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Articles

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Properties of (Trifluoromethanesulfonato)pentacarbonylmanganese(I) and -rhenium(I). Reactions in Superacid Solvents

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The complexes $M(CO)_5(O_3SCF_3)$, where M = Mn and Re, are prepared by the reaction between $M(CO)_5Br$ and $Ag(O_3SCF_3)$ in CH_2Cl_2 solvent. These complexes readily lose the triflate $(O_3SCF_3)^-$ ligand when attacked with nucleophiles. The stoichiometry of the trifluoromethanesulfonate substitution reactions was studied for L = THF, acetone, ether, CH_3CN, and $P(n\text{-}Bu)_3$. For poor nucleophiles (L = THF, acetone, and ether) only the manganese complex reacts to form $[Mn(CO)_5L][CF_3SO_3]$ first and $[Mn(CO)_3L_3][CF_3SO_3]$ at longer reaction times. For $Mn(CO)_5(O_3SCF_3)$ and THF the rate law was shown to obey first-order kinetics, $k_1[Mn(CO)_5(O_3SCF_3)]$, with $\Delta H^* = 25.5 \pm 0.7$ kcal/mol, $\Delta S^* = 6.9 \pm 4.0$ cal/(deg mol). A two-term rate law was found for the reaction between $Mn(CO)_5(O_3SCF_3)$ and CH_3CN, $k_1[Mn(CO)_5(O_3SCF_3)] + k_2[Mn(CO)_5(O_3SCF_3)][CH_3CN]$. In contrast, for M = Re and L = CH_3CN the rate law was found to be exclusively second order, $k_2[Re(CO)_5(O_3SCF_3)][CH_3CN]$, with $\Delta H^* = 11.8 \pm 0.4$ kcal/mol and $\Delta S^* = 34.5 \pm 2.6$ cal/(deg mol). In the superacid solvents CF_3SO_3H, FSO_3H, CF_3SO_3H/SbF_5, and FSO_3H/SbF_5, the triflate derivatives react with CO to yield $M(CO)_6^+$ and this reaction proceeds dramatically faster in the presence of SbF_5. Addition of SbF_5 to a CF_3SO_3H solution of $Re(CO)_5(O_3SCF_3)$ causes a specific shift in the ^{13}C NMR resonance trans to the triflate ligand. Solutions of the $M(CO)_5(O_3SCF_3)$ complexes can also be generated in high yield by the oxidation reaction between anhydrous CF_3SO_3H and $M_2(CO)_{10}$ complexes or by protonation reactions of $Mn(CO)_5B$ species, where B = a base such as pyridine, Br^-, and H^-. The reaction between $H_3Mn_3(CO)_{12}$ and CF_3SO_3H produces 2 $Mn(CO)_5(O_3SCF_3)$ and the unusual complex $\{Mn(CO)_2(O_3SCF_3)\}_n$. The $M(CO)_5(O_3SCF_3)$ complexes exhibit an intense low-energy electronic absorption (380 nm for M = Mn and 322 nm for M = Re) in CH_2Cl_2 solution. In CF_3SO_3H solvent $Mn(CO)_5(O_3SCF_3)$ exhibits an absorption, $\epsilon = 1400\ M^{-1}\ cm^{-1}$, at 396 nm. SCF-$X\alpha$-DV calculations for $Mn(CO)_5^+$ predict the d–d transition $8e \rightarrow 10a_1$ to occur at 409 nm; however, the unoccupied $10a_1$ orbital is expected to contain substantial CO π^* character. This rationalizes the high intensity of the "d–d" transition.

Introduction

Metal complexes that readily dissociate a ligand to produce coordinatively unsaturated complexes find application in synthesis and catalysis. It is well-known from studies of Werner complexes that oxygen donor groups such as NO_3^- or ClO_4^- bind weakly to transition-metal ions and are excellent leaving groups. The triflate ion $(O_3SCF_3)^-$ has been found to be displaced easily from metals in high oxidation states.[2] Hard and soft acid–base theory[3] would suggest even weaker binding of such an ion to a soft metal center as found in carbonyl complexes. Indeed, low-valent transition-metal complexes containing the ClO_4^-,[4a–d] AsF_6^-,[4e] PF_6^-,[5] NSF_3,[6] BF_4^-,[5,7] $CR_3SO_3^-$ (R = H, F),[8] $NHSO_2F_2^-$,[9] $NCNSF_2$,[10] $OTeF_5^-$,[11] and $PO_2F_2^-$[3] ligands exhibit high reactivity and behave as Lewis acids. Normally weak ligands like H_2O, HOR, and ROR (R = alkyl group) displace those listed above. Lewis acidities of main-group complexes have been further enhanced by using acidic solvent systems.[12]

Ferrocene was the first organo transition-metal complex to be studied in strong acids.[13] Subsequently, the protonation of basic metal centers in H_2SO_4,[14a] HBF_4,[14b,c] HBF_3OH,[14a] CF_3COOH,[15] $HClO_4$,[16] and HX (X = Cl, Br, I)[17] was investigated; however, there are few reports[18] of reactions carried out in superacid media.

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Superacid solvents have been used[19] to stabilize carbocations. It seemed possible that electron-deficient metal carbonyl cations of Mn and Re[20] might also be produced in this medium. We now report the properties of carbonyl cations of Mn(I) and Re(I) in CF_3SO_3H, FSO_3H, CF_3SO_3H/SbF_5, and FSO_3H/SbF_5 and in nonaqueous solvents.

Experimental Section

The preparations were performed at room temperature under an atmosphere of dry nitrogen. When necessary, solids were manipulated and stored in a Vacuum Atmospheres glovebox equipped with an HE-493 Dri-Train. Manganese decacarbonyl (Alfa or Strem) was sublimed before use. Rhenium decacarbonyl (Strem), silver trifluoromethanesulfonate (Aldrich), acetone (Mallinckrodt), and SbF_5 (Aldrich) were used as received. Preparations of $H_3Mn(CO)_{12}$,[21a] $H_3Re_3(CO)_{12}$,[21b,c] $[Mn(CO)_6]BF_4$,[22a] $Mn(CO)_5Br$,[22b] $Re(CO)_5Br$,[23] $H_2Re_2(CO)_8$,[24] $[Re(CO)_6]BF_4$,[25] and $[PNN][Mn(CO)_5]$[26] followed the published procedures ($PNN^+ = (Ph_3P)_2N^+$). Trifluoromethanesulfonic acid (Aldrich or Eastman Kodak) and tributylphosphine (Aldrich) were distilled under N_2 before use (the phosphine from Na). Acetonitrile and CH_2Cl_2 were refluxed over P_2O_5 and distilled. Tetrahydrofuran and diethyl ether were dried over sodium–benzophenone ketyl and distilled.

Infrared spectra were recorded with a Perkin-Elmer 283 or Nicolet 7199 FT-IR spectrometer using CaF_2 cells (0.1- or 0.2-mm path length). Most superacid solutions were too reactive to obtain IR spectra in CaF_2 cells; however, with CF_3SO_3H it was possible to obtain solution IR spectra with use of CaF_2 cells containing Teflon spacers. One must work quickly to avoid damaging the cell windows and metal inlet ports. The ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer or JEOL FX-270 spectrometer. Lock and reference values were achieved with use of a coaxial inner tube filled with C_6D_6. Chemical shifts are referenced to Me_4Si with use of a value of δ 128.0 for the C_6D_6 signal. Thermal decoupling[27a] was used to obtain ^{13}C NMR spectra on the JEOL FX-270 with chemical shifts referenced by using δ 77.0 for the $CDCl_3$ signal. The ^{55}Mn NMR spectra were measured at 22.15 MHz on a JEOL FX-90 spectrometer and referenced in ppm to an external aqueous $KMnO_4$ solution. Electronic absorption spectra were recorded with a Perkin-Elmer 320 or 330 spectrophotometer, and the samples were contained in 1.00-cm quartz cells adapted for use with air-sensitive compounds. For the kinetics experiments concentrations were determined by using the molar extinction coefficients measured for solutions of pure compounds.

