(CF_3)_2$ species is likely.[136]

Intermolecular activation of C–F bonds in hexafluorobenzene with the chloride $Cp_2ZrCl(NBu^tSiMe_2H)$ leads to a complex mixture of products. Use of the sterically more hindered perfluoro-*o*-xylene allows isolation of **118** in reasonable yield (50%) (eq 46). Nonclassical Zr–H–Si interactions in the series of related silylamido zirconocenes $Cp_2ZrX(NBu^tSiMe_2H)$ follows the order X = H > I > Br > Cl > F (**118**), reflecting the relative electrophilicity of the zirconium center in these compounds.[137]



(46)

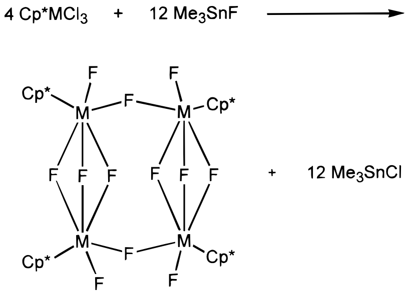
2. Zirconium and Hafnium Monocyclopentadienyl

Table 6 represents an up-to-date list of monocylopentadienyl zirconium and hafnium fluorides. Halide metathesis of the chlorides with trimethyltin fluoride provides a convenient route to Cp^*MF_3 (M

Table 6. Cyclopentadienylzirconium and Hafnium Fluorides

no.	complex	starting material/reagent (yield %)	ref
119	Cp^*ZrF_3	Cp^*ZrCl_3/Me_3SnF (94), X-ray	16
		tmpy·2HF (90)	22
120	Cp^*HfF_3	Cp^*HfCl_3/Me_3SnF (93), X-ray	16
		tmpy·2HF (95)	22
121	$(EtCp)HfF_3$	$(EtCp)_2HfCl_2/F_2$	138
124	Cp^*ZrF_2Cl	Cp^*ZrF_3/Me_3SiCl (82), X-ray	70
125	Cp^*HfF_2Cl	Cp^*HfF_3/Me_3SiCl (90), X-ray	70
126	Cp^*ZrF_2Br	Cp^*ZrF_3/Me_3SiBr (84), X-ray	139
127	$[(Cp^*ZrF_2Cl)_2(Cp^*ZrFCl_2)_2]$	Cp^*ZrF_3/Me_2AlCl, X-ray	70
128	$[(Cp^*HfF_2Cl)_2(Cp^*HfFCl_2)_2]$	Cp^*HfF_3/Me_2AlCl, X-ray	70
130	$(Cp^*Zr)_6F_{18}Li_4O_2$	$Cp^*ZrF_3/LiO(2,6\text{-}Bu^t{}_2C_6H_3)$, X-ray	141

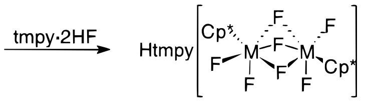
= Zr (**119**); Hf (**120**)) compounds in almost quantitative yields (eq 47).[16] A more unusual procedure involves reaction of trimethylpyridine hydrofluoride (tmpy·2HF) with a metal alkyl. In this procedure generation of alkane accompanies formation of the metal fluoride (eq 48).[22] Under rather drastic conditions, using elemental fluorine in chlorinated biphenyls at 480 K, Gorsich claimed to have prepared $(EtCp)HfF_3$ (**121**) from the chloride $(EtCp)_2HfCl_2$.[138] Novel anionic organo group 4 fluorides (**122** and **123**) are obtained when an excess of tmpy·2HF is employed in the fluorination (eq 48).[22] Successful fluorination of Cp^*TiCl_3 using arsenic trifluoride has been described (section V.A.2). A complicating feature in the reaction of Cp^*ZrCl_3 with AsF_3 involves transfer of Cp* from zirconium to arsenic in addition to the desired fluorine–chlorine exchange (eq 49).[16]



(47)

M = Zr (**119**), Hf (**120**)

$$2\,Cp^*MR_3 + 3\,(tmpy)\cdot 2HF \rightarrow 2\,Cp^*MF_3 + 6\,RH + 3\,tmpy$$



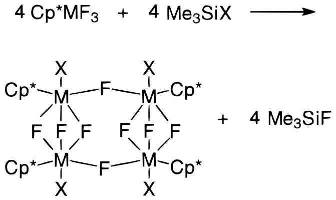
M = Zr (**122**), Hf (**123**)

R = CH$_2$Ph; tmpy = trimethylpyridine (48)

$$Cp^*ZrCl_3 + \text{excess } AsF_3 \longrightarrow \underset{\mathbf{119}}{Cp^*ZrF_3} + Cp^*AsCl_2 \qquad (49)$$

In the crystal **119** exhibits a symmetric arrangement of four Cp^*ZrF_3 units with alternate single and triple fluorine bridges between the four zirconiums, and four terminal fluorines. Compound **122** is a triply-bridged zirconium dimer in the solid with two terminal fluorines per zirconium. Zirconium atoms are coordinated in a highly distorted octahedral geometry with one Cp* group on each metal.[16] Terminal ($Zr-F_{av}$, 1.96 Å (**119**),[16] 1.95 Å (**122**)[22]) and bridging ($Zr-F_{av}$, 2.14 Å (**119**),[16] 2.16 Å (**122**)[22]) zirconium distances do not vary significantly for the fluorine-bridged neutral and anionic compounds. Cp^*HfF_3 (**120**) is isostructural with **119**.[16] ^{19}F NMR spectra of **119** and **120** exhibit four signals, confirming the persistence of the tetrameric structures in solution.[16] Multiplets found at 97.5 and 41.8 ppm (C_6D_6) in **119** and **120**, respectively, have been definitively assigned to terminal fluorine resonances.[70] ^{19}F resonances for **122** show the nonequivalence of the two terminal and three bridging fluorines.[22]

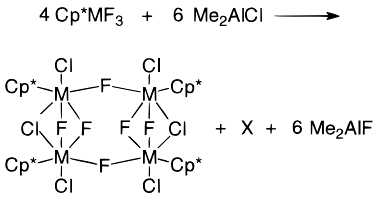
Mixed fluoro–chloro group 4 compounds provide the possibility to combine elements of the chemistries of the respective halides. In contrast to the ease with which zirconocene and hafnocene fluoro–chloro compounds are prepared, monocyclopentadienyl mixed fluoro–chloro compounds $Cp^*MF_nX_{3-n}$ (M = Zr, Hf; X = Cl, Br, I) cannot be prepared from the trihalides using Me_3SnF. A reverse strategy employs fluoro–chloro exchange of Cp^*MF_3 (M = Zr, Hf) with Me_3SiCl at room temperature to furnish the fluoro–chloro compounds Cp^*MF_2Cl (M = Zr (**124**), Hf (**125**)) in almost quantitative yields (eq 50). Selective replacement of the four terminal fluorines in Cp^*MF_3 by chlorines is accompanied by formation of Me_3SiF. The exchange proceeds with retention of the tetrameric core structure of Cp^*ZrF_3.[70] The bromide analogue Cp^*ZrF_2Br (**126**) has been prepared similarly (eq 50). Failure to isolate the iodide Cp^*ZrF_2I suggests that it is not stable.[139] Dimethylaluminum chloride serves as a more exceptional fluoro–chloro exchange reagent. In the reaction of Cp^*ZrF_3 (**119**) with an equimolar quantity of dimethylaluminum chloride a mixture of **124** and the more highly chlorinated complex $[(Cp^*ZrF_2Cl)_2(Cp^*ZrFCl_2)_2]$ (**127**) is obtained (eq 51). Fractional recrystallization of the



(50)

M = Zr; X = Cl (**124**), Br (**126**)

M = Hf, X= Cl (**125**)



(51)

M = Zr (**127**), X = **124**

M = Hf (**128**), X = **125**

reaction mixture allowed an X-ray study of **127**. Compound **127** is isostructural to **124** with two of the bridging fluorines replaced by chlorines. Interestingly, replacement of two bridging fluorines by chlorines does not disrupt the tetrameric structure present in Cp^*ZrF_3. Similarly, Cp^*HfF_3 reacts with dimethylaluminum chloride to give a mixture of **125** and $[(Cp^*HfF_2Cl)_2(Cp^*HfFCl_2)_2]$ (**128**).[70]

Russian chemists described the interaction of 40% aqueous HF with Cp_2ZrCl_2 as giving $CpZrF_2OH$ (**129**) in 55% yield on the basis of spectroscopic and analytic data.[140] Recent work has shown that group 4 fluorides cleave the carbon−oxygen bond of lithium alkoxides bearing electron-rich substituents.[18] Advantageous use of this fact has been made in preparing the intercalated oxide **130** via reaction of Cp^*ZrF_3 with lithium-2,6-di-*tert*-butylphenoxylate (eq 52). The

$$6\ Cp^*ZrF_3 + 4\ LiO(2,6\text{-}Bu^t_2C_6H_3) \rightarrow (Cp^*Zr)_6F_{18}Li_4O_2 + 2\ (2,6\text{-}Bu^t_2C_6H_3)_2O \quad (52)$$

130

metal−fluorine backbone in **130**, described as a “waisted-ellipsoid”, contains two oxygens intercalated into the cavities (Figure 6). Terminal Zr−F (2.15 Å) are comparatively long and bridging distances (Zr−F−Li, 2.00 Å; Zr−F−Zr, 2.02 Å) significantly shorter for **130** than in Cp^*ZrF_3. The reduction in bond lengths and the octahedral coordination of oxygen in **130** is typical for compounds having interstitial oxygen. Cp^*ZrF_3 does not react directly with Li_2O probably due to the high lattice energy of the oxide.[141]

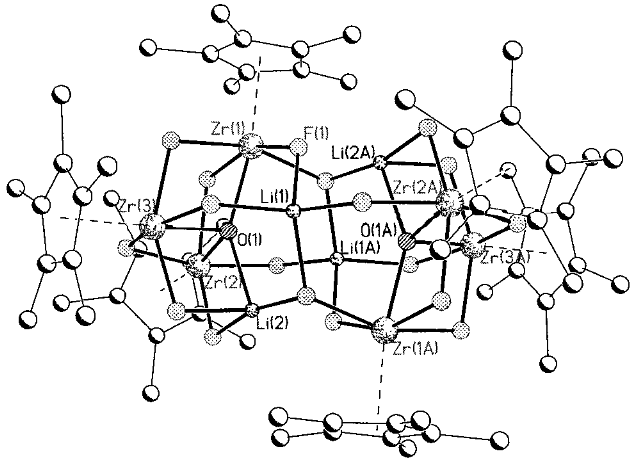
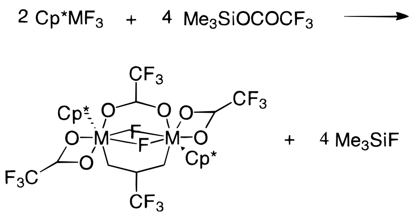


Figure 6. Structure of $(Cp^*Zr)_6F_{18}Li_4O_2$ (**130**). (Reprinted with permission from ref 141. Copyright 1995 Royal Society of Chemistry.)

Regardless of the molar ratios employed, fluorides Cp^*MF_3 (M = Zr, Hf) react with the trimethylsilyl ester of trifluoroacetic acid to give dinuclear complexes **131** and **132** (eq 53). The X-ray structure of **131** shows two seven-coordinated zirconiums bridged by two acetate groups and two fluorine atoms, leading to a symmetrical four-membered Zr_2F_2 ring (Zr−F, 2.15 Å).[127] In the related complex **55**, titanium is six-coordinated probably as a result of the smaller ionic radius of the metal.[91] The presence of chelating and bridging trifluoroacetate groups in **131** is confirmed by ^{19}F NMR and, in particular, IR spectroscopy.[127]



(53)

M = Zr (**131**), Hf (**132**)

Using trimethyltin fluoride, $Cp^*Zr(acac)_2Cl$ is converted to the corresponding fluoride **134** via the fluorine-bridged intermediate **133** (eq 54). Coordination of Me_3SnCl produced during the reaction by the product leads to **133** which is stable and has been structurally characterized. On standing in vacuo, **133** decomposes with elimination of trimethyltin chloride to the fluoride **134**. The metal−fluorine distances in **133** (Zr−F, 2.03 Å; Sn−F, 2.46 Å; Sn−Cl, 2.13 Å) confirm the weak nature of the tin−fluorine interaction even in the solid state.[51] The Sn−F distance (2.46 Å) is notably longer than the typical Sn−F single bond distance in Mes_3SnF (1.96 Å)[142] and also longer than the weak Sn···F interactions (2.30 Å) in polymeric $(C_6H_{11})_3SnF$.[143]

$$Cp^*Zr(acac)_2Cl + Me_3SnF \rightarrow Cp^*Zr(acac)_2(\mu\text{-}F)SnMe_3Cl$$

133 (54)

$$\rightarrow Cp^*Zr(acac)_2F + Me_3SnCl$$

134

An interesting comparison has been made of the catalytic activities of bis-amido and amido−cyclopentadienyl zirconium/hafnium chlorides and fluorides (eq 55) for the polymerization of ethylene. In the presence of MAO as cocatalyst the amido−cyclopentadienyl-substituted compounds are more active than the bis-amido compounds. Although no clear trend is evident the fluorides do exhibit activities comparable with the chlorides. The absence of any silicon−fluorine interaction (Zr−F, 2.18 Å) in the solid-state structure precludes the use of **135** as a precursor for imido compounds via elimination of Me_3SiF.[144]

$$Cp^*\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}MCl_2 + Me_3SnF \rightarrow$$

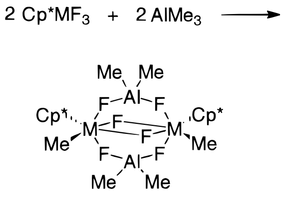
$$Cp^*[(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)]MCl(F) + Me_3SnCl$$

M = Zr (**135**), Hf (**136**) (55)

3. Group 4 Fluorides and Aluminum Reagents

One of the exciting observations in the chemistry of early organotransition metal fluorides is the high catalytic activity of cyclopentadienylzirconium and titanium fluorides in the presence of methylalumoxane (MAO) as cocatalyst for the polymerization of ethylene and styrene, respectively. The organometallic fluoride-catalyzed polymerization of styrene is noteworthy as syndiotactic polymer is obtained in the absence of any chiral discriminating reagent.[145] MAO is thought to play a bifunctional role in these systems. Firstly, methylation of the transition metal complex occurs, followed by halide abstraction generating the active cationic species which is, in some way, stabilized in the presence of MAO.[39]

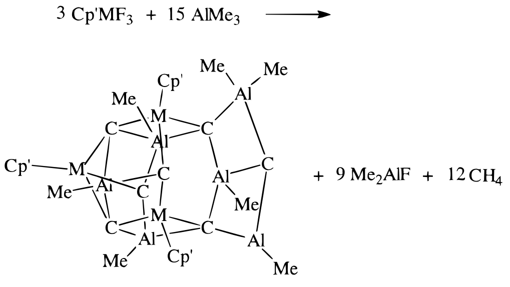
It has been shown that reactions of Cp*MF_3 (M = Zr, Hf) with trimethylaluminum (TMA) in a 1:1 molar ratio proceed with selective exchange of fluorine atoms for methyl groups (eq 56). Dimethylaluminum fluoride formed during the fluoro−methyl exchange does not give tetrameric $[Me_2AlF]_4$, but instead acts as a ligand bridging two transition metals in compounds **137** and **138**. X-ray analysis of **137** shows the presence of Zr−F−Zr and Zr−F−Al bridges (Zr−F, 2.11−2.18 Å and Al−F, 1.77−1.79 Å) with the zirconium and aluminum atoms having distorted octahedral and tetrahedral coordination spheres, respectively. Compound **138** is isostructural with **137**. An exceptional structural feature of **137** and **138** is the *cis* disposition of the two methyl groups bonded to zirconium and hafnium, respectively. Stereospecific formation of *cis* isomers of **137** and **138** is confirmed by ^1H NMR spectroscopy. Variable-temperature NMR studies show there is no *cis*−*trans* isomerism in solution even at 340 K. Three signals in the ^{19}F NMR spectra of **137** and **138** are assigned to distinct types of bridging fluorine environments, indicating that the solid-state structures persist in solution.[146]



(56)

M = Zr (**137**), Hf (**138**)

Methane gas evolution is observed on reaction of **137**, or Cp*ZrF_3, with excess trimethylaluminum and the fluorine free cluster core $Zr_3Al_6C_7$ (**139**) is obtained in good yield (eq 57). In contrast, reaction of Cp*HfF_3 with excess trimethylaluminum affords Cp*$HfMe_3$ in 85% yield. The hafnium cluster $Hf_3Al_6C_7$ (**140**) is isolated only as a reaction byproduct. X-ray analyses of **139** and **140** show them to be structurally comparable. Remarkably short metal−metal bond distances, shorter than the sum of the metal radii, are observed in both clusters. Whether these short metal−metal distances arise as a result of an electron deficiency at the metal centers is not clear. The different short metal−carbon distances give rise to the unsymmetrical shaped structures for **139** and **140**. Methylene and methyne groups cap the cube-like structure and are detected by ^1H NMR in $CDCl_3$ solution. Surprisingly, no reacton of the cluster with this solvent occurs. Unambigious assignment of ^1H NMR signals in the high-field region of the spectra using 2D methods and ^{13}C NMR spectroscopy has been hampered by poor solubility of the compounds following precipitation from solution. Substitution of EtCp* for Cp* in **139** did not improve solubility of the cluster. Methylidene-transfer reactions of **139** with various organic substrates have been studied and alkenes are obtained in reasonable yields.[133,146]



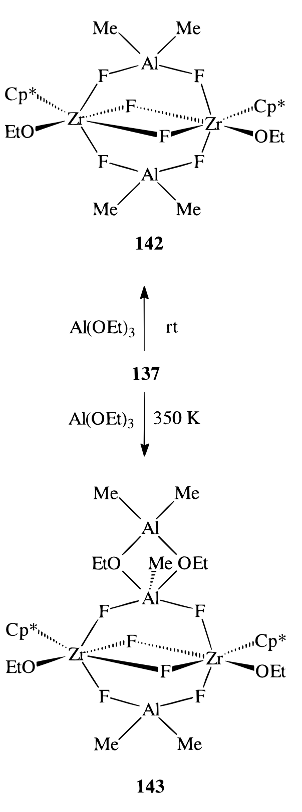
(57)

Cp' = Cp*; M = Zr (**139**), M = Hf (**140**)

Cp' = EtCp*; M = Zr (**141**)

hydrogen atoms at the cage corners are omitted for clarity

Stereospecific substitution of the two *cis*-methyl groups of **137** occurs on treatment with aluminum ethoxide (eq 58). Two products are isolated depending on the reaction temperature. At room temperature substitution of the two *cis*-methyl groups leads to **142**. Raising the reaction temperature to 350 K affords **143** where substitution of the two *cis*-methyl groups is accompanied by formation of a four-membered Al_2O_2 ring. These reactions represent a potentially useful route to modification of the transition metal coordination sphere of **137**.[147] In addition **142** and **143** constitute rare examples of the broad class of mixed halide−alkoxide group 4 compounds. This class of compound has proven difficult to prepare especially in the case of sterically undemanding alcohols such as ethanol.[148]



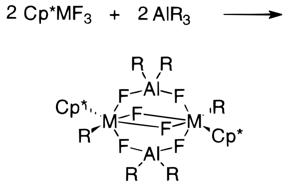
(58)

The relationship between stereochemistry (i.e., *cis* vs *trans* disposition of the alkyl groups) and steric bulk of the alkyl group in the reactions of homoleptic aluminum compounds with group 4 fluorides has

