

Metal Complexes of Weakly Coordinating Anions. Precursors of Strong Cationic Organometallic Lewis Acids[†]

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I. Introduction

Organometallic compounds of weakly coordinating anions, e.g., BF_4^- , PF_6^- , AsF_6^- , and SbF_6^- , have been the object of many studies in recent years. These complexes contain a hard anion coordinated to a soft metal center in a low oxidation state with π -acceptor ligands (e.g., CO , PR_3).¹ They are highly reactive; the anions are excellent leaving groups and can easily be replaced by other ligands under very mild conditions, so they have proven to be useful starting materials in preparative organometallic synthesis.

The first metal carbonyl compounds of this type that could be isolated were $\text{MCl}(\text{FBF}_3)(\text{NH}=\text{NR})(\text{CO})-(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$),² $\text{Re}(\text{CO})_5(\text{FAsF}_5)$,³ and $\text{Cr}(\text{CO})_3(\text{PMe}_3)(=\text{CMe})(\text{FBF}_3)$.⁴ Our group in Munich entered this field when Klaus Schloter in his Master's thesis examined the reaction between $\text{Mo}(\text{CO})_3(\text{Cp})(\text{SiMe}_3)$ and $\text{Ph}_3\text{C}^+\text{BF}_4^-$. Instead of the desired $\text{Me}_2\text{Si}=\text{CH}_2$ ligand, he discovered $\text{Mo}(\text{CO})_3(\text{Cp})(\text{FBF}_3)$ ⁵ as a byproduct. Other good examples of such complexes are $\text{Re}(\text{CO})_5(\text{FBF}_3)$ and $\text{Au}(\text{PPh}_3)\text{X}$. They react as coordinatively and electronically unsaturated $\text{Re}(\text{CO})_5^+$ or $\text{Au}(\text{PPh}_3)^+$ with a series of nucleophiles analogously to the isolobal carbenium ions or to the proton.⁶ We call these compounds "organometallic Lewis acids", in contrast to the "organometallic bases".⁷ It was recognized early that all the anions mentioned above have coordinating abilities, at least in the solid state;⁸ however, examples are known in which in spite of electronic unsaturation of the metal, the anion remains uncoordinated [e.g., $[\text{Rh}(\text{PPh}_3)_3]^+ \text{PF}_6^-$ ^{9,10} or $[\text{Co}(\text{P}(\text{OR})_3)_4]^+ \text{PF}_6^-$,¹⁰ also in $\text{Cu}(\text{CO})(\text{AsF}_6)$ the anion is apparently not coordinated to the metal, in contrast to the corresponding sulfonato complexes¹¹].

The cationic fragment in these complexes must have low-lying acceptor orbitals as was shown for the d^6 $\text{M}(\text{CO})_5$ fragment.^{12a} A theoretical investigation of the $[\text{Cp}_2\text{ZrCl}]^+$ moiety showed two low-lying δ - and π -acceptor MOs.^{12b} It appears that the more acidic the corresponding hydrides L_nMH are, the lower are the LUMOs and the higher is the electrophilicity of ML_n^+ . There are many such complexes of metals in "normal" oxidation states which can only be mentioned briefly here. Examples include $\text{M}(\text{N-vinylimidazole})_4\text{SiF}_6$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$), $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})\text{BF}_4]\text{BF}_4$, $\text{Cu}(\text{PPh}_3)_3\text{BF}_4$, and $\text{Mn}(2,6\text{-lutidine } N\text{-oxide})(\text{F})(\text{BF}_4)$.¹³ Often the anions BF_4^- and ClO_4^- occur as bridging or "semicoordinating" ligands.¹⁴

[†] Dedicated to Professor Heinrich Nöth on the occasion of his 60th birthday.



Prof. Wolfgang Beck was born in 1932 in München, West Germany. He received his Ph.D. under the supervision of Professor Walter Hieber at the Technische Hochschule München in 1960. He was appointed Professor of Inorganic Chemistry at the Ludwigs-Maximilians Universität München and Director of the Institute of Inorganic Chemistry in 1968. In 1977 he spent a term as Visiting Professor at the University of Wisconsin, Madison. Prof. Beck is the author of over 300 publications. He started his research with pseudohalide complexes, particularly fulminate and azido complexes, and with reactions at coordinated ligands. His current interests involve metal complexes of biologically important ligands, especially palladium and platinum compounds of α -amino acids and their derivatives and organometallic chemistry. In the latter field he presently studies with his co-workers metal complexes of weakly coordinating anions and nucleophilic attack of organometallic anions on coordinated unsaturated hydrocarbons.



Dr. Karlheinz Sünkel was born in 1955 in München, West Germany. He received his Diplomchemiker degree in 1979 and his Dr. rer. nat. degree with a thesis on organometallic compounds of weakly coordinating anions under the supervision of Prof. W. Beck in 1982 at the University of Munich. After postdoctoral study with Prof. R. Bau at the University of Southern California, Los Angeles, he returned to Munich and is presently working for his "Habilitation" on complexes of functionalized cyclopentadienyls and of other unsaturated hydrocarbons.

Reviews on perchlorato,¹⁵ trifluoroacetato,¹⁶ trifluoromethanesulfonato, and fluorosulfonato¹⁷ complexes and of palladium(II) and platinum(II) compounds with such anions¹ have been published. A review on the synthesis of such complexes by ion exchange has also appeared.¹⁸ The preparation of several of the compounds described here will appear in Vol. 26 of *Inorganic Synthesis*.

II. Scope of the Review

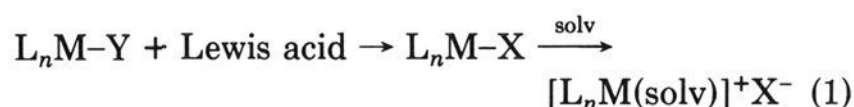
Here, we try to focus on complexes with π -acidic ligands and with the very weakly coordinating anions. ClO_4^- and CF_3SO_3^- usually are stronger ligands and will be considered here only for the sake of comparison,

where appropriate. Pentaammine fluorosulfato and triflato complexes of Os^{III} , Co^{III} , and Ru^{III} $[\text{M}(\text{NH}_3)_5(\text{OSO}_2\text{R})]^{2+}$, which have been used extensively as starting materials for many interesting complexes, e.g., η^2 -benzene or η^2 -acetone,¹⁹ will not be discussed here. Reactions of cationic with anionic metal complexes to give metal-metal-bonded compounds will also not be covered.

III. Methods of Preparation

Several methods of preparation of organometallic Lewis acids or their precursors have been developed.

A. Abstraction of an Anionic Ligand by a Lewis Acid

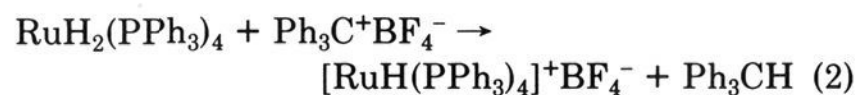


Y	Lewis acid	X ⁻	solvent
H ⁻	H ⁺ , Ag ⁺	FBF ₃ ⁻	THF
CH ₃ ⁻	Tl ⁺ , NO ⁺	FPF ₅ ⁻	Me ₂ CO
Hal ⁻	R ₃ O ⁺ , Ph ₃ C ⁺	FAsF ₅ ⁻	H ₂ O
N ₃ ⁻	BF ₃ , AlCl ₃	FSbF ₅ ⁻	CH ₂ Cl ₂
	CH ₃ OSO ₂ F	OCIO ₃ ⁻	CH ₃ CN
	C ₇ H ₇ ⁺	OReO ₃ ⁻	SO ₂
	ArN ₂ ⁺	OSO ₂ R ⁻	
	SbCl ₅	OTeF ₅ ⁻	
	CoCl ₂	CH(SO ₂ R) ₂ ⁻	
	HgCl ₂	ClAlCl ₃ ⁻	

In the complexes $\text{L}_m\text{M}-\text{X}-\text{EX}_n$ the organometallic Lewis acid competes with the Lewis acid EX_n for the base X⁻. In AlCl_4^- complexes, the transition metal is usually the "winner"; i.e., formation of AlCl_3 and $\text{L}_n\text{M}-\text{Cl}$ is often observed. In the presence of coordinating solvents (e.g., THF, CH₃CN, liquid SO₂) the cationic solvent complexes $[\text{L}_n\text{M}(\text{solv})]^+$ are formed. From some cationic SO₂ complexes the neutral L_nMX can be obtained by simple evacuation.^{3,20}

1. Abstraction of Anionic Group X with Triphenylcarbenium Salts

The reaction of iridium hydrido complexes with trityl salts to give triphenylmethane was first reported in 1962.²¹ The organometallic product was not studied. A ruthenium dihydride yielded a cationic monohydrido complex with no coordination of anion or solvent.²²



However, phosphine transfer was observed in the analogous reaction of the corresponding iron hydride.^{22a}

A cationic complex $[\text{CpW}(\text{NO})_2\text{NCMe}]^+$ with coordinated solvent was obtained in the reaction of $\text{CpW}(\text{NO})_2\text{H}$ with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ in CH₃CN.²³ The first time a complex of coordinated BF_4^- could be obtained by this route was the synthesis of $\text{Cp}(\text{CO})_3\text{MoFBF}_3$ from $\text{CpMo}(\text{CO})_3\text{H}$ and Ph_3CBF_4 in CH₂Cl₂.⁵ A similar reaction of $\text{Mn}(\text{CO})_4(\text{PR}_3)\text{H}$ in moist CH₂Cl₂ gave the aqua complex $[\text{Mn}(\text{CO})_4(\text{PR}_3)(\text{H}_2\text{O})]^+\text{BF}_4^-$,²⁴ $(\text{OC})_5\text{ReH}$ and $\text{Ph}_3\text{C}^+\text{BF}_4^-$ afford $(\text{OC})_5\text{ReFBF}_3$.⁴² Molybdenum and tungsten compounds of coordinated PF_6^- , AsF_6^- ,

obtained with HBF_4/CO .^{84b} $\text{RuH}_2(\text{PPh}_3)_4$ yields on protonation with *p*-TsOH,^{85a} $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2/\text{toluene}$,^{85b} or HBF_4 or phenol^{85c} η^6 -arene complexes $[\text{RuH}(\text{PPh}_3)_2(\text{arene})]^{n+}$ ($n = 0, 1$), where the arene is either the phenyl ring of OTs^- , toluene, PPh_3 , or OPh^- . Also $\text{OsH}_4(\text{PPh}_3)_3$ undergoes a similar reaction with sulfonic acids in refluxing benzene.^{85d}

This method is especially convenient for metal carbonyl systems where the carbonyl metalate can be protonated without isolation of the intermediate hydride: complexes $[\text{Fe}(\text{CO})_3(\text{NO})\text{L}]^+$ ⁸⁶ and $\text{Mn}(\text{CO})_5\text{O}-\text{SO}_2\text{CF}_3$ ⁸⁷ have been produced from $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ and $[\text{Mn}(\text{CO})_5]^-$, respectively.

The best and cleanest method for the isolation of organometallic Lewis acids seems to be the protonation of methyl complexes:



This method made the isolation of the following complexes possible: $\text{Re}(\text{CO})_5\text{FBF}_3$,⁸⁸ $\text{CpM}(\text{CO})(\text{L})(\text{OSO}_2\text{R})$ ($\text{M} = \text{Fe}, \text{Ru}, \text{L} = \text{CO}, \text{PMe}_3$),⁸⁹ $\text{Cp}(\text{OC})_2\text{FeOTeF}_5$,⁵⁴ $\text{CpM}(\text{CO})_3\text{X}$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{FBF}_3, \text{OSO}_2\text{R}$),⁹⁰ $\text{M}(\text{CO})_5\text{OTeF}_5$ ($\text{M} = \text{Mn}, \text{Re}$),⁵⁴ $\text{CpRe}(\text{NO})(\text{PPh}_3)\text{X}$ ($\text{X} = \text{OSO}_2\text{CF}_3, \text{FBF}_3, \text{FPF}_3$).⁹¹

However, it could be shown that isolation of these complexes and of " $(\text{C}_6\text{H}_6)\text{Ru}(\text{PR}_3)(\text{CH}_3)^+$ " is not necessary for many reactions.⁹²⁻⁹⁵ Also ethyl⁹⁶ and other σ -alkyl and σ -allyl⁹⁷ complexes can be used. $\text{H}_3\text{CCo}[\text{P}(\text{OR})_3]_4$ can be protonated by NH_4PF_6 to give $[(\text{H}_3\text{N})\text{Co}[\text{P}(\text{OR})_3]_4]^+\text{PF}_6^-$.¹⁰

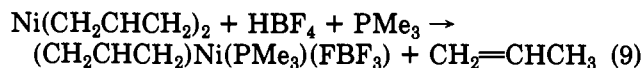
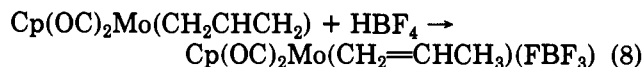
Some mechanistic investigations on the reaction of metal alkyl complexes with strong acids have been undertaken.^{98,99} The protonation of the optically active $\text{CpRe}^*(\text{NO})(\text{PPh}_3)\text{R}^*$ by HBr proceeds with retention of configuration at both carbon and rhenium,⁹⁸ which "can be visualized as a net addition of HX across the rhenium-carbon σ -bond".

