kcal/mol.[66] The effect of different metal centers on the rate of C–C bond rotation was also examined. Although the difference is small, C–C bond rotation is slightly more hindered in $Mn(CO)_5CCl_2CF_3$ than $Re(CO)_5CCl_2CF_3$. This is expected since the third-row metal has a larger covalent radius and forms longer M–C bonds. Rotation around the C–C bond in the formally seven-coordinate $CpMo(CO)_3CCl_2CF_3$ complex is more facile than in the octahedral $M(CO)_5CCl_2CF_3$ systems. Indeed, $\Delta G^*$ for $CpMo(CO)_3CCl_2CF_3$ is nearly the same as that for $ICCl_2CF_3$ (but significantly higher than $CCl_3CCl_2CF_3$) and this implies that steric interactions between the trifluoromethyl group and the $CpMo(CO)_3$ moiety are small. As can be seen in Table V, the facility of C–C bond rotation in $MCCl_2CF_3$ increases in the series $Mn(CO)_5 < Re(CO)_5 < CpMo(CO)_3 < I < CCl_3$.

## Conclusion

We have demonstrated that facile regioselective electrophilic halogen exchange takes place when transition-metal perfluoroalkyl complexes are treated with Lewis acids such as $BX_3$. In this context, the reactivity observed at the α-carbon is akin to that at benzylic or allylic positions in organic compounds. The α-regioselectivity appears to be a consequence of the ability of the transition-metal center to stabilize the cationic dihalocarbene complex that is the proposed intermediate in the exchange reaction. Although electronically quite similar, the trihalomethyl (X = Cl, Br, I) are much more reactive than their thermally stable fluorocarbon precursors.[33]

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**Registry No.** $Mn(CO)_5CF_3$, 13601-14-4; $Mn(CO)_5CHF_2$, 15022-34-1; $Mn(CO)_5CH_2F$, 15337-23-2; $Mn(CO)_5C_2F_5$, 20791-80-4; $Re(CO)_5C_2F_5$, 20774-63-4; $Re(CO)_5CFCF_2$, 14882-07-6; $CpFe(CO)_2CF_3$, 52409-72-0; $CpFe(CO)_2C_6F_5$, 12176-60-2; $CpMo(CO)_3CF_3$, 12152-60-2; $CpMo(CO)_3C_2F_5$, 88180-66-9; $CpMo(CO)_3$-*n*-$C_3F_7$, 12093-00-4; $CpFe(CO)_2C(O)CF_3$, 70910-76-8; $[CpFe(CO)_2]_2$, 38117-54-3; $Mn(CO)_5CCl_3$, 86392-59-8; $Mn(CO)_5CHCl_2$, 86392-64-5; $Mn(CO)_5CH_2Cl$, 71374-84-0; $Mn(CO)_5CBr_3$, 86392-60-1; $Mn(CO)_5CHBr_2$, 86392-65-6; $Mn(CO)_5CH_2Br$, 86392-63-4; $Mn(CO)_5CI_3$, 86392-61-2; $Mn(CO)_5CCl_2CF_3$, 88180-67-0; $Re(CO)_5CCl_2CF_3$, 86392-62-3; $Re(CO)_5C_2ClF_2$, 88180-68-1; $Re(CO)_5Cl$, 14099-01-5; $CpFe(CO)_2CCl_3$, 86392-66-7; $CpFe(CO)_2CBr_3$, 88180-69-2; $CpMo(CO)_3CCl_3$, 88180-70-5; $CpMo(CO)_3CCl_2CF_3$, 88180-71-6; $CpMo(CO)_3CCl_2C_2F_5$, 88180-72-7; $CpFe(CO)_2Me$, 12080-06-7; $CpMo(CO)_3CBr_3$, 88180-73-8; $Re(CO)_5CBr_2CF_3$, 88180-74-9; $BCl_3$, 10294-34-5; $BBr_3$, 10294-33-4; $Bi_3$, 13517-10-7; $SiF_4$, 7783-61-1; $B_2H_6$, 19287-45-7.

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# Nucleophilic, Electrophilic, and Homolytic Reaction Chemistry of Transition-Metal Carbonyl Trihalomethyl (X = F, Cl, Br) Complexes