Table 7. Products from Reactions of Group 13 Alkyls/Alkoxides with Zirconium/Hafnium Fluorides

no.	compound	starting material/reagent	ref(s)
137	*cis*-$[(Cp^*ZrFMe)_2(\mu\text{-}F_2AlMe_2)_2]$	$Cp^*ZrF_3/AlMe_3$, X-ray	133, 146
138	*cis*-$[(Cp^*HfFMe)_2(\mu\text{-}F_2AlMe_2)_2]$	$Cp^*HfF_3/AlMe_3$, X-ray	133, 146
139	$(Cp^*Zr)_3Al_6Me_8(CH)_5(CH_2)_2\cdot$toluene	Cp^*ZrF_3/excess $AlMe_3$, X-ray	133, 146
140	$(Cp^*Hf)_3Al_6Me_8(CH)_5(CH_2)_2\cdot$toluene	Cp^*HfF_3/excess $AlMe_3$, X-ray	133, 146
141	$(EtCp^*Zr)_3Al_6Me_8(CH)_5(CH_2)_2\cdot$toluene	$EtCp^*ZrF_3$/excess $AlMe_3$	133, 146
142	*cis*-$[\{Cp^*ZrF(OEt)\}_2(\mu\text{-}F_2AlMe_2)_2]$	*cis*-$[(Cp^*ZrFMe)_2(\mu\text{-}F_2AlMe_2)_2]/Al(OEt)_3$, 300 K, X-ray	147
143	*cis*-$[\{Cp^*ZrF(OEt)\}_2\{\mu\text{-}F_2AlMe(\mu\text{-}OEt)_2AlMe_2\}(\mu\text{-}F_2AlMe_2)]$	*cis*-$[(Cp^*ZrFMe)_2(\mu\text{-}F_2AlMe_2)_2]/Al(OEt)_3$, 350 K, X-ray	147
145	*trans*-$[\{Cp^*ZrF(CH_2Ph)\}_2\{\mu\text{-}F_2Al(CH_2Ph)_2\}_2]$	$Cp^*ZrF_3/Al(CH_2Ph)_3$, X-ray	147
146	*trans*-$[\{Cp^*ZrF(CH_2SiMe_3)\}_2\{\mu\text{-}F_2Al(CH_2SiMe_3)_2\}_2]$	$Cp^*ZrF_3/Al(CH_2SiMe_3)_3$, X-ray	147
147	*trans*-$[\{Cp^*HfF(CH_2SiMe_3)\}_2\{\mu\text{-}F_2Al(CH_2SiMe_3)_2\}_2]$	$Cp^*HfF_3/Al(CH_2SiMe_3)_3$, X-ray	147

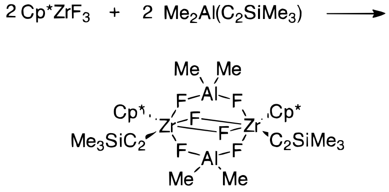
been investigated (eq 59). In all cases studied similar clusters were isolated and the two alkyl groups adopt a *trans* arrangement with respect to one another in the solid state. It appears that the *cis* arrangement arises only in the reactions of group 4 fluorides with trimethylaluminum. The complexity of these reactions increases dramatically when unsymmetrically substituted aluminum compounds are introduced. Reaction of dimethylaluminum acetylide $[Me_2Al(C{\equiv}CSiMe_3)]_2$ with Cp^*ZrF_3 illustrates this point clearly (eq 60). A complex mixture of products including *cis*-diacetylide **147** and compound **137** is isolated from this reaction. Compound **147** was structurally characterized but the structure could not be fully refined. Aminodimethylaluminum $Me_2AlN(SiMe_2Pr^i)(2,6\text{-}Me_2C_6H_3)$ reacts with Cp^*ZrF_3 to give the *cis* product **148** (eq 61). Steric demands of the bulky amino group are probably responsible for the isolation of **145** as the major product in this case.[147]



(59)

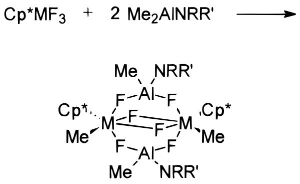
M = Zr; R = CH_2Ph (**144**), CH_2SiMe_3 (**145**)

M = Hf, R = CH_2SiMe_3 (**146**)



(60)

147



(61)

148

R = $SiMe_2Pr^i$, R' = $2,6\text{-}Me_2C_6H_3$

Products from the reactions of group 4 fluorides and aluminum compounds are gathered in Table 7. These preliminary studies of the reactions of aluminum compounds with organo group 4 fluorides are all the more remarkable given that the area of organo group 4 chloride/aluminum compound mixtures has been under active investigation for the last 30 years.[39]

VI. Group 5

Table 8 contains many of the group 5 fluorides currently known. Although one low-valent vanadium fluoride has been described, organometallic group 5 fluorides generally display a preference for higher oxidation states. In practice, the presence of two cyclopentadienyl groups and three halide atoms would result in a severely crowded coordination sphere in high oxidation state metallocene fluorides and this type of compound has not been reported. The stability of paramagnetic and coordinatively unsaturated Cp'_2MX_2 (M = Nb, Ta; X = halide) systems has been ascribed to a balance between electronic and steric factors.[149]

For group 5 fluorides, ^{19}F NMR signals for metal–fluorine and fluorines of coordinated anions are typically found downfield and upfield, respectively, of external standards $CFCl_3$ or CF_3Cl. Typically, ^{19}F NMR singlets characteristic of monomeric solution species are observed. This is consistent with weak metal–fluorine bridging interactions found in the solid state.

A. Vanadium

Treatment of Cp_2VCl_2 with 3 equiv of AsF_5 affords $Cp_2V(AsF_6)_2$ (**149**) in quantitative yield (eq 62).

$$Cp_2VCl_2 + 3\,AsF_5 \rightarrow Cp_2V(AsF_6)_2 + Cl_2 + AsF_3 \qquad (62)$$

Cp_2VCl_2 is readily oxidized to $[Cp_2V(AsF_6)_2][AsF_6]$ (**150**) in the presence of anhydrous HF using either AsF_5 or $AgAsF_6$.[150] $Cp_2V(SbF_6)_2$ (**151**) is prepared from Cp_2VCl_2 and $AgSbF_6$ in SO_2 as solvent and recrystallized from a SO_2/SO_2ClF mixture.[151] The Cp_2VF_2 fragments in **149** and **151** are isostructural having V–F distances of 2.04 Å. Compounds **149** and **151** are also isostructural with the titanium compounds $Cp_2Ti(AsF_6)_2$ (**33**)[77] and $Cp_2Ti(SbF_6)_2$ (**34**)[78] (section V.A.1).

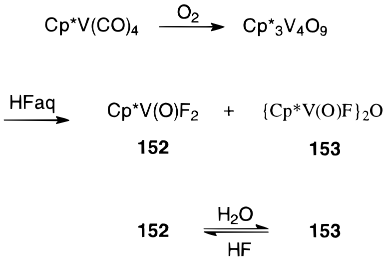
Aerial oxidation of $Cp^*V(CO)_4$ followed by treatment of the dark-red intermediate "$Cp^*_3V_4O_9$" toluene solution with aqueous HF gives a mixture of the oxo fluorides $Cp^*V(O)F_2$ (**152**) and $[Cp^*V(O)F]_2O$ (**153**) in low yields. Compound **152** and **153** have been identified by ^{51}V NMR. Compound **152** displays a triplet ($^1J(^{51}V,^{19}F)$ 234 Hz) and **153** a broad doublet

Table 8. Vanadium, Niobium, and Tantalum Fluorides

no.	compound	starting material/reagent	ref
149	$Cp_2V(AsF_6)_2$	Cp_2VCl_2/AsF_5, X-ray	150
150	$[Cp_2V(AsF_6)_2][AsF_6]$	Cp_2VCl_2/AsF_5 or $AgAsF_6/HF$	150
151	$Cp_2V(SbF_6)_2$	$Cp_2VCl_2/AgSbF_6$ in SO_2, X-ray	151
152	$Cp^*V(O)F_2$	$Cp^*V(CO)_4/HF(aq)$ mix of **149** and **150**	152
153	$[Cp^*V(O)F]_2O$	**152**/H_2O	152
154	$[Et_4P][CpVF(CO)_3]$	$[Et_4P][CpVI(CO)_3]/NaF$ in CH_2Cl_2	153
155	$CpNbF_4{\cdot}2AsF_3$	$CpNbCl_4/AsF_3$	154
156	$Cp^*NbF_4{\cdot}2AsF_3$	Cp^*NbCl_4/AsF_3	154
157	$Cp^*TaF_4{\cdot}2AsF_3$	Cp^*TaCl_4/AsF_3, X-ray	154, 155
158	$CpNbF_4$	**155**/vacuo 420 K	154
159	Cp^*NbF_4	**156**/vacuo 420 K	154
160	Cp^*TaF_4	**157**/vacuo 420 K	154, 155
161	$(EtCp^*)TaF_4$	$(EtCp^*)TaCl_4/AsF_3$, vacuo 420 K	154, 155
162	$Cp^*NbF_3[OC(Me)CHC(Me)O]$	**159**/LiOC(Me)CHC(Me)O	156, 157
163	$Cp^*NbF_3[OC(Ph)CHC(Ph)O]$	**159**/LiOC(Ph)CHC(Ph)O, X-ray	156, 157
164	$Cp^*TaF_3[OC(Me)CHC(Me)O]$	**160**/LiOC(Me)CHC(Me)O	156, 157
165	$Cp^*TaF_3[OC(CF_3)CHC(CF_3)O]$	**160**/$LiOC(CF_3)CHC(CF_3)O$	156, 157
166	$Cp^*TaF_3[OC(OEt)CPhC(OEt)O]$	**160**/LiOC(OEt)CPhC(OEt)O	156, 157
167	$Cp^*TaF_3[OC(Ph)CHC(Ph)O]$	**160**/LiOC(Ph)CHC(Ph)O, X-ray	156, 157
172	$Cp^*TaF_3[(NSiMe_3)_2(C_6H_4\text{-p-OMe})]$	**160**/$Li[(NSiMe_3)_2(C_6H_4\text{-}p\text{-OMe})]$, X-ray	159
174	$Cp^*TaF_4{\cdot}HN{=}PPh_3$	**160**/$HN{=}PPh_3$	160
175	$(Bu^tCH_2)_3TaF_2$	$(Bu^tCH_2)_3Ta{=}CHBu^t/HBF_4$, $(Bu^tCH_2)_4TaCl/TlBF_4$	161
			161
176	$[(MeCp)_2NbF(CH_2SiMe_3)][PF_6]$	$[(MeCp)_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)]/LiPF_6$	162
179	$[(Me_3SiCp)NbF\{\eta^2\text{-}(C,N)\text{-}R_2HCCNR\}][BF_4]$	**178**/$AgBF_4$	164, 165
180	$[(EtCp^*)_2NbF_2][PF_6]$	$(EtCp^*)_2NbCl_2/Na/Hg$ and HPF_6	166
181	$(EtCp^*)_2NbF_2$	**180**/electrochemical reduction	166
182	$(EtCp^*)_2Nb(\eta^2\text{-}S_2)F$	**180**/Li_2S_2	166

($^1J(^{51}V,^{19}F)$ 190 Hz). Mononuclear **152** is somewhat more volatile and less stable than the dinuclear oxo-bridged **153**. Slow conversion of **152** to **153** is observed in solution and also in the solid state. This equilibrium may be controlled in solution by addition of water or HF, and monitored by ^{51}V NMR spectroscopy (Scheme 9).[152] Halide exchange of $[Et_4P][CpVI(CO)_3]$ with sodium fluoride in dichloromethane furnishes a rare example of a low-valent vanadium complex $[Et_4P][CpVF(CO)_3]$ (**154**). IR and ^{51}V NMR data for **154** have been correlated with related species $[CpVX(CO)_3]^-$ (X = Cl, Br, I). Vanadium 51 shielding follows a normal halogen dependence within this series.[153]

Scheme 9



B. Niobium and Tantalum

Exothermic halogen metatheses of $CpNbCl_4$ and Cp^*MCl_4 (M = Nb, Ta) in the presence of excess arsenic trifluoride afford $CpNbF_4{\cdot}2AsF_3$ (**155**) and $Cp^*MF_4{\cdot}2AsF_3$ (M = Nb (**156**), M = Ta (**157**)). Sublimation of the arsenic trifluoride adducts at 420 K in vacuo gives $CpNbF_4$ (**158**), Cp^*NbF_4 (**159**), and Cp^*TaF_4 (**160**), respectively. While **158** is only sparingly soluble, Cp*-substituted **159** and **160** display good solubility properties. Recrystallization of **156** from arsenic trifluoride yields crystals of composition $[Cp^*NbF_4{\cdot}2AsF_3]_2[Cp^*NbF_4(HF)AsF_3]_2$ (Figure 7). The presence of a bridging HF molecule in the structure has been attributed to impurities in the arsenic trifluoride which arose as a result of the preparative procedure. X-ray structural analysis of the $Cp^*NbF_4{\cdot}2AsF_3$ (**156**) fragment shows it to be dimeric with two bridging (Nb−F, 2.18 Å and 2.04 Å) and three terminal fluorines (Nb−F_{av}, 1.92 Å). Niobium atoms enjoy a distorted octahedral geometry in **156**. $[Cp^*TaF_4]{\cdot}2AsF_3$ (**157**) is also dimeric in the solid state with a four-membered Ta_2F_2 ring with long (2.19 Å) and short (2.04 Å) Ta−F distances. Three terminal fluorines (Ta−F_{av}, 1.90 Å) and one Cp* ring complete a distorted octahedral coordination geometry about each tantalum. There are no metal−AsF_3 interactions in **156** and **157**. A singlet in the ^{19}F NMR spectrum shows **160** is monomeric in solution. $(EtCp^*)TaF_4$ (**161**) has been prepared by an identical procedure.[154,155] Further reaction of **160** with excess trimethylaluminum leads to the tetramethyl derivative Cp^*TaMe_4 in quantitative yield.[133]

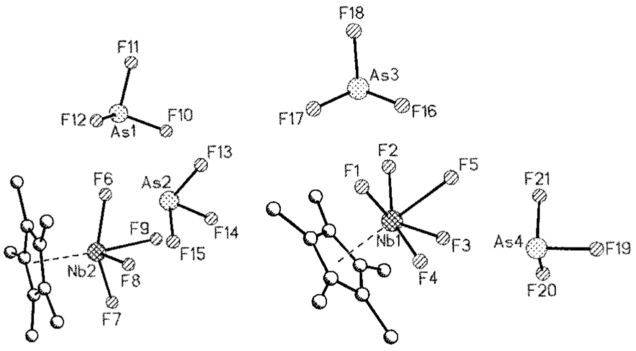
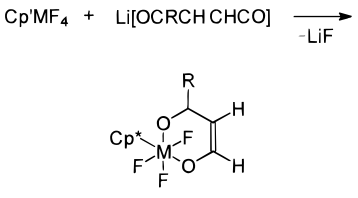


Figure 7. Structure of $[Cp^*NbF_4{\cdot}2AsF_3]_2[Cp^*NbF_4(HF)AsF_3]_2$ (**156**). (Reprinted with permission from ref 157. Copyright 1989 Springer Verlag.)

Substitution reactions of **159** and **160** with lithium salts of substituted chelating β-diketonate ligands proceed as shown in eq 63. The high Lewis acidity

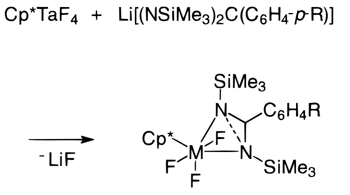


(63)

R = Ph; M = Nb (**163**), Ta (**167**)

of **159** and **160** makes it possible to prepare compounds with higher coordination numbers. X-ray crystal structures of $Cp^*MF_3[OC(Ph)CHCH(Ph)O]$ (M = Nb (**163**); Ta (**167**)) show the two oxygens from the β-diketonate moieties occupying one axial and one equatorial position. Three terminal fluorines ($Nb-F_{av}$, 1.92 Å; $Ta-F_{av}$, 1.92 Å) and the Cp* group, complete the distorted octahedral environments of the niobium and tantalum centers in **163** and **167**, respectively.[156-158]

Similarly, reactions of **160** with the lithium salts of *para*-substituted benzamidinates proceed with elimination of LiF and formation of $Cp^*TaF_3[(NSiMe_3)_2C\text{-}C_6H_4\text{-}p\text{-}R]$ (eq 64). In **172** two nitrogens of the chelating benzamidinate ligand occupy one axial and one equatorial position as for the diketonate **167**. As a consequence of steric restraints one fluorine is forced to lie *trans* to the Cp* ring ($Ta-F_{eq}$, 1.91 Å), while the other fluorines occupy axial positions ($Ta-F_{ax}$, 1.95 Å) of the *pseudo*-octahedral coordination sphere. Compounds **168**–**179** are soluble even in hydrocarbon solvents. Consistent with **168**–**179** being isostructural they all exhibit triplet/doublet splitting patterns in their ^{19}F NMR spectra. The unexpected appearance of a single singlet for the Me_3Si groups in **172** is probably a consequence of fluxional behavior in solution at room temperature.[159] Formation of the adduct $Cp^*TaF_4{\cdot}HN{=}PPh_3$ (**174**), on mixing **160** and $HN{=}PPh_3$, is consistent with the high Lewis acidity of **160**. Compound **174** has a distorted octahedral geometry at tantalum with four equatorial fluorines tilted toward the iminophosphorane ligand and a Ta–N distance in the range of a coordinative bond. Adduct formation with PPh_3 or $P(OMe)_3$ does not occur for **160**.[160]



(64)

R = H (**168**) Me, (**169**), CF_3 (**170**), CN (**171**), OMe (**172**), NMe_2 (**173**)

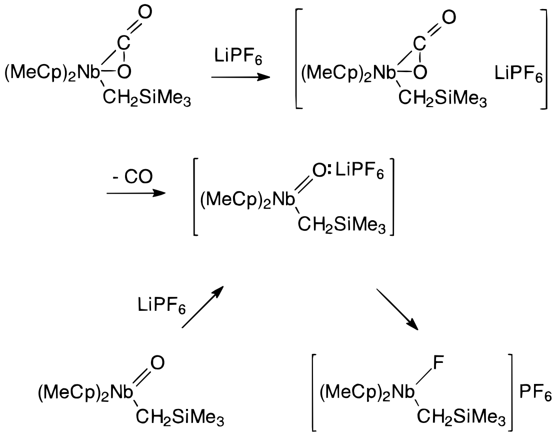
$(Bu^tCH_2)_3TaF_2$ (**175**) represents the only example of an early transition metal non-cyclopentadienyl-substituted organometallic fluoride. Schrock and Fellman succeeded in preparing **175** in moderate yields via two different routes. Attempts to form $[(Bu^tCH_2)_4Ta][BF_4]$ from $(Bu^tCH_2)_4TaCl$ and $TlBF_4$ led instead to the pentane soluble complex **175** (eq 65). Consistent with this result is the isolation of **175** on reaction of the tantalum neopentylidene complex $(Bu^tCH_2)_3Ta{=}CHBu^t$ with HBF_4 (eq 66). Apparently, in these reactions $[(Bu^tCH_2)_4Ta]^+$ readily abstracts fluoride from BF_4^- and then exchanges a second Bu^tCH_2 ligand for fluoride in BF_3.[161]

$$(Bu^tCH_2)_4TaCl + TlBF_4 \rightarrow \underset{\textbf{175}}{(Bu^tCH_2)_3TaF_2} \qquad (65)$$

$$(Bu^tCH_2)_3Ta{=}CHBu^t + HBF_4 \rightarrow \underset{\textbf{175}}{(Bu^tCH_2)_3TaF_2} \qquad (66)$$

Decarbonylation, accompanied by deoxygenation, of $(MeCp)_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)$ with $LiPF_6$, or $BF_3{\cdot}OEt_2$, produces $[(MeCp)_2NbF(CH_2SiMe_3)][Z]$ ($Z = PF_6^-$ (**176**), BF_4^- (**177**)). The reaction probably proceeds by decarbonylation to an oxoadduct, which then reacts with $LiPF_6$ to give **176** (Scheme 10).