The intermediate complex $[\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}(\text{CH}_3)\text{H}]^+\text{BF}_4^-$ from the protonation of $\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}(\text{CH}_3)$ with HBF_4 could be isolated.^{99b} Further examples for the cleavage of the metal-carbon σ -bond by protonic acids are summarized in ref 100.

The cleavage of the cyclopentadienyl ligand from nickelocene via $[\text{NiCp}]^+$ has led to the first "triple-decker" compound $[\text{Ni}_2\text{Cp}_3]^+$,^{101a} which can be used as an excellent source for the extremely reactive $[\text{NiCp}]^+$ unit.^{101b}

Interestingly, protonation of $(\eta^6\text{-C}_7\text{H}_9)\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) by HBF_4 yields the 16e system $[(\text{C}_7\text{H}_9)\text{M}(\text{CO})_3]^+\text{BF}_4^-$ with no coordination of the anion.¹⁰² In contrast to the analogous tungsten compound, the molybdenum atom is not electrophilic, since addition of phosphine takes place at the C_7H_9 group.

In contrast to these reactions, the cyclohexadienyl complex CpFeC_6H_7 is protonated by $\text{HBF}_4\cdot\text{OEt}_2$ to give the very reactive diene-tetrafluoroborato complex $\text{CpFe}(\eta^4\text{-C}_6\text{H}_8)(\text{FBF}_3)$.¹⁰³ Protonation of the η^3 -allyl complex $\text{CpMo}(\text{CO})_2(\text{C}_3\text{H}_5)$ with HBF_4 yielded $\text{Cp}(\text{CO})_2\text{Mo}(\text{CH}_2=\text{CHMe})(\text{FBF}_3)$, an organometallic Lewis acid bearing two accessible coordination sites (eq 8).^{104a} Similarly, protonation of η^3 -allyl complexes $(\text{C}_3\text{H}_5)\text{ML}_n$ ($\text{ML}_n = \text{Co}[\text{P}(\text{OMe})_3]_3$,¹⁰ $\text{Mn}(\text{CO})_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2$,^{104b} and $\text{Ru}(\eta^4\text{-diene})$ ^{104c}) gives compounds with two reactive coordination sites. $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$, PMe_3 , and HBF_4 yield $(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{PMe}_3)(\text{FBF}_3)$, which was characterized by ³¹P NMR (eq 9).¹⁰⁵

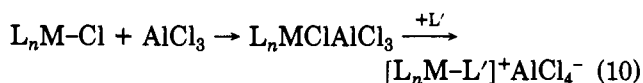


The aryl complexes $\text{CpRe}(\text{CO})(\text{NO})(\text{C}_6\text{H}_4\text{R})$ gave cationic η^2 -arene complexes $[\text{CpRe}(\text{CO})(\text{NO})(\eta^2\text{-C}_6\text{H}_5\text{R})]^+$ upon protonation with HBF_4 .^{29b} Evidence for the formation of $\text{CpFe}(\text{CO})_2\text{BF}_4$ from $\text{CpFe}(\text{CO})_2\text{SO}_2\text{OR}$ and HBF_4 has been reported.¹⁰⁶

Closely related are the reactions of metal alkyl complexes with metal hydrides to give alkanes and dimeric species with metal-metal bonds.¹⁰⁷

4. Reactions Using BF_3 , AlCl_3 , NO^+ , R_3O^+ , $\text{CH}_3\text{OSO}_2\text{F}$, CoBr_2 , and Hg^{2+}

A general applicable method for the synthesis of cationic metal carbonyl complexes is the halide abstraction promoted by BF_3 or AlCl_3 in the presence of neutral ligands;¹⁰⁸⁻¹¹¹ e.g.



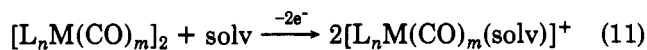
Thus the first homoleptic metal carbonyl cations $[\text{M}(\text{CO})_6]^+$ ($\text{M} = \text{Mn}, \text{Re}$) could be isolated.^{108,109} In several cases evidence for the intermediacy of coordinated AlCl_4^- and similar anions could be found.¹¹² Due to their sensitivity to water and the easy loss of AlCl_3 , relatively few AlCl_4^- complexes could be isolated. Addition of AlCl_3 to chloro complexes yielded the structurally characterized $\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\eta^2\text{-Cl}_2\text{AlCl}_2)_3$,^{113a,b} $\text{U}(\eta^6\text{-C}_6\text{Me}_6)(\text{ClAlCl}_3)_3$,^{113b} $[\text{U}(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_3(\mu_1\text{-}\eta^2\text{-Cl}_2\text{AlCl}_2)_3(\eta^6\text{-C}_6\text{Me}_6)][\text{AlCl}_4]^-$,^{113c} $[\text{Pd}(\eta^1\text{-ClAlCl}_3)(\mu_2\text{-}\eta^6\text{-C}_6\text{H}_6)_2]_2$,¹¹⁴ $(\eta^6\text{-C}_6\text{R}_6)\text{Ti}(\eta^2\text{-Cl}_2\text{AlCl}_2)_2$,^{115a} $(\eta^3\text{-C}_3\text{H}_5)\text{-}[(\text{C}_6\text{H}_{11})_3\text{P}]\text{NiClAlMe}_2\text{Cl}$,^{105c} and $\text{Cp}_2\text{Ti}(\text{Cl})(\text{ClAlCl}_2\text{Me})$.^{115b} Other examples are 1:1 adducts of AlCl_3 with Cp_2TiCl_2 ^{116a} and $(\text{H})(\text{OC})(\text{Ph}_3\text{P})_2\text{IrCl}_2$.^{116b} An unusual tricoordinate ylide complex $[\text{Pt}(\text{CH}_2\text{PPh}_3)(\text{PPh}_3)\text{Cl}]\text{AlCl}_4^-$ could be obtained by chloride abstraction from $\text{Pt}(\text{CH}_2\text{PPh}_3)(\text{PPh}_3)\text{Cl}_2$ by AlCl_3 .¹¹⁷ Abstraction of a SiCl_3 group from $\text{Re}(\text{CO})_5\text{SiCl}_3$ by SbCl_5 produced $\text{Re}(\text{CO})_5\text{ClSbCl}_5$.¹¹⁸ The carbon-iron bond in $[(\text{HNC}_5\text{H}_4)\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}]^+$ can be cleaved by Hg^{2+} salts in aqueous solution to give the $[\text{CpFe}(\text{CO})_2(\text{H}_2\text{O})]^+$ cation.¹¹⁹

Reaction of several Fischer-type carbene complexes with BF_3 led to the isolation of $(\text{MeC})\text{Cr}(\text{CO})_3(\text{PMe}_3)\text{FBF}_3$ ⁴ and $(\text{RC})\text{W}(\text{CO})_4\text{FBF}_3$.¹²⁰ A niobium hydride was reported to react with BF_3 to give a complex of BF_3H^- .¹²¹ Also a general examination of the interaction of metal carbonyl hydrides with Lewis acids BCl_3 and AlBr_3 was undertaken.¹²² The titanium boranate complex Cp_2TiBH_4 and $\text{BF}_3\cdot\text{OEt}_2$ give Cp_2TiBF_4 with bidentate BF_4^- .¹²³

Trialkyl oxonium salts have also been used for the abstraction of halide,^{24,124} methyl,²⁴ or azide^{125a-c} ligands. Halide and pseudohalide abstraction using R_3O^+ , $\text{SO}_2\text{F}(\text{OMe})$, NO^+ , or BF_3 is a directed way for the preparation of halide- and pseudohalide-bridged complexes.¹²⁴⁻¹²⁶ $(\text{C}_8\text{H}_{14})\text{AuCl}$ and $\text{SO}_2\text{F}(\text{OMe})$ give the fluorosulfate complex $(\text{C}_8\text{H}_{14})_3\text{AuOSO}_2\text{F}$.¹²⁷ Cp_2ReH and AlX_3 form the hydride-bridged compounds $\text{Cp}_2\text{Re}-\text{H}-\text{AlX}_3$,^{128a} while with CoBr_2 in MeCN , hydride abstraction and formation of $(\text{Cp}_2\text{Re})_2\text{CoBr}_4$ are observed.^{128b}

B. Oxidation of Neutral Monomeric or Dimeric Complexes

The oxidation of dimeric metal carbonyls in coordinating solvents has been used to produce cationic complexes of many metals.

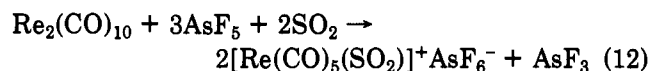


A quite general method for the preparation of cationic complexes is oxidation of neutral monomeric and dimeric carbonyl complexes by nitrosyl salts,¹²⁹ e.g., from $M_2(CO)_{10}$ and NO^+ in MeCN the cations $[(OC)_5MNCMe]^+$ ($M = Mn, Re$) have been obtained, which are useful starting compounds for other cations $[(OC)_5ML]^+$.^{129d}

Other oxidants that have been used to produce $[(OC)_5MNCMe]^+$ are Cu^{2+} , Fe^{3+} , and TCNE.^{129e,f}

$[CpFe(CO)_2]_2$ and its derivatives can be oxidized by Fe^{3+} ,¹³⁰ O_2 in the presence of $HBf_4 \cdot OEt_2$,¹³¹ Ag^+ ,¹³² Ph_3C^+ ,¹³³ quinone,¹³⁴ or Cp_2Fe^+ ¹³⁵ to give $[CpFe(CO)_L(\text{solv})]^+$. Similarly, from $[CpM(CO)_3]_2$ ($M = Cr, Mo$) and Ag^+ ,¹³⁶ Cp_2Fe^+ ,^{135c} or Ph_3C^+ ,¹³⁷ $[CpRu(CO)_2]_2$ and Ag^+ ,¹³⁸ and $[CpCr(NO)_2]_2$ and $HBf_4 \cdot OEt_2$,¹³⁹ the organometallic Lewis acids $[CpM(CO)_3]^+$, $[CpRu(CO)_2]^+$, and $[CpCr(NO)_2]^+$ have been generated in situ. Oxidation of the bis(carbene) complex $Mo(CO)_4L_2$ with HO_3SCF_3 gave the bis(triflate) complex $Mo(CO)_2L_2(O_2SO_2CF_3)_2$ ¹⁴⁰ ($L = =CN(Et)(CH_2)_2NEt$). It should be noted that in the oxidation of the dimeric rhodium complexes $Cp_2Rh_2(\mu-CO)(\mu-L)$ ($L = CO, dpmm$) with AgX , the cluster compounds $(\mu-AgX)[Cp_2Rh_2(\mu-CO)(\mu-L)]$ are obtained.^{141,142}

An elegant way for the synthesis of $[CpFe(CO)_2(SO_2)]^+$, $[Mn(CO)_5(SO_2)]^+$, $[Re(CO)_5(SO_2)]^+$, and $[Co(CO)_4(SO_2)]^+$ is the oxidation of the corresponding neutral dimers with AsF_5 in liquid SO_2 ,¹⁴³ e.g.