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The nucleophilic, electrophilic, and homolytic reaction chemistry of transition-metal carbonyl trihalomethyl complexes (X = F, Cl, Br) has been surveyed. The complexes $CpFe(CO)_2CX_3$ (X = F, Cl, Br) were found to readily react with electrophiles to afford cationic carbene complexes $[CpFe(CO)_2(CX_2)]^+$ that were characterized by NMR and IR spectroscopic methods. These carbenes are extremely moisture sensitive, and hydrolysis affords $[CpFe(CO)_3]^+$. Difluorocarbene complexes are also implicated in the proton acid induced hydrolysis of $MCF_3$ to afford $[MCO]^+$ (M = $CpFe(CO)_2$, $CpMo(CO)_3$, $Mn(CO)_5$). The trihalomethyl complexes $CpFe(CO)_2CX_3$ (X = Cl, Br) are much more reactive with nucleophiles than the corresponding trifluoromethyl complexes. Treatment of $CpFe(CO)_2CCl_3$ with $NH_3$, *i*-$PrNH_2$, or $H_2O$ at room temperature affords high yields of $CpFe(CO)_2CN$, $[CpFe(CO)_2(CN$-*i*-$Pr)]^+$, or $[CpFe(CO)_3]^+$, respectively. In contrast, $CpFe(CO)_2CF_3$ is inert to these reagents. Reaction of $Mn(CO)_5CBr_3$ with olefins, cumene, or toluene takes place by a radical process to afford a large number of products including $Mn(CO)_5CHBr_2$, $Mn(CO)_5Br$, $CH_2Br_2$, $CHBr_3$, $C_2HBr_3$, and $C_2Br_4$. Carbon–bromine bond cleavage is proposed to be the major initiation step for these reactions. Accordingly, $Mn(CO)_5CCl_3$ is much less reactive with these reagents and $Mn(CO)_5CF_3$ is completely inert. Addition of 2 equiv of $HSn(n\text{-}Bu)_3$ to a solution of $Mn(CO)_5CBr_3$ results in a rapid exothermic reaction to afford $Mn(CO)_5CHBr_2$ and $Mn(CO)_5CH_2Br$. The latter complex is converted to $Mn(CO)_5CH_3$ by reaction with $HSn(n\text{-}Bu)_3$ for 1 h at 60 °C.

## Introduction

The great stability of (trifluoromethyl)metal carbonyl complexes toward nucleophiles is in part a consequence of resistance of the $CF_3$ group to chemical attack.[1-5] In the preceding paper, we have shown that the $CF_3$ group readily undergoes electrophilic attack and halogen exchange occurs to afford trihalomethyl complexes (X = Cl, Br, I) in high yield under mild conditions.[6] The replacement of fluorine by the lower halogens would be expected to greatly enhance the reactivity of the methyl group in these complexes. Accordingly, we have explored

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the reaction chemistry of these new complexes with electrophiles, nucleophiles, olefins, and reagents that react by radical pathways. Additional reactions of the trifluoromethyl ligand with electrophiles are also reported. As detailed below, the trihalomethyl complexes exhibit much greater reactivity with several classes of reagents than their trifluoromethyl precursors.

## Experimental Section

Transition-metal trihalomethyl complexes were synthesized as described in the preceding paper.[6] Olefins and cumene (isopropylbenzene) were distilled and freed of oxygen prior to use, and their purities were checked by $^1H$ NMR spectroscopy. Commercial $HSn(n\text{-}Bu)_3$ (Aldrich), 40% aqueous $HBF_4$, and $NH_3$ were used as received. Isopropylamine was distilled from BaO and dried with activated molecular sieves. Other solvents and reagents were purified as previously described.[6]

**$[CpFe(CO)_2(CF_2)][BF_4]$.** Boron trifluoride (0.80 mmol) was condensed into a benzene solution (10 mL) of $CpFe(CO)_2CF_3$ (0.146 g, 0.59 mmol) and the mixture warmed to room temperature. The extremely hygroscopic white solid that formed was collected on a frit, washed with 5 mL of benzene, and dried under vacuum (0.15 g, 0.48 mmol, 81% yield). This salt was not sufficiently soluble in nonreactive solvents to permit NMR measurements. Exposure of a Nujol mull of $[CpFe(CO)_2(CF_2)][BF_4]$ to the atmosphere resulted in rapid hydrolysis to afford $[CpFe(CO)_3][BF_4]$. Anal. Calcd for $C_8H_5BF_6O_2Fe$: C, 30.62; H, 1.61; B, 3.45; F, 36.33. Found: C, 30.90; H, 1.69; B, 3.16; F, 36.58.

**Tensimetric Titration of $CpFe(CO)_2CF_3$ with $BF_3$.** A grease-free tensimeter of standard design[7] was employed, and the temperature of the reaction flask was maintained at 0 °C in an ice-water bath. Boron trifluoride uptake by a 0.1421-g (0.578 mmol) sample of $CpFe(CO)_2CF_3$ in 5 mL of toluene was monitored by measuring the pressure of the system following incremental addition of $BF_3$. The mull IR of the white precipitate formed in this experiment was identical with that of the analytical sample prepared above.