Scheme 10

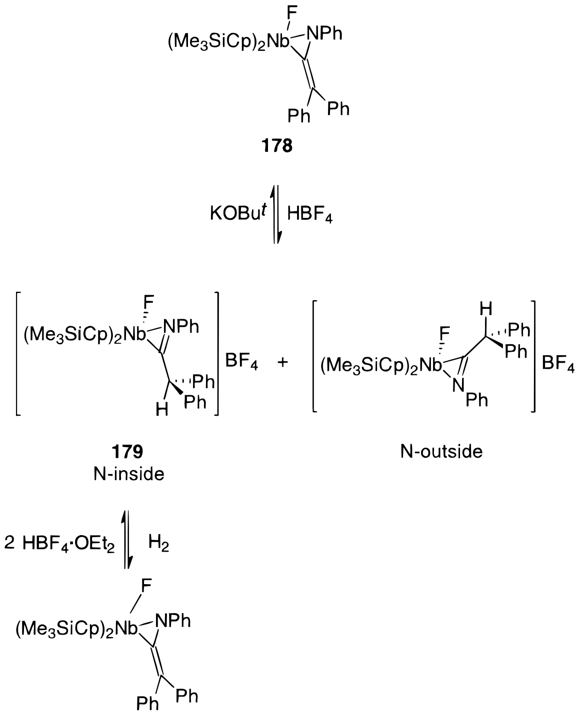


176

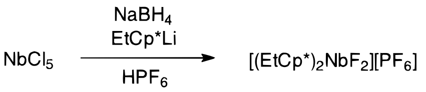
Compound **176** has also been isolated on reaction of the oxo derivative $(MeCp)_2Nb(O)(CH_2SiMe_3)$ with $LiPF_6$, confirming the proposed reaction pathway. The fate of the carbon dioxide derived oxygen has not been determined. The basic pseudotetrahedral geometry found for **176** is typical of Cp_2MXY complexes. Compound **176** provides the first measured niobocene Nb–F distance at 1.91 Å.[162]

One-step reaction of (ketenimine)niobocene fluoride $[(Me_3SiCp)_2NbF\{\eta^2(C,N)\text{-}Ph_2CCNPh\}]$[163] (**178**) with 1 equiv of $HBF_4{\cdot}OEt_2$ gives the η^2-iminoacyl $[(Me_3SiCp)_2NbF\{\eta^2(C,N)\text{-}Ph_2HCCNPh\}][BF_4]$ (**179**). The reaction proceeds via protonation at the free end of the uncomplexed ketenimine ligand (Scheme 11). This route affords the *N*-inside conformer, with the bulky fragments pointing away from the fluoride, as the major product. Compound **179** is also isolated as a 50:50 mixture of *N*-outside and *N*-inside conformers in the three-step reaction: oxidation, fluoride abstraction, and protonation of $(Me_3SiCp)_2Nb[\eta^2(C,N)\text{-}Ph_2HCCNPh]$ with 2 equiv of $HBF_4{\cdot}OEt_2$. The molecular structure of **179** and the related chloride exhibit typical bent-metallocene geometry around niobium (Nb–F, 2.20 Å) with a $\eta^2(C,N)$-bonded iminoacyl ligand similar to that of related η^2-iminoacyl complexes. Curiously, niobocene **179** exhibits a rather spurious value of 2.20 Å for a Nb–F terminal distance. Facile chemical and electrochemical one-electron reduction of **179** affords the starting ketenimine **178** with evolution of hydrogen (Scheme 11).[164,165]

Scheme 11



Solutions of the niobocene(IV) compound $(\mathrm{EtCp^*})_2\mathrm{NbCl_2}$ are prepared from $\mathrm{NbCl_5}$, $(\mathrm{EtCp^*})\mathrm{Li}$, and $\mathrm{NaBH_4}$. Treatment of this reduced solution with excess $\mathrm{HPF_6}$ leads to the first stable difluoroniobocene derivative $[(\mathrm{EtCp^*})_2\mathrm{NbF_2}][\mathrm{PF_6}]$ (**180**) (eq 67).

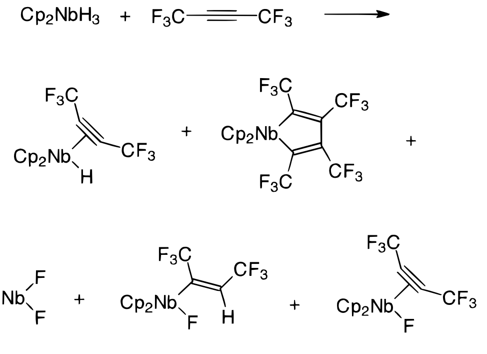


$$\mathrm{NbCl_5} \xrightarrow[\mathrm{HPF_6}]{\mathrm{NaBH_4}\ \ \mathrm{EtCp^*Li}} [(\mathrm{EtCp^*})_2\mathrm{NbF_2}][\mathrm{PF_6}] \qquad (67)$$

180

Related Cp*-substituted niobocenes gave yellow oils which did not crystallize. Compound **180** has a bent metallocene structure in which niobium is surrounded by two EtCp* and two fluoro ligands (Nb–$\mathrm{F_{av}}$, 1.91 Å). Repulsive effects of unpaired electrons in the related niobium(IV) dichloride $(\mathrm{EtCp^*})_2\mathrm{NbCl_2}$ (Cl–Nb–Cl, 85.2°) are absent in **180** (F–Nb–F, 102.3°). IR and ^{19}F NMR show absorptions characteristic of the two types of fluorines present, niobocene -$\mathrm{NbF_2}$ and the anion $\mathrm{PF_6^-}$, respectively. Cocrystallization of **180** and $[(\mathrm{EtCp^*})_2\mathrm{NbCl_2}][\mathrm{PF_6}]$ has been investigated using X-ray diffraction. Electrochemical reduction of **180** yields paramagnetic $(\mathrm{EtCp^*})_2\mathrm{NbF_2}$ (**181**). Compound **181** exhibits a 10-line ESR spectrum with triplet hyperfine structure. As noted in the case of $\mathrm{Cp_2NbF_2}$ (**183**), **181** also proved impossible to isolate. Compound **180** reacts with lithium sulfide ($\mathrm{Li_2S_2}$) to form $(\mathrm{EtCp^*})_2\mathrm{Nb}(\eta^2\text{-}\mathrm{S_2})\mathrm{F}$ (**182**). Interestingly, the corresponding dichloride is reduced by $\mathrm{Li_2S_2}$.[166]

Formation of the "extremely air-sensitive" compound $\mathrm{Cp_2NbF_2}$ (**183**), as a mixture with monofluorides **184** and **185**, has been observed in fluoride transfer from hexafluorobutyne to $\mathrm{Cp_2NbH_3}$ (eq 68). Reduced niobium species **183**–**185** were described as extremely air-sensitive, while the other reaction products were stable.[167] Photolysis of a toluene solution of $\mathrm{Cp_2NbH_3}$ and hexafluorobutyne gives the same result.[168] Examples of C–F bond activation mediated by group 5 organometallic compounds are limited to this one report.



(68)

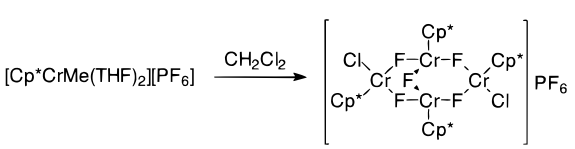
183 **184** **185**

VII. Group 6

Group 6 fluorides are collected in Table 9. As early as 1976 Fischer and co-workers had prepared the first transition metal alkylidyne fluoride.[169] Few developments in organochromium fluoride chemistry have occurred in the intervening time. Protonation of various molybdenum and tungsten hydride compounds, using $\mathrm{HBF_4{\cdot}OEt_2}$, has proven to be a convenient route to a diverse range of fluoroborate, and fluoride-substituted products. Recently, several fluorine-bridged bimetallic compounds $\mathrm{M}(\mu\text{-F})_3\mathrm{M}$ (M = Mo, W) have been described.

A. Chromium

Fischer isolated the very moisture sensitive *mer*-$(\mathrm{Me_3P})(\mathrm{CO})_3\mathrm{Cr}(\mathrm{CMe})(\mathrm{FBF_3})$ (**186**) on reaction of boron trifluoride with the alkylidyne *cis*-$(\mathrm{Me_3P})(\mathrm{CO})_3\mathrm{Cr}(\mathrm{CMe})(\mathrm{OMe})$. Compound **186** was characterized by IR and NMR spectroscopy. Reaction of **186** with water gives *mer*-$[(\mathrm{H_2O})\mathrm{Cr}(\mathrm{CO})_3(\mathrm{PMe_3})(\mathrm{CMe})][\mathrm{BF_4}]$.[169] Substitutionally labile $[\mathrm{Cp^*CrMe(THF)_2}][\mathrm{PF_6}]$ is catalytically active for the polymerization of ethylene, but exhibits a short lifetime in solution. One of the decomposition products is the tetranuclear $[\mathrm{Cp^*_4Cr_4}(\mu\text{-F})_5\mathrm{Cl_2}][\mathrm{PF_6}]$ (**187**). Compound **187** arises as a result of halogen abstraction from the $\mathrm{PF_6^-}$ anion and dichloromethane solvent (eq 69). In **187** four chromiums bridged by five fluorines (Cr–$\mathrm{F_{av}}$, 1.95 Å) give a butterfly-type core.[170] Cr–Cr distances (3.61 Å) are well outside the documented Cr–Cr single bond distance (2.21–2.54 Å).[171] The chromium(III) centers exhibit strong antiferromagnetic coupling mediated by the fluoride bridges. Mass spectroscopy indicates that $\mathrm{Cp^*_4Cr_4F_7}$, $\mathrm{Cp^*_4Cr_5F_8}$, $\mathrm{Cp^*_4Cr_6F_{10}}$, $\mathrm{Cp^*_5Cr_5F_8}$, and $\mathrm{Cp^*_5Cr_6F_{10}}$ are other possible decomposition products of $[\mathrm{Cp^*CrMe(THF)_2}][\mathrm{PF_6}]$.[170]



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187

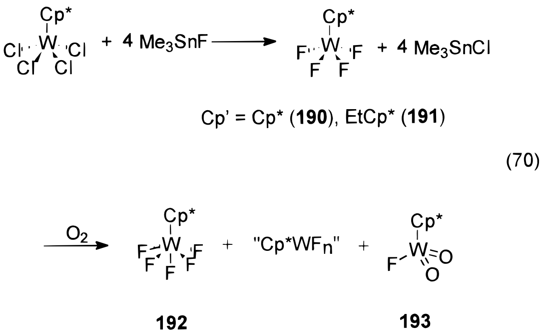
B. Molybdenum and Tungsten

High oxidation state tungsten alkyne compounds $[\mathrm{WCl_4}(\mathrm{R{-}C{\equiv}C{-}H})]_2$ and $[\mathrm{WCl_4}(\mathrm{R{-}C{\equiv}C{-}R'})]_2$ un-

Table 9. Chromium, Molybdenum, and Tungsten Fluorides

no.	complex	starting material/reagent	ref
186	*mer*-$(Me_3P)(CO)_3Cr(CMe)(FBF_3)$	$(Me_3P)(CO)_3Cr(CMe)(OMe)/BF_3$	169
187	$[Cp^*_4Cr_4(\mu\text{-}F)_5Cl_2][PF_6]$	$[Cp^*CrMe(THF)_2][PF_6]/CH_2Cl_2$, X-ray	170
190	Cp^*WF_4	Cp^*WCl_4/Me_3SnF	176
191	$(EtCp^*)WF_4$	$(EtCp^*)WCl_4/Me_3SnF$	176
192	Cp^*WF_5	**190**/O_2 and H_2O	176
193	$Cp^*W(O)_2F$	**190**/O_2 and H_2O	176
194	$W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2$	$W(O)(CHCMe_3)(Cl)_2(PEt_3)_2/TlBF_4$	177
195	$[MoF(\equiv CCH_2Bu^t)(dppe)_2][BF_4]$	$MoH_3(C\equiv CBu^t)(dppe)_2/HBF_4{\cdot}OEt_2$	178
196	$[MoF(MeHNC\equiv CNHMe)(dppe)_2][BF_4]$	$[Mo(CNHMe)(CNMe)(dppe)_2]/HBF_4{\cdot}OEt_2$	179
197	$[WF(MeHNC\equiv CNHMe)(dppe)_2][BF_4]$	$[W(CNHMe)(CNMe)(dppe)_2]]/HBF_4{\cdot}OEt_2$	179
198	$WF(\equiv CCH_2CO_2Me)(dppe)_2$	$WH_2(C\equiv CCO_2Me)_2(dppe)_2/HBF_4{\cdot}OEt_2$	180, 181
199	$[WF(=CHCH_2Ph)(dppe)_2][BF_4]$	$WH_2(C\equiv CPh)_2(dppe)_2/HBF_4{\cdot}OEt_2$	180, 181
200	$(MeCp)WF(H)(dmpe)$	$[(MeCp)W(dmpe)][PF_6]/LiAlH_4$, X-ray	182
201	$WH(BF_4)(CO)_3(PCy_3)_2$	$W(CO)_3(PCy_3)_2/HBF_4{\cdot}OEt_2$, X-ray	183
202	$(Me_3P)(NO)(CO)_3W(\mu\text{-}F)SbF_5$	$(Me_3P)W(CO)_3/[NO][SbF_6]$	184, 185
203	$(Me_2PhP)(NO)(CO)_3W(\mu\text{-}F)SbF_5$	$(Me_2PhP)W(CO)_5/[NO][SbF_6]$, X-ray	184, 185
204	$(Cy_3P)(NO)(CO)_3W(\mu\text{-}F)SbF_5$	$(Cy_3P)W(CO)_5/[NO][SbF_6]$, X-ray	184, 185
205	$(Me_3P)(NO)(CO)_3W(\mu\text{-}F)BF_3$	$(Me_3P)W(CO)_5/[NO][BF_4]$, X-ray	184, 185
206	$(Me_3P)(NO)(CO)_3W(\mu\text{-}F)PF_5$	$(Me_3P)W(CO)_5/[NO][PF_6]$, X-ray	184, 185
207	$[Et_4N][Mo(CO)_2F(S_2CNMe_2)_2]$	$Mo(CO)_2(S_2CNMe_2)_2/[Et_4N]F$	186
208	$[Et_4N][W(CO)_2F(S_2CNMe_2)_2]$	$W(CO)_2(S_2CNMe_2)_2/[Et_4N]F$	186
209	$[Et_4N][W(CO)_2F(S_2CNEt_2)_2]$	$W(CO)_2(S_2CNEt_2)_2/[Et_4N]F$	186
210	$[MoF(CO)_2(dppe)_2][PF_6]$	$Mo(CO)_2(dppe)_2/AgPF_6$	187
211	$[MoF(PhCCH)(dppe)_2][BF_4]$	$MoH_4(dppe)_2/HBF_4{\cdot}OEt_2$, $PhC\equiv CH$, X-ray	188
212	$[MoF(NH)(dppe)_2][BF_4]$	$MoH_4(dppe)_2/HBF_4{\cdot}OEt_2$, N_3^-	188
217	$[W_2(\mu\text{-}F)_3(CO)_4(PPhMe_2)_4][BF_4]$	$WH_6(PPhMe_2)_2/HBF_4{\cdot}OEt_2$, X-ray	189
218	$[Mo_2(\mu\text{-}F)_3(CO)_4(PEt_3)_4]$	$MoH_4(PEt_3)_4/HBF_4{\cdot}OEt_2$	189
219	$[Mo_2(\mu\text{-}F)_3(CO)_4(PPh_2Me)_4]$	$MoH_4(PPh_2Me)_4/HBF_4{\cdot}OEt_2$	189
220	$[Mo_2(\mu\text{-}F)_3(CO)_4(PPh_3)_4][BF_4]$	$Mo_2(CO)_4(PPh_3)_4Br_2/AgBF_4$, X-ray	190
221	$[W_2(\mu\text{-}F)_3(CO)_4(PPh_3)_4][BF_4]$	$W(CO)_2(PPh_3)_2Br_2/AgBF_4$	190
222	$[Mo_2(\mu\text{-}F)_2(\mu\text{-}Br)(CO)_4(PPh_3)_4][BF_4]$	$Mo_2Br_2(CO)_4(PPh_3)_4/NaBF_4$, X-ray	191
223	$[Mo_2(\mu\text{-}F)_2(\mu\text{-}Cl)(CO)_4(PPh_3)_4][BF_4]$	Mixture with **222**	191
224	$[Mo_2(\mu\text{-}F)_2(\mu\text{-}OH)(CO)_4(PPh_3)_4][BF_4]$	Mixture with **222**	191
225	$[W_2(\mu\text{-}F)_2(\mu\text{-}Br)(CO)_4(PPh_3)_4][BF_4]$	$W(CO)_2(PPh_3)_2Br_2/NaBF_4$	191
226	$[W_2(\mu\text{-}F)(\mu\text{-}Br)_2(CO)_4(PPh_3)_4][BF_4]$	$W(CO)_2(PPh_3)_2Br_2/NaBF_4$	191

dergo halide metathesis with NaF and KF in acetonitrile solution in the presence of crown ethers to afford fluoro complexes [Na(15-crown-5)][$WF_5(R{-}C{\equiv}C{-}R')$] (**188**) and [K(18-crown-6)][$WF_5(R{-}C{\equiv}C{-}R')$] (**189**), respectively. [Na(15-crown-5)][$WF_5(Ph{-}C{\equiv}C{-}Ph)$] (**188a**) and [Na(15-crown-5)][$WF_5(Ph{-}C{\equiv}C{-}H)$] (**188b**) form ion pairs in the solid state. In **188a** and **188b** the tungsten of the anion is coordinated by five fluorines and two carbons of the acetylenic group in a side-on manner corresponding to a metallacyclopropene structure. W−C distances are similar in **188a** and **188b**. Na−F distances are considerably longer in **188a**.[172,173] Similar structural features are observed for [Na(15-crown-5)][$WF_5(Ph{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3)$] (**188b**) and [K(18-crown-6)][$WF_5(Ph{-}C{\equiv}C{-}H)$]·MeCN (**189a**).[174,175]



Cp' = Cp* (**190**), EtCp* (**191**)

(70)

192 **193**

A relatively straightforward route to novel high oxidation state cyclopentadienyl tungsten fluorides Cp^*WF_4 (**190**) and $(EtCp^*)WF_4$ (**191**) involves reaction of the tetrachlorides with trimethyltin fluoride (eq 70). A dimeric or higher oligomeric structure is likely for **190** on the basis of a low *g* value (1.82) in the ESR spectrum and the beige color of the solid. Strong absorptions in the IR spectra of **190** and **191** at 576 and 572 cm^{-1}, respectively, have been assigned to tungsten−fluorine vibrations. On exposure to air **190** disproportionates to the tungsten(VI) complex Cp^*WF_5 (**192**) and other fluorine containing species “Cp^*WF_n”. Workup of the reaction solution affords the unusual mixed fluoro−oxide $Cp^*W(O)_2F$ (**193**) (eq 70). Compound **192** has a square-bipyramidal geometry with the Cp* occupying one apex and tungsten lying out of the plane of the square base (W−F_{av}, 1.90 Å; F−W−F_{av}, 158°). ^{19}F NMR spectroscopy highlights the nonequivalence of the four equatorial and one apical fluorine with the expected splitting patterns.[176]

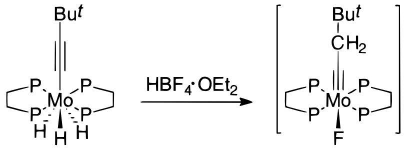
Attempts to prepare coordinatively unsaturated cationic complexes of $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ with BF_4^- or PF_6^- counteranions yielded the monofluoride $W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2$ (**194**) instead (eq 71).

$$W(O)(CHCMe_3)Cl_2L_2 + TlBF_4 \rightarrow W(O)(CHCMe_3)(Cl)(F)L_2 + TlCl + BF_3 \quad (71)$$

L = PEt_3 (**194**)