Reactions in Superacids. All reactions of transition-metal complexes with acids were performed in a Pyrex reaction cell equipped with a 1 cm path quartz cuvette side arm and a Teflon valve. The side arm was charged with the transition-metal compound, and the cell was evacuated and filled with N_2. In an N_2-atmosphere glovebox ~2.5 mL of acid was pipetted into the cell. Antimony pentafluoride, if used, was also added (in excess) at this time. The cell was removed from the box and attached to a vacuum line. The acid was freeze–pump–thaw degassed (three cycles), and the cell was then wrapped in aluminum foil (all solutions are photosensitive) and shaken for 15–30 min. Samples that were used for IR studies were prepared and transferred in the glovebox.

Preparation of $[PPN][O_3SCF_3]$. A hot-water solution of $Ag(O_3SCF_3)$ (0.5 g, 1.9 mmol) was added to 1.0 g (1.7 mmol) of PPN^+Cl^- that was dissolved in the minimum amount of hot water. The mixture was stirred for 15 min and allowed to cool to room temperature. A precipitate was collected by filtration and dissolved in CH_2Cl_2, and the solution was filtered to remove insoluble AgCl and $Ag(O_3SCF_3)$. The crude product obtained by removal of solvent was recrystallized from CH_2Cl_2 and ether to yield 1.09 g (91% yield) of white crystals: the Nujol mull IR spectrum [ν_{SO} 1182 (m) and 1028 (s) cm^{-1}] may be compared with that of NaO_3SCF_3[27b] [ν_{SO} 1168 (s) and 1036 (s) cm^{-1}].

Preparation of (Trifluoromethanesulfonato)pentacarbonylmanganese(I), $Mn(CO)_5(O_3SCF_3)$.[28] $Mn(CO)_5Br$ (0.84 g, 3.0 mmol) was dissolved in CH_2Cl_2 (40 mL) in a flask under a nitrogen atmosphere. From an ampule, $Ag(O_3SCF_3)$ (0.98 g, 3.8 mmol) was added and the suspension was stirred at room temperature for 1 h. After filtration, the volume of solution was reduced under vacuum and hexane was added. Solvent was removed under vacuum, and orange-yellow $Mn(CO)_5(O_3SCF_3)$ formed in 87% yield (0.90 g). IR (CH_2Cl_2): ν_{SO} 1013 (m), 1179 (m), 1336 (s) cm^{-1}; ν_{CF} 1202 (s), 1234 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 209.2 (ax), 202.0 (eq); ^{55}Mn NMR (CH_2Cl_2): δ 152 ($\Delta\nu_{1/2}$ = 3400 Hz). UV (CH_2Cl_2): 380 nm (d–d, ϵ = 1320 cm^{-1} M^{-1}). Anal. Calcd for $MnC_6O_8F_3S$: C, 20.94; S, 9.32; Mn 15.98. Found: C, 20.38; S, 9.39; Mn 15.83.

Preparation of (Trifluoromethanesulfonato)pentacarbonylrhenium(I), $Re(CO)_5(O_3SCF_3)$.[28] This complex was prepared from $Re(CO)_5Br$ in 80% yield by a procedure analogous to that employed for the manganese compound. IR (CH_2Cl_2): ν_{SO} 1006 (s), 1174 (m), 1343 (m) cm^{-1}; ν_{CF} 1202 (s), 1235 (m) cm^{-1}. UV (CH_2Cl_2): 322 nm (d–d, ϵ = 1290 cm^{-1} M^{-1}). Mass spectrum: parent ion at 476 (*m*/*e*). ^{13}C NMR ($CDCl_3$): δ 179.2 (eq), 177.9 (ax). Anal. Calcd for $ReC_6O_8F_3S$: C, 15.16; F, 11.99. Found: C, 15.20; F, 12.68.

Spectral Studies and Kinetics Procedures. Solutions of $Mn(CO)_5(O_3SCF_3)$ and $Re(CO)_5(O_3SCF_3)$ must be prepared immediately before use by dissolution of pure samples in CH_2Cl_2. With $Mn(CO)_5(O_3SCF_3)$, the solution obtained was filtered, to remove traces of insoluble material (from decomposition), and was stored at −78 °C. Details of a typical spectral study that identified ligand substitution products is given below. The same procedures or slight modifications thereof apply to the reactions of $Mn(CO)_5(O_3SCF_3)$ and $Re(CO)_5(O_3SCF_3)$ with C_4H_8O, CH_3CN, $P(n\text{-}Bu)_3$, and $(CH_3)_2CO$.

$Mn(CO)_5(O_3SCF_3)$ + $P(n\text{-}Bu)_3$. To a stirred yellow solution of $Mn(CO)_5(O_3SCF_3)$ (0.14 mmol in 10 mL of CH_2Cl_2) was added $P(n\text{-}Bu)_3$ (0.2 mL, 0.8 mmol). An immediate color change to red-orange occurred, and the infrared spectrum revealed complete conversion to $[Mn(CO)_5[P(n\text{-}Bu_3)]][CF_3SO_3]$. IR: ν_{CO} 2140 (m), 2056 (sh), 2044 (s) cm^{-1}; ν_{SO} 1031 (s), 1161 (m) cm^{-1}. After 5 min of stirring at room temperature the red-orange color disappears and *mer*- and *fac*-$[Mn(CO)_3[P(n\text{-}Bu)_3]_3][CF_3SO_3]$ are observed in the IR spectrum. IR: ν_{CO} (*mer*) 2020 (w), 1895 (w), 1943 (s) cm^{-1}; ν_{CO} (*fac*) 2020 (w), 1953 (s) cm^{-1}. The isomerization process has been reported[3b] for the analogous reaction with $Mn(CO)_5(OClO_3)$. In general, the occurrence of multiple substitution is limited to the Mn derivative. An experiment for $Re(CO)_5(O_3SCF_3)$ under similar conditions showed rapid reaction to produce $[Re(CO)_5P(n\text{-}Bu)_3][CF_3SO_3]$. Conversion to the *fac*- and *mer*-tricarbonyl complexes occurs slowly.