Another interesting example is $Re(CO)_5FReF_5$, which can be obtained from $Re_2(CO)_{10}$ and ReF_6 or XeF_2 , respectively.¹⁴⁴

The hydrido complex $CpFeL_2H$ and $[CpFe(CO)_2L']^+$ ($L' = \text{olefin, carbene}$) undergo redox reactions to give $[CpFeL_2(\text{solv})]^+$ and $CpFe(CO)_2(\text{alkyl})$.¹⁴⁵ Cp_2ReH is oxidized by $CuCl_2$ to $[Cp_2Re]^+[CuCl_2]^-$.¹⁴⁶

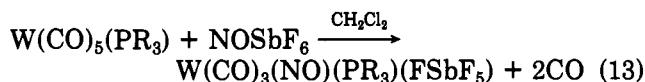
Examples of dicationic complexes obtained by the oxidation of monomeric complexes include $[Pd(PPh_3)_4]^{2+}$ (from $Pd(PPh_3)_4$ and Ph_3C^+),¹⁴⁷ $[MoH_2(PR_3)_4(NCMe)_2]^{2+}$ (from $MoH_4(PR_3)_4$ and $AgBF_4$),⁷⁸ $[CpCoL_2]^{2+}$ (from $CpCoL_2$ and $AgBF_4$),¹⁴⁸ $[CpCoL_3]^{2+}$ (from $CpCo(CO)_2$, L , and $[Cp_2Fe]^+BF_4^-$),¹⁴⁹ $[M(NO)_2(NCCH_3)_4]^{2+}$ (from $M(CO)_6$ ($M = Mo, W$) and $NOBF_4$),¹⁵⁰ and $[Mo(CO)_2(bpy)_2(OH_2)]^{2+}(BF_4^-)_2$ (from $Mo(CO)_2(bpy)_2$ and $AgBF_4$).¹⁵¹

A report of the synthesis of $[Mo(NO)_5]^{5+}[BF_4^-]_5$ from $Mo(CO)_6$ and $NOBF_4$ in $Cl_2C_2H_4$ is highly surprising¹⁵² and certainly wrong. Reactions of $M(CO)_6$ with NOX ($X = Cl, PF_6$) give polymeric $[M(NO)_2X_2]_n$.^{153,185} $[Mo(NO)_5]^{5+}[BF_4^-]_5$ and $Mo(NO)_2(PF_6)_2$ ¹⁸⁵ show identical $\nu(NO)$ bands.

Seventeen-electron species can also be obtained^{148,154} by oxidation of 18-electron complexes, e.g., $[CpFe(dppe)I]^+PF_6^-$.¹⁵⁵ In the electrochemical oxidation of

$[M(CO)_3Cp]_2$ and $Mn_2(CO)_{10}$ the radicals $[M(CO)_3Cp]^*$ and $[Mn(CO)_5]^*$ are key intermediates.^{156,157} Electrochemical preparations of cationic complexes include $[CpFe(CO)_2(\text{solv})]^+$,¹⁵⁸ $[IrR(CO)(PPh_3)_3]^+$,¹⁵⁹ $[CpRh(CO)(PPh_3)]^+$,¹⁶⁰ and $[CpCr(NO)_2(\text{solv})]^+$.¹⁶¹

Recently, a complex of coordinated SbF_6^- could be prepared by oxidation of $W(CO)_5(PPh_3)$ with $NOSbF_6$.¹⁶²

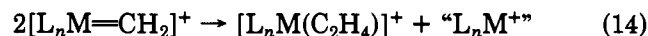


C. Oxidative Addition of RX to Metal d^8 Systems

The oxidative addition of strong acids, of alkyl fluorosulfates, or of oxonium salts to Vaska's compound $IrCl(CO)(PPh_3)_2$ gives the complexes $Ir(CO)(Cl)(PPh_3)_2(R)(X)$ (where $R = H$ or Me and $X = FBF_3, FPF_5, OPOF_2, OSO_2CF_3, OSO_2C_4F_9, OSO_2F$, or $OCIO_3$).^{124a,b,163,164} Similarly, $Ir(N_2)(PPh_3)_2Cl$ and RX give $Ir(N_2)(PPh_3)_2(Cl)(R)(X)$ ($R = H, Me; X = OSO_2F, OSO_2CF_3, FBF_3$),^{163,165} which have two good leaving groups, similar to the above-mentioned $[CpMo(CO)_2(CH_2=CHMe)(FBF_3)]$.¹⁰⁴ The Brønsted acidity of strong acids HX is transferred to Lewis acidity at the metal by these reactions. Reacting $Pt(PPh_3)_2(C_2H_4)$ with HBf_4 or HSO_3CF_3 gives $Pt(PPh_3)_2H_2X_2$ ($X = BF_4, CF_3SO_3$),¹⁶⁶ and addition of $H_2C(SO_2CF_3)_2$ yields $(PPh_3)_2PtH[HC(SO_2CF_3)_2]$.¹⁶⁷ $Pt(PPh_3)_2Cl_2$ adds two molecules of RX to give $Pt(PPh_3)_2HCIX_2$ ¹⁶⁶ or $[Pt_2(PPh_3)_4Cl_2][FSO_3]_2$,^{124b} depending on the nature of RX . Addition of HBf_4 to the dinuclear complex $[RhCl(\mu-dppm)]_2(\mu-CO)$ gives the mixed Rh^I/Rh^{III} dimer $[RhCl(\mu-dppm)]_2(\mu-CO)(\mu-H)(Fbf_3)$.³⁹

D. Miscellaneous

Photochemical-induced disproportionation of dimeric complexes $[(MeCp)Mo(CO)_3]_2$ to give $[(MeCp)Mo(CO)_3(\text{solv})]^+$ and $[(MeCp)Mo(CO)_3]^-$ has been reported.¹⁶⁸ The highly reactive $[CpFe(dppe)]^+$ is formed by irradiation of $[CpFe(CO)(dppe)]^+$; it coordinates a large variety of ligands.¹⁶⁹ Abstraction of Cl^- from $CpCr(NO)_2CH_2Cl$ by Ag^+ leads via the intermediate $[CpCr(NO)_2=CH_2]^+$ to $(C_5H_4CH_3)Cr(NO)_2^{+}$.¹⁷⁰ The disproportionation of cationic methylene complexes gives the intermediate organometallic Lewis acids and cationic ethylene compounds:^{90,171-173}



where $L_nM = CpL_2Fe$,¹⁷¹ $Cp(OC)_2LMO$, $Cp(OC)_2LW$,^{90,172} or $Cp(ON)(Ph_3P)Re$.¹⁷³ ($L = CO, PR_3$). Triflate complexes can be isolated by this route.^{90,171d,e} An unusual weak ligand is $V(CO)_6^-$ in $V(THF)_4[(\mu-OC)V(CO)_5]_2$ ¹⁷⁴ and $(C_5Me_5)_2V(\mu-OC)V(CO)_5$,¹⁷⁵ which is coordinated via the oxygen atom of one carbonyl ligand to the Lewis acid $[V(THF)_4]^{2+}$ and $[(C_5Me_5)_2V]^+$, respectively. In the latter complex $V(CO)_6^-$ is easily displaced by nitrogen donors.¹⁷⁵

IV. Proof of Coordination

In Table I a listing of isolated and characterized complexes of coordinated fluoro anions, $OTeF_5^-$, and carborane anions is given.

TABLE I. Representative Examples of Proposed or Isolated Complexes with Fluoro-, Teflate- and Carborane anions

complex	X, L	ref
CrCp(NO) ₂ X	X = FBF ₃ , FPF ₅ , FAsF ₅	20, 60, 161
Cr(CO) ₃ (CMe)(PMe ₃)X	X = FBF ₃	4
MoCp(CO) ₂ (L)X	L = CO, PPh ₃ , PEt ₃ , P(OPh) ₃ ; X = FBF ₃	5, 182
	L = CO; X = FPF ₅ , FAsF ₅ , FSbF ₅	5, 25
WCp(CO) ₂ (L)X	L = CO, PR ₃ ; X = FBF ₃	5, 186a
	L = CO; X = FPF ₅ , FAsF ₅ , FSbF ₅	5, 202
WCp(NO) ₂ X	X = FBF ₃	222
W(CO) ₅ (NO)(PR ₃)X	X = FSbF ₅ ; PR ₃ = PMe ₂ Ph, PMe ₃	162
Mn(CO) ₅ X	X = FBF ₃ , FAsF ₅ , OTeF ₅	3, 54, 183
Re(CO) ₃ (L) ₂ X	L = bpy, tmen; X = FBF ₃ , FAsF ₅	56c
	L = CO; X = FBF ₃ , FAsF ₅ , OTeF ₅ , FReF ₅	3, 42, 54, 88, 144
Re(Cp)(NO)(PPh ₃)X	X = FBF ₃ , FPF ₅	91b
FeCp(CO) ₂ X	X = FBF ₃	53
Fe(TPP)X	X = FSbF ₅ , B ₁₁ CH ₁₂	179, 180
[Rh ₂ Cl ₂ (μ-H)(μ-CO)(dppm) ₂ X]	X = FBF ₃	39
Ir(L)(Cl)(PPh ₃) ₂ (H)X	L = CO, N ₂ ; X = FBF ₃	164
	L = CO, X = FPF ₅	252
U ₂ (C ₅ H ₃ (SiMe ₃) ₂) ₄ (μ-F) ₂ (μ-X) ₂	X = F ₂ BF ₂	176
trans-(Ph ₃ P) ₂ PtHX	X = [HC(SO ₂ CF ₃) ₂]	167

TABLE II. Bond Lengths in Some M-F-EF_n Complexes

compd	d(M-F _b)	d(F _b -E)	d(E-F ₁)	ref
Cu(PPh ₃) ₃ FBF ₃	2.31	1.39	1.35	13c
[UCp'' ₂ (μ-BF ₄)(μ-F)] ₂	2.41	1.34	1.38/1.23	176
[Cu(bpy) ₂ (F ₂ BF ₂)] ⁺ BF ₄ ⁻	2.56/2.66	1.37/1.35	1.39	14a
IrClCO(PPh ₃) ₂ (H)(FBF ₃)	2.27	1.45	1.34	164b
Ag(CNR) ₂ F ₂ PF ₄	2.67	1.56	1.51	178
Fe(TPP)FSbF ₅	2.11	1.90	1.88-1.93	180a
(Me ₂ PhP)(CO) ₂ ONWFSbF ₅	2.17	1.95	1.86	162
(OC) ₅ ReFReF ₅	2.13/2.20	1.98/1.95	1.84	144

TABLE III. ν(E-F) Bands (cm⁻¹) of Hexafluorophosphato-, arsenato-, and -antimonato Complexes L_nM-X^a

L _n M	X	A ₁ (ν ₁)	A ₁ (ν ₂)	B ₁ (ν ₂)	A ₁ (ν ₃)	E(ν ₃)	A ₁ (ν ₄)	E(ν ₄)	ref
Cu(py) ₄	(FPF ₅) ₂	742			852	828		551	181
CpMo(CO) ₃	FPF ₅	739			879	810		488	5
IrHCl(PPh ₃) ₂ CO	FPF ₅	734			880	810		488	116b
CpMo(CO) ₃	FAsF ₅	669	511	550	699	726	395, 384, 367		25
CpW(CO) ₃	FAsF ₅	668			697	726			34
Re(CO) ₅	FAsF ₅	675			712	730			3
Mn(CO) ₅	FAsF ₅	676			710	725			3
Re(CO) ₃ (bpy)	FAsF ₅		530		705	765		390	56c
CpMo(CO) ₃	FSbF ₅	642			662	679			25

^aThe ν(E-F) bands (F_{1u}) of the free octahedral anions are at ca. 830 cm⁻¹ (PF₆⁻), 700 cm⁻¹ (AsF₆⁻), and 670 cm⁻¹ (SbF₆⁻).