Compound **194** has only been identified in solution and isolated (60% NMR yield) as a mixture with $W(O)(CHCMe_3)Cl_2(PEt_3)_2$. Reaction in the absence of PEt_3 gives lower yields of **194**. No cationic species was observed.[177]

trans-[MoF($\equiv$CCH$_2$Bu^t)(dppe)$_2$][BF$_4$] (**195**) constitutes the first example of a stable paramagnetic alkylidyne compound. Protonation of [MoH$_3$(C$\equiv$CBu^t)(dppe)$_2$] with HBF$_4$·OEt$_2$ gives *trans*-(**195**) (eq 72), among other products. In **195** the alkylidyne ligand *trans* to fluorine (Mo–F, 2.02 Å) is disordered with two possible orientations.[178] HBF$_4$·OEt$_2$ promotes reductive coupling of aminocarbyne compounds *trans*-[M(CNHMe)(CNMe)(dppe)$_2$][BF$_4$] to the corresponding bis(amino)acetylene fluorides *trans*-[MF(MeHNC$\equiv$CNHMe)(dppe)$_2$][BF$_4$] M = Mo (**196**), M = W (**197**) (eq 73). In **196** four phosphorus atoms of two dppe ligands occupy equatorial positions of the octahedral molybdenum coordination sphere. Apical sites are occupied by fluoride (Mo–F, 2.02 Å) and the midpoint of the alkyne. The C$\equiv$C distance (1.37 Å) indicates extensive π-delocalization along the bis(amino)acetylene framework. Base-induced cleavage of the acetylenic bond occurs with deprotonation of the amino groups and defluorination of the metal, regenerating the starting compound [M(CNHMe)(CNMe)(dppe)$_2$][BF$_4$].[179] Protonation of the tungsten complexes [WH$_2$(C$\equiv$CR)$_2$(dppe)$_2$] (R = CO$_2$Me, Ph) leads to the alkylidyne [WF($\equiv$CCH$_2$R)(dppe)$_2$] (R = CO$_2$Me) (**198**) and the alkylidene [WF(=CHCH$_2$R)(dppe)$_2$][BF$_4$] (R = Ph) (**199**) fluorides, respectively (eq 74). Mechanisms for these reactions have not been investigated. It has been suggested that formation of **198** involves loss of one alkyne, with two successive protonations of the remaining alkynyl ligand to give the alkylidyne group followed by fluorination of the metal.[180,181]



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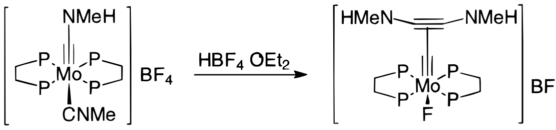
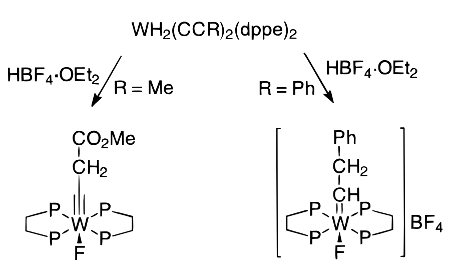


(73)

M = Mo (**196**), W (**197**)

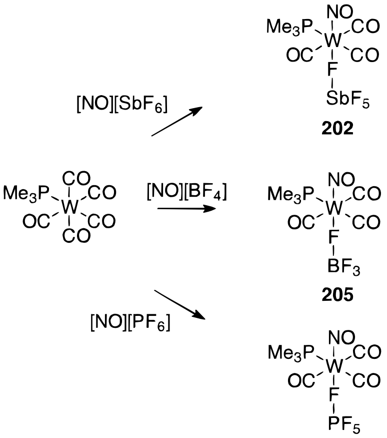


198 **199**

(74)

The fluoro hydride (MeCp)WF(H)(dmpe) (**200**) has been isolated as an unexpected product in the LiAlH$_4$ reduction of [(MeCp)W(dmpe)][PF$_6$]. Compound **200** has essentially a four-legged piano stool geometry with the chelating dmpe ligand spanning two *trans* sites and a terminal W–F distance of 2.04 Å. It is likely that fluoride abstraction from PF$_6^-$ occurs; however, the mechanism has not been fully investigated as the preparation is not reproducible.[182]

Scheme 12



202

205

206

Protonation of 16-electron W(CO)$_3$(PCy$_3$)$_2$ with equimolar HBF$_4$·OEt$_2$ in toluene leads to the kinetically labile 18-electron WH(BF$_4$)(CO)$_3$(PCy$_3$)$_2$ (**201**). The structure of **201** reveals two *trans* PCy$_3$ groups, two *trans* carbonyls and a η^1-coordinated BF$_4^-$ (W–F, 2.15 Å). Disorder prevented location of the hydride ligand. Formulation of the protonation product as a molecular species is consistent with its solubility in noncoordinating solvents. Reactivity studies show that protonation is initiated by proton transfer and not by coordination of a lone pair of the conjugate base BF$_4^-$.[183]

Hersh and Honeychuck described the preparation of the isostructural transition metal adducts *mer*-(*cis*-L)(*trans*-NO)(CO)$_3$W(μ-F)EF$_n$ (EF$_n$ = SbF$_5$, L = PMe$_3$ (**202**), PMe$_2$Ph (**203**); PCy$_3$ (**204**); EF$_n$ = BF$_3$, L = PMe$_3$ (**205**); EF$_n$ = PF$_5$, L = PMe$_3$ (**206**)) from LW(CO)$_5$ and [NO][EF$_{n+1}$] (Scheme 12). Within this series, thermal stability of the adducts decreases in the order SbF$_6^-$ > BF$_4^-$ > PF$_6^-$. As might be expected on the basis of this qualitative observation it was found that the BF$_4^-$ and SbF$_6^-$ adducts, **203** and **205**, display the shortest W–F distances while the unstable PF$_6^-$ adduct **206** and the sterically hindered **204** have longer W–F bond lengths. Similarity of the W–F distances for compounds **202**–**206** to that of M(μ-F)$_3$M (M = Mo, W) bond lengths infers that the anions are in fact covalently bound to tungsten. A comparison of bond lengths and bond length distortions allows the order of ligand binding strength to be determined as SbF$_6^-$ > BF$_4^-$ > PF$_6^-$. Definitive evidence for the coordination of the anions of these compounds in solution is provided in the form of ^{19}F, ^{31}P, and ^{13}C NMR spectra, which clearly exhibit coupling between the fluorines of the anion and the phosphorus and carbon atoms attached to tungsten. Neutral donors such as phosphine readily displace the anions to give [*mer*-(*cis*-Me$_3$P)(*trans*-NO)(CO)$_3$WL][EF$_{n+1}$].[184,185]

Addition of fluoride to 16-electron M(CO)$_2$(S$_2$CNR$_2$)$_2$ (M = Mo, W) furnishes the seven-coordinated complex anions [Et$_4$N][MF(CO)$_2$(S$_2$CNR$_2$)$_2$] (M = Mo, R = Me (**207**); M = W, R = Me (**208**), Et (**209**)) (eq 75).

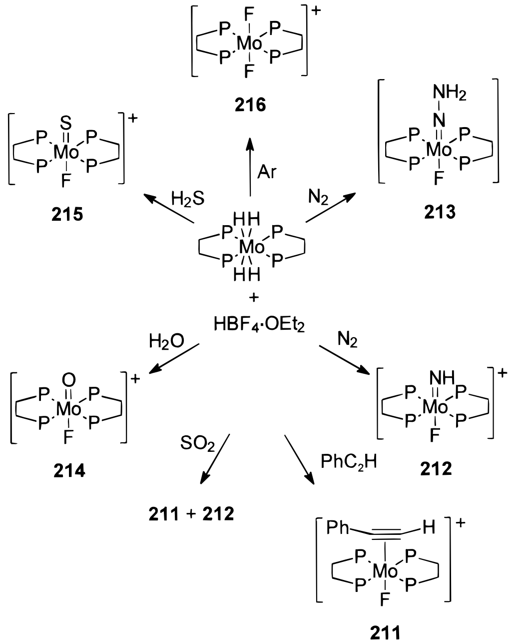
$$M(CO)_2(S_2CNR_2)_2 + [Et_4N]F \rightarrow [Et_4N][MF(CO)_2(S_2CNR_2)_2] \quad (75)$$

M = Mo, W

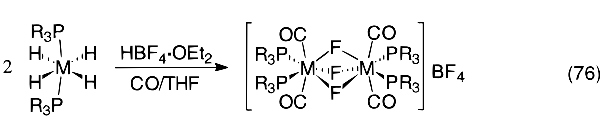
Lability of the fluorides in **207**−**209** to ligand substitution by phosphines and carbon monoxide affords neutral complexes.[186] The geometries exhibited by $[Et_4N][MoF(CO)_2(S_2CNMe_2)_2]$ (**207**)[186] and $[MoF(CO)_2(dppe)_2][PF_6]$ (**210**)[187] are almost identical and approximate a capped trigonal prism. Fluoride is the capping ligand in both complexes, lying over the face formed by the four dithiocarbamate sulfurs in **207**, and by the four dppe phosphorus in **210**. The Mo−F distances in **207** (2.06 Å) and **210** (2.04 Å) are similar. The nominally shorter distance for **210** is likely due to the cationic charge on the complex and the dppe π-acid character.

The highly reactive $MoH_4(dppe)_2/HBF_4{\cdot}OEt_2$ system exhibits a rapid and diverse range of reactivity with small molecules (Scheme 13). Reactions with various substrates fall into one of three categories: (i) binding without activation **211**, (ii) binding with activation **212** and **213**, and (iii) atom abstraction reactions **214** and **215**. All compounds in Scheme 13 have been characterized by NMR spectroscopy and magnetic susceptibility measurements. Under a nitrogen atmosphere low concentrations of **213** have been detected in the product mixtures. Protonation of the dinitrogen ligand gives the hydrazido species **213**. Cleavage of sulfur dioxide to **215** and **214** has been established by the isolation of these products from the independent reactions of $MoH_4(dppe)_2/HBF_4{\cdot}OEt_2$ with hydrogen disulfide and water, respectively. $[MoF(PhC{\equiv}CH)(dppe)_2]^+$ (**211**) has a quasi-octahedral molybdenum geometry (Mo−F, 1.98 Å) with the phenylacetylene ligand coordinated side on.[188]

Scheme 13



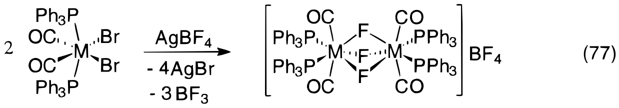
Henderson and co-workers obtained the bright-yellow $[W_2(\mu\text{-}F)_3(CO)_4(PPhMe_2)_4][BF_4]$ (**217**) on reaction of $WH_4(PPhMe_2)_2$ with $HBF_4{\cdot}OEt_2$ in CO saturated THF (eq 76). In **217** the coordination geometry and dimensions around both tungsten atoms are similar. Three bridging fluorines form a basal plane for each tungsten atom (W−F_{av}, 2.12 Å). Virtually parallel to this plane, beyond each tungsten atom, lie rhombic arrangements of two carbonyl carbons and two phosphine phosphorus donors. Compound **217** was obtained in low yield as a consequence of the presence of other species such as $[W_2(\mu\text{-}F)_2(THF)(CO)_4(PPhMe_2)_4]^{2+}$, the hydride-bridged compound $[W_2(\mu\text{-}F)_2(\mu\text{-}H)(CO)_4(PPhMe_2)_4]^+$, and $[PHR_3][BF_4]$ contaminant in the reaction mixture. A quartet pattern in the $^{31}P\text{-}\{H\}$ NMR and a quintet in the ^{19}F NMR are consistent with the presence of three equivalent fluorines and four phosphoruses in **217**. Assignment of $(\mu\text{-}F)_3$-bridged structures to $[Mo_2(\mu\text{-}F)_3(CO)_4(PEt_3)_4]$ (**218**) and $[Mo_2(\mu\text{-}F)_3(CO)_4(PPh_2Me)_4]$ (**219**) was based on the similarity of spectra to those of **217**.[189] This was confirmed in 1993 when Beck and co-workers, while attempting to prepare $[M(CO)_2(PPh_3)_2]^{2+}$ (M = Mo, W) derivatives via reaction of $M(CO)_2(PPh_3)_2Br_2$ with $AgBF_4$, succeeded in isolating the triply fluorine-bridged compound $[M_2(\mu\text{-}F)_3(CO)_4(PPh_3)_4][BF_4]$ (M = Mo (**220**), W = (**221**)) in excellent yield (eq 77).



(76)

M = W, R_3 = $PhMe_2$ (**217**)

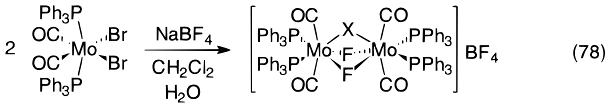
M = Mo, R_3 = Et_3 (**218**), Ph_2Me (**219**)



(77)

M = Mo (**220**), W (**221**)

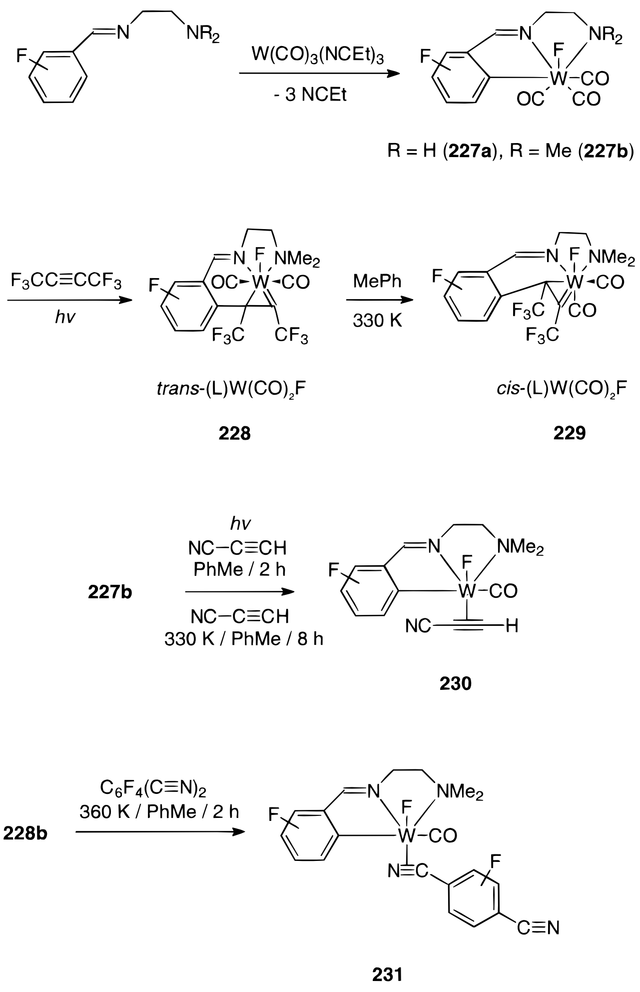
Compounds **217** and **220** are isostructural with each Mo having coordination number seven. In contrast to **217**, the Mo−F(2)−Mo in **220** is asymmetric (Mo−F(2), 2.10 and 2.21 Å). ^{19}F and ^{31}P NMR data demonstrate that the three fluorine and four phosphorus are equivalent in solution. Low-temperature ^{19}F NMR studies suggest the role of intermediates of the type $(F_3BF)_2Mo(PPh_3)_2(CO)_2$ in the formation of **220**.[190] Reactions of $MoBr_2(CO)_2(PPh_3)_2$ with aqueous $NaBF_4$ in a two-phase CH_2Cl_2/water mixture lead to the simultaneous formation of a number of triply bridged species including $[Mo_2(\mu\text{-}F)_2(\mu\text{-}X)(CO)_4(PPh_3)_4]^+$ (X = Br (**222**), Cl (**223**), OH (**224**)) and $[Mo_2(\mu\text{-}F)_3(CO)_4(PPh_3)_4]^+$ (**220**) (eq 78). Fractional recrystallization of the reaction mixture afforded crystals of **222** as the fluoride salt. This is surprising given that the bulk composition of the material was purportedly a BF_4^- salt. The structure of **222** shows a triply bridged dimer (Mo−F_{av}, 2.15 Å) with a long Mo−Br distance (Mo−Br, 2.69 Å) due to the *trans* influence



(78)

X = Br (**222**), Cl (**223**), OH (**224**)

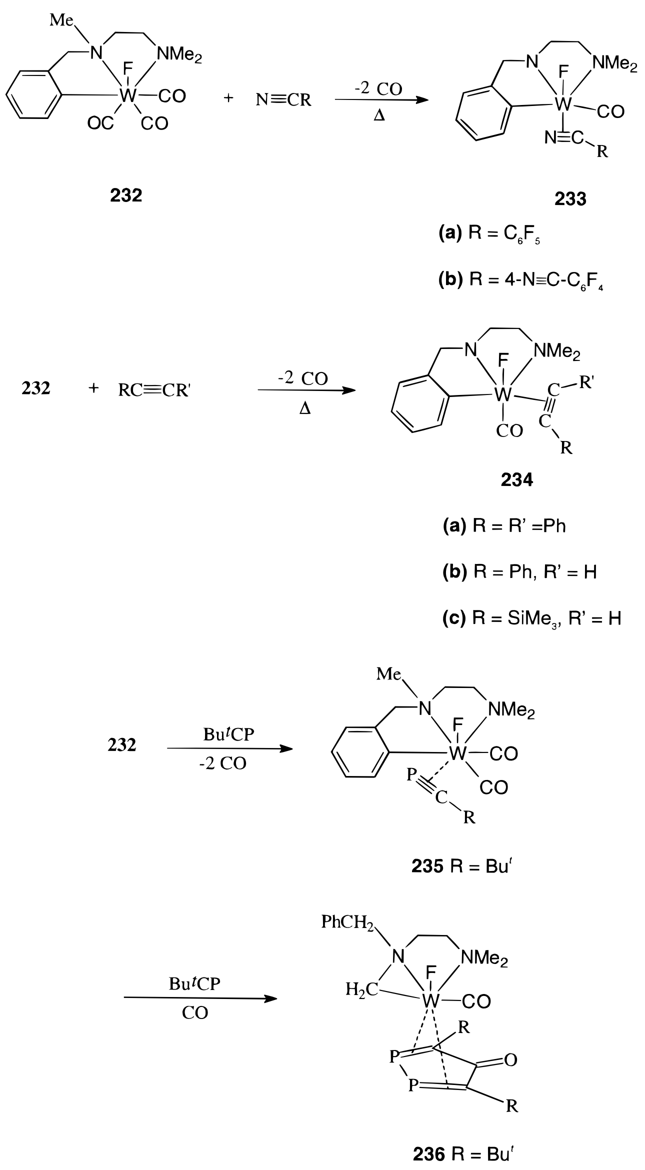
Scheme 14



of two carbonyl ligands. It was suggested that fluxional behavior of the bromide leads to facile substitution by fluoride, chloride, and hydroxide anions, leading to the product mixtures. “Adventitious” HCl present in dichloromethane appears to be the source of chloride in **223**. $WBr_2(CO)_2(PPh_3)_2$ reacts with $NaBF_4$ under identical conditions to give $[W_2(\mu\text{-}F)_n(\mu\text{-}Br)_{3-n}(CO)_4(PPh_3)_4]^+$ ($n = 2$ (**225**), 1 (**226**)). In general, the composition of the mixtures of products in these systems appears to be highly dependent on reaction conditions employed.[191] M−M distances of 3.35 Å remove any speculation of M−M interactions in these compounds.