Infrared spectral studies show that the stoichiometry of the ligand substitutions can be described by eq 1–3. All products exhibited carbonyl stretches in the IR spectra that are consistent with the given stoichiometry.[3b,20a,b] The positions of the sulfonate stretches show conclusively the change in coordination from covalent (through the oxygen) to ionic.[27b] In addition, the compounds $[Mn(CO)_5(C_4H_8O)][CF_3SO_3]$ and $[Mn(CO)_5(NCCH_3)][CF_3SO_3]$ exhibit d–d transitions at 397 and 332 nm, respectively.

$$Re(CO)_5(O_3SCF_3) + L \xrightarrow{CH_2Cl_2} [Re(CO)_5L][CF_3SO_3] \qquad (1)$$

$$L = P(n\text{-}Bu)_3,\ CH_3CN$$

$$Mn(CO)_5(O_3SCF_3) + L \xrightarrow{CH_2Cl_2} [Mn(CO)_5L][CF_3SO_3] \qquad (2)$$

$$L = CH_3CN,\ THF,\ OC(CH_3)_2,\ O(CH_2CH_3)_2,\ P(n\text{-}Bu)_3$$

$$[Mn(CO)_5L][CF_3SO_3] \xrightarrow[L]{CH_2Cl_2} mer\text{-},fac\text{-}[Mn(CO)_3L_3][CF_3SO_3] + 2CO \qquad (3)$$

$$L = THF,\ OC(CH_3)_2,\ O(CH_2CH_3)_2,\ P(n\text{-}Bu)_3$$

Rates of triflate substitution in $Mn(CO)_5(O_3SCF_3)$ (M = Mn, Re) were determined by measuring changes in the UV–vis or IR spectra as a function of time. In the UV–vis experiments a specially adapted

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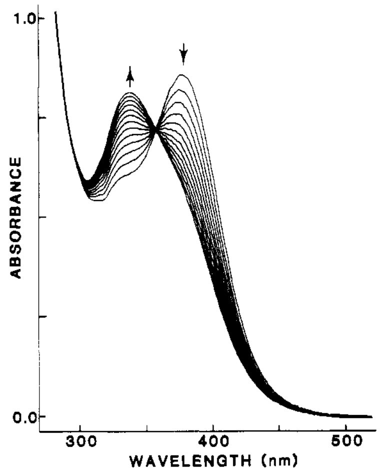

Figure 1. UV-visible spectral changes during the reaction between 5.7 × 10^{-4} M $Mn(CO)_5(O_3SCF_3)$ and 0.912 M CH_3CN in CH_2Cl_2 at 26.0 °C.

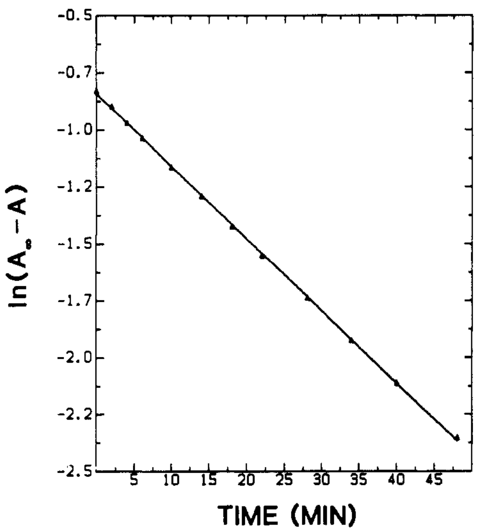

Figure 2. Plot of ln ($A_\infty - A$) at time t for the reaction of $Mn(CO)_5(O_3SCF_3)$ (7.01 × 10^{-4} M) with CH_3CN (0.958 M) at 26.0 °C in CH_2Cl_2. A is the absorbance at 337 nm from $[Mn(CO)_5(NCCH_3)][CF_3SO_3]$.

1.00-cm quartz cell was thermostated in the cell holder of a Perkin-Elmer 320 or 330 spectrophotometer (±0.2 °C). A solution of the complex was prepared in the cell and allowed to thermally equilibrate for at least 20 min, then the appropriate amount of ligand was injected (gastight syringe), and the cell was vigorously shaken for ca. 20 s. The appearance of $[Mn(CO)_5L][CF_3SO_3]$ or the disappearance of $M(CO)_5(O_3SCF_3)$ (M = Mn, Re) can be followed for 3 half-lives. Every kinetic run was monitored for at least 5 half-lives to determine the value of A_∞. A typical experiment for the UV–vis spectral changes during the ligand substitution reaction between $Mn(CO)_5(O_3SCF_3)$ and CH_3CN is shown in Figure 1.

Observed rate constants were measured under pseudo-first-order conditions with the concentration of entering ligand greater than 300 times that of the complex. The precise concentration of metal complex and ligand was determined by weighing the cell and calculating the dilution. Plots of ln ($A_\infty - A$) or ln ($A - A_\infty$) vs. time were linear ($r^2 >$ 0.997) for 2–3 half-lives for all reactions investigated. A typical plot is shown in Figure 2. The reproducibility of an individual run is estimated to be within 5%. Rate constants (k_{obsd}) were calculated from the slope of the line obtained from a least-squares program. For the ligand concentration dependence plots and Arrhenius plots least-squares error analyses are provided in the data tables (errors are 3 standard deviations, within 95% confidence limits).

Xα Calculations. These studies employed the SCF-Xα–DV method at the (l = 0) level[29] for the species $[Mn(CO)_5]^+$. Seven radical degrees of freedom were allowed for in the least-squares expansion of the density (in addition to the radial atomic densities). Numerical atomic orbital basis sets were generated from exact atomic Hartree–Fock–Slater calculations. Neutral-atom basis sets were employed for C and O, while Mn 1+ atomic functions were assumed. Minimal basis sets were used for the light atoms, and the metal orbitals include 4s and 4p functions. The 1s, 2s, and 2p orbitals on Mn^+ and the 1s orbitals on carbon and oxygen were treated as a frozen core[29] in the molecular calculations. Optical transitions were computed by the transition-state procedure.[30] The geometry for the $Mn(CO)_5^+$ fragment was taken by idealizing the structural parameters of the corresponding moiety in $Mn(CO)_5(O_3SCF_3)$[31] to C_{4v} symmetry.

Table I

$$Mn(CO)_5(O_3SCF_3) + C_4H_8O \xrightarrow{CH_2Cl_2} [Mn(CO)_5(C_4H_8O)][CF_3SO_3]$$

T, °C	$10^4[Mn(CO)_5(O_3SCF_3)]$, M	$[C_4H_8O]$,[a] M	k_{obsd},[b] s^{-1}
25.2	7.15	0.207	3.81 × 10^{-5}
25.2	6.85	0.529	4.35 × 10^{-5}
25.2	6.45	1.21	3.97 × 10^{-5}
39.5	6.60	1.20	2.93 × 10^{-4}
17.5	6.59	1.20	1.25 × 10^{-5}

[a] Pseudo-first-order excess of C_4H_8O. [b] Monitoring the appearance of $[Mn(CO)_5(C_4H_8O)][CF_3SO_3]$ at 418 nm.

Table II

$$Mn(CO)_5(O_3SCF_3) + CH_3CN \xrightarrow{CH_2Cl_2} [Mn(CO)_5(NCCH_3)][CF_3SO_3]$$

T, °C	$10^4[Mn(CO)_5(O_3SCF_3)]$, M	$[CH_3CN]$,[a] M	k_{obsd},[b] s^{-1}
26.0	7.31	0.571	3.46 × 10^{-4}
26.0	6.81	1.93	1.03 × 10^{-3}
26.0	7.01	0.958	5.29 × 10^{-4}
26.0	7.27	0.244	1.95 × 10^{-4}
37.7	7.25	0.977	1.31 × 10^{-3}
37.7	3.77	0.508	8.65 × 10^{-4}
37.7	7.83	2.05	2.92 × 10^{-3}
37.7	7.03	1.23	2.05 × 10^{-3}
16.8	6.42	2.21	6.01 × 10^{-4}
16.8	7.28	1.59	4.55 × 10^{-4}
16.8	7.24	0.840	2.54 × 10^{-4}

[a] Pseudo-first-order excess of CH_3CN. [b] Monitoring the appearance of $[Mn(CO)_5(CH_3CN)][CF_3SO_3]$ at 337 nm.