A. Crystal Structure Determinations

A series of crystal structures of non-carbonyl complexes show BF₄⁻ as a monodentate or bidentate bridging ligand.^{13,14,176,177} Also the structures of complexes with PF₆⁻,¹⁷⁸ AlCl₄⁻, and AlCl₂R₂⁻^{105c,113-115} have been elucidated. A group of Fe(TPP)X complexes, particularly with the weak anionic ligands X = SbF₆⁻¹⁷⁹ and B₁₁CH₁₂⁻,¹⁸⁰ was examined by X-ray crystallography. The crystal structure of AgB₁₁CH₁₂·2C₆H₆^{180c} shows a bridging carborane and an η¹-coordinated benzene ligand, which is "interpreted as resulting from the poor ligation properties of the *closo*-carborane anion". Only a few crystal structures of carbonyl complexes with BF₄⁻, SbF₆⁻, ReF₆⁻, and OTeF₅⁻ have been reported, e.g., IrCl(CO)(PPh₃)₂(H)(FBF₃),^{164b} (Me₂PhP)(CO)₃(NO)WFSbF₅,¹⁶² (OC)₅ReFReF₅,¹⁴⁴ and (OC)₅MnOTeF₅.⁵⁴ In most of these compounds the bridging E-F bonds are longer than the terminal E-F bonds. The metal-fluorine interaction is stronger in complexes of π-acceptor ligands than it is in complexes of metals in normal oxidation states with nitrogen donors. The two very different terminal B-F bond lengths in [UCp''₂(μ-BF₄)(μ-F)]₂ (Cp'' = C₅H₃(SiMe₃)₂) are unusual.¹⁷⁶

The coordination of CH(SO₂CF₃)₂⁻ to platinum via the carbon atom was shown in a crystal structure determination of Pt(PPh₃)₂(H)(CH(SO₂CF₃)₂).^{167b} This appears interesting since RHC(SO₂CF₃)₂ are strong protic acids and the negative charge of the corresponding anion should be delocalized.

Bond lengths of relevant examples are summarized in Table II.

B. IR Spectroscopy

Coordination of the highly symmetric anions BF₄⁻ (T_d), PF₆⁻, AsF₆⁻, or SbF₆⁻ (O_h) to a metal center leads to a significant lowering of the symmetry. This results in a characteristic splitting of the E-F stretching vibrations^{13c,181} (Table III). The ν(BF₄) vibrations are especially sensitive to changes in the neighborhood of the BF₄⁻ anion. Four ν(BF) bands are expected for the C_s symmetry of the M-F-BF₃ group, as has been observed with M(CO)₅FBF₃ (M = Mn, Re); sometimes only three bands are visible (Table IV).

Splitting of the ν(BF₄) band may also be observed without coordination of the anions to a metal center, due to hydrogen bonds to coordinated water or amines.^{4,56c,184}

TABLE IV. $\nu(^{11}\text{B-F})$ Bands of Tetrafluoroborate Complexes^a

compd	$\nu(^{11}\text{B-F})$				ref
CpMo(CO) ₃ FBF ₃	1130	884	722	5	
CpMo(CO) ₂ (PPh ₃)FBF ₃	1119	901	732	182	
CpMo(CO) ₂ (PEt ₃)FBF ₃	1137	891	730	182	
Cu(PPh ₃) ₃ FBF ₃		984	769	13c	
Cr(CMe)(CO) ₃ (PMe ₃)FBF ₃	1110		910	745	4
Re(CO) ₅ FBF ₃	1162	1128	902	738	42
Mn(CO) ₅ FBF ₃	1145	1118	919	738	183
[Cu(bpy) ₂ F ₂ BF ₂] ⁺ BF ₄ ⁻	1105	1070	1030		14a
[SnMe ₃ F ₂ BF ₂] ⁺ BF ₄ ⁻	1170	1085	1005	758	14a

^aThe free BF₄⁻ ion absorbs at ca. 1050–1080 cm⁻¹.

We have found that some very labile complexes can react with the material of the IR cell windows rapidly under formation of halide compounds. Then only the IR spectrum of the free anions is observed. In other cases the presence of water leads also to splitting of $\nu(\text{BF}_4^-)$ bands (see below).

Evidence for bridging F₂PF₄ groups in polymeric [Mo(NO)₂(PF₆)₂]_n has been obtained by IR spectroscopy.¹⁸⁵

C. NMR Spectroscopy

In a few cases it has been possible to demonstrate the coordination by NMR spectroscopy. The ¹⁹F NMR low-temperature spectra of CpM(CO)₂(L)(FBF₃)¹⁸⁶ in CD₂Cl₂ show two widely separated signals; a doublet due to the terminal fluorine nuclei close to free BF₄⁻ and a quartet at very high field due to the bridging fluorine atom. Similarly, coordination of BF₄⁻ in CpFe(C₆H₅)(FBF₃) was proven by ¹⁹F NMR spectroscopy.¹⁰³ In phosphorus-containing compounds (L = PR₃) additional coupling to the ³¹P nuclei can be observed.^{186,187} The ³¹P NMR spectra of these complexes as well of (MeC≡)Cr(CO)₃(PMe₃)FBF₃,⁴ W(CO)₃-(PR₃)(NO)(FSbF₅),¹⁶² and (η^3 -C₃H₅)(Me₃P)NiFBF₃^{105a} also reveal a doublet at low temperature due to coupling of the ³¹P nucleus to a single fluorine atom. At higher temperatures typical coalescence behavior in both ³¹P and ¹⁹F NMR spectra is observed, which is consistent with an intramolecular exchange of coordinated and noncoordinated fluorine atoms.

In some cases only signals of freely rotating or uncoordinated fluoro anions could be obtained.^{30,56c,60,91b,186a} This was explained by an equilibrium between the coordinated and free BF₄⁻ anion^{56c} or by rapid rotation of PF₆⁻ on the NMR time scale;⁶⁰ a fast exchange of solvent and coordinated PF₆⁻ may also be an explanation.^{186a} For CpRe(NO)(PPh₃)BF₄ ¹³C NMR evidence of coordinated CD₂Cl₂ in CD₂Cl₂ solution has been obtained.^{91b} The relatively small number of NMR "proofs" is a consequence of the low solubility of many of these complexes in weakly coordinating solvents. In stronger donor solvents substitution of the coordinated anion by the solvent occurs.

V. Reactivity

Organometallic Lewis acids such as "Re(CO)₅⁺" or "AuPPh₃⁺" can serve as a probe for the behavior of all kinds of ligands, including ambivalent ligands. "Re(CO)₅⁺" is especially useful since the pentacarbonyl group can easily be detected by its characteristic pattern of the $\nu(\text{CO})$ bands in the IR spectrum.

TABLE V

A. CO Frequencies (cm⁻¹) of Carbonyl Complexes L_n(CO)_nMX of Weakly Coordinating Anions

L _n (CO) _n M	X	$\nu(\text{CO})$ (in CH ₂ Cl ₂)			ref
Mn(CO) ₅	FBF ₃	2163	2081	2023	183
	OCIO ₃	2158	2074	2023	54
	OSO ₂ CF ₃	2158	2073	2020	54
	OTeF ₅	2155	2070	2016	54
	OCOCF ₃	2149	2063	2012	54
Re(CO) ₅	I	2129	2045	2008	54
	FBF ₃	2166	2066	2008	42
	OSO ₂ CF ₃	2166	2059	2004	54
	OTeF ₅	2164	2055	1998	54
	OReO ₃	2163	2051	1995	239d
CpFe(CO) ₂	Cl	2157	2046	1985	54
	FBF ₃	2078	2032		53
	OTeF ₅	2069	2024		54
	I	2043	1998		53
	Cp(CO) ₃ Mo	FSbF ₅	2079	2001	
FPF ₅		2079	1997		5
FAsF ₅		2072	1985		25
FBF ₃		2067	1975		5
Cl		2057	1977		5
Ir(PPh ₃) ₂ (CO)(Cl)H (in Nujol)	FPF ₅		2072		252
	FBF ₃		2061		164b, 190
	OSO ₂ CF ₃		2055		164b, 190
	OSO ₂ F		2048		90
	OReO ₃		2044		57
	Cl		2027		190

B. NO Frequencies (cm⁻¹) of Complexes CpW(NO)₂X

X	$\nu(\text{NO})$		ref
FBF ₃	1770	1640	222
OTs	1737	1650	222
Cl	1705	1625	222

TABLE VI. $\delta(\text{C}_5\text{H}_5)$ Signals of Several Cyclopentadienyl Complexes CpL_nMX of Weakly Coordinated Anions

CpL _n M	X	$\delta(\text{C}_5\text{H}_5)$ ^a	ref
Cp(CO) ₃ Mo	FSbF ₅	6.02	25
	FAsF ₅	6.02	25
	FBF ₃	5.98	90
	OSO ₂ F	5.88	90
	OSO ₂ CF ₃	5.85 ^b	90
Cp(CO) ₃ W	Cl	5.70	5
	FBF ₃	6.11	90
	OSO ₂ F	6.00	90
	OSO ₂ CF ₃	5.96 ^b	90
	Cl	5.79	5

^aIn CD₂Cl₂ unless otherwise noted. ^bIn CDCl₃.

A. Relative Donor Strengths of Several Weakly Coordinating Anions

The cationic character of the metal carbonyl fragment, corresponding to a weak donor strength of the coordinated anions, can easily be derived from the $\nu(\text{CO})$ data. The complex "Cu(CO)AsF₆" shows the highest $\nu(\text{CO})$ frequency (2180 cm⁻¹) for monocarbonyls.^{11a} In the complexes M(CO)₅X (M = Mn, Re), CpM(CO)₃X (M = Mo, W), or CpFe(CO)₂X the $\nu(\text{CO})$ frequencies are considerably higher for X = EF_n⁻, ClO₄⁻, OTeF₅⁻, etc. than in the corresponding halides. In the nitrosyl complex CpW(NO)₂X the same observation can be made for $\nu(\text{NO})$ (Table V).

Similar results can be obtained by comparing the ¹H NMR spectra of CpM(CO)₃X (M = Mo, W), where the shifts for the cyclopentadienyl group occur at lower fields for weaker σ -donor ability of X (see Table VI). The IR and NMR data indicate the following order of

TABLE VII

A. ¹H NMR Chemical Shifts and $\nu(\text{Ir-H})$ Wavenumbers for $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{Cl})(\text{H})\text{X}^{190}$

X	$\delta(\text{Ir-H})$	$\nu(\text{Ir-H})$
FBF ₃	-26.5	2333
OSO ₂ CF ₃	-21.77	2305
NCS _e	-16.1	
Cl		2240
SeCN	-11.4	2180

B. ³¹P NMR Data for $\text{trans}-(\text{OC})_3(\text{ON})(\text{Me}_3\text{P})\text{WL}]^{+191}$

L	$\delta(^{31}\text{P})$	$^1J(\text{P-W})$
FSbF ₆ ⁻	-16.25	282.9
FBF ₃ ⁻	-17.46	282.0
OPOF ₂ ⁻	-21.48	274.4
NCS _e	-27.03	263.8
Cl ⁻	-28.34	263.8
PPh ₃	-35.96	252.4

relative σ -donor strength:^{5,54,57,90} FAsF_5^- , FSbF_6^- , FPF_5^- < FBF_3^- < OSO_2F^- , $\text{OSO}_2\text{CF}_3^-$ < OCIO_3^- < OTeF_5^- , $\text{OReO}_3^- \ll \text{Cl}^-$.

A similar order was found earlier from electronic spectra and magnetic data of complexes $\text{M}(\text{en})_2\text{X}_2$ and $\text{M}(\text{py})_4\text{X}_2$.^{14c,188} Calculations of the "group electronegativities"¹⁸⁹ of the coordinating anions are consistent with this series. For complexes of the same type this trend is qualitatively also observed in the chemical reactivity. For instance, the reaction of $\text{HRh}(\text{PP}_3)$ ($\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$) with HBF_4 yields an $\eta^2\text{-H}_2$ complex $[\text{H}_2\text{Rh}(\text{PP}_3)]^+\text{BF}_4^-$, which spontaneously loses H_2 on addition of CF_3SO_3^- to give the triflate complex $(\text{PP}_3)\text{RhOSO}_2\text{CF}_3$.^{76a}

Two correlations have been found by comparing either the $\delta(\text{Ir-H})$ chemical shifts and $\nu(\text{Ir-H})$ in compounds $\text{HIr}(\text{CO})(\text{PPh}_3)_2(\text{L})\text{Cl}^{190}$ or the ³¹P NMR data of $\text{LW}(\text{NO})(\text{PMe}_3)(\text{CO})_3^{191}$ ($\text{L} = \text{anionic or neutral ligand}$). Linear relationships between the $\delta(\text{Ir-H})$ shift and the electronegativity of the ligand trans to hydrogen in the first case and between ³¹P NMR shifts and one-bond coupling constants $^1J(^{31}\text{P}-^{183}\text{W})$ in the second case were found. Both measurements allow one to derive a general order of σ -donor strengths for both anionic or neutral ligands: F donor < O donor < N donor (Table VII).