Facile oxidative addition of the C−F bond of a perfluoroaromatic Schiff base bonded to a tungsten(0) center leads to fluoride compounds **227a** (R = H) and **227b** (R = Me) (W−F, 2.03 Å) (Scheme 14).[192] Alternatively **227b** is prepared by fluoride metathesis of the related chloride with potassium fluoride dihydrate.[193] Insertion of tungsten into a C−F bond in the presence of C−H bonds has also been observed.[194] Photolysis of a toluene solution of **227b** and perfluorobutyne at room temperature produces the *kinetic* η^2-vinyl complex **228**. In **228** the fluoride (W−F, 1.99 Å) lies *trans* to the inserted acetylene and *cis* to two carbonyl groups. On heating in solution, **228** undergoes isomerization to the *thermodynamic* η^2-vinyl product **229**. Here the fluoride ligand (W−F, 2.00 Å) is *cis* to the inserted alkyne and one carbonyl, and *trans* to the other carbonyl group. Kinetics of the

Scheme 15



$P(OMe)_3$-promoted η^2-vinyl isomerization have been studied. The geometry around the tungsten(II) centers in **228** and **229** are roughly octahedral if one considers the η^2-vinyl ligand to occupy a single coordination site.[195] Cyanoacetylene acts as a four-electron donor alkyne ligand in **230** (W−F, 1.96 Å). Compound **230** is obtained by two routes in equally poor yields (5%) (Scheme 14). Tests show that **230** is inactive for the polymerization of cyanoacetylene to poly(cyanoacetylene).[196] Treatment of **227b** with tetrafluoroterephthalonitrile furnishes the tungsten(II) nitrile complex **231**. Compound **231** provides a unique opportunity to compare and contrast a coordinated and uncoordinated nitrile function within the same complex.[197]

Related η^2-vinyl complexes have been obtained on reaction of **227b** with substituted alkynes and the products structurally characterized.[198] Scheme 15 summarizes reactions in which nitrile, alkyne, and phosphaalkyne complexes act as four-electron donor ligands. On the basis of spectroscopic and crystallographic data Richmond and co-workers have shown that the nitrile ligand functions as a better π-acid/poorer π-base than the η^2-alkyne ligand in complexes

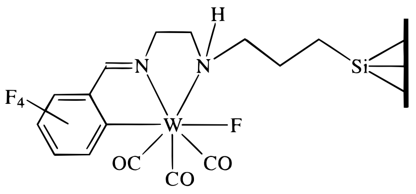


Figure 8. Surface-tethered tungsten fluoride.

233 and **234**. This leads to greater electron density at the metal centers for the alkyne complexes **234** compared with the nitrile complexes **233**. The difference is reflected in the coordination geometry of the flexible $\eta^3[C,N,N']$ chelate ligand system. In the nitrile complexes, the nitrile is *trans* to fluorine and the tridentate ligand adopts a meridonal geometry. To avoid π-conflicts with the fluoride ligand at the basic metal center, the tridentate ligand takes on a facial geometry in the alkyne complexes with the alkyne *cis* to fluoride.[199] Related phosphaalkyne complexes have been observed in solution (Scheme 15). Although **235** is not isolable in crystalline form, further reaction with $Bu^tC{\equiv}P$ affords **236**, containing an η^2-ligated 3,4-diphosphacyclopentadieneone group and a three-membered NCH_2W ring system.[200] This behaviour is different to that of the η^2-ligated nitrile complex whose chemistry is dominated by ready dissociation of the nitrile ligand.

Generation of surface tethered tungsten(II) species (Figure 8) has been achieved by two routes. Oxidative addition of a suitable tungsten complex to a surface-bound aryl halide and reaction of a tungsten complex with a pendant siloxane group followed by condensation with silica afford the surface-bound species. Metathesis with potassium fluoride leads to the surface-bound tungsten fluoride complex and substitution of one carbonyl group occurs on treatment with PEt_3. Reactivity studies show no surface effect on substitution reactions, but surface effects may lead to additional modes of reactivity.[201]

VIII. Group 7

Manganese and rhenium fluorides are listed in Table 10. In general organotechnetium chemistry is underdeveloped relative to the chemistry of the other transition metals. Technetium halocarbonyls (Cl, Br) constitute an important route to organotechnetium chemistry but no reports of fluorides have appeared.

A. Manganese

Selective replacement of the edge-bridging ethoxy group in $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$ on treatment with boron trifluoride generates $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}F)$ (**237**). X-ray analysis of **237** shows three $Mn(CO)_3$ units in a triangular cluster, with two face-bridging ethoxy groups and one edge-bridging fluoride ligand (Mn−F, 1.95 Å) (Figure 9).[202] The structure of $[Mn(CO)_3]_4(\mu_3\text{-}F)_2(\mu_3\text{-}OH)_2$ (**238**) ($Mn{-}F_{av}$, 2.05 Å) has been determined, but was highly disordered.[203]

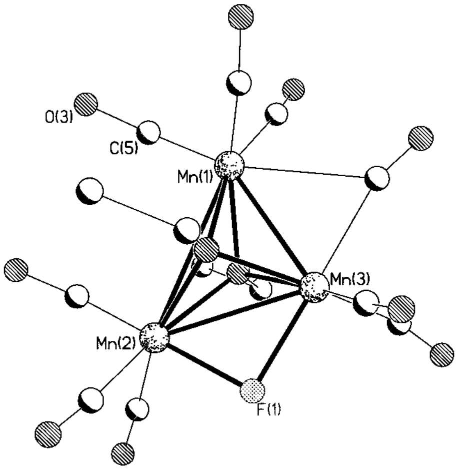


Figure 9. Structure of $[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}F)]$ (**237**). (Reprinted with permission from ref 202. Copyright 1979 Royal Society of Chemistry.)

B. Rhenium

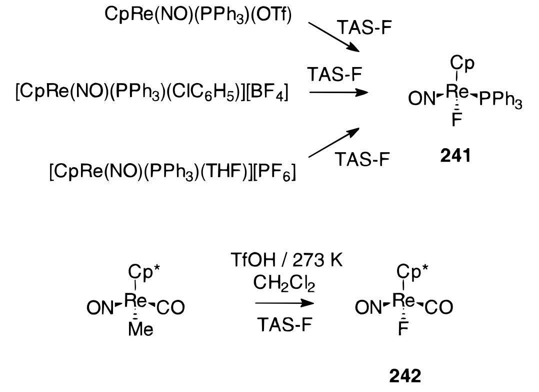
$(Cp^*ReO_2)_2$ is converted quantitatively to the mononuclear difluoro−oxo derivative $Cp^*Re(O)F_2$ (**239**) on treatment with aqueous hydrogen fluoride.[204] ^{17}O-enriched **239** and a series of $Cp^*Re(O)X_2$ (X = halide, alkyl, alkoxy) derivatives have been prepared and chemical shifts of the terminal oxo functions determined. $\delta(^{17}O)$ values are dependent on the σ-donor ability of the ligand (X) and correlate roughly to the electron density at rhenium.[205]

Treatment of a dichloromethane solution of *trans*-$[ReCl({=}C{=}CHBu^t)(dppe)_2]$ with $HBF_4{\cdot}OEt_2$ followed

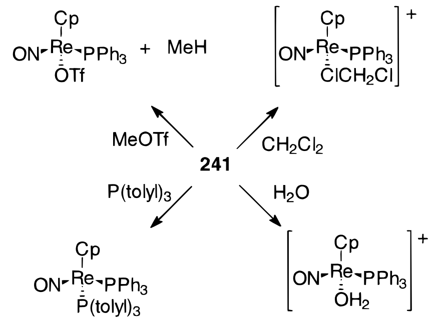
Table 10. Manganese and Rhenium Fluorides

no.	compound	starting material/reagent	ref
237	$Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}F)$	$Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)/BF_3{\cdot}OEt_2$, X-ray	202
238	$[Mn(CO)_3]_4(\mu_3\text{-}F)_2(\mu_3\text{-}OH)_2$	X-ray	203
239	$Cp^*Re(O)F_2$	$(Cp^*ReO_2)_2/HF(aq)$	204
240	*trans*-$[ReF({\equiv}CCH_2Bu^t)(dppe)_2][BF_4]$	trans-$ReCl({=}C{=}CHBu^t)(dppe)_2/HBF_4{\cdot}OEt_2$, X-ray	206
241	$CpReF(NO)(PPh_3)$	$CpRe(NO)(PPh_3)(OTf)$/TAS-F	207
242	$Cp^*ReF(NO)(CO)$	$Cp^*ReMe(NO)(CO)$/TfOH, TAS-F	207
243	$[ReF(CO)(NO)(PPh_3)_2][ClO_4]$	$ReH_2(NO)(PPh_3)_3/HBF_4$ or HPF_6, CO, X-ray	207
244	$ReFH(CO)(NO)(PPh_3)_2$	**243**/$Na[BH_4]$	207
245	$ReF(OMe)(CO)(NO)(PPh_3)_2$	**243**/NaOMe	207
246	$ReF_2(CO)(NO)(PPh_3)_2$	**243**/NaF	207
248	$[Re(CO)_3F]_4$	$Re(CO)_5Br/AgF$	210
249	$Re(CO)_3L_2F$ (L_2 = tmen)	$Re(CO)_3L_2Br/AgF_2H$	210
250	$[Re(CO)_3(L_2)F]_2H{\cdot}HOBF_3$	$Re(CO)_3L_2Br/AgF_2H$ in Pyrex glass vessel	24
252	*cis*-$Re(CO)_4(PPh_3)F$	*cis*-$Re(CO)_4(PPh_3)Me$/anhydrous HF, X-ray	212
253	*trans*-$Re(CO)_3(PPh_3)_2F$	*trans*-$Re(CO)_3(PPh_3)_2Cl/Ag(SO_3CF_3)$, [PPN]F	213
254	$[Et_4N]_2[Re_3H_2(CO)_9(\mu\text{-}FBF_3)]$	$Re_4H_4(CO)_{12}/[Et_4N][BF_4]$	216
255	$(OC)_5Re(\mu\text{-}F)ReF_5$	$Re_2(CO)_{10}/ReF_6$, anhydrous HF	217

Scheme 16



Scheme 17

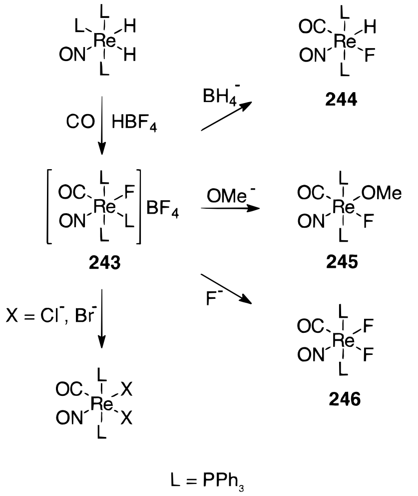


by addition of diethyl ether gives the alkylidyne complex *trans*-$[ReF(\equiv CCH_2Bu^t)(dppe)_2][BF_4]$ (**240**). In *trans*-**240** the Re−F bond length is 2.13 Å and the Re−C distance (1.77 Å) is slightly greater than that predicted from the sum of the triply bonded covalent radii of rhenium and sp-C.[206]

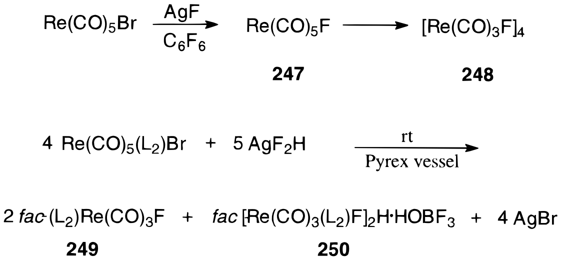
Reactions of substitutionally labile precursors with TAS-F in THF at room temperature give $CpReF(NO)(PPh_3)$ (**241**) in 65−75% yield and in high chemical purity (Scheme 16). Compound **241** decomposes quickly in solution at room temperature. Suggestion of $CpRe(NO)(PPh_3)FBF_3$ as an intermediate to **241** seems likely. Generation of $Cp^*ReF(NO)(CO)$ (**242**) via a slightly modified procedure has been described. Thermal stability and reactions of **241** with electrophiles and nucleophiles have been studied via ^1H and ^{31}P NMR (Scheme 17). These substitution reactions clearly demonstrate the synthetic utility of fluorides such as **241**. Loss of triphenylphosphine to give a fluorine-bridged dimer $[CpRe(NO)(\mu\text{-}F)]_2$ is not detected on thermal decomposition of **241**. IR ν_{NO} and ν_{CO} frequencies for **241** and **242** appear much lower than for corresponding chloride, bromide and iodide complexes. This suggests that the fluoride ligand behaves as *electron releasing* relative to other halide ligands, in this rhenium fragment at least.[207] Interest in compounds of the type $[CpReF(NO)(PPh_3)]$ stems from their potential use as precursors of chiral Lewis acids $[CpRe(NO)(PPh_3)]^+$ which have proven useful in asymmetric transformations.[208]

Treatment of $ReH_2(NO)(PPh_3)_3$ with HBF_4, or HPF_6, in the presence of carbon monoxide gives the novel fluoro cation $[ReF(CO)(NO)(PPh_3)_3]^+$ (**243**). Anion exchange affords the perchlorate salt $[ReF(CO)(NO)(PPh_3)_3][ClO_4]$. A meridonal arrangement of four phosphine ligands and fluoride ligand (Re−F, 1.97 Å) *trans* to a linear nitrosyl group completes the distorted octahedral rhenium coordination. Further reaction of **243** with coordinating anions provides neutral complexes $ReFX(CO)(NO)(PPh_3)_2$ (X = H (**244**), OMe (**245**), F (**246**)) (Scheme 18). In the formation of **244**, where fluoride is *trans* to carbon monoxide, the fluoride ligand has changed from a *trans* to nitric oxide position in **243**. Attempts to thermally isomerize **244** resulted only in decomposition. Compound **244** is also unusual in that its stereochemistry has been determined absolutely by a combination of IR and ^1H NMR spectroscopy.[209]

Scheme 18

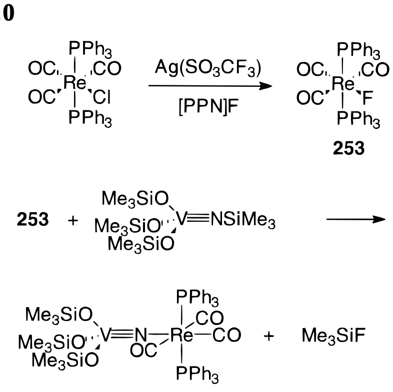


Scheme 19



Facile bromide abstraction from $Re(CO)_5Br$ with excess silver fluoride in fluorobenzene followed by removal of silver bromide and reflux leads to tetrameric $[Re(CO)_3F]_4$ (**248**) (Scheme 19). The reaction intermediate $Re(CO)_5F$ (**247**) was not isolated due to facile conversion to **248** even at room temperature. Compound **248** forms a cubane-type structure whose corners are alternately occupied by rhenium and μ_3-fluorine atoms (Re−F_{av}, 2.20 Å).[210] Bromide abstraction from $Re(CO)_3L_2Br$ (L = $SbPh_3$; L_2 = bpy, dppe, tmen) with silver bifluoride in plastic reaction vessels produces $Re(CO)_3L_2F$ (L_2 = tmen, (**249**)). When the same reaction was conducted in Pyrex flasks attack of the silver bifluoride led to the introduction of trifluoroborate into the system and the product crystallized as *fac*-$[Re(CO)_3(L_2)F]_2H{\cdot}HOBF_3$ (L_2 = tmen (**250**)).[24] The stereochemistry of the rhenium atoms is the same for **249** (Re−F, 2.04 Å) and **250** (Re−F, 2.24 Å). Hydrogen bonding between fluoride and $HOBF_4$ in **250** leads to the increased Re−F distance. HF solvates the silver fluoride thus preventing water solvation and subsequent formation of aqua complexes.[24] $(OC)_5ReFBF_3$ reacts with trimethylmethoxysilane to give the neutral complex $(OC)_5ReO(Me)BF_3$ (**251**).[211]

Scheme 20



Elimination of methane gas is a strong driving force in the formation of *cis*-$Re(CO)_4(PPh_3)F$ (**252**) on reaction of *cis*-$Re(CO)_4(PPh_3)Me$ with anhydrous HF. ^1H and ^{19}F NMR and IR spectroscopy confirm the *cis* formulation of **252**. Compound **252** completes the series $ReF(CO)_{5-x}(PPh_3)_x$ ($x = 0-2$)[3] and highlights the additional stability conferred on these complexes by substituting the more basic phosphine for CO.[212] Related methyl fluoride exchange using Olah's reagent (py·*x*HF) has been used in the preparation of $Mo_2F_4(PR_3)_4$.[26]

trans-$Re(CO)_3(PPh_3)_2F$ (**253**) is prepared on reaction of *trans*-$Re(CO)_3(PPh_3)_2Cl$ with $Ag(SO_3CF_3)$ and a large excess of [PPN]F in dichloromethane (Scheme 20). Carbonyl groups in **253** are considerably more labile than for the chlorine compound. The rate of *cis* ^{13}CO incorporation into the rhenium coordination sphere of **253** is roughly 2 orders of magnitude greater than at the *cis* positions in $Re(CO)_3(PPh_3)_2Cl$. *Trans*, as opposed to *cis*, incorporation of ^{13}CO is more than 10-fold slower for **253** giving essentially stereospecific substitution of the *cis* carbonyl group. Condensation of coordinatively saturated **253** with silylimido derivative $[(Me_3SiO)_3V{\equiv}NSiMe_3]$ leads to the nitride-bridged $[(Me_3SiO)_3V{\equiv}NRe(CO)_3(PPh_3)_2]$ in quantitative yield (Scheme 20).[213] The corresponding chloride reaction is complicated by side reactions involving trimethylsilyl chloride. Related syntheses of vanadium−platinum- and diiridium-bridged compounds suggest that this condensation reaction provides a general route to main group atom-bridged transition metal compounds.[214,215]

At room temperature in dichloromethane, reaction between $Re_4H_4(CO)_{12}$ and acetone followed by addition of $[Et_4N][BF_4]$ gives $[Et_4N]_2[Re_3H_2(CO)_9(\mu\text{-}FBF_3)]$ (**254**) in good yield. Compound **254** provides another example of a different bonding mode for the BF_4^- group. In **254** the regular triangular trirhenium cluster is capped by a μ_3-FBF_3 ligand (Figure 10). The Re−F distance for **254** (2.14 Å) is similar to that found for related systems. The B−F distance (1.50 Å) is longer than in the uncoordianted BF_4^- (1.41 Å) anion and the average of terminal BF_3 distances (1.36 Å). In order to fulfill the 18-electron rule for each rhenium center the bridging fluorine must be considered as a six-electron donor in this trirhenium cluster.[216]

Fluoride-bridged $(OC)_5Re(\mu\text{-}F)ReF_5$ (**255**) is a remarkable compound given that the fluoride bridges rhenium centers in two such dissimilar oxidation states. Both rhenium atoms are coordinated approximately octahedrally and are linked by a bent (Re−F−Re, 140°) fluorine bridge. Compound **255** is obtained by condensing ReF_6 on $Re_2(CO)_{10}$ in anhydrous HF.[217]

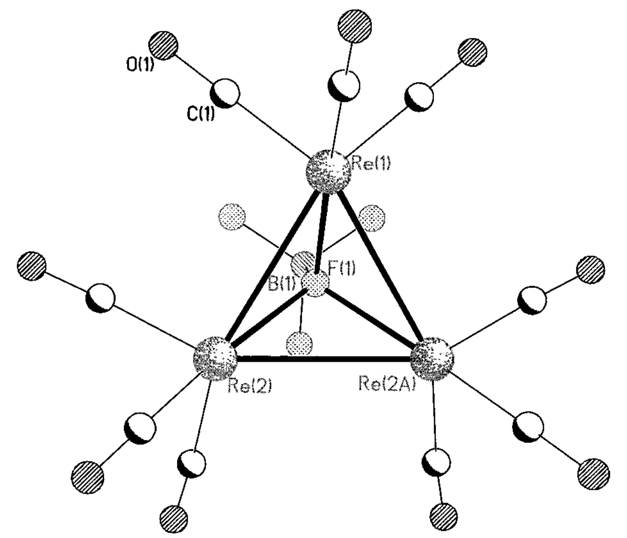


Figure 10. $[Et_4N]_2[Re_3H_2(CO)_9(\mu\text{-}FBF_3]$ (**254**). (Reprinted with permission from ref 216. Copyright 1994 Royal Society of Chemistry.)

IX. Groups 8−10

Group 8−10 fluorides are listed in Table 11. In general the organometallic fluoride chemistry of groups 8−10 is dominated by carbonyl and mixed carbonyl−phosphine systems. Cyclopentadienyl-substituted metal fluorides have only been described for iridium. There are no examples of organo iron and cobalt fluorides.