Table III

$$Re(CO)_5(O_3SCF_3) + CH_3CN \xrightarrow{CH_2Cl_2} [Re(CO)_5(NCCH_3)][CF_3SO_3]$$

T, °C	$10^4[Re(CO)_5(O_3SCF_3)]$, M	$[CH_3CN]$,[a] M	k_{obsd},[b] s^{-1}
25.5	7.33	0.551	2.33 × 10^{-4}
25.5	7.06	1.22	5.15 × 10^{-4}
25.5	6.64	2.74	1.15 × 10^{-3}
25.5	7.33	0.257	1.27 × 10^{-4}
17.7	7.19	0.905	2.22 × 10^{-4}
37.3	7.11	0.555	6.56 × 10^{-4}

[a] Pseudo-first-order excess of CH_3CN. [b] Monitoring the disappearance of $Re(CO)_5(O_3SCF_3)$ at 332 nm.

Results and Discussion

Kinetics of Ligand Substitutions. Replacement of the triflate ligand in $M(CO)_5(O_3SCF_3)$ (M = Mn, Re) with a variety of ligands proceeds rapidly in solution at room temperature according to eq 1–3. These ligand substitutions were monitored by observing changes in the UV–vis spectra as a function of time (Figure 1). Isosbestic points were observed in the reactions whose kinetics were studied.

The case of triflate substitution with $P(n\text{-}Bu)_3$ is more complicated because of a marked increase in reaction rate with stronger nucleophiles. Mixing a 7.0 × 10^{-4} M solution of $Mn(CO)_5(O_3$-

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Table IV. Rate Constants and Activation Parameters for Substitution of M(CO)$_5$(O$_3$SCF$_3$) (M = Mn or Re) by Ligand L, According to Eq 1-3, in CH$_2$Cl$_2$

complex	L	T, °C	10^5k_1,[a] s^{-1}	10^4k_2,[a] s^{-1} M^{-1}	ΔH^*, kcal/mol	ΔS^* cal/(deg mol)
Mn(CO)$_5$(O$_3$SCF$_3$)[b]	C$_4$H$_8$O	25.2	4.35 ± 0.11		+25.5 ± 0.70	+6.9 ± 4.0
Mn(CO)$_5$(O$_3$SCF$_3$)[c]	CH$_3$CN	26.0	6.46 ± 3.06	4.97 ± 0.27	+14.7 ± 1.0[d]	−24.5 ± 3.4[d]
Re(CO)$_5$(O$_3$SCF$_3$)[e]	CH$_3$CN	25.5	1.21 ± 1.99	4.15 ± 0.13	+11.8 ± 0.4[d]	−34.6 ± 2.3[d]

[a] Uncertainties are 3 standard deviations from a linear least-squares analysis. [b] Monitoring rate of appearance of [Mn(CO)$_5$(C$_4$H$_8$O)][CF$_3$SO$_3$] at 418 nm. [c] Monitoring rate of appearance of [Mn(CO)$_5$(CH$_3$CN)][CF$_3$SO$_3$] at 337 nm. [d] Activation parameters are for the k_2 pathway; the relative contribution of the k_1 path was so small for Mn that accurate activation parameters were not obtained. For Re the k_1 path is zero within experimental error. [e] Monitoring rate of disappearance of [Re(CO)$_5$(O$_3$SCF$_3$)] at 332 nm.

SCF$_3$) with 1.8 × 10^{-2} M P(n-Bu)$_3$ results in an immediate color change and formation of the monosubstituted derivative [Mn(CO)$_5$P(n-Bu)$_3$][CF$_3$SO$_3$]. The pseudo-first-order rate constant was estimated to be 4.8 × 10^{-3} s^{-1}. As described in the Experimental Section, trisubstituted complexes form within 5 min.

The ligands CH$_3$CN and THF were chosen for kinetic study over a range of concentration and temperature. Complete listings of pseudo-first-order rate constants as a function of temperature and concentration are provided in Tables I–III. For the entering ligand THF, with Mn(CO)$_5$(O$_3$SCF$_3$), substitution obeys the first-order rate law given in eq 4. No ligand-dependent (i.e.,

$$-d[\mathrm{Mn(CO)_5(O_3SCF_3)}]/dt = k_1[\mathrm{Mn(CO)_5(O_3SCF_3)}] \qquad (4)$$

associative) reaction pathway exists under these conditions. The concentration of THF was varied from 0.21 to 1.21 M, and the observed rate constants were unaffected. In contrast, the reaction of Re(CO)$_5$(O$_3$SCF$_3$) with THF in CH$_2$Cl$_2$ or with pure THF as solvent gave no trace of monosubstituted product, in the IR spectrum. The Re derivative was also observed to be inert toward other oxygen-containing solvents such as (CH$_3$)$_2$CO, CH$_3$OH, and (CH$_3$CH$_2$)$_2$O.

The rate of triflate substitution could be studied in detail with CH$_3$CN as the nucleophile. Plots of k_{obsd} vs. [CH$_3$CN] are shown in Figure 3 for the monosubstitution process of eq 1 and 2. The rate law exhibits two terms for M = Mn (eq 5). Also, the values

$$-d[\mathrm{M(CO)_5(O_3SCF_3)}]/dt = k_1[\mathrm{M(CO)_5(O_3SCF_3)}] + k_2[\mathrm{M(CO)_5(O_3SCF_3)}][\mathrm{CH_3CN}] \qquad (5)$$

$$k_1 = 0 \text{ for M = Re}$$

of k_1 for the reactions between Mn(CO)$_5$(O$_3$SCF$_3$) and either CH$_3$CN or THF are the same within experimental error. Within experimental error, no ligand-independent (S$_\mathrm{N}$1) pathway exists for the reaction between Re(CO)$_5$(O$_3$SCF$_3$) and CH$_3$CN; the rate law is strictly second order.

For the strongest nucleophiles used, CH$_3$CN and P(n-Bu)$_3$, substitutions depend on the concentration of the incoming ligand. Furthermore, activation parameters (Table IV) provide additional support for an associative process. The small energies of activation (14.7 and 11.8 kcal mol^{-1}) and the large, negative entropies of activation (−24.5 and −34.6 cal/(deg mol)) are typical for transition states that exhibit an expanded coordination number.[32] Several carbonyl complexes that react by an associative mechanism show similar activation parameters.[32,33] An alternative to a true seven-coordinate intermediate in the associative reactions of M(CO)$_5$(O$_3$SCF$_3$) complexes is that the metal–nucleophile interaction occurs at a long distance in an associative-interchange process. This could explain the lack of a steric effect in going from Mn to Re, the values of k_2 for reaction with CH$_3$CN being (4.97 ± 0.27) × 10^{-4} and (4.15 ± 0.13) × 10^{-4} s^{-1} M^{-1}, respectively.

Alternatively, the lack of a rate difference between metals may be attributed to offsetting effects of increased metal size and stronger metal–triflate bonding. Apparently the Mn–O$_3$SCF$_3$ bond is weaker than the Re–O$_3$SCF$_3$ bond. This is evidenced by the substitution reactions of the Mn(CO)$_5$(O$_3$SCF$_3$) complex (but not Re) that proceed by triflate dissociation in the presence of weak nucleophiles. The effect of the stronger Re–O$_3$SCF$_3$ bond may be offset by the larger Re radius that would make associative attack easier.