From the porphyrin core coordination parameters of five-coordinate ferric porphyrins, e.g., the iron-nitrogen distances, or the distance of iron atoms from the porphyrin plane, the following order of decreasing strength of anion bonding has been found:^{180b} $\text{I}^- > \text{OCIO}_3^- > \text{FSbF}_6^- > \text{B}_{11}\text{CH}_{12}^-$. Thus the carborane ligand is the least coordinating anion, at least for the $\text{Fe}(\text{TPP})^+$ moiety.^{179,180} A "new" candidate for the least coordinating anion is the $\text{B}(\text{OTeF}_5)_4^-$ anion.¹⁹² An "old" candidate for this position may be the $\text{C}(\text{SO}_2\text{R})_3^-$ ion, which has been shown to be a very weak ligand.¹⁹³

B. Substitution of Weakly Coordinating Ligands by Neutral σ - and π -Donors

The weakly coordinated anions are readily displaced under very mild conditions by a large number of neutral σ - and π -donors to give ionic complexes



where $\text{X} = \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^-, \text{SbF}_6^-, \text{OTeF}_5^-, \text{OCIO}_3^-, \text{CF}_3\text{SO}_3^-, \text{AlCl}_4^-, \text{and SbCl}_6^-$ and $\text{L}' = \text{H}_2\text{O}$, ROH ,^{84a,194,195} R_2O ,^{58,195,196} $\text{R}_2\text{C}=\text{O}$,^{5,42,49,50,55,56a,134,194,198,199}

RNO_2 ,^{134,200} H_2S ,^{24,201,202} RSH ,^{202,203} R_2E_n ($n = 1, 2$; $\text{E} = \text{S, Se, Te}$),^{103,200,202,204,205} R_2SO ,^{202,205} N_2 ,^{74,169} NR_3 ,^{169,206-209,282} R-CN ,^{134,210-213} ER_3 ($\text{E} = \text{P, As, Sb, Bi}$),^{135e,205,214-218} R_3EX ($\text{E} = \text{P, As, Sb}$; $\text{X} = \text{S, Se, Te, O, NR}$),^{219,282} $\text{RN}=\text{C}$,^{220,245} $\text{R}_2\text{C}=\text{CR}_2$,^{10,134,136a,182,221-226} $\text{R-C}\equiv\text{C-R}$,^{5,51,136b,225,227-229} CO ,^{5,42,62} SO_2 ,^{194,213} O, S , and N heterocycles,^{230,239b} and guanine^{239c} and xanthine derivatives.⁷⁷ Easy uptake of H_2 even in the solid state has been reported for $[\text{Co}(\text{P}(\text{OMe})_3)_4]^+\text{PF}_6^-$ to give $[\text{H}_2\text{Co}(\text{P}(\text{OMe})_3)_4]^+\text{PF}_6^-$.¹⁰

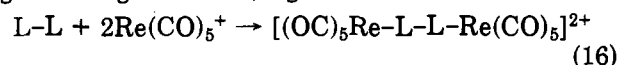
The systems $\text{CpFe}(\text{CO})_2\text{X}$,^{231a} CpML_2X ($\text{M} = \text{Ru, Os}$),^{231b} and $\text{CpM}(\text{CO})_2(\text{L})\text{X}$ ($\text{M} = \text{Mo, W}$) have been intensively studied. It should be noted that the starting compounds $\text{CpM}(\text{CO})_2(\text{L})\text{X}$ ($\text{M} = \text{Mo, W}$) are extremely sensitive to moisture. The formation of the much less reactive red aqua complexes $[\text{CpM}(\text{CO})_2\text{L}(\text{H}_2\text{O})]^+\text{X}^-$ from the violet BF_4^- complexes can easily be recognized. In the system $\text{CpM}(\text{CO})_2(\text{L})\text{X}$ we observed the following order of increasing ability to substitute weaker ligands:^{5,195,196,202} $\text{CH}_2\text{Cl}_2 \sim \text{PF}_6^- \sim \text{AsF}_6^- \sim \text{SbF}_6^- < \text{OEt}_2 < \text{BF}_4^- < \text{H}_2\text{S} < \text{THF} < \text{Me}_2\text{CO} < \text{H}_2\text{O} < \text{CF}_3\text{SO}_3^- < \text{CO} \sim \text{MeCN} \sim \text{PR}_3$.

Other systems examined for substitution reactions include $\text{CpW}(\text{NO})_2\text{BF}_4$,²²² $\text{CpCr}(\text{NO})_2\text{PF}_6$,⁶⁰ $\text{Mn}(\text{CO})_5\text{OCIO}_3$,^{55,56a,217} $(\text{Mn,Re})(\text{CO})_5\text{OSO}_2\text{CF}_3$,⁵⁸ $(\text{Mn,Re})(\text{CO})_5\text{FBF}_3$,^{42,56c,224,239a,b} $\text{Mn}(\text{CO})_4(\text{L})\text{BF}_4$,²⁴ $\text{Mn}(\text{CO})_3(\text{L})_2\text{X}$ ($\text{X} = \text{ClO}_4^-, \text{PO}_2\text{F}_2^-$,^{56a,220} $(\text{Mn,Re})(\text{CO})_5\text{F-AsF}_5$,^{194,213,234} $\text{Cp}'\text{Os}(\text{CO})_2\text{BF}_4$,³⁰ $(\text{Rh,Ir})(\text{CO})(\text{PPh}_3)_2\text{ClO}_4$,^{62,210,211} $\text{HIr}(\text{Cl})(\text{CO})(\text{PPh}_3)_2\text{FBF}_3$,¹⁶⁴ Cp_2TiX_2 ,^{198,206,212} and $\text{W}(\text{CO})_3(\text{PR}_3)(\text{NO})\text{X}$.¹⁹¹ $(\text{OC})_5\text{-ReOSO}_2\text{CF}_3$ undergoes substitution of triflate with nucleophiles according to an associative process.⁵⁸ Interestingly, the reactions of $\text{CpRe}(\text{NO})(\text{PPh}_3)\text{X}$ ($\text{X}^- = \text{BF}_4^-, \text{PF}_6^-$) with σ - and π -donors proceed with retention of configuration at rhenium.^{91b}

Many substitution reactions have been carried out by in situ generation of $\text{L}_n\text{M-X}$ or from cationic solvent complexes in the presence of donors. As far as these syntheses have been carried out in dichloromethane, coordination of CH_2Cl_2 may occur.^{5,52,53,56b,91b,186a,221}

Interesting ligands that could be coordinated to the metal via this method in cationic complexes are acetic and trifluoroacetic acid,²³² CH_3I ,^{233a,e,236} $\text{C}_6\text{H}_4\text{I}_2$,^{233b} NS^+ ^{234a} (thus a dicationic carbonyl complex $[(\text{OC})_5\text{ReNS}]^{2+}$ could be obtained), NSF_3 ,^{234b} HNSO ,^{234c} HNSOF_2 ,^{234d} $\text{Ph}_3\text{PCHCOCH}_3$,²³⁵ and Et_3PCS_2 .²³⁷ The alkyl iodide complexes $[\text{Ir}(\text{PPh}_3)_2\text{H}_2(\text{MeI})_2]^+$ ^{233a} and $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{ICH}_2\text{SiMe}_3)]^+\text{BF}_4^-$ ²³⁶ have been characterized by crystal structure determination. Closely related are $[(\text{COD})\text{Ir}(\eta^2\text{-}(\text{P,Br})\text{-}(\text{Ph}_2\text{PC}_6\text{H}_4\text{Br}))]^+$ ^{233c} and $[\text{IrH}_2(\text{PPh}_3)_2(\eta^2\text{-}(\text{8-fluoroquinoline}))]$.^{233d}

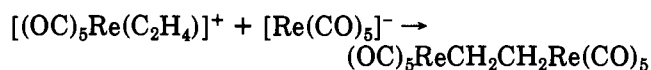
With diphosphines mono- and dinuclear cationic complexes can be obtained, e.g., $[(\text{CO})_5\text{Re-PPh}_2\text{-X-PPh}_2\text{-Re}(\text{CO})_5]^{2+}$, with $\text{X} = \text{CH}_2, \text{NH}$, or O , or the two tautomers $[(\text{CO})_5\text{Re-PPh}_2\text{-NH-PPh}_2]^+$ and $[(\text{CO})_5\text{Re-PPh}_2\text{-N-PPh}_2\text{H}]^+$.²³⁸ Several polyfunctional neutral ligands, such as pyrazine,^{239b} TCNE , TCNQ ,^{239a} 1,3- or 1,4-dithiane, 1,3,5-trithiane,^{219b,239d} or 1,4-dioxane,¹⁹⁶ can also be metalated by more than one $\text{Re}(\text{CO})_5^+$ to give ligand-bridged cations; e.g.



Trithiane and TCNQ can be trimetalated by $\text{Cp}(\text{OC})_2\text{Fe}^+$ ^{219b} or $\text{Re}(\text{CO})_5^+$,^{239a} respectively.

CO readily displaces AlCl_4^- , BF_4^- , or ReF_6^- in $(\text{Mn}, \text{Re})(\text{CO})_5\text{X}^{42,108,109,144}$ in a CO atmosphere, while for $\text{X} = \text{OTeF}_5^-$ or CF_3SO_3^- no reaction occurs under these conditions.^{54,58} On the other hand, in $(\text{OC})_5\text{MnX}$ with $\text{X} = \text{OTeF}_5^-$ and CF_3SO_3^- ligands CO is substituted by nucleophiles while the anionic ligand remains coordinated.^{54,58} Interestingly, the metal-triflate bond of $(\text{OC})_5\text{MOSO}_2\text{CF}_3$ ($\text{M} = \text{Mn}, \text{Re}$) is seriously weakened in superacidic solvents ($\text{CF}_3\text{SO}_3\text{H}$, FSO_3H , SbF_5). In these systems the triflate complexes react with CO to give $[\text{M}(\text{CO})_6]^+$.⁵⁸

Introducing alkenes or alkynes to form cationic complexes with coordinated unsaturated hydrocarbons is particularly easy by this method. Cationic complexes are important starting materials for nucleophilic addition reactions at coordinated unsaturated hydrocarbons, carbon monoxide, isonitriles, or ketones.^{51a,199,240-243} The use of carbonyl metalates, e.g., $\text{Re}(\text{CO})_5^-$, instead of organic nucleophiles for the attack on the coordinated unsaturated hydrocarbon leads to a series of hydrocarbon-bridged bimetallic complexes in a directed way,²⁴⁴ e.g.



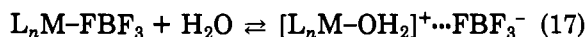
C. Reaction of Tetrafluoroborate and Hexafluorophosphato Complexes with Water

Three different types of reaction with water have been observed.

1. Formation of Aqua Complexes

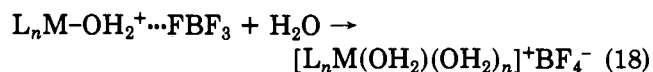
The anion can be substituted by H_2O to give cationic aqua complexes. So $[\text{Mn}(\text{CO})_5(\text{H}_2\text{O})]^+$,²⁴⁶ $[\text{Re}(\text{CO})_5(\text{H}_2\text{O})]^+$,^{42,56c,194,201} $[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{H}_2\text{O})]^+$,²⁴ $[(\text{Mn}, \text{Re})(\text{CO})_3\text{L}_2(\text{H}_2\text{O})]^+$,^{56c} $[\text{Cp}(\text{Mo}, \text{W})(\text{CO})_2(\text{L})(\text{H}_2\text{O})]^+$,^{5,195} $[\text{CpOs}(\text{CO})_2(\text{H}_2\text{O})]^+$,³⁰ $[\text{Cr}(\text{CO})_3(\text{PMe}_3)(\text{CMe})(\text{H}_2\text{O})]^+$,⁴ $[\text{CpFe}(\text{CO})_2(\text{H}_2\text{O})]^+$,^{41,53} $[\text{Pt}(\text{PPh}_3)_2(\text{Cl})(\text{H}_2\text{O})]^+$,²⁴⁷ $[\text{Cp}_2\text{Ti}(\text{H}_2\text{O})_2]^{2+}$,²⁴⁸ $[\text{Cp}_2\text{Zr}(\text{H}_2\text{O})_3]^{2+}$,²⁴⁹ and $[\text{W}(\text{PMe}_3)_4(\text{H}_2\text{O})\text{H}_2\text{F}]^+$ ²⁵⁰ have been obtained. The origin of the water can be moist solvent²⁴ or traces of water in the silver salts^{56c} used in synthesis.