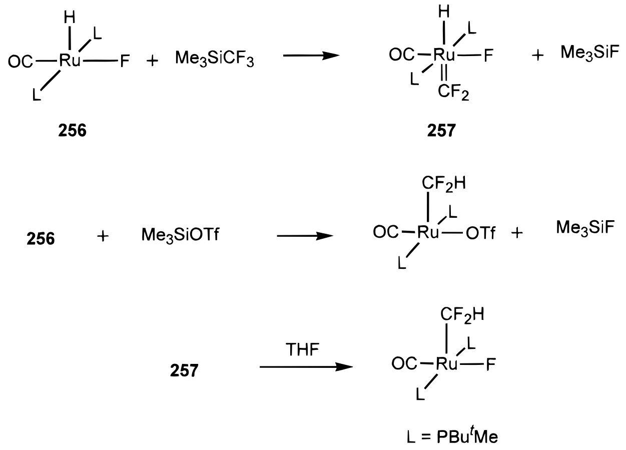
A. Ruthenium and Osmium

Caulton and Huang have described a very effective method for introducing fluorocarbon ligands, CF_2 and CF_3, based on the reaction of Me_3SiCF_3 with an appropriate organometallic fluoride.[218] Me_3SiCF_3 reacts smoothly with $RuHF(CO)(PBu^t{}_2Me)$ (**256**)[219] forming Me_3SiF and a six-coordinated product (**257**) where α-F migration has occurred in the proposed reaction intermediate $RuH(CF_3)(CO)(PBu^t{}_2Me)_2$ (Scheme 21). The CF_2 group is readily converted to CO by addition of water to **257**. Fluoride abstraction using Me_3SiOTf leads to an unusual rearrangement in which coordinated hydride migrates to the carbene forming CF_2H. Compound **257** is stable in benzene for extended periods but rearranges within hours in tetrahydrofuran via hydrogen migration to CF_2. Experimental evidence suggests that this rearrangement occurs by a mechanism involving dissociation of one phosphine ligand (Scheme 21).[218] The ν(CO) frequency has been investigated as a probe to determine the nature of the Ru−X bond in $RuHX(CO)(PBu^t{}_2Me)_2$ (X = halide, alkoxide) compounds. In all cases, the CO frequency is lower than that of free CO and the reduction increases in the order $I < Br < Cl < F <$ alkoxide.[219] In earlier work the modulation of reactivity and stereochemistry of substrate binding on variation of the X group in $RuHX(CO)(PBu^t{}_2Me)_2$ was described. In summary reactivity of

Table 11. Ruthenium and Osmium Fluorides

no.	compound	starting material/reagent	ref
256	$\mathrm{RuHF(CO)(PBu^t{}_2Me)_2}$	$\mathrm{RuHCl(CO)(PBu^t{}_2Me)_2/CsF}$	219
257	$\mathrm{RuHF(CF_2)(CO)(PBu^t{}_2Me)_2}$	$\mathrm{RuHF(CO)(PBu^t{}_2Me)_2/Me_3SiCF_3}$	218
258	$\mathrm{[RuF(\mu\text{-}F)(CO)_3]_4}$	$\mathrm{RuF_5/CO}$, X-ray	221, 222
259	$\mathrm{RuF(CO)_2[C(F)O](PPh_3)_2}$	$\mathrm{Ru(CO)_3(PPh_3)_2/XeF_2}$, HF at 200 K	223
260	$\mathrm{OsF(CO)_2[C(F)O](PPh_3)_2}$	$\mathrm{Os(CO)_3(PPh_3)_2/XeF_2}$, HF at 200 K	223
261	$\mathrm{RuF_2(CO)_2(PPh_3)_2}$	**259**/thermal decomposition, X-ray	223
262	$\mathrm{OsF_2(CO)_2(PPh_3)_2}$	**260**/thermal decomposition	223
263	*cis*-$\mathrm{Os(CO)_4F_2}$	$\mathrm{Os_3(CO)_{12}/XeF_2}$, anhydrous HF	224
268	*mer*-$\mathrm{Os(CO)_3F_3}$	*mer*-$\mathrm{K[Os(CO)_3Cl_3]}$ *mer*-$\mathrm{[\{Os(CO)_3Cl_2\}_2]/XeF_2}$ in HF or $\mathrm{IF_5}$	229
269a	$\mathrm{Cp'IrF(PMe_3)(aryl)}$	X-ray	230
272	$\mathrm{Cp^*IrF(PF_3)(PF_2)}$	$\mathrm{Cp^*IrF(PF_3)_2)}$/thermal decomposition	233
275	$\mathrm{Ir(CO)ClF(NSF_2)(PPh_3)_2}$	$\mathrm{Ir(CO)Cl(PPh_3)_2/NSF_3}$, X-ray	235
276	$\mathrm{Ir(CO)ClF(NSO)(PPh_3)_2}$	**275**/$\mathrm{H_2O}$	235
277	$\mathrm{Ir(CO)F_2X(PEt_3)_2}$ (X = Cl, Br, I)	*trans*-$\mathrm{Ir(CO)X(PEt_3)_2/XeF_2}$ 240 K	7
280	$\mathrm{[IrF\{C(F)O\}(CO)_2(PEt_3)_2][BF_4]}$	$\mathrm{[Ir(CO)_3(PEt_3)_2][BF_4]/XeF_2}$	7
287	$\mathrm{Ir(CO)FCl(PEt_3)_2SF_3}$	$\mathrm{Ir(CO)Cl(PEt_3)_2/SF_4}$, 200 K	7
288	$\mathrm{Rh(CO)FCl(PEt_3)_2SeF_3}$	$\mathrm{Rh(CO)Cl(PEt_3)_2/SeF_4}$, 200 K	7
289	*fac*- and *mer*-$\mathrm{IrF_3(CO)_3}$	$\mathrm{Ir_4(CO)_{12}/XeF_2}$, HF 230 K	238
291	$\mathrm{[IrF(NHNC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2][BF_4]}$	$\mathrm{Ir(NHNC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2/AgBF_4}$	240
292	$\mathrm{[RhF(C_2F_4)(C_2H_4)]_4}$	$\mathrm{RhCl(C_2F_4)(C_2H_4)/AgBF_4}$, TAS-F, X-ray	241
293	$\mathrm{RhF(C_2F_4)(PPh_3)_2}$	**292**/$\mathrm{PPh_3}$	241
294	$\mathrm{RhF(CO)(PPh_3)_2}$	**293**/CO, X-ray	242, 243

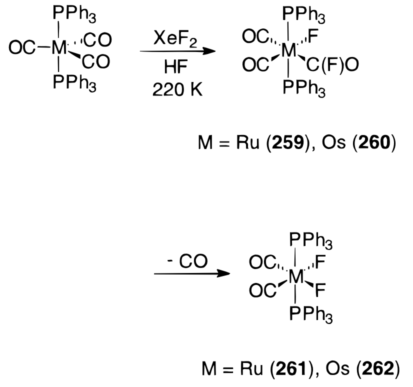
Scheme 21



$\mathrm{RuHX(CO)(PBu^t{}_2Me)}$ with substrates G−H (G = H, $\mathrm{SiR_3}$, $\mathrm{C_2Ph}$) occurs exclusively at the Ru−H bond for X = Cl and I. In contrast the fluoro analogue $\mathrm{RuHX(CO)(PBu^t{}_2Me)_2}$ displays reactivity at both the Ru−H and the Ru−F bonds.[220]

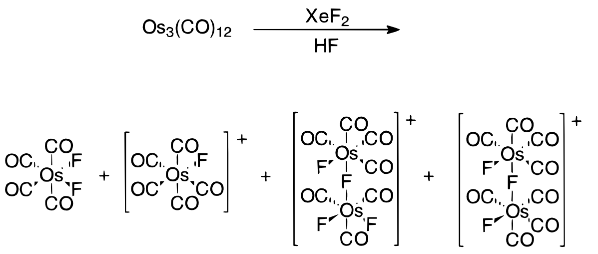
Tetrameric $\mathrm{[RuF(\mu\text{-}F)(CO)_3]_4}$ (**258**) is one of the earlier carbonyl fluorides to be structurally characterized. Compound **258** is isolated on reaction of ruthenium pentafluoride with carbon monoxide. Four terminal (Ru−$\mathrm{F_{av}}$, 1.99 Å) and four bridging (Ru−$\mathrm{F_{av}}$, 2.04 Å) fluorines give the tetrameric structure which is based on the ruthenium pentafluoride tetramer. Disorder in the structure solution gives rise to large uncertainties in bond lengths and angles, and is probably responsible for the very similar terminal and bridging Ru−F distances.[221,222]

Stepwise fluorination of ruthenium(0)- and osmium(0)-mixed carbonyl−phosphine compounds occurs at low temperatures via metal fluoroacyl intermediates $\mathrm{RuF(CO)_2[C(F)O](PPh_3)_2}$ (**259**) and $\mathrm{OsF(CO)_2[C(F)O](PPh_3)_2}$ (**260**), leading to low-valent metal difluorides $\mathrm{MF_2(CO)_2(PPh_3)_2}$ (M = Ru (**261**), Os (**262**)) (eq 79). Compound **259** decomposes at room temperature with elimination of one carbonyl group to $\mathrm{RuF_2(CO)_2(PPh_3)_2}$ (**261**). Compound **262** is prepared by heating fluoroacyl **260** in solution for several hours. Structural analysis of **261** confirmed the octahedral ligand geometry assigned on the basis of ^{31}P and ^{19}F NMR. Ru−C, Ru−P, C−O, and Ru−F (2.01 Å) bond lengths for **261** are comparable with those for related Ru(II) complexes. Addition of $\mathrm{BF_3{\cdot}OEt_2}$ to the thermally more stable osmium fluoroacyl **260** results in fluoride abstraction from the acyl fluoride group. Curiously, even in the presence of excess $\mathrm{BF_3{\cdot}OEt_2}$ fluoride abstraction does not occur at the Os−F bond. A reaction mechanism involving oxidation by $\mathrm{XeF^+}$ followed by nucleophilic attack of fluoride at coordinated CO is reasonable on the basis of these abstraction reactions. Subsequent elimination of CO yields stable compounds **261** and **262**. Low-temperature NMR reveals the formation of a thermally unstable adduct $\mathrm{Ru(CO)_3(PPh_3)_2(\mu\text{-}FBF_3)}$ as a reaction intermediate. No corresponding osmium adduct was detected.[223]



(79)

Oxidative fluorination of $\mathrm{Os_3(CO)_{12}}$ with $\mathrm{XeF_2}$ in anhydrous HF proceeds at 220 K with liberation of xenon gas and formation of a number of HF-soluble osmium complexes (eq 80).[224] *cis*-$\mathrm{OsF_2(CO)_4}$ (**263**), first reported in 1978,[225] is the major product (70%) and $\mathrm{[Os\ F(CO)_5]^+}$ (**264**), $\mathrm{[Os_2F_4(CO)_7]^+}$ (**265**), and $\mathrm{[Os_2F_3(CO)_8]^+}$ (**266**) are minor products in this reaction. Formation of **264** with a higher carbonyl to osmium ratio than the starting material confirms



263 **264** **265** **266**

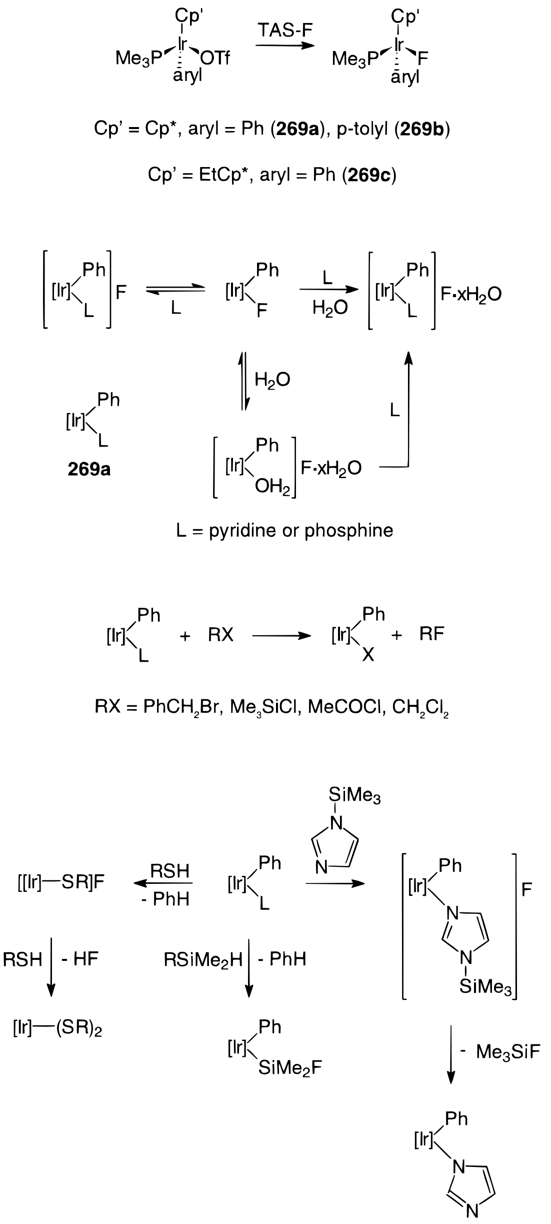
that carbonyl scrambling occurs during metal–metal bond cleavage. Addition of Lewis acids (BF_3 and AsF_5) leads to total decomposition and formation of an insoluble precipitate which is likely a product of fluoride abstraction. Compounds **263**–**266** represent the only examples of carbonyl/fluoride ligand-stabilized osmium(II) complexes.[224] Hope and co-workers recently reinvestigated the related oxidative florination of $Ru_3(CO)_{12}$ with XeF_2 in anhydrous HF. This reaction affords solution species *cis*-$RuF_2(CO)_4$ as the major product with $[RuF(CO)_5]^+$, $Ru_2F_4(CO)_7$, $[\{RuF(CO)_4\}_2(\mu\text{-}F)]^+$, *mer*- and *fac*-$[RuF_3(CO)_3]^-$, $[RuF_2(CO)_3]_n$, and $[\{RuF_2(CO)_3\}(\mu\text{-}F)\{Ru(CO)_5\}]^+$ as minor products.[226] Previously on the basis of ESR and magnetic susceptibility measurements oxidation to an unusual 17-electron complex $RuF_3(CO)_3$ had been incorrectly reported for this reaction.[227]

Compound **263** has also been prepared via reaction of *cis*-$Os(CO)_4Me_2$ with HF. Elimination of methane gas is a strong thermodynamic driving force in this reaction and as expected no carbonyl scrambling is observed. Compound **263** has been identified by a combination of multinuclear NMR studies.[228] Reactions of osmium carbonyl chloride complexes *mer*-$K[Os(CO)_3Cl_3]$ and *mer*-$[Os(CO)_3Cl_2]_2$ with XeF_2 in anhydrous HF or IF_5 give *mer*-$Os(CO)_3F_3$ (**268**) as characterized by EPR and IR spectra.[229]

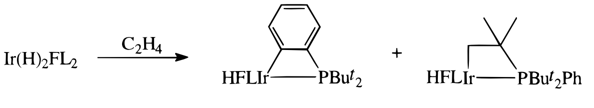
B. Rhodium and Iridium

Bergman and co-workers showed that facile Ir–F ionization of aryliridium(III) fluorides $Cp'IrF(PMe_3)(aryl)$ **269a**–**c** (Scheme 22) leads to exceptionally high reactivity for these compounds. In anhydrous solutions at room temperature, Lewis bases such as pyridines and phosphines slowly displace fluoride from **269a**. An equilibrium is established between the resultant salt and the covalent starting material. Remarkably the rate of establishment and magnitude of the equilibrium constant are increased dramatically on addition of water. The high reactivity of the hydrates $[Cp'Ir(PPh_3)(aryl)(OH_2)]F{\cdot}xH_2O$ enables these species to serve as intermediates in water catalyzed substitutions of fluoride by various Lewis bases. Failure to detect a related hydroxide compound indicates that the ability of fluoride to abstract a proton from $[Cp'Ir(PPh_3)(aryl)(OH_2)]F{\cdot}xH_2O$ in aqueous media is highly attenuated by solvation.[230] The greater propensity of fluoride ion to dissociate from the iridium center, even in nonpolar solvents, leads to reactivity which is substantially different from the related halide compounds and similar to that of corresponding triflates.[231] Compound **269a** undergoes exchange reactions with organic halides including dichloromethane. Reactions with (trimethylsilyl)imidazole, boranes and silanes have been studied (Scheme 22). Compound **269a** has a typical three-legged piano stool geometry (Ir–F, 2.07 Å).[230]

Scheme 22



Caulton demonstrated how fluorine, acting as a π-acid ligand in unsaturated metal complexes, can be used to promote C–H bond activation. Heating $Ir(H)_2FL_2$ (L = $PBu^t{}_2Ph$) in toluene in excess ethylene leads to **270** and **271** (eq 81). These products are the result of irreversible ethylene scavenging of hydride ligands from Ir. Rapid trapping of highly unsaturated intermediates, via intramolecular C–H oxidative addition, then leads to **270** and **271**. This



270 **271**

L = $PBu^t{}_2Ph$

dehydrogenation only proceeds when the halide substituent X in $Ir(H)_2XL_2$ is fluoride.[232]

Thermally induced oxidative isomerization of one trifluorophosphine ligand in $Cp^*IrI(PF_3)_2$ gives the iridium(III) fluoride $Cp^*IrF(PF_3)(PF_2)$ (**272**) (eq 82).

$$Cp^*Ir(PF_3)_2 \xrightarrow{\Delta} Cp^*IrF(PF_3)(PF_2) \qquad (82)$$

272

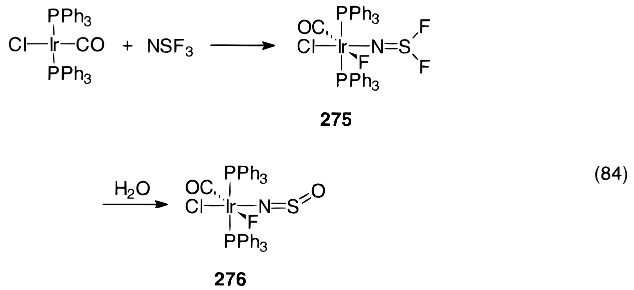
Structural assignment of **272** was made by ^{19}F NMR spectroscopy.[233] Compound **272** is unusual given that trifluorophosphine typically acts as a donor ligand and P−F bonds are not normally active in oxidative addition.

Stoichiometric protonation of $MMe_3(PMe_2Ph)_3$ in dichloromethane leads to molecular *cis,mer*-$MMe_2(PMe_2Ph)_3(BF_4)$ (M = Rh (**273**), Ir (**274**)) with generation of methane gas (eq 83). In the solid **274** shows an η^1-coordinated BF_4^- group (Ir−F, 2.39 Å) *trans* to methyl and an octahedrally coordinated iridium(III) center. In dichloromethane the BF_4^- anion is not coordinated to iridium and it is not certain whether a 18-electron solvated $[IrMe_2(CH_2Cl_2)(PMe_2Ph)_3]^+$ or a 16-electron $[IrMe_2(PMe_2Ph)_3]^+$ cation persists. Reactions of **273** and **274** with unsaturated nucleophiles (CO and ethylene) highlight the differences in reactivities and stabilities of analogous rhodium and iridium complexes.[234]

$$MMe_3(PMe_2Ph)_3 + HBF_4{\cdot}OEt_2 \rightarrow MMe_2(PMe_2Ph)_3(BF_4) + MeH$$

M = Rh (**273**), Ir (**274**) (83)

A novel thiazyl difluoride complex Ir(CO)Cl(F)-$(NSF_2)(PPh_3)_2$ (**275**) is obtained on reaction of Ir(CO)-$Cl(PPh_3)_2$ with NSF_3 (eq 84). Compound **275** is extremely moisture sensitive and readily undergoes hydrolysis to the corresponding NSO complex **276**. Compound **275** (Ir−F, 2.09 Å) represents the first example of a complex where thiazyl difluoride acts as ligand. Oxidative addition across an S−F bond of NSF_3 is also a novel feature of this reaction.[235]

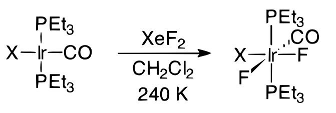


275

(84)

276

Four-coordinated iridium(I) compounds *trans*-$Ir(CO)X(PEt_3)_2$ oxidatively add XeF_2 at 240 K to give $Ir(CO)F_2X(PEt_3)_2$ (**277a**−**c**) as major products (eq 85).