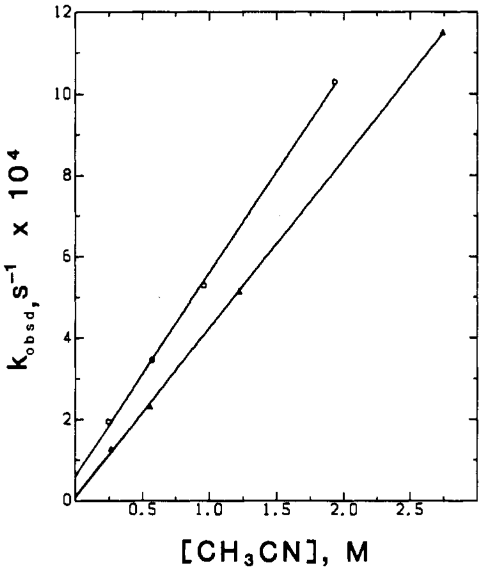

Figure 3. Plot of k_{obsd} (s^{-1}) vs. CH$_3$CN concentration (M) for the triflate substitution in M(CO)$_5$(O$_3$SCF$_3$) by CH$_3$CN in CH$_2$Cl$_2$ solution: (△) M = Re; (○) M = Mn.

Qualitative comparisons may be made with other effective leaving groups. Usón and co-workers reported[4b] the preparation of Mn(CO)$_5$(OClO$_3$) and observed substitution reactions that yield product distributions similar to those reported here. Kinetic studies were not carried out; however, it appears that the reactivities of the perchlorate and triflate ligands are comparable. Given the treacherous properties of organometallic perchlorates, the triflate derivatives are to be preferred for synthetic and physical studies. On the other hand, differences are noted between triflate and the fluoroanions in Re(CO)$_5$FBF$_3$[7a] and Re(CO)$_5$FAsF$_5$.[4] The latter complexes are reported to react with H$_2$O, CH$_3$OH, acetone, and other σ and π donors. The fluoroanions appear to be more weakly associated to the Re center than triflate.

The reactivity trend found in the formation of tris-substituted derivatives [M(CO)$_3$L$_3$][CF$_3$SO$_3$] (M = Mn, Re) parallels that found for monosubstitution. Infrared spectral studies show trace quantities of [M(CO)$_3$(P(n-Bu)$_3$)$_3$][CF$_3$SO$_3$] as soon as P(n-Bu)$_3$ and Mn(CO)$_5$(O$_3$SCF$_3$) are mixed. With THF ligand, the tris-substituted complex forms more slowly. The tendency of the triflate complex, or solvated species, to yield tricarbonyl derivatives has been exploited in the synthesis of thiophene complexes of Mn(I).[34] In contrast, the reaction between Re(CO)$_5$(O$_3$SCF$_3$) and P(n-Bu)$_3$ produces [Re(CO)$_5$P(n-Bu)$_3$][CF$_3$SO$_3$] initially and formation of [Re(CO)$_3$(P(n-Bu)$_3$)$_3$][CF$_3$SO$_3$] occurs later in the reaction. The mechanism of multiple ligand substitution probably proceeds by cis labilization of the carbonyls. It has been established that in substituted metal carbonyl compounds the positions cis to non-carbonyl ligands are labilized toward dissociation.[35]

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First-order rate constants for multiple substitution at Re are significantly smaller than those found for similar Mn compounds.

Manganese Carbonyl Cations in Superacids. Reactions 6–10 generated $Mn(CO)_5(O_3SCF_3)$ in neat CF_3SO_3H solution. In

$$[PPN][Mn(CO)_5] + 2CF_3SO_3H \rightarrow H_2 + (PPN)(CF_3SO_3) + Mn(CO)_5(O_3SCF_3) \quad (6)$$

$$Mn_2(CO)_{10} + 2CF_3SO_3H \rightarrow 2Mn(CO)_5(O_3SCF_3) + H_2 \quad (7)$$

$$[Mn(CO)_5py]BF_4 + 2CF_3SO_3H \rightarrow Mn(CO)_5(O_3SCF_3) + [pyH][CF_3SO_3] + BF_3 + HF \quad (8)$$

$$Mn(CO)_5Br + CF_3SO_3H \rightarrow Mn(CO)_5(O_3SCF_3) + HBr \quad (9)$$

$$H_3Mn_3(CO)_{12} + 3CF_3SO_3H \rightarrow 3H_2 + 2Mn(CO)_5(O_3SCF_3) + (1/n)[Mn(CO)_2(O_3SCF_3)]_n \quad (10)$$

those cases where H_2 was evolved, the expected stoichiometry was confirmed (±10%) by Toepler pumping the evolved gas through a series of liquid-nitrogen-cooled traps. Quantitative infrared analysis confirmed that CO was not evolved or was but a minor (<10%) component of the final products. The presence of the $Mn(CO)_5(O_3SCF_3)$ product was characterized by weak IR bands at 2164 and 2113 cm^{-1}, an absorption of medium intensity at 2042 cm^{-1}, and a strong absorption at 2083 cm^{-1}. Resonances were found at δ 209.6 and 202.4 in the ^{13}C NMR spectra of these acid solutions, and the relative intensities were ca. 1:4, suggesting they be assigned to axial and equatorial carbon monoxide ligands. Electronic absorption spectra exhibited a transition at 396 nm ($\epsilon \approx 1400$ M^{-1} cm^{-1}) and weaker features at 304 and 280 nm. These spectroscopic properties are identical with those of $Mn(CO)_5(O_3SCF_3)$, prepared from $Mn(CO)_5Br$ and $Ag(O_3SCF_3)$, when dissolved in CF_3SO_3H solution.

The solution prepared according to eq 10 exhibited an additional intense and broad IR band at 1980 cm^{-1} (Figure 4), and the electronic absorption spectum tailed further into the visible spectral region. Difference spectra revealed a weak absorption centered near 450 nm. The H_2 and $Mn(CO)_5(O_3SCF_3)$ stoichiometry determined for reaction 10 (established by quantitative Toepler and IR measurements) requires an $[Mn(CO)_2(O_3SCF_3)]_n$ formulation for the second carbonyl species. A linear $Mn(CO)_2^+$ fragment would be expected to display an antisymmetric CO stretch at the low frequency (1980 cm^{-1}) observed. We could not detect resonances attributable to the second carbonyl species in the ^{13}C NMR spectrum, even though this complex does not appear to be paramagnetic (by susceptibility measurements with the NMR technique).[36] The inability to see ^{13}C NMR spectra of certain Mn carbonyl complexes has been attributed to the quadrupole moment of Mn.

When small amounts of CO were added to a solution prepared according to eq 10, the 1980-cm^{-1} band disappeared immediately and only IR absorptions attributable to $Mn(CO)_5(O_3SCF_3)$ and $Mn(CO)_6^+$ remained. This suggests the second species is indeed a carbonyl-deficient Mn(I) complex. Solutions of $Mn(CO)_5(O_3SCF_3)$ and $[Mn(CO)_2(O_3SCF_3)]_n$ are photosensitive and yield $Mn(CO)_6^+$ and an unidentified precipitate when irradiated at 366 nm. The identification of $Mn(CO)_6^+$ in this and in the previous reactions was indicated by an intense IR peak at 2102 cm^{-1} and a sharp ($\Delta\nu_{1/2} = 40$ Hz) ^{55}Mn NMR resonance at −1447 ppm.[37] An authentic sample[22a] of $[Mn(CO)_6]BF_4$ when dissolved in CF_3SO_3H yielded identical parameters.