A variable-temperature ^{19}F NMR study of $[\text{Re}(\text{CO})_3(\text{tmen})(\text{H}_2\text{O})]^+$ has been undertaken.^{56c} The coalescence of two singlets was interpreted as evidence for an equilibrium:



However, the characteristic pattern of coordinated BF_4^- has not been observed.

In complexes $[\text{L}_n\text{M}-\text{OH}_2]^+\text{BF}_4^-$ IR spectroscopy clearly reveals hydrogen bridges between coordinated H_2O and BF_4^- .^{4,5,56c,184,247,251} The characteristic pattern of the $\nu(\text{BF})$ absorptions in H-bridged species can easily be distinguished from the pattern of coordinated BF_4^- and of free BF_4^- , as was shown for $[\text{CpMo}(\text{CO})_3(\text{H}_2\text{O})]^+$.^{5,184} When more than stoichiometric amounts of water are present, hydrates are formed and the IR spectrum of free BF_4^- is observed.



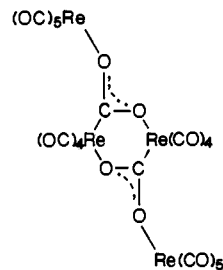
The crystal structure determinations of the aqua complexes $[\text{Ir}(\text{PPh}_3)_2(\text{Cl})\text{H}(\text{H}_2\text{O})]^+\text{BF}_4^-$ ²⁵² and

$[(\text{C}_7\text{H}_7)\text{Mo}(\text{acac})(\text{H}_2\text{O})]^+\text{BF}_4^-$ ²⁵³ show a cyclic structure of two water molecules doubly hydrogen bridged to two different bridging BF_4^- anions. BF_4^- and AsF_6^- was shown to be hydrogen bonded to two coordinated water molecules of $[\text{Re}(\text{CO})_3(\text{tmen})(\text{H}_2\text{O})]^+$.^{56c} Also in $[\text{Cp}_2\text{Zr}(\text{H}_2\text{O})_2(\text{OTs})]^+$ hydrogen bridges between H_2O and the sulfonato group have been proven.²⁵⁴

2. Condensation Reactions

In the presence of weak bases cationic aqua complexes can be deprotonated, and condensation gives dinuclear hydroxo-bridged or tris(metallaonium) species. With $[\text{CpCr}(\text{NO})_2(\text{OH}_2)]^+$ ¹³⁹ or $[\text{Cp}_2\text{Zr}(\text{H}_2\text{O})_3]^{2+}$ ²⁵⁵ the hydroxo-bridged $\{[\text{CpCr}(\text{NO})_2]_2(\mu\text{-OH})\}^+\text{BF}_4^-$ and $[\text{Cp}_2\text{Zr}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_6]^{4+}$ have been obtained. On the other hand, $[\text{CpMo}(\text{CO})_3(\text{H}_2\text{O})]^+$ and $[\text{CpMo}(\text{NO})_2(\text{H}_2\text{O})]^+$ give $\{[\text{CpMo}(\text{CO})_2]_3\text{O}\}^+$ ¹⁸⁴ and $\{[\text{CpMo}(\text{NO})(\text{OH})]_3\text{O}\}^+$.²⁵⁶ $\{[\text{CpMo}(\text{CO})_2]_3\text{O}\}^+$ contains semibringing CO groups, while the homologous $\{[\text{CpMo}(\text{CO})_2]_3\text{S}\}^+$ does not.²⁵⁷ Oxonium salt formation is also observed in the system $\text{AuPPh}_3\text{Cl}/\text{AgBF}_4$, where $\{[\text{Au}(\text{PPh}_3)]_3\text{O}\}^+$ is the reaction product in the presence of moisture.²⁵⁸ Oxo- and/or hydroxo-bridged oligomers are also obtained by alkaline hydrolysis of $\text{Fe}(\text{TPP})\text{-Cl}$,²⁵⁹ $[\text{Cp}'\text{CoX}_2]_2$,²⁶⁰ or Cp_2ZrCl_2 ²⁶¹ and have been structurally characterized.

Nucleophilic attack of hydroxide on a carbon atom of a carbonyl ligand (Hieber base reaction²⁶²) gives the CO_2 -bridged complex^{201,263}



as the final product.

3. Hydrolysis of the Anion

Hydrolysis of the anion occurs especially with the PF_6^- anion, where the very stable PO_2F_2^- ion is formed,²⁶⁴ which is also a much stronger donor. Examples are $\text{Mn}(\text{CO})_3(\text{L})_2\text{OPOF}_2$ ⁵⁶ and $\text{IrCl}(\text{H})(\text{PPh}_3)_2(\text{CO})(\text{PO}_2\text{F}_2)$,²⁵² the crystal structures of which have been determined.

In some cases hydrolysis of BF_4^- and BPh_4^- to give BF_3OH^- and BPh_3OH^- is observed.^{42,139,201,265} The structure of $(\text{OC})_5\text{Re}(\text{OH})\text{BF}_3$, which crystallized with $\{[(\text{CO})_5\text{Re}]_3\text{S}\}^+\text{BF}_4^-$ in the same crystal, has been determined.²⁶⁶ Interestingly, the BF_3OH^- ion was formed also by the reaction of AgF_2H with $\text{Re}(\text{CO})_3(\text{tmen})\text{Br}$ in a glass apparatus to give $\{[\text{Re}(\text{CO})_3(\text{tmen})\text{F}]_2\text{H}\}^+\text{BF}_3\text{OH}^-$, as was shown by crystal structure determination.²⁶⁷

D. Reaction with Monoanionic Ligands

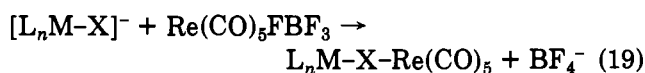
Particularly for $\text{Re}(\text{CO})_5\text{X}$ compounds the substitution of the BF_4^- ion in $\text{Re}(\text{CO})_5\text{BF}_4$ by a large number of anionic ligands is a straightforward way under very mild conditions. In these reactions the $\text{Re}(\text{CO})_5$ moiety remains intact, whereas in reaction of the corresponding

halides with silver salts loss of CO may occur. In several cases $\text{Re}(\text{CO})_5\text{FBF}_3$ can be reacted in aqueous solution, where substitution of the aqua ligand in $[\text{Re}(\text{CO})_5(\text{H}_2\text{O})]^+$ takes place. Thus complexes $\text{Re}(\text{CO})_5\text{X}$ with $\text{X} = \text{SCN}, \text{SeCN}, \text{OReO}_3, \text{ONO}_2, \text{NO}_2, \text{OCHO}, \text{NCNC-N}^-, \text{NCC}(\text{CN})_2^-,$ or TCNQ^- could be obtained.^{57,201,239a} Dicyanamide and tricyanomethanide have been shown to coordinate through the nitrile N atom to the metal.^{239a} Related substitutions with halide, pseudohalide, or nitrate ligands have been reported for $[\text{CpFe}(\text{CO})_2(\text{OH}_2)]^+\text{BF}_4^-$,¹³¹ $\text{W}(\text{CO})_4(\text{CR})\text{FBF}_3$,¹²⁰ $\text{Cp}_2\text{Ti}(\text{CF}_3\text{SO}_3)_2$,²⁶⁸ and $\text{W}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2(\text{OCIO}_3)$.²⁶⁹ In the perchlorato complexes $\text{Mn}(\text{CO})_5(\text{OCIO}_3)$ the ClO_4^- anion can be substituted by acetylde.²⁷⁰ Similar reactions with $[\text{CpFe}(\text{CO})\text{L}]^+$ ²⁷¹ and with $\text{Os}(\text{C}_6\text{H}_6)(\text{P}-i\text{-Pr}_3)_2/\text{AgPF}_6$ and an alkyne²⁷² also yield σ -acetylde complexes $\text{L}_n\text{M}-\text{C}\equiv\text{C}-\text{R}$. Carboxylate complexes are obtained from $[(\text{Rh}, \text{Ir})(\text{CO})(\text{PPh}_3)_2(\text{MeCN})]^+$ and peroxocarboxylates,²⁷³ from halide complexes with silver carboxylates,²⁷⁴ or from $[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3(\text{Ni}, \text{Pt})(\text{H}_2\text{O})]^+$ and NaOCHO .²⁷⁵ In an interesting reaction the highly electrophilic $[(\text{OEP})\text{Rh}]^+$ (from $(\text{OEP})\text{RhCl}$ and AgBF_4 or AgClO_4) yields in the presence of arenes $\text{Ph}-\text{X}$ the σ -aryl compounds $(\text{OEP})\text{Rh}-\text{C}_6\text{H}_4\text{X}$.²⁷⁶ Recently, the reaction of $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_3\text{CH}_3/\text{HBF}_4$ ($\text{M} = \text{Mo}, \text{W}$) with hydrogen selenide was reported to give $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_3\text{SeH}$.²⁷⁷ Metal-metal-bonded complexes can be obtained from the substitution of the weakly coordinated anion by an organometallic anion,²⁷⁸ e.g., $(\text{OC})_5\text{MnRe}(\text{CO})_5$ from $(\text{O}^{13}\text{C})_5\text{ReOSO}_2\text{CF}_3$ and $\text{KMn}(\text{CO})_5$.¹⁹⁷

E. Directed Synthesis of Ligand-Bridged Complexes

1. Neutral Ligand-Bridged Bimetallic Complexes

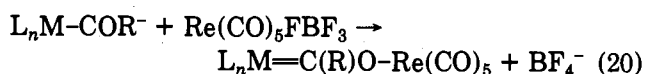
It is well-known that Lewis acids of main-group elements ($\text{BF}_3, \text{SiF}_4, \text{AlR}_3$) add to the nitrogen atom of cyanide complexes.²⁷⁹ Similarly, the Lewis acids $[\text{Me}(\text{CO})(\text{PR}_3)_2(\text{Cl})\text{Ir}]^+$,²⁸⁰ $[\text{Cp}_2\text{Zr}]^{2+}$,²⁸¹ and $[\text{Re}(\text{CO})_5]^+$ ²⁰¹ form cyanide-bridged complexes with $[\text{Pt}(\text{CN})_4]^{2-}$ or $[\text{Au}(\text{CN})_2]^-$, e.g., $\text{NCAuCNRe}(\text{CO})_5$ and $(\text{NC})_2\text{Pt}[\text{CNRe}(\text{CO})_5]_2$. By the reaction of anionic carbonyl halide or pseudohalide complexes with $\text{Re}(\text{CO})_5\text{FBF}_3$ the neutral compounds $\text{L}_n\text{M}-\text{X}-\text{Re}(\text{CO})_5$ can be obtained



where $\text{L}_n\text{M} = \text{Cr}(\text{CO})_5$ or $\text{W}(\text{CO})_5$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{NCS}, \text{NCO}, \text{SH},$ or $\text{NCC}(\text{CN})_2$.²⁸² Three $\text{Re}(\text{CO})_5^+$ groups can be added to $[\text{Cr}(\text{NCS})_6]^{3-}$ to afford $(\text{SCN})_3\text{Cr}[\text{NCSRe}(\text{CO})_5]_3$.²⁰¹ Examples of chalcogenide-bridged complexes obtained in a similar fashion are $[(\text{C}_5\text{R}_5)(\text{CO})_3\text{M}]_2(\mu\text{-E})$, with $\text{M} = \text{Mo}$ or W and S or Se .⁹⁵

An interesting compound, $[(\text{OC})_5\text{Re}-\text{O}(\text{O})_2\text{CrOCr}(\text{O})_2\text{O}-\text{Re}(\text{CO})_5]$, that shows that high and low oxidation states are compatible within one complex is precipitated from an aqueous solution of $[\text{Re}(\text{CO})_5(\text{H}_2\text{O})]^+\text{BF}_4^-$ and $\text{K}_2\text{Cr}_2\text{O}_7$.^{239d}

From anionic acyl complexes and $\text{Re}(\text{CO})_5\text{FBF}_3$ Fischer-type bimetallic carbene complexes can be prepared. These reactions are another example for the isolobal⁶ analogy between $\text{Re}(\text{CO})_5^+$ and carbenium ions.