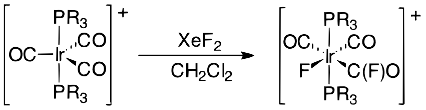


(85)

X = Cl, Br, I

Relatively small amounts of two isomeric monofluorides $Ir(CO)FX_2(PEt_3)_2$ (**278a**−**c**) and trifluoride $Ir(CO)F_3(PEt_3)_2$ (**279**) have also been detected. $Ir(CO)F_2X(PEt_3)_2$ are stable in solution at room temperature while analogous rhodium complexes are less thermally stable.[7]

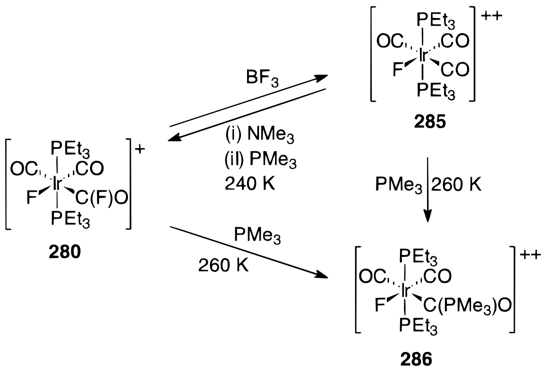
Oxidative addition of XeF_2 across the M−C(*CO*) bonds of five-coordinated iridium(I) complexes $[Ir(CO)_3(PR_3)_2][BF_4]$ produces unusual fluoroacyl compounds $[IrF\{C(F)O\}(CO)_2(PR_3)_2][BF_4]$ (**280**-**284**) (eq 86). In **280** the coordination around iridium is essentially octahedral. The acyl fluorine is *cis* to the iridium-bound fluorine (Ir−F, 2.00 Å).[236] Reactions of various phosphine-substituted $Ir(CO)_4L_2$ (L = PMe_3, PEt_3, PMe_2Ph, PEt_2Ph) compounds show that complexes of the most basic phosphines react more readily with XeF_2 (eq 86). This is expected if electron density at iridium(I) is important in this oxidative reaction. Bulkier phosphines such as triphenyl, methyldiphenyl, and the very basic tricyclohexyl phosphines sterically hinder the reaction. In a related reaction, $[Ir(CO)(PMe_3)_4]Cl$ reacts with XeF_2 to give stable $[Ir\{C(F)O\}F(PMe_3)_4]Cl$. Formation of two fluoroacyl species is observed on reaction of $Ir(CO)_2Cl(PMe_3)_2$ with XeF_2.[7]



(86)

$R_3 = Et_3$ (**280**), Me_3 (**281**), Me_2Ph (**282**), Et_2Ph (**283**), $EtPh_2$ (**284**)

Boron trifluoride-mediated fluoride abstraction of the acyl fluoride in **280** leaves an unusual *tris*-carbonyl Ir(III) dication **285** (eq 87). Compound **285** has been structurally characterized.[3] The reverse process is observed when the BF_4^- salt **285** is treated with trimethylamine. Reaction of **285** with trimethylphosphine at 240 K also regenerates **280**. At higher temperatures (260 K) an unusual dication **286**, derived from **280,** in which the acyl fluoride has been replaced by trimethylphosphine is detected. Fluoroacyl complexes have been investigated as synthetic intermediates (eq 88). The substituted acyl compounds are all unstable at room temperature.

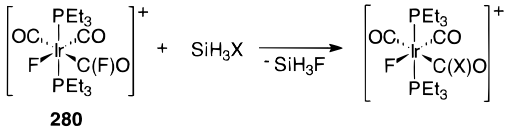


285

280

(87)

286



(88)

280

X = CN, NCO, NCS

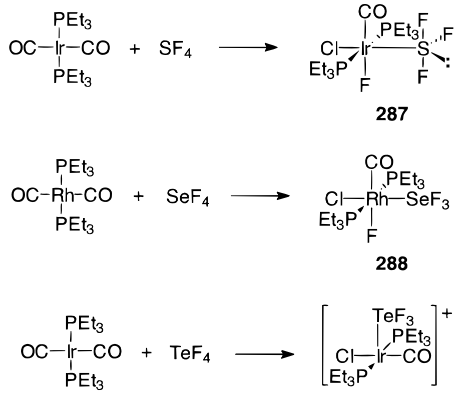
Attempts to form a chloroacyl compound using trimethylsilyl chloride lead mainly to mixtures of fluoroacyl species.[7]

Consistent with the reactions of **280** with Lewis bases, the mechanism of the fluorination in eq 87 probably involves attack of a formally positive XeF^+ fragment to give the metal fluoride. This step is followed by nucleophilic attack of fluoride at the carbonyl group or alternatively fluoride migration from iridium to carbonyl and fluorination of iridium (eq 89). In this system it is not possible to differentiate between attack of fluoride at the coordinated CO or migration of the metal-bound fluoride to carbonyl. There is, however, no evidence for fluorination of the carbonyl group *trans* to fluorine. Six-coordinated iridium(III) complexes $Ir(CO)XYZ(PEt_3)_2$ are unaffected by XeF_2 up to 300 K at which temperature the compounds start to decompose. Well-defined reactions for this system include fluorination of unsaturated or easily oxidized ligands.[237]

$$[Ir(CO)_3(PEt_3)_2]^+ + XeF^+ \longrightarrow IrF(CO)_3(PEt_3)_2 \xrightarrow{F^-} [IrF\{C(F)O\}(CO)_2(PEt_3)_2]^+ \quad (89)$$

Cockman and co-workers conducted an extensive multinuclear NMR study of the reactions of nonmetal fluorides SF_4, SeF_4, and TeF_4 with $M(CO)Cl(PEt_3)_2$ (M = Rh, Ir). These reactions, summarized in Scheme 23, are carried out at 200 K. Raising the solution temperature gives rise to several fluxional processes. Variation of the ^{19}F NMR spectrum with temperature indicates that there are at least two and possibly three processes involved in the $Ir(CO)FCl(PEt_3)_2SF_3$ (**287**) system: rotation or rocking of the SF_3 group about the Ir–S bond, intermolecular fluorine exchange, and possibly an intramolecular component or pseudorotation. A strong dependence of this fluxional behavior on the nature of the other ligands present is observed. Coalescence temperatures for the fluxional processes increase in the order F < Cl < Br < I. Analogous rhodium complexes display poorer stability and preparations are complicated by the formation of a large number of isomeric products. Fluxional processes are also observed for the rhodium analogues, for example $Rh(CO)FCl(PEt_3)_2SeF_3$ (**288**). Evidence here suggests that a reversible intermolecular exchange between Rh–F and SeF_5^- occurs in solution at room temperature. TeF_4 appears to be a strong enough Lewis acid to abstract fluoride from rhodium. Main group fluorides NF_3 and SF_6 were either unreactive or yielded many products on reaction with $M(CO)X(PEt_3)_2$ (M = Ir, Rh).[7]

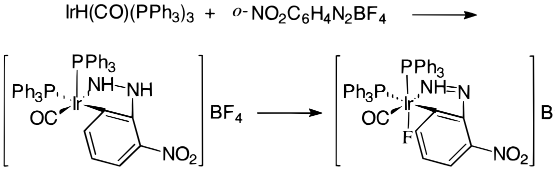
Scheme 23



Reaction of $Ir_4(CO)_{12}$ with XeF_2 in anhydrous HF solution at low temperatures (230 K) proceeds via sequential fluorination. This leads initially to neutral 18-electron *fac*- and *mer*-$IrF_3(CO)_3$ (**289a**,**b**) and finally in the presence of excess XeF_2 to the iridium(V) salt $[XeF][IrF_6]$ (eq 90). Removal of solvent followed by dissolution in HF shows ^{13}C and ^{19}F NMR signals of the *fac* isomer only, indicating that it is the thermodynamically more stable isomer. Compounds **289a** and **b** constitute the only examples of iridium(III) complexes coordinated solely by carbonyl and fluoride ligands.[238] In **289** the Ir–F (1.92 Å) distance as determined by EXAFS is shorter than in related compounds. Similarily the Ir–C bond length is unusually long (2.03 Å) and the C–O bond length (1.01 Å) unusually short by comparison with most metal-bound carbonyl ligands.[239]

$$Ir_4(CO)_{12} \xrightarrow[230\ K]{XeF_2\ /\ HF} \underset{\mathbf{289}}{IrF_3(CO)_3} \xrightarrow{XeF_2} [XeF][IrF_6] \quad (90)$$

Nitrobenzenediazonium tetrafluoroborate reacts with the hydride $IrH(CO)(PPh_3)_3$ to give the orthometalated arylhydrazido complex **290**. Compound **290** is unstable and readily converts to the related diazene $[IrF(NHNC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2][BF_4]$ (**291**) (eq 91). Two *trans* phosphine ligands and fluorine (Ir–F, 2.21 Å) *trans* to the Ir–aryl bond of the aryldiazene chelate give a pseudooctahedral arrangement around iridium in **291**. Limited accuracy of the structure determination allowed basically an assignment of the stereochemistry of the complex.[240]



(91)

290 **291**

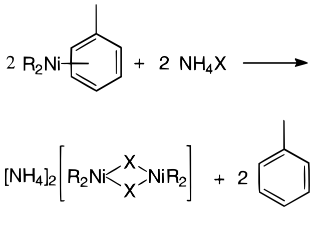
Novel chemistry involving fluoroorganometallic fluorides appeared as early as 1987. Fluorine metathesis of the chloro fluoroolefin $RhCl(C_2F_4)(C_2H_4)$, using $AgBF_4$ and TAS-F, affords the fluoro–fluoroolefin compound $[RhF(C_2F_4)(C_2H_4)]_4$ (**292**) (eq 92). Addition of triphenylphosphine leads to fragmentation and formation of monometallic **293**. Facile substitution of CO for C_2F_4 occurs on exposing **293** to 1 equiv of carbon monoxide. Fluoride abstraction is achieved by addition of trimethylsilyl triflate to **293**. In the distorted cubane structure of **292** the

$$RhCl(C_2F_4)(C_2H_4) \xrightarrow[TAS\text{-}F]{AgBF_4} \underset{\mathbf{292}}{[RhF(C_2F_4)(C_2H_4)]_4} \xrightarrow{PPh_3} \underset{\mathbf{293}}{RhF(C_2F_4)(PPh_3)_2} \xrightarrow{CO} \underset{\mathbf{294}}{RhF(PPh_3)_2(CO)} \quad (92)$$

Rh−C bond distances are shorter and the C−C distances somewhat longer for the tetrafluoroethylene than for the ethylene ligands. The ethylene units are *trans* to face-bridging fluorides. Rh−F bond distances fall into two ranges: two short (2.07−2.09 Å) and four longer (2.24−2.33 Å). In solution, an equilibrium exists between **292** and a dimeric species. Insertion of fluoroethylene into the metal−fluorine bond is not observed in this system.[241] Structures of *trans*-RhX$(PR_3)_2$(CO) (X = F, Cl, NCO; R = H, Me, Ph) predicted on the basis of density functional theory calculations compare favorably with experimental data. *trans*-RhF$(PPh_3)_2$(CO) (**294**) has a slightly distorted square-planar structure (Rh−F, 2.05 Å) with moderate bending of the phosphine ligand toward the fluoride and a nonlinear configuration of P−Rh−P atoms.[242,243]

C. Group 10

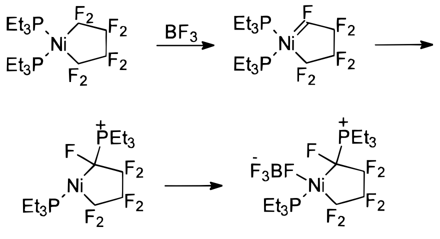
Displacement of labile η^6-arene ligands in nickel(II) compounds (R_2Ni(arene)) by halide (Cl, F) provides a convenient route to nickel(II) halides. Halide-bridged organometallic complexes $[(R_2M)_2(\mu\text{-}X)_2]^{2-}$ with σ-bonded perfluorogroups have been prepared according to eq 93. A square-planar geometry about nickel is present in both fluoride and chloride compounds. Expected structural changes are observed on substitution of fluoride for chloride; a decrease in X···X distance (0.60 Å), the Ni···Ni separation is shorter (0.40 Å), and a slight decrease in the Ni−C_6F_5 distance are found. Compound **295** is one of the few structurally characterized perfluoroorganometallic fluorides and the only fluoride-bridged (Ni−F, 1.89 and 1.91 Å) organo nickel compound.[244]



(93)

X = F (**295**), Cl

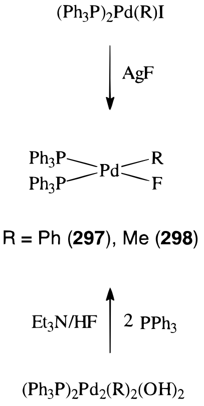
Perfluorometallacyclic Ni$(PEt_3)_2(CF_2)_4$ reacts irreversibly with BF_3·OEt_2 to afford the unprecedented perfluorometallacycle **296** (eq 94). Compound **296** has a phosphonium ylide structure. A reaction sequence involving extraction of fluoride ions from the coordinated perfluorometallacycle followed by quenching the transiently stable carbene species by migration of an ancillary phosphine ligand from the metal to a carbon of the metallacyclic ring is likely.



(94)

296

Scheme 24



R = Ph (**297**), Me (**298**)

The monodentate BF_4^- occupies the coordination site vacated by the phosphine (Ni−F, 1.98 Å). Displacement of BF_4^- occurs readily on addition of water. A bis-ylide bis-tetrafluoroborate compound is isolated when a 2-fold excess of boron trifluoride etherate is employed in the reaction.[245]

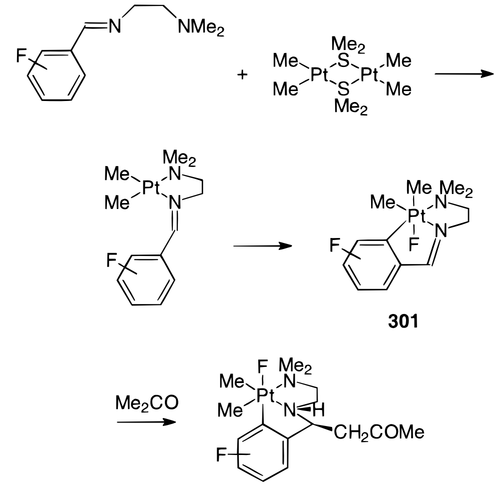
Air-stable palladium(II) compounds $(Ph_3P)_2$Pd(R)F (R = Ph (**297**), Me (**298**)) are prepared by sonication of a benzene solution of $(Ph_3P)_2$Pd(R)I and AgF (Scheme 24). This reaction proceeds only slowly, with poor yields and selectivities, when the reaction solution is simply stirred. An alternative route to **297** involves reaction of the hydroxo compound $(Ph_3P)_2Pd_2(Ph)_2(OH)_2$ and Et_3N·3HF in the preence of PPh_3. Compound **297** has a square-planar geometry (Pd−F, 2.09 Å).[246] The existence of **297** and **298** is unusual given that the hydroxo palladium cogeners, $[(Ph_3P)_2$Pd(OH)R] (R = Me, Ph), are kinetically and thermodynamically unstable.[247] In contrast, fluorides **297** and **298** are stable even in “wet” deuterated solvents. The reactivity of **297** and **298** toward CO also differs from the other halogen analogues. Instead of forming a stable $[(Ph_3P)_2$Pd(COPh)F] compound, carbonylation of **297** leads to reductive elimination of PhCOF and formation of palladium(0) phosphine carbonyl complexes.[246]

Conversion of covalent cyclopalladated chloride dimers to the corresponding ionic tetrafluoroborates leads to enhanced reactivity allowing reactions with alkynes at room temperature. Multiple insertion of 3-hexyne into cyclopalladated 8-methylquinoline tetrafluoroborate leads to **299**. The main structural feature of **299** is a square-planar palladium(II) center which is part of a six-membered metallacycle with no evidence of ring strain. In the solid state, bond lengths indicate the BF_4^- group is only weakly coordinated (Pd−F, 2.36 Å).[248,249]

cis-PtF$[CH(CF_3)_2](PPh_3)_2$ (**300**) is isolated as a minor product in the reaction of bis(trifluoromethyl)diazomethane with Pt(stilbene)$(PPh_3)_2$. Attack of trace amounts of hydrogen fluoride on the initially formed $(Ph_3P)_2$Pt·NNC$(CF_3)_2$ adduct leads to a mixture of *cis*- and *trans*-**300**. *cis*-**300** has a square-planar configuration about platinum. The phosphine *trans* to fluorine (Pt−F, 2.03 Å) exhibits a remarkably short Pt−P distance (2.22 Å).[250]

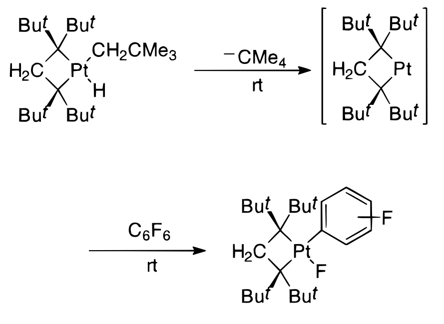
Reports of intramolecular oxidative addition of aryl−fluorine bonds to square-planar platinum complexes is relatively surprising given the low affinity

Scheme 25



of group 10 elements for the fluoride ligand. Intramolecular oxidative addition of the aryl−fluorine bond in $Me_2NCH_2CH_2N{=}CHC_6F_5$ to platinum(II) occurs sequentially to give **301** (Scheme 25). Addition of a C−H bond of acetone across the imine group in **301** leads to **302**. Dimers associated by hydrogen bonding in the solid state lead to an exceptionally low ν(NH) frequency for **302**. In **302** the platinum is octahedrally coordinated by three carbon donors in a facial arrangement, two nitrogen donors, and a fluoride ligand (Pt−F, 2.07 Å).[251] As mentioned earlier (section VII.B) the ability to produce chelate-assisted aryl C−F oxidative-addition processes is a function of several factors including the degree of fluorination of the aryl ring. Intramolecular activation of C−F bonds of difluoro- and monofluoro-substituted rings fail at Pt(II). In the former case no reaction occurs as for the ligand $Me_2NCH_2CH_2N{=}CH(2,6\text{-}C_6H_3F_2)$, or in the latter C−H bond activation takes place as for the ligand $Me_2NCH_2CH_2N{=}CH(2,6\text{-}C_6H_4F)$.[251] Crespo and co-workers have shown that trifluorinated ligands $Me_2NCH_2CH_2N{=}CHR$ (R = $2,4,6\text{-}C_6H_2F_3$, $2,3,6\text{-}C_6H_2F_3$) with two *ortho* fluorines undergo C−F bond activation. Acetone addition on the iminic bond of the coordinated ligand leads to $PtFMe_2(Me_2NCH_2CH_2NHCH(CH_2COMe)R$ (R = $2,4\text{-}C_6H_2F_2$ (**303a**), $2,3\text{-}C_6H_2F_2$ (**303b**)). The slightly longer Pt−F distance in **303a** (2.08 Å) in comparison with that observed in **302** is likely a result of the greater *trans* influence of the less fluorinated group. In contrast to the above reactions, treatment of the platinum substrate with trifluorinated ligands containing only one or no fluorine in the ortho positions yields [C,N,N′] cyclometalated platinum(II) $PtMe(Me_2NCH_2CH_2N{=}CHC_6HF_3)$ by ortho metalation accompanied by loss of methane.[252] Kinetic studies of C−X (X = H, F, Cl, Br) bond activation of ring-substituted $PhCHNCH_2Ph$-type imines, via intramolecular oxidative addition to the platinum(II) complex $[PtMe_2(\mu\text{-}SMe_2)]_2$, have been made. The bond activation is solvent independent, indicating that no polar transition state is formed during the reaction and that a common highly ordered three-centered C−Pt−X interaction is present for all the imines used.[253]

A highly reactive platinum(0) intermediate formed on reductive elimination of neopentane from (dtbpm)-PtNp(H) activates C−F bonds of hexafluorobenzene giving the thermally stable fluoride **304** in almost quantitative yield (eq 95). All nuclei of **304** are NMR active thus allowing an unequivocal assignment of the structure.[254]



(95)

304

X. Groups 11 and 12

Very little is known of the organometallic fluorides of groups 11 and 12. Organocopper and -gold fluorides have not been reported. Similarily the chemistry of organozinc and -cadmium fluorides remains largely unexplored. The isocyanide chemistry of silver provides the only well-characterized fluorides in this section. One example of an organomercury fluoride has appeared this year.