Rhenium Carbonyl Cations in Superacids. Reactions 11 and 12 generate $Re(CO)_5(O_3SCF_3)$ in neat CF_3SO_3H solution. With

$$Re_2(CO)_{10} + 2CF_3SO_3H \rightarrow H_2 + 2Re(CO)_5(O_3SCF_3) \quad (11)$$

$$H_2Re_2(CO)_8 + 2CF_3SO_3H \rightarrow H_2 + Re(CO)_5(O_3SCF_3) + \text{“U”} \quad (12)$$

$H_3Re_3(CO)_{12}$ as reactant, only 1 mol of H_2/mol of cluster was evolved initially ($^1/_2$ h) to produce a blue solution. Longer reaction times at 60 °C yielded an additional 1 mol of hydrogen, and the species generated in this reaction (IR: 2161, 2127, 2059, 2025, 1980, 1960 cm^{-1}) did not include $Re(CO)_5(O_3SCF_3)$. The reaction of eq 12 appeared to be somewhat analogous to that of eq 10. A strong and broad absorption was observed at 1960 cm^{-1} in addition to those of $Re(CO)_5(O_3SCF_3)$ (IR: 2170 (w), 2108 (w), 2070 (s), 2026 (m) cm^{-1}) and other unidentified absorptions designated as product(s), "U".

Table V. Infrared Spectra of $Mn(CO)_5(O_3SCF_3)$, Where M = Mn or Re, in HO_3SCF_3 and in CH_2Cl_2 Solvents.

		CO str freq, cm^{-1}			
complex	solvent	$a_1^{(2)}$	b_1	e	$a_1^{(1)}$
$Mn(CO)_5(O_3SCF_3)$	CH_2Cl_2	2158 w	2042 w	2073 s	2020 m
$Mn(CO)_5(O_3SCF_3)$	HO_3SCF_3	2164 w	2113 w[a]	2083 s	2042 m
$Re(CO)_5(O_3SCF_3)$	CH_2Cl_2	2166 w	2031 w	2059 s	2004 m
$Re(CO)_5(O_3SCF_3)$	HO_3SCF_3	2170 w	2111 w[a]	2070 s	2026 m

[a] Because of the very weak intensity of this peak and the photosensitivity of the $M(CO)_5(O_3SCF_3)$ complexes, the assignment of this weak feature to the b_1 mode must be regarded as tentative.

Table VI. Frontier Orbitals, Eigenvalues, and Atomic Orbital Character[a] for $Mn(CO)_5^+$

orbital	energy, eV	orbital type and dominant atomic composition
$6b_1$	−9.12	26% $d_{x^2-y^2}$; 50% CO_{eq} π^*; 24% CO_{eq} 5σ
$11a_1$	−9.21	27% d_{z^2}; 50% CO_{eq} π^*; 15% CO_{ax} 5σ
$3b_2$	−9.27	30% d_{xy}; 70% CO_{eq} π^*
$5b_1$	−9.35	29% $d_{x^2-y^2}$; 21% CO_{eq} 5σ; 50% CO_{eq} π^*
10e	−9.37	13% $d_{xz,yz}$; 40% CO_{ax} π^*; 41% CO_{eq} π^*
9e	−9.61	31% CO_{ax} π^*; 55% CO_{eq} π^*
$10a_1$	−11.07	35% d_{z^2}; 48% CO_{eq} π^*
8e	−13.99[b]	79% $d_{xz,yz}$; 9% CO_{ax} π^*; 10% CO_{eq} π^*
$2b_2$	−14.34	79% d_{xy}; 21% CO_{eq} π^*
7e	−17.96	84% CO_{eq} 5σ
$4b_1$	−18.82	9% $d_{x^2-y^2}$; 75% CO_{eq} π; 16% CO_{eq} 5σ
$9a_1$	−18.87	7% d_{z^2}; 68% CO_{eq} π; 18% CO_{ax} 5σ
6e	−18.92	98% CO π
$1a_2$	−18.97	pure CO_{eq} π

[a] The coordinate system is such that *z* points along the C_4 axis and *x* and *y* lie along orthogonal Mn–C_{eq} bonds. [b] This is the highest occupied molecular orbital.

CO-Uptake Experiments and Spectroscopic Properties. Unusual behavior was observed for the rate of reaction 13. In CH_2Cl_2

$$CO + Mn(CO)_5(O_3SCF_3) \rightarrow [Mn(CO)_6][CF_3SO_3] \quad (13)$$

the reaction did not take place over a period of several hours. In CF_3SO_3H the reaction proceeded within 2–4 h. In CF_3SO_3H, containing small (ca. 1–5 equiv) amounts of SbF_5 or $[PPN][CF_3SO_3]$, the reaction was complete within minutes, possibly limited by the rate of CO dissolution. A similar rapid reaction with CO occurred in FSO_3H/SbF_5 mixed solvent, but only a slow reaction took place in FSO_3H. The rhenium analogue exhibited analogous behavior in the rate of formation of $[Re(CO)_6][O_3SCF_3]$. One possible explanation for these observations would be Lewis acid (SbF_5 or PPN^+) assisted dissociation of the $CF_3SO_3^-$ ligand. The equilibria of eq 14 have been identified in the FSO_3H acid sys-

$$SbF_5 + FSO_3^- \rightarrow [FSO_3 \cdot SbF_5]^- + SbF_5 \rightarrow [FSO_3 \cdot 2SbF_5]^- \quad (14)$$

tems.[38] Spectroscopic evidence below suggests that SbF_5 can bind to the triflate ligand when it is bound to $Mn(CO)_5^+$ and $Re(CO)_5^+$.

The UV–vis and IR spectra for the complexes showed slight differences between solutions that contained and did not contain SbF_5. The sulfonate stretches shifted from 1013, 1179, and 1336 cm^{-1} to 1043, 1143, and 1347 cm^{-1} when 3 equiv of SbF_5 was added to a CH_2Cl_2 solution of $Mn(CO)_5(O_3SCF_3)$. In this same experiment ν_{CO} shifted from the values listed in row 1 of Table

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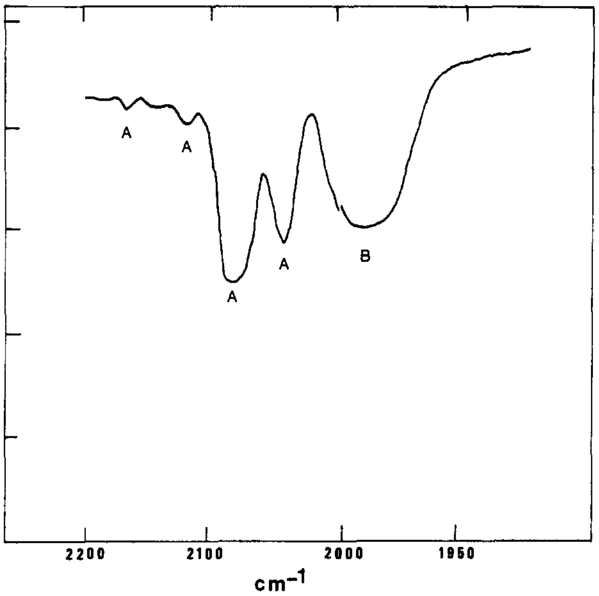

Figure 4. Infrared spectrum of the solution obtained by allowing HO$_3$SCF$_3$ and H$_3$Mn$_3$(CO)$_{12}$ to react. Peaks marked A are attributable to Mn(CO)$_5$(O$_3$SCF$_3$), and peak B is assigned to {Mn(CO)$_2$(O$_3$SCF$_3$)}$_n$.