where $\text{L}_n\text{M} = \text{Cr}(\text{CO})_5, \text{W}(\text{CO})_5, \text{Cr}(\text{CO})_4(\text{PPh}_3)$, or $\text{W}(\text{CO})_4(\text{PPh}_3)$ and $\text{R} = \text{Me}, \text{Ph},$ or Fc .^{282,283}

$\text{CpRe}(\text{CO})(\text{NO})\text{COOH}$ and $\text{Cp}_2\text{Zr}(\text{Cl})\text{Me}$ yield $\text{Cp}(\text{ON})(\text{OC})\text{Re}(\mu-(\eta^1\text{-C}:\eta^2\text{-O}, \text{O}'))\text{ZrCp}_2\text{Cl}$; $\text{CpRe}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ and $\text{Cp}_2\text{Zr}(\text{Cl})\text{Me}$ give $\text{Cp}(\text{ON})(\text{OC})\text{Re}-\text{CH}_2\text{O}-\text{ZrCp}_2\text{Cl}$.²⁸⁴ The anionic η^2 -acetaldehyde complex $[\text{CpMo}(\text{CO})_2(\eta^2\text{-MeCHO})]^-$ and $\text{CpMo}(\text{CO})_3\text{BF}_4$ give $\text{CpMo}(\text{CO})(\mu-\eta^1, \eta^2\text{-MeCHO})(\mu\text{-CO})\text{Mo}(\text{CO})_2\text{Cp}$.²⁸⁵

Closely related is the reaction of $\text{Cp}(\text{CO})(\text{NO})\text{Mo}(\text{CROLi})^-$ with $[\text{CpFe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$, which led to the crystallographically characterized $\text{Cp}(\text{NO})\text{Mo}(\mu\text{-CO})[\mu\text{-C}(\text{O})\text{R}]\text{FeCp}(\text{CO})$ ²⁸⁶ with a π -bonded μ -acyl bridge. Here, however, metal-metal bonds are involved. From iron-bonded enolates and the Lewis acid precursors AuPPh_3Cl or Cp_2ZrCl_2 bimetallic complexes with either a "keto" or an "enol" bridge are obtained: $[\text{Cp}(\text{Ph}_3\text{P})(\text{OC})\text{Fe}-\text{C}(\text{CH}_2)\text{O}-\text{ZrCp}_2\text{Cl}]$ and $[\text{Cp}(\text{Ph}_3\text{P})(\text{OC})\text{Fe}-\text{C}(\text{O})\text{CH}_2-\text{AuPPh}_3]$.²⁸⁷ Bimetallic μ -malonyl compounds have been obtained from in situ generated $\text{Cp}^*\text{Re}(\text{NO})(\text{PPh}_3)(\text{COCH}_2\text{Li})$ and $\text{M}(\text{CO})_5(\text{CF}_3\text{SO}_3)$ ($\text{M} = \text{Mn}, \text{Re}$).²⁸⁸ Also oxalate, squarate, and tetrathiosquarate dianion can function as bridges between two $\text{Re}(\text{CO})_5$ or $\text{CpM}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) moieties.^{201,289}

2. Formation of Ligand-Bridged Cationic Complexes

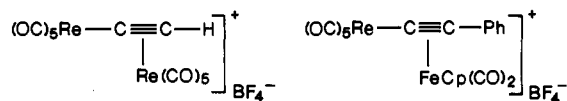
Metalation of halide, pseudohalide, or chalcogenide ligands by organometallic Lewis acids has led to a large variety of dimeric metal cations:



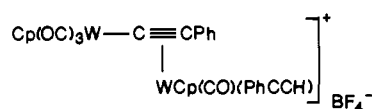
Multifunctional compounds L_nMX_m can be metalated more than once. Examples for these reactions include $\{[\text{CpM}(\text{CO})_3]_2\text{I}\}^+$ ($\text{M} = \text{Mo}, \text{W}$),²⁹⁰ $[\text{Cp}(\text{CO})_2\text{Fe}-\text{X}-\text{Re}(\text{CO})_5]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{NCO}, \text{NCC}(\text{CN})\text{CN}, \text{SR}, \text{CSSMe}, \text{PPh}_2$,²⁸² $[(\text{Ph}_3\text{PAu})_2(\mu\text{-Cl})]^+$,²⁹¹ $\{[(\text{CO})_5\text{M}]_2(\mu\text{-X})\}^+$ ($\text{M} = \text{Mn}, \text{Re}; \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$,²⁹² $\text{CN}, \text{HCOO}, \text{F}$,²⁰¹ N_3 ³²⁴), $\{[\text{Mo}(\text{CO})_2(\text{dppe})_2]_2(\mu\text{-F})\}^+$,²⁹³ $\{[\text{CpFe}(\text{CO})_2]_2(\mu\text{-X})\}^+$ ($\text{X} = \text{I}$,^{20,53} Cl, Br ,²⁹⁴ O_2CR ²⁹⁵), $\{[\text{CpCr}(\text{NO})_2]_2(\mu\text{-Cl})\}^+$,²⁰ $[\text{Pd}_3(\text{dppe})_3(\mu\text{-CN})_3]^{3+}$,²⁹⁶ $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{L}_2]_2(\mu\text{-X})^+$ ($\text{X} = \text{CN}, \text{SCN}, \text{N}_3$),²⁹⁷ $\{[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Pt}\}_2(\mu\text{-X})^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}$),²⁹⁸ $\{[\text{CpW}(\text{CO})_3]_2(\mu\text{-SH})\}^+$,²⁰² $\{[\text{Re}(\text{CO})_5]_4(\mu_4\text{-C}_4\text{S}_4)\}^{2+}$,²⁰¹ $\{[\text{Au}[\text{CNRe}(\text{CO})_5]_2]\}^+$, $\{[\text{Pt}[\text{CNRe}(\text{CO})_5]_4]^{2+}$,²⁰¹ and $\{[\text{Ir}(\text{PPh}_3)_2(\text{Cl})(\text{H})(\text{CO})]_2(\mu\text{-SeCN})\}^+$.²⁹⁹ A compound $[\text{Cp}(\text{OC})_2\text{Fe}]_2(\mu_3\text{-CS}_2)\text{Re}(\text{CO})_5]^+$, in which carbon disulfide bridges three metals, has been obtained and structurally characterized.²⁸² It is isoelectronic with the neutral $[\text{Cp}(\text{OC})_2\text{Fe}]_2(\mu_3\text{-CS}_2)[\text{W}(\text{CO})_5]$.³⁰⁰ Tricyanomethanide coordinated to three metals via its nitrile N atoms has been obtained in $\{(\text{OC})_5\text{WNCC}[\text{CNRe}(\text{CO})_5]_2\}^+\text{BF}_4^-$.²⁸² Cationic thiolate-bridged heterometallic complexes $[\text{CpNi}(\mu\text{-SR})_2\text{MCp}_2]^+\text{BF}_4^-$ can be obtained from thiolates $\text{Cp}_2\text{M}(\text{SR})_2$ ($\text{M} = \text{Ti}, \text{Mo}$) and $[\text{Cp}_3\text{Ni}]^+$.^{101b} Tris(metalla)sulfonium, tris(metalla)selenonium, or tris(metalla)telluronium salts $[(\text{L}_n\text{M})_3\text{E}]^+$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) have been obtained from chalcogenides and organometallic Lewis acids. Structurally characterized were the star-shaped cations $\{[\text{Re}(\text{CO})_5]_3\text{E}\}^+$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$)²⁶⁶ and $\{[\text{CpFe}(\text{CO})_2]_3\text{Se}\}^+$.³⁰¹ Unexpectedly, the compounds $\{[\text{CpFe}(\text{CO})_2]_3\text{Se}\}^+$ and $\{[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{Se}-\text{Fe}(\text{CO})_2\text{Cp}\}^+$ are formed by reaction of $[\text{CpFe}(\text{CO})_2]_2\text{Se}_n$ ($n = 1, 2$) with $\text{Re}(\text{CO})_5\text{FBF}_3$.³⁰² They are

closely related to the $[E(HgX)_3]^+^{303}$ and $\{[Au(PPh_3)_3E]^+\}$ salts,³⁰⁴ which were obtained in a different way.

Di- and tricationic ligand-bridged systems with neutral bridge ligands have been mentioned before. Other examples are $\{[(OC)_5Re]^{2+}(\mu-(NS)_2NMe)\}^{2+}$,³⁰⁶ $\{[CpFe(CO)_2](\mu-Ph_2E_2)\}^{2+}$ ($E = S, Se, Te$),³⁰⁷ and $\{[Re(CO)_5]_n(\mu-L_{CN})\}^{n+}$ ($L_{CN} = TCNE$ ($n = 2$), $TCNQ$ ($n = 3$)).^{239a} Two interesting types of ligand bridges occur with acetylides. From $Re(CO)_5FBF_3$ and $SiMe_3C\equiv CH$ or $CpFe(CO)_2C\equiv CPh$ the σ -, π -bridged complexes



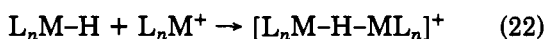
are obtained.^{282,308} The unexpected formation of the latter compound with a rhenium-carbon σ -bond was confirmed by X-ray crystal structure determination.²⁸² $CpW(CO)_3C\equiv CPh$ and HBF_4 yield the structurally characterized³⁰⁹



$[HPtL_2(\text{acetone})]^+BF_4^-$ and $PtL_2(C\equiv CPh)_2$ ³¹⁰ or $Cp(CO)_2W\equiv CAr$ ³¹¹ give μ -alkylidene complexes.

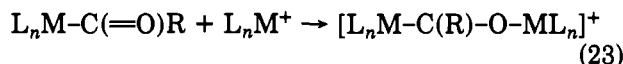
3. Formation of Cationic Hydride- and Acyl-Bridged Complexes

The concept of Lewis acid-Lewis base coupling, i.e., the reaction of organometallic Lewis acids with metal hydrides, has been proven to be a directed way for the synthesis of homo- and heterobimetallic hydride-bridged complexes, which has been reviewed.³¹²

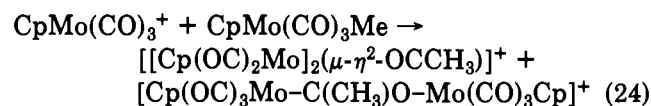


Thus the complexes $[(R_3P)_2(R')Pt(\mu-H)M(PR''_3)]^+$ ($M = Ag, Au$),³¹³ $[Cp_2M(\mu-H)_2Rh(PPh_3)_2]^+$ ($M = Mo, W$),³¹⁴ $[Cp_2W(\mu-H)_2Pt(Ph)(PEt_3)]^+$,³¹⁵ $[(CpFe)_2(\mu-dppe)(\mu-H)]^+$,²⁸ $[[CpMo(CO)_3]_2(\mu-H)]^+$ ($M = Mo, W$),^{5,316} and $[[CpM(NO)_2]_2(\mu-H)]^+$ ($M = Mo, W$)³¹⁷ have been obtained. Protonation of the dihydride $CpRh(PR_3)_2H_2$ by CF_3COOH yields $\{[CpRh(PR_3)_2(\mu-H)]_3\}^+$.³¹⁸ Also protonation of bimetallic neutral complexes $[CpM(CO)_3]_2$ ($M = Mo, W$),⁷⁵ $[CpFe(CO)_2]_2$,¹³⁹ or $Mn_2(CO)_5-(dpmm)_2$ ³¹⁹ gives hydride-bridged cationic complexes.