Reaction of isocyanides with the silver salt of hexafluorophosphate affords $Ag(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_2PF_6$ (**305**). Compound **305** has a novel structure and represents the only structurally characterized example of a bidentate chelating hexafluorophosphate group (eq 96). In **305** the silver is tetrahedrally coordinated in a distorted fashion by two isocyanide ligands and two fluorine atoms of the hexafluorophosphate group. Conductivity measurements indicate **305** exists as a 1:1 salt in solution.[255]

$$\mathrm{RNC} + \mathrm{AgPF_6} \longrightarrow \mathrm{Ag(RNC)(PF_6)} \xrightarrow{\mathrm{RNC}} \underset{\mathbf{305}}{\mathrm{Ag(RNC)_2(PF_6)}} \quad (96)$$

Aliphatic diisonitriles are potentially good ligands to bring two silver atoms into close proximity. 2,5-Dimethyl-2,5-diisocyanohexane (TMB) reacts with AgX to afford two series of compounds (eqs 97 and 98). In $Ag(TMB)BF_4$ (**306**) the silver is two coordinated and interacts weakly with a monodentate BF_4^- group (Ag−F, 2.85 Å, B−F_b, 1.25 Å). The structure of $Ag_2(TMB)_3(PF_6)_2$ (**307**) consists of pairs of chains cross-linked by extra TMB ligands leading to a ladder-like pattern (Ag−F, 2.87 Å, P−F, 1.59 Å). Acetonitrile in the crystal is not coordinated to silver.

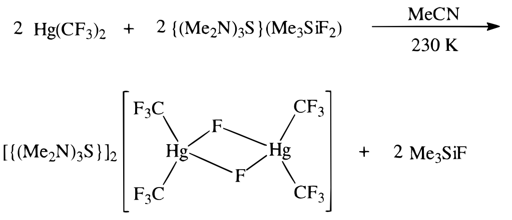
$$\mathrm{TMB} + \mathrm{AgX} \rightarrow \mathrm{Ag(TMB)X} \quad (97)$$

$$3\,\mathrm{TMB} + 2\,\mathrm{AgX} \rightarrow \mathrm{Ag_2(TMB)_3X_2} \quad (98)$$

$$\mathrm{X} = \mathrm{BF_4^-, PF_6^-, NO_3^-}$$

Compound **307** is isostructural with the perchlorate $Ag_2(TMB)_3(ClO_4)_2$.[256]

The first example of a perfluorinated organometallic, namely $Hg(CF_3)_2$, was prepared as early as 1949.[257] $Hg(CF_3)_2$ undergoes halide addition to give halide-bridged dimers $(F_3C)_2Hg(\mu\text{-}X)_2Hg(CF_3)_2$ (X = Cl, Br, I). Until very recently attempts to prepare the corresponding fluoride were unsuccessful. Using TAS−F as fluorinating reagent, Mews and co-workers isolated the first anionic fluoro−mercury complex $[(F_3C)_2Hg(\mu\text{-}X)_2Hg(CF_3)_2]^{2-}$ (**308**) (eq 99). Compound **308** is isostructural with the analogous chloro derivative (Hg−F, 2.40 and 2.42 Å; F−Hg−F, 82.4°). Experimental evidence suggests that **308** can be employed as a trifluoromethanide equivalent. Treatment of **308** with NSF_3 provides $NSF_2(CF_3)$ which was previously inaccessible (eq 100). The presence of fluoride ion in **308** leads to labilization of the Hg−C(*CF₃*) bond.[258] In contrast $Hg(CF_3)_2$ cannot be used for nucleophilic transfer of CF_3^- due to the very strong Hg−C bond.



(99)

308

$$\mathbf{308} + 2\ NSF_3 \xrightarrow[240\ K]{MeCN} 2\ NSF_2(CF_3) + 2\ \{(Me_2N)_3S\}(CF_3)HgF_2 \qquad (100)$$

XI. Concluding Remarks and Outlook

The organometallic chemistry of fluoride derivatives is now reaching a respectable level of development. Even in the absence of convincing evidence fluoride has rightly gained the reputation of being distinctly different from the heavier halides. In an article which bears special relevance to organometallic fluorides, Caulton has discussed the influence of π-stabilized unsaturation and filled/filled repulsions in transition metal chemistry.[259] The term saturated refers to a complex where the metal is assigned 18 valence electrons.

In organometallic halide chemistry it is reasonable to expect that filled/filled interactions will be at a maximum for the short distances which are characteristic of M−F bonds. Evidence in support of this hypothesis is found in the body of the review. For instance in $IrX(CO)(PPh_3)_2$ and $CpReNO(PPh_3)X$ (X = halide) compounds the ranking of ν(CO) and ν(NO) frequencies is F << Cl < Br < I. For $CpReNO(PPh_3)X$ this ordering is not in agreement with predictions based on halide electronegativity but is consistent with filled/filled interactions being delocalized into π*(NO), especially in the case of fluoride. CO labilization reaches an extreme limit for $ReF(CO)_3(PPh_3)_2$ where CO loss is much faster than for the chloro analog. Similarily, repulsion between fluorine lone pairs and filled d_π orbitals in the saturated complex $Cp'IrF(PMe_3)(aryl)$ is at least partly responsible for the ready ionization of fluoride.

Nonclassical Zr−H−Si interactions in the series of related silylamido zirconocenes $Cp_2ZrX(NBu^tSiMe_2H)$ follows the order X = H > I > Br > Cl > F, reflecting the relative electrophilicity of the zirconium center in these compounds. The π-donating ability of halide ligands in d^1-bent metallocene compounds (Cp'_2TiX) follows the order F > Cl > Br > I consistent with strong overlap between the p orbitals of fluoride and d orbitals of the bent metallocene. Fluoride ligand on W(II) also forms bonds to water, phenols, and coordinated amines. This originates from the highly polar nature of the W−F bond and also because of filled/filled repulsions.

The ν(CO) frequency has been investigated as a probe to determine the nature of the Ru−X bond in $RuHX(CO)(PBu^t_2Me)$ (X = halide, alkoxide) compounds. In all cases, the CO frequency is lower than that of free CO and the reduction in frequency increases in the order I < Br < Cl < F. The realization that the reactivity and stereochemistry of substrate binding in organometallic systems may be manipulated by the switching of halide substituent, in particular fluorine and chlorine (and to a lesser extent bromine), will have far-reaching effects. This is one of the many exciting avenues that the availability of organometallic fluorides is now opening to the chemist.

A. Structure and Spectroscopy

Tables 12 and 13 provide a comprehensive overview of organometallic fluoride M−F bridging and terminal bond distances. A casual glance reveals the many gaps which remain to be filled. In some cases no range is quoted as only one value is to be found in the literature. Exceptions to the ranges in Table 12 are found in the text. These values have been omitted since they are wildly different to the common values observed. The information in Tables 12 and 13 may be used to determine whether metal fluorine interactions in the solid state are weak or strong, as in the case of coordinated fluorinated anions.

A substantial number of organotitanium(IV) fluorides have been structurally characterized establishing values for terminal and bridging distances.

Table 12. Bond Distances in Organometallic Fluorides (in Å)

metal	M−F−M bridging	terminal M−F[a]
Sc	2.05	
Ti(IV)	1.99−2.06	1.81−1.85
Ti(III)	2.06	1.86
Zr/Hf	2.11−2.18	1.95−1.98
Nb/Ta	2.04−2.19	1.90−1.95
Cr	1.95	
Mo/W	2.10−2.21	1.99−2.06
Mn	1.95−2.05	2.05
Re		
Ru/Os	2.04	1.99−2.01
Rh/Ir	2.07−2.33	2.00−2.07
Ni	1.89−1.91	
Pd/Pt	2.09	2.07−2.08
Hg	2.40−2.42	

[a] Terminal bond distance with no other bonding interaction(s).

Table 13. Structural Parameters of Organometallic Compounds with Coordinated Fluorinated Anions

compound	M	M−F (Å)	E	$E-F_{bridge}$ (Å)	$E-F_n$ (Å)	ref
33	Ti(IV)	2.00	As	1.80	1.65	77, 78
34	Ti(IV)	1.99	Sb	1.94	1.82	77, 78
149	V(IV)	2.04	As	1.78	1.65	150
157	V(IV)	2.04	Sb	1.89	1.80	151
201	W(II)	2.15	B	1.45	1.36	183
203	W(0)	2.17	Sb	1.95	1.86	184
204	W(0)	2.19	Sb	1.98	1.85	184
205	W(0)	2.17	B	1.50	1.38, 1.32	184
206	W(0)	2.19	P	1.73	1.57	184
254	Re(I/II)	2.14	B	1.50	1.36	216
255	Re(I)	2.17	Re(V)	1.97	1.85	217
299	Pd(II)	2.36	B	1.34	1.33, 1.42	248
305	Ag(I)	2.67	P	1.56	1.51	255
306	Ag	2.85	B	1.25	1.26, 1.28	256
307	Ag	2.87	P	1.59	1.59, 1.54	256

Dicyclopentadienyltitanium(III) fluorides exhibit terminal and bridging bond distances which fall at the long ends of the titanium(IV) ranges. This is expected given the reduced Lewis acidity of the titanium(III) centers. Molybdenum and tungsten fluorine bond distances, both terminal and bridging are well scattered. Many of the examples of structurally characterized tungsten fluorides are derived from intramolecular C−F bond activation of coordinated Schiff bases bearing fluorinated substituents. M−F bond lengths for d^6 group 8 and 9 metals typically fall in the range 2.00−2.09 Å with fluoride *trans* to carbonyl. There are no examples of structurally characterized organometallic fluorides with F_{trans}−F. M−F distances measured for group 8 and 9 complexes with fluorinated anions show that the anions are only weakly coordinated (Table 13).

In organometallic systems with weakly coordinating anions ($M-F_b-EF_n$) the bridging fluorine−chalcogen (F_b-E) relative to the remaining fluorine−chalcogen (EF_n) bond distances provides the best measure of the metal−fluorine (M−F) bond strength. A long F_b-E distance, relative to the average $E-F_n$ distance, is taken to indicate a strong M−F bond. For example the structures of $Ir(Me)_2(PMe_2Ph)(BF_4)$ and *trans*-$Ir(Cl)(H)(CO)(PPh_3)_2(BF_4)$ show the expected distortion on coordination of BF_4^-; elongation of the (μ-F)−B distances over that of the terminal B−F distances. Long M-F bonds in these compounds indicate the weak nature of the anion/cation interaction.

In complexes of weakly coordinating fluorinated anions the fluoride may adopt several coordination modes, fluoride abstraction may occur leading to the formation of a neutral fluoride complex, or it may remain as a noncoordinating anion. Fluorinated anions which may have been considered as weakly or noncoordinating anions are now found to exhibit a wide range of coordination chemistry. The tetrafluoroborate anion exhibits the greatest variety of coordination modes. It typically adopts a monodentate coordination mode as in $WH(BF_4)(CO)_3(PCy_3)_2$, and recently has been shown as monodentate, bridging three metals in $[Et_4N]_2[Re_3H_2(CO)_9(\mu\text{-}FBF_3)]$. BF_4^- acts as a bridging bidentate ligand in the uranium compound $[(Me_3SiCp)_2U(\mu\text{-}F)(\mu\text{-}F_2BF_2)]_2$[260] and probably bidentate chelating in $Cp_2Ti(\mu\text{-}F_2BF_2)$. The hexafluorophosphate anion acts as a bidentate chelating ligand in $Ag_2(TMB)_3(PF_6)_2$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane). A comprehensive list of structurally characterized compounds with fluorinated anions is given in Table 13.

Frequently, structures of organometallic fluorides of weakly coordinated fluorinated anions in the solid and in solution structures differ markedly. Unfortunately complexes with weakly coordinated fluorinated anions exhibit low solubilities in nonpolar solvents making it difficult to record their NMR spectra. In cases where solubility is not a problem, equilibria involving coordinated and free anion, and ligand rotation typically lead to complex ^{19}F NMR spectra. Proof of coordination in solution is commonly observed in the form of coupling with other nuclei coordinated to the same metal. ^{19}F NMR spectroscopy is a useful tool in identifying bridging and terminal fluorines in early transition metal fluorides. IR spectroscopy provides less convincing evidence of fluoride formation. For early transition metal fluorides the metal−fluorine vibrations typically appear above 500 cm^{-1} with the remaining metal−halide absorptions below 400 cm^{-1}. Interestingly the increase in bond length on going from $Cp_2Ti(AsF_6)_2$ to $Cp_2Ti(SbF_6)_2$ is reflected in a decrease of 30 cm^{-1} in the Ti−F absorption for the latter. On coordination to a metal center highly symmetric fluorinated anions undergo a significant reduction in symmetry. This leads to characteristic splitting patterns in the IR spectra of the anions. Caution must be exercised in this respect, since the same splitting patterns may also be observed as a consequence of hydrogen bonding of the anion with solvent or water molecules, without coordination to a metal center.

Complexities involved in determining molecular formulas for low oxidation state metal carbonyl fluorides have made it difficult to definitively assign structures in the absence of X-ray data. As a result simple empirical formulas found in the earlier literature often represent more complex species and, in some cases, mixtures of products. An early review of carbonyl fluoride systems suggested that they exist in certain specific configurations which contain particularly stable units or “building blocks”.[261] Recent X-ray structural studies have confirmed many structures predicted on the basis of NMR spectroscopic data. This endorses the usefulness and reliability of these techniques.

B. Applications in Synthesis and Catalysis

As a consequence of exceptionally strong M−F bonds organometallic fluorides have been long thought of as synthetically and catalytically inert. Anomalous reactivity patterns frequently encountered with fluoride complexes of low oxidation state organometallic fragments have also contributed to this misconception. Currently organometallic fluorides are being successfully applied in many areas of synthesis and catalysis. These uses are summarized in Table 14.

Group 4 fluorides have provided several excellent examples clearly demonstrating that the strong M−F bond does not preclude their use in catalysis. Group 4 cyclopentadienyl fluorides are active, in combina-

Table 14. General Applications of Organometallic Fluorides in Catalysis and Synthesis

application	fluoride	ref(s)
catalytic olefin polymerization	Cp'_2MF_2 (M = Ti, Zr)	145
catalytic enantioselective hydrosilylation of prochiral amines	(*S*,*S*)-EBTHITiF_2	64
catalytic reduction of perfluorocarbons	Cp'_2MF_2 (M = Ti, Zr)	63
transamination of group 4 fluorides	Cp'_2MF_2 (M = Ti, Zr)	20
synthesis of main group−transition metal bonds	$ReF(CO)_3(PPh_3)_3$	3, 213
intramolecular C−F bond activation	tungsten and platinum fluorides	5, 194
C−H bond activation	$Ir(H)_2FL_2$ (L = phosphine)	232
trifluoromethanide transfer equivalent	$(F_3C)_2Hg(\mu\text{-}F)_2Hg(CF_3)_2$	258
highly reactive Lewis acids with applications in asymmetric catalysis	complexes of weakly coordinating fluorinated anions	4, 207
host−guest chemistry	tungsten fluorides	3

tion with methylaluminoxane as cocatalyst, for the polymerization of ethylene and the stereoregular polymerization of styrene. These catalyst systems display activities comparable with those of the known metallocene chlorides. Investigations have shown that activation of the catalyst with MAO probably involves methylation of the fluoride as a first step. Using very similar group 4 metallocene difluorides Richmond has shown that they mediate as electron-transfer "shuttles" in the catalytic reduction of saturated perfluoro compounds and in the stoichiometric activation of saturated perfluorocarbons. This is a remarkable result and opens the door to the activation of a wide variety of fluorocarbon substrates. An unprecedented catalyst activation step involving conversion of a Ti−F bond to a Ti−H bond in ethylenebis(η^5-tetrahydroindenyl))titanium difluoride offers a highly enantioselective route for the catalytic hydrosilylation of prochiral imines. This procedure operates with remarkably high substrate:catalyst ratios and with a broad range of substrates. Metallocene difluorides are used as catalysts for the addition of nucleophiles to aldehydes.[263]

The work of Bergman and Caulton highlights two conceptually distinct ways to manipulate reactivity by incorporation of the fluoride ligand. Easy Ir−F ionization of aryliridium(III) fluorides $Cp'IrF(PMe_3)(aryl)$ leads to the exceptionally high reactivity of these compounds. Caulton has shown how fluorine, acting as a π-acid ligand in unsaturated metal complexes $Ir(H)_2F(PBu^t{}_2Ph)_2$, can be used to promote C−H bond activation. This reaction proceeds only when the halide substituent X in $Ir(H)_2XL_2$ is fluoride.

The extremely strong silicon−fluorine bond has been utilized in the preparation of transition metal compounds not accessible from chloro, bromo, or iodo starting materials. Silaphilicity of fluoride ligands in the condensation of coordinatively saturated *trans*-$MF(CO)_3(PPh_3)_2$ and $[(Me_3SiO)_3V{\equiv}NSiMe_3]$ lead to the nitride-bridged compounds $[(Me_3SiO)_3V{\equiv}NM(CO)_3(PPh_3)_2]$ in quantitative yield. Curiously the reactivity of the organometallic fluorides in these reactions depends strongly on the method of preparation. Formation of the strong Al−F bond has been investigated in transamination reactions of aminoalanes with organotitanium and zirconium fluorides

$[(F_3C)_2Hg(\mu\text{-}F)_2Hg(CF_3)_2]^{2-}$ has been employed as a trifluoromethanide equivalent making the synthesis of previously inaccessible compounds such as $NSF_2(CF_3)$ possible. The presence of fluoride is responsible for the labilization of the Hg−C(*CF*$_3$) bond since $Hg(CF_3)_2$. Fluoride may be viewed as a useful reactive site given its propensity to form hydrogen bonds with hydroxylic compounds. These hydrogen-bonding capabilities have been exploited in host−guest chemistry.

Organometallic compounds coordinated by "weakly coordinating" anions such as BF_4^-, PF_6^-, AsF_6^-, and SbF_6^- are highly reactive. These ligands act as good leaving groups, being readily substituted by other ligands under mild conditions, thereby giving organometallic moieties with greatly enhanced Lewis acidity. A very attractive application of these compounds is in the generation of chiral Lewis acids for use in asymmetric synthesis.

It is not uncommon that the mode of preparation of inorganic and organometallic fluorides dictates subsequent reactivity patterns. For instance, Ziegler found that aluminum fluoride obtained commercially could not be used in the preparation of organoalane fluorides. Aluminum fluoride generated *in situ*, however, reacted readily with alkylating reagents to give the desired products.[262] In the preparation of transition metal−main group bonds via condensation reactions the mode of preparation of the metal fluoride also plays an important role. The recently employed strategy of *in situ* generation of solids followed by immediate capture in an organometallic fluoride host is interesting from a synthetic point of view and opens a new field of chemistry on the border of inorganic/organometallic chemistry.

The ability to produce chelate-assisted aryl C−F oxidative−addition processes has been attributed to the basicity, chelating nature, and restricted conformation of the ligand, as well as the perfluorination of the aryl ring. Intramolecular activation of C−F bonds at tungsten has been extended from substrates containing perfluorinated to difluoro- and monofluoro-substituted aromatic rings, an extension which fails at platinum.

In conclusion the extraordinary reactivity of organometallic fluorides is and has been under investigation for some time and the preparation of these fluorides is no longer a contentious issue. The synthetic value of this class of compound has just been touched on in the synthesis of transition metal−main group bonds for example. These reactions demonstrate that formation of a strong metal−fluorine bond is a powerful reaction driving force. Equally intriguing is the finding that such strong bonds do not preclude the use of organometallic fluorides in catalysis. Structural characterization of a large number of fluorides constitutes a novel feature of recent work. There can be no doubt that the introduction of the fluorine ligand into organometallic systems will continue to provide some of the most intriguing chemistry of the next decade.

XII. Acknowledgments

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