V to 2158 (w), 2111 (w), 2079 (s), and 2032 (m) cm^{-1}. Also, Re(CO)$_5$(O$_3$SCF$_3$) exhibited ^{13}C NMR resonances at δ 176.8 and 179.9 that shifted to δ 175.3 and 179.7 when SbF$_5$ was added to a CF$_3$SO$_3$H solution of the complex. The preferential shift of the axial (δ 176.8) carbon monoxide resonance suggests a specific interaction between SbF$_5$ and the trans-CF$_3$SO$_3^-$ ligand.

The enhanced reactivity of the M(CO)$_5$(O$_3$SCF$_3$) complexes in the superacid solvents is accompanied by differences in their IR (Table V) and optical spectra. Generally, the IR stretches in HO$_3$SCF$_3$ are shifted to higher frequency than in CH$_2$Cl$_2$ (Table V) and the optical transition red shifts from 380 to 396 nm for Mn(CO)$_5$(O$_3$SCF$_3$). The Cr(CO)$_5$ moiety, which is isoelectronic with Mn(CO)$_5^+$, has been studied in rare-gas matrices.[39] A low-energy optical transition, ca. 500 nm, characterizes the coordinatively unsaturated Cr(CO)$_5$ fragment; however, there is considerable dependence of the energy of this transition on the inert medium. The low-energy transition has been assigned to the allowed "d–d" transition $^1A_1 \rightarrow {}^1E$ ($b_2^2e^4a_1^0b_1^0 \rightarrow b_2^2e^3a_1^1b_1^0$). It should involve promotion of an electron into the d_{z^2} (a_1) orbital that is localized along the "empty" coordination position.[40] Thus, the distinct red shift of the analogous transition in Mn(CO)$_5$(O$_3$SCF$_3$) on a change of the solvent from CH$_2$Cl$_2$ to SbF$_5$/HO$_3$SCF$_3$ is consistent with weakening of the Mn–triflate bond. SCF–Xα–DV calculations (Table VI and Figure 5) for the limiting case of the free Mn(CO)$_5^+$ ion predict the optical transition 8e ($d_{xz,yz}$) $\rightarrow$ 10a$_1$ (d_{z^2}) to be of lowest energy at 409 nm. That agrees closely with the value found in the superacid solvent.

For considering the bonding in Mn(CO)$_5^+$, we choose the metal coordinate system with the z direction oriented along the C_4 axis and x and y aligned along the equatorial ligand directions. The highest occupied molecular orbitals (Figure 5) are primarily $d_{xz,yz}$ (8e) and d_{xy} (2b$_2$). In M(CO)$_6^+$ these orbitals would be degenerate (t_{2g}); however, the loss of the axial CO results in less π bonding to the $d_{xz,yz}$ orbitals and they become destabilized relative to d_{xy}. As expected, the absence of the axial CO lowers the energy of the axial metal–ligand σ^* orbital 10a$_1$; however, calculations suggest a more complex description of 10a$_1$ than simple ligand field models. This orbital consists of 35% Mn d_{z^2}, 10% axial CO 5σ, and 48% equatorial CO π^*. Although CO π^* levels are orthogonal to the axial metal orbital in O_h symmetry, this is no longer required in the C_{4v} point group. The presence of substantial

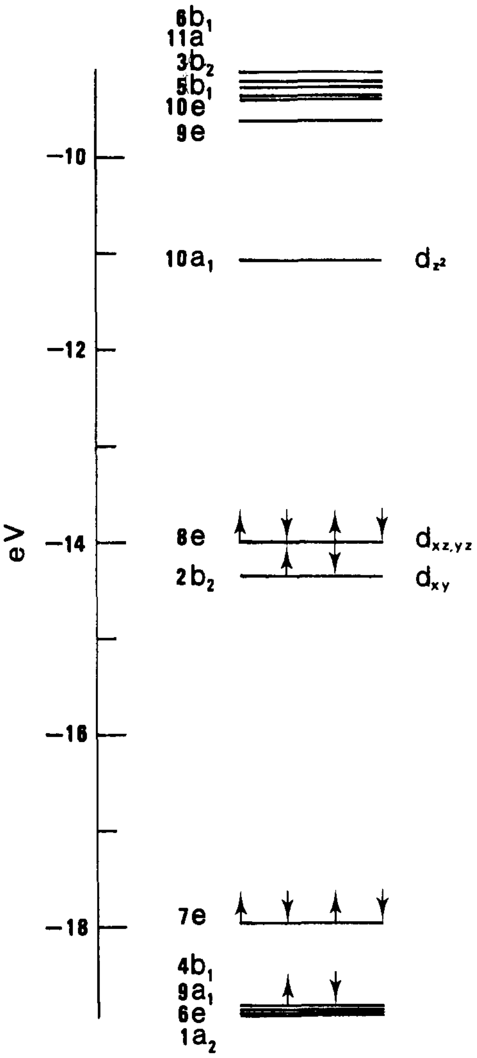

Figure 5. Orbital energy diagram from SCF–Xα–DV calculations of Mn(CO)$_5^+$. The ligand-field "d" orbitals are noted; however, the 10a$_1$ orbital contains significant CO π^* orbital character.

CO π^* character in 10a$_1$ helps to explain the anomalous high intensity of the 8e $\rightarrow$ 10a$_1$ ($\epsilon \approx 1400$ M^{-1} cm^{-1}) electronic transition. In a crystal field sense this would be a d–d transition with an expected ϵ of about 100 M^{-1} cm^{-1}. If one considers that the 10a$_1$ orbital contains substantial CO π^* character, then the exception intensity of the 8e $\rightarrow$ 10a$_1$ transition can be attributed to its partial MLCT character.

Conclusions

In organic solvents the M(CO)$_5$(O$_3$SCF$_3$) complexes undergo substitution of the triflate ligand with a variety of nucleophiles according to an associative process. Only for Mn(CO)$_5$(O$_3$SCF$_3$) and only with use of weak nucleophiles, such as THF, is there evidence for triflate dissociation. The weakly basic triflate ligand should be a poor one for a soft metal center; however, electrostatic forces prevent ready dissociation of the anion in nonpolar solvents. If a good nucleophile such as P(n-Bu)$_3$ is present, then displacement of triflate proceeds rapidly by an associative mechanism. The lack of reaction with CO is expected due to its poor nucleophilicity. We concur with the description[8f] of metal–triflate bonds in organometallics as "moderately strong" and "predominantly ionic" that was arrived at from a consideration of an X-ray structure of (η^5-C$_5$Me$_5$)(CO)$_2$Fe(O$_3$SCF$_3$). This must be qualified with the observation that the infrared absorptions of bound triflate in the M(CO)$_5$(O$_3$SCF$_3$) complexes are quite different from those of ionic Na(O$_3$SCF$_3$) or [PPN][O$_3$SCF$_3$]. Unfortunately, the X-ray study[8f] did not report the triflate vibrational stretches. Another point that is difficult to reconcile, if a simple ionic model is assumed, is the absence of triflate

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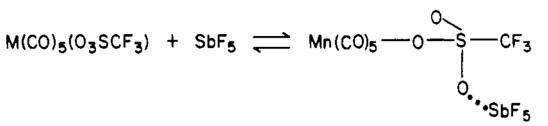
dissociation from $\mathrm{Re(CO)_5(O_3SCF_3)}$, since the Re–triflate separation must be greater than in the Mn complex. Differing crystal field activation energy barriers[32] may [Re(I) is expected to show larger splittings than Mn(I)] account for the difference.