From transition-metal acyl complexes and organometallic Lewis acids cationic acyl-bridged bimetallic complexes can be obtained



e.g., $[Cp(CO)(L)Fe-C(CH_3)O-Mo(CO)_2(L)Cp]^+$ ^{25,320,321} and $[Cp(L)(OC)_2Mo-C(CH_3)O-Mo(CO)_2(L)Cp]^3$ ^{320b}. These compounds can also be obtained by the reaction of transition-metal alkyl complexes with organometallic Lewis acids. It could be confirmed by a crystal structure determination³²¹ that a symmetric acyl bridge can also be formed:³²⁰



This reaction is another example of a Lewis acid me-

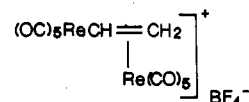
diated methyl migration.³²² Careful reexamination of the reaction of $CpMo(CO)_3H$ with " $CpMo(CO)_3^+$ "⁵ showed that actually hydrido bridges are formed and—due to the stable metal-hydrogen bond—migration of hydride to a carbonyl ligand does not occur.³¹⁶

Coordination of the acyl oxygen atom in $[Cp(OC)_2Fe-CH_2CO-FeCp(CO)_2]$ to " $CpFe(CO)_2^+$ " or " Cp_2ZrMe " yields cationic trinuclear $\mu_3-\eta^3-(C,C)_3O$ -ketene complexes $[Cp(OC)_2Fe-CH_2C(OML_n)-Fe(CO)_2Cp]^+$ ($ML_n = CpFe(CO)_2, Cp_2ZrMe$).³²³

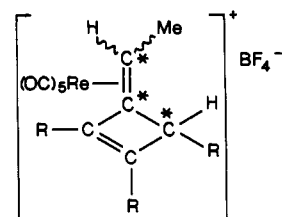
F. Miscellaneous Reactions

1. Stoichiometric Reactions

Organometallic Lewis acids are sufficiently electrophilic to cleave M-C linkages in organo derivatives of the main-group elements ($M = B, Al, Si, Sn$). Thus from the reaction of $CpW(NO)_2BF_4$ with AlR_3 or SnR_4 the compounds $CpW(NO)_2R$ are produced.²²² $CpW(NO)_2BF_4$ and $Re(CO)_5BF_4$ react with $NaBPh_4$ to give $CpW(NO)_2Ph$ ²²² and $Re(CO)_5Ph$.³²⁴ respectively. $CpRu(L)_2X$ and $NaBPh_4$ yield either $CpRu(L)_2Ph$, $[CpRu(L)_2]_2$, or $[CpRu(\eta^6-Ph-BPh_3)]$, depending on the reaction conditions.³²⁵ Alkynylstannanes and -silanes and $Re(CO)_5FBF_3$ give σ -alkynyl complexes $Re(CO)_5-C\equiv CR$.³⁰⁸ For $R = H$ the σ,π -ethynide-bridged $\{[(OC)_5Re-C\equiv CH]Re(CO)_5\}^+BF_4^-$ is formed as the stable product, as was mentioned before. This compound can easily be deprotonated in a reversible reaction by Brønsted bases to give $(OC)_5Re-C\equiv C-Re(CO)_5$.³⁰⁸ In a similar manner, the reaction of $Re(CO)_5F-BF_3$ and $Me_3SiCH=CH_2$ produced the σ,π -vinyl-bridged complex²³⁸



While with the organometallic Lewis acids $CpMo(CO)_2(L)FBF_3$ and alkynes cationic π -alkyne compounds $[CpM(CO)(L)(RCCR)]^+BF_4^-$,^{5,136,227} are obtained, $M(CO)_5FBF_3$ ($M = Mn, Re$) and $MeCCMe$ produce derivatives of a $(2\pi + 2\pi)$ -cycloaddition: $Mn(CO)_5FBF_3$ yields the π -cyclobutadiene compound $Mn(CO)_4(\eta^4-C_4Me_4)^+BF_4^-$ with loss of carbon monoxide.³²⁶ With $Re(CO)_5FBF_3$ a 1,3-H shift is observed and the pentacarbonyl complex



is formed as a consequence of the more stable $Re(CO)_5$ unit.⁸⁸

Terminal alkynes and $[CpRu(L)_2(MeOH)]^+$ give rise to cationic vinylidene complexes $[Cp(L)_2Ru=C=CHR]^+$,^{228a,b} while $[CpRu(CO)_2(MeCN)]^+BF_4^-$ and toluene afford the cyclobutadiene complex $[CpRu(\eta^4-C_4Ph_4)(MeCN)]^+BF_4^-$.¹³⁸

Similar to other Lewis acids $CpMo(CO)_3FBF_3$ induces ring opening and dimerization of oxirane, and the 1,4-dioxane complex $[CpMo(CO)_3O(CH_2)_4O]^+$ is formed.¹⁹⁶

$\text{CpCo}(\text{CO})_2$ reacts with $\text{CpMo}(\text{CO})_3\text{FBF}_3^{25}$ but not with $\text{Re}(\text{CO})_5\text{FBF}_3^{282}$ to yield a cationic bimetallic complex with a metal-metal bond.²⁵ Similarly, $\text{CpM}(\text{PMe}_3)_2$ ($M = \text{Co}, \text{Rh}$) or $(\text{C}_6\text{H}_6)\text{Os}(\text{PMe}_3)(\text{CNR})$ and AuPPh_3Cl yield $[\text{Cp}(\text{Me}_3\text{P})_2\text{M}-\text{AuPPh}_3]^+\text{X}^-$ ³²⁷ and $[(\eta^6\text{-C}_6\text{H}_6)(\text{Me}_3\text{P})(\text{RNC})\text{Os}-\text{AuPPh}_3]^+\text{X}^-$ ³²⁸ respectively.

2. Catalytic Reactions

The acetone complex $[\text{CpMo}(\text{CO})_3(\text{OCMe}_2)]^+\text{BF}_4^-$ catalyzes the reaction of acetone with oxirane to form 1,3-dioxolane.¹⁹⁶ E.g., alkene polymerization, oligomerization, or rearrangements can be catalyzed by $[\text{Fe}(\text{NO})_2\text{Cl}]_2/\text{AgPF}_6$,³²⁹ $[\text{Mo}(\text{NO})_2(\text{MeCN})_4]^{2+}$,¹⁵⁰ $\text{CpW}(\text{NO})_2\text{BF}_4$,²²² $\text{L}_2\text{PdCl}_2/\text{AgBF}_4$ mixtures,³³⁰ or $(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{PMe}_3)(\text{FBF}_3)$ and related systems $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)(\text{PR}_3)(\text{ClAlR}_3)$.¹⁰⁵ Olefin metathesis can be induced by $\text{MoCl}_2(\text{NO})_2(\text{PR}_3)_2/\text{AlEtCl}_2$ mixtures and similar systems, where the intermediate formation of a $\text{Mo}-\text{Cl}-\text{AlCl}_3$ moiety is discussed.³³¹ Claisen ester condensation reactions as well as the formation of 1,3-dicarbonyl compounds from 1-alkynes and acid anhydrides are catalyzed by $\text{TiCl}_2(\text{OSO}_2\text{CF}_3)$.³³² Diene polymerization and Diels-Alder reactions are catalyzed by $(\text{Me}_3\text{P})(\text{ON})(\text{OC})_3\text{WFSbF}_5$,³³³ the X-ray structure of the presumed catalytic intermediate $[(\text{Me}_3\text{P})(\text{ON})(\text{OC})_3\text{W}(\text{acrolein})]^+$ was determined. Hydroformylation of olefins is catalyzed by $[(\text{PPh}_3)_3\text{Rh}(\text{CO})]^+[\text{HC}(\text{SO}_2\text{CF}_3)_2]^-$.³³⁴

$\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{OCIO}_3)$ catalyzes the hydrogenation of unsaturated aldehydes.³³⁵ The most important cationic complexes are $[(\text{R}_3\text{P})_2\text{Rh}(\text{solvent})_2]^+$ and $[\text{IrH}_2\text{L}_2(\text{solvent})_2]^+$ for olefin hydrogenation or C-H bond cleavage reactions, e.g., benzene formation from cyclohexane.³³⁶ This subject appears to be, however, beyond the scope of this review.

VI. Addendum

The rapid growth of this field is documented by a series of recent interesting communications.

The complexes $\text{Cp}_2\text{Ti}(\text{FEF}_5)_2$ ($E = \text{As}, \text{Sb}$) have been prepared in SO_2 from AgEF_6 and Cp_2TiCl_2 ³³⁷ and from Cp_2TiF_2 and AsF_5 ³³⁸ and the complexes $[\text{Cp}_2\text{Ti}(\text{NCCH}_3)_3]^{2+}$ ³³⁹ and $\text{CpTi}(\text{SO}_2)_n(\text{EF}_6)_3$ have been studied.³⁴⁰ $\text{Cp}_2\text{Ti}(\text{FAsF}_5)_2$ has been characterized by X-ray diffraction.³³⁸ The extremely reactive organometallic Lewis acid $[\text{Cp}(\text{OC})(\text{R}_2\text{O})\text{Fe}(\eta^2\text{-CH}_2=\text{CHCH}_3)]^+\text{BF}_4^-$ was obtained by protonation of $\text{Cp}(\text{OC})\text{Fe}(\eta^3\text{-allyl})$ with $\text{HBF}_4\cdot\text{OR}_2$.³⁴¹ In this paper³⁴¹ previous work on the chemistry of CpL_2Fe^+ cations is thoroughly described. Coordination of tetrafluoroborate could be shown by ^{19}F NMR in $\text{Cp}(\text{OC})_2\text{Fe}(\text{FBF}_3)$,³⁴¹ $\text{Cp}(\text{OC})_2\text{Mo}(\eta^2\text{-CH}_2=\text{CHCH}_3)(\text{FBF}_3)$ ³⁴¹ and in $\text{Ph}_3\text{P}(\text{OC})_4\text{Mn}(\text{FBF}_3)$.³⁴² Ligation of CH_2Cl_2 to the chiral Lewis acid $\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{Re}^+$ has been definitely proven by low temperature ^{13}C NMR spectra.³⁴³ A hydrido-methyl complex $[\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{Re}(\text{H})(\text{Me})]^+$ has been detected as intermediate in the formation of $\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{Re}^+$ from $\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{ReCH}_3$ and $\text{HBF}_4\cdot\text{OEt}_2$.³⁴³ The chemistry of the stereochemically rigid Lewis acid $\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{Re}^+$ has been extended.³⁴³⁻³⁴⁵ Impressive is the selective binding of one enantioface of monosubstituted alkenes to this cation.³⁴⁶ In a comprehensive study, preparation, reactions, and structures of a series of complexes $(\text{R}_3\text{P})(\text{ON})(\text{OC})_3\text{W}(\text{FSbF}_5, \text{FPF}_5,$

$\text{FBF}_3)$ have been described.³⁴⁷ NMR spectra and crystal structure determination confirmed that the anions are coordinated to tungsten both in solution and in the solid state. Apparently the strongly electron-withdrawing NO ligand—trans to the coordinated anion—increases the Lewis acidity of the metal. "Spinning" of the coordinated SbF_6^- and BF_4^- ligands in these complexes also has been observed by ^{19}F NMR spectroscopy. Bond length comparison has been made in a series of adducts of SbF_6^- , BF_4^- , PF_6^- , and ReF_6^- . The order of binding strength in these tungsten complexes is $\text{SbF}_6^- > \text{BF}_4^- > \text{PF}_6^-$.³⁴⁷ ClO_4^- , BF_4^- , and PF_6^- complexes of Cd^{2+} , Pb^{2+} , and Tl^+ have been electrochemically generated in noncoordinating solvents and the equilibrium constants show that PF_6^- ligation is considerably weaker than that of ClO_4^- and BF_4^- .³⁴⁸ $\text{Cp}(\text{Ph}_3\text{P})_2\text{RuOSO}_2\text{CF}_3$ reacts with thiirane to give $[\text{Cp}(\text{Ph}_3\text{P})_2\text{Ru}(\text{CH}_2\text{CH}_2\text{S})]^+\text{SO}_3\text{CF}_3^-$.³⁴⁹ Protonation of $\text{H}_2\text{Ru}[\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3\text{P}]$ by HBF_4 yields the coordinatively unsaturated complex $\text{HRu}[\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3\text{P}]^+\text{BF}_4^-$.³⁵⁰ The reaction of arenes with $(\text{OC})_5\text{MFBF}_3$ ($M = \text{Mn}, \text{Re}$) provides an efficient route to cationic complexes $[(\eta^6\text{-arene})\text{M}(\text{CO})_3]^+\text{BF}_4^-$.^{351,352}

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VIII. Abbreviations

bpy	2,2'-bipyridine
COD	cyclooctadiene
Cp	η^5 -cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
dmpe	bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
en	ethylene diamine
Fc	ferrocenyl
nbd	norbornadiene
OEP	octaethylporphyrinate
OTs	<i>p</i> -toluenesulfonate
py	pyridine
THF	tetrahydrofuran
tmen	tetramethylethylenediamine
TPP	tetraphenylporphyrinate

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