The enhanced kinetic lability in superacid solvents as well as the shifts in spectroscopic parameters suggest that the metal–triflate bond is seriously weakened in acidic solvent systems. For the case of $\mathrm{CF_3SO_3H/SbF_5}$ the equilibria of eq 15 and/or 16 may be important. Either type of complexation would lead to labilization of the triflate complex. The surprising finding on addition of $\mathrm{[PPN][O_3SCF_3]}$ (in place of $\mathrm{SbF_5}$) to $\mathrm{CF_3SO_3H}$ implies that a cation, $\mathrm{[PPN]^+}$, may aid in the dissociation of bound $\mathrm{O_3SCF_3^-}$. Because of the poor nucleophilicity of CO it is likely that the enhanced rate of reaction between $\mathrm{M(CO)_5(O_3SCF_3)}$ and carbon monoxide in superacid solvents results from increased triflate dissociation. The premise[88] that one can stabilize coordinatively unsaturated complexes (or molecules that behave as such) in highly acidic media seems justified.

$$\mathrm{M(CO)_5(O_3SCF_3) + SbF_5 \rightleftharpoons M(CO)_5^+ + CF_3SO_3{\cdot}SbF_5^-} \qquad (15)$$



$$\mathrm{M(CO)_5(O_3SCF_3) + SbF_5 \rightleftharpoons Mn(CO)_5{-}O{-}\overset{\overset{O}{\diagdown}}{\underset{\underset{O\cdots SbF_5}{|}}{S}}{-}CF_3} \qquad (16)$$

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Reactions of Chloro Complexes of Dimolybdenum(II) Containing Quadruple Metal–Metal Bonds with Bidentate Tertiary Phosphines $\mathrm{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2}$ (n = 1–3) and $\mathrm{(C_6H_5)_2P(CH_2)_2As(C_6H_5)_2}$ in Alcohol Media. Effect of Ligand Hydrocarbon Chain Length and Solvent on Product Formation and Isomerization

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The reactions of $\mathrm{K_4Mo_2Cl_8}$ with the bidentate tertiary phosphines bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos), and 1,3-bis(diphenylphosphino)propane (dppp) in methanol, ethanol, and 1-propanol produce complexes of the type $\mathrm{Mo_2Cl_4(LL)_2}$. The reactions of $\mathrm{Mo_2Cl_4(py)_4}$ and $\mathrm{Mo_2Cl_4(P(}n\mathrm{\text{-}Pr)_3)_4}$ with dppe and dppp have also been explored. The only form of $\mathrm{Mo_2Cl_4(dppm)_2}$ isolated from the three alcoholic solvents is the species known to have a bridging dppm structure. In refluxing methanol both $\mathrm{Mo_2Cl_8^{4-}}$ and $\mathrm{Mo_2Cl_4(py)_4}$ yield α-$\mathrm{Mo_2Cl_4(LL)_2}$ complexes (LL = dppe, dppp), whose spectral properties are consistent with structures containing chelating phosphine ligands. In 1-propanol these reactants lead to β-$\mathrm{Mo_2Cl_4(LL)_2}$ complexes (LL = dppe, dppp), which are believed to exhibit structures with a trans disposition of donor atoms in the $\mathrm{MoCl_2P_2}$ moiety and with the phosphine bridging the $\mathrm{Mo_2}$ unit. Reaction in ethanol gives rise to mixtures. Under refluxing conditions only β-$\mathrm{Mo_2Cl_4(arphos)_2}$ is produced in pure or nearly pure form from $\mathrm{K_4Mo_2Cl_8}$ and arphos, whereas in methanol at lower temperatures mixtures of α and β isomers result from reaction with $\mathrm{(NH_4)_5[Mo_2Cl_8]Cl{\cdot}H_2O}$. The chelating isomers are converted to the bridging forms on reflux in 1-propanol or prolonged reflux in methanol (arphos, dppp). These results indicate a thermodynamic stabilization of the β-$\mathrm{Mo_2Cl_4(LL)_2}$ species in the higher alcohols while the α isomers are the kinetically favored products in methanol. Although the reaction of $\mathrm{Mo_2Cl_4(P(}n\mathrm{\text{-}Pr)_3)_4}$ and dppe in methanol yields a mixture of α- and β-$\mathrm{Mo_2Cl_4(dppe)_2}$, the reaction with dppp produces $\mathrm{Mo_2Cl_4(P(}n\mathrm{\text{-}Pr)_3)_2(dppp)}$, whose spectral properties are similar to those of the known $\mathrm{Mo_2Cl_4(PR_3)_4}$ species.

Introduction

Hundreds of complexes containing quadruple bonds between transition-metal atoms are known, and the essential features of this multiple-bonding type are now well established.[1] In recent years there has been considerable interest in understanding geometric factors affecting the δ component of such bonds.[2] Although maximum overlap in the δ bond is achieved in an $\mathrm{M_2L_8}$ framework when the donor atoms are in an eclipsed configuration, several examples exist of crystallographically characterized species in which substantial movement toward a staggered array of pendant atoms occurs.[3–5] In an earlier study we prepared a number of tetrahalodimolybdenum(II) complexes containing bidentate tertiary phosphines and arsines.[6] On the basis of interpretation of spectroscopic and other physical measurements, we proposed structures for certain of these $\mathrm{Mo_2X_4(LL)_2}$ compounds (X = Cl, Br) in which bridging of two molybdenum atoms by the organic ligands is accompanied by such staggering of ligand atoms about the Mo–Mo axis.

An intriguing observation resulting from our investigation was the isolation of two isomers of $\mathrm{Mo_2Cl_4(dppe)_2}$ (dppe = 1,2-bis(diphenylphosphino)ethane) depending upon reaction conditions. One of these was assigned a molecular structure in which each dppe binds to a molybdenum atom in a chelating mode while in the other dppe appeared to bridge the $\mathrm{Mo_2}$ moiety. In an effort to further examine the effect of the length of the hydrocarbon chain of these organic ligands and solvent on isomer formation of $\mathrm{Mo_2Cl_4(LL)_2}$ complexes, we recently explored the reactions of chloro complexes of $\mathrm{Mo^{II}_2}$ with the bidentate ligands $\mathrm{Ph_2P(CH_2)_nPPh_2}$ (n = 1–3) and $\mathrm{Ph_2P(CH_2)_2AsPh_2}$. The results reported here indicate that the occurrence of structural isomers is a common feature among $\mathrm{Mo_2Cl_4(LL)_2}$ systems.

While this study was in progress, Professor Malcolm Chisholm informed us of the results of a similar investigation in his laboratory.

Experimental Section

Starting Materials. $\mathrm{K_4Mo_2Cl_8}$ and $\mathrm{(NH_4)_5[Mo_2Cl_8]Cl{\cdot}H_2O}$ were prepared by established procedures.[7,8] $\mathrm{Mo_2Cl_4(py)_4}$ and $\mathrm{Mo_2Cl_4(P(}n\text{-}$

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