**$[CpFe(CO)_2(CCl_2)][BCl_4]$.** Addition of 3 equiv of $BCl_3$ to a frozen toluene solution of $CpFe(CO)_2CF_3$ followed by warming to room temperature resulted in quantitative precipitation of the product as a yellow powder. Large orange crystals (ca. 1 mm on edge) were isolated from concentrated $CH_2Cl_2$ solutions of $[CpFe(CO)_2(CCl_2)][BCl_4]$. Both powdered and crystalline compounds darkened on storage under nitrogen or vacuum at room temperature. Solutions of this complex form significant quantities of $CpFe(CO)_2CCl_3$ when left at room temperature for several days: $^{13}C$NMR ($CD_2Cl_2$, -40 °C) $\delta$ 319.5 (s, $CCl_2$), 202.2 (s, CO), 95.9 (d, $J$ = 185 Hz, Cp); $^1H$ NMR ($CD_2Cl_2$) $\delta$ 5.99 (s, Cp).

**$CpFe(CO)_2CN$.** Addition of excess $NH_3$ (4.3 mmol) to a frozen solution of 0.18 g (0.61 mmol) of $CpFe(CO)_2CCl_3$ in 20 mL of $CH_2Cl_2$ and warming to room temperature resulted in a rapid reaction as evidenced by lightening of the color of the solution and formation of a white solid that was collected on a frit and identified as $NH_4Cl$ by its mull IR spectrum.[8] Addition of 20 mL of hexane and slow evaporation of the $CH_2Cl_2$ gave 0.096 g (0.47 mmol, 78%) of $CpFe(CO)_2CN$ as yellow-orange crystals. The identity of this complex was ascertained by IR, $^1H$ NMR, and mass spectral measurements that were in agreement with literature reports.[9-11]

**$[CpFe(CO)_2(CN\text{-}i\text{-}Pr)][PF_6]$.** A $CH_2Cl_2$ solution (25 mL) of 0.58 g (2.36 mmol) of $CpFe(CO)_2CF_3$ was treated with 2.4 mmol of $BCl_3$ to afford a solution of $CpFe(CO)_2CCl_3$. The IR spectrum of this solution indicated the presence of ca. 10% $[CpFe(CO)_2(CCl_2)]^+$. Following removal of the $BF_3$ under vacuum, $i\text{-}PrNH_2$ (11 mmol) was condensed into the flask and rapid reaction occurred upon warming the solution to room temperature. At this point the IR spectrum indicated the presence of $[CpFe(CO)_2(CN\text{-}i\text{-}Pr)]^+$ and $CpFe(CO)(CN\text{-}i\text{-}Pr)(C(O)NH(i\text{-}Pr))$ (2120 (m), 1950 (s) cm$^{-1}$).[12] The latter compound was converted into $[CpFe(CO)_2(CNR)]^+$ (2218 (m), 2064 (s), 2043 (s) cm$^{-1}$) by removing the excess amine under vacuum. Ion exchange with 0.39 g (2.38 mmol) of $[NH_4][PF_6]$ in acetone followed by crystallization at -20 °C from $CH_2Cl_2/Et_2O$ and washing with $H_2O$ to remove alkylammonium salts gave solid $[CpFe(CO)_2(CN\text{-}i\text{-}Pr)][PF_6]$. The complex (0.62 g, 1.58 mmol, 67% yield) was identified by its IR and $^1H$ NMR spectra.[13]

**$CPFe(CO)_2CCl_3 + H_2O$.** A yellow solution of $CpFe(CO)_2CCl_3$ in 5 mL of MeCN was treated with 0.5 mL of $H_2O$. Complete spectroscopic conversion to $[CpFe(CO)_3]^+$ was confirmed by comparison of its IR spectrum with an independently prepared sample.[14]

**$Mn(CO)_5CF_3 + BF_3$.** Addition of 1.5 equiv of $BF_3$ to a $CH_2Cl_2$ solution of $Mn(CO)_5CF_3$ resulted in a cloudy solution with new CO bands at 2174 (w), 2130 (m, sh), and 2092 (s, br) cm$^{-1}$ which were similar in intensity to bands assigned to unreacted $Mn(CO)_5CF_3$. Unchanged starting material was obtained by removing the $BF_3$ gas under vacuum. A white precipitate that readily evolved $BF_3$ formed when this reaction was carried out in benzene solution. The mull spectrum of this solid showed weak IR bands assigned to $\nu_{CF_2}$ at 1260 and 1233 cm$^{-1}$ and strong bands at 1050 cm$^{-1}$ assigned[15] to $[BF_4]^-$ in addition to the carbonyl bands observed in the solution spectrum. A tensimetric titration of 0.1036 g (0.392 mmol) of $Mn(CO)_5CF_3$ in 3 mL of toluene at 0 °C with $BF_3$ was performed as previously described for $CpFe(CO)_2CF_3$.

**$[Mn(CO)_6][BF_4]$.** A $MeNO_2$ solution (10 mL) of 0.174 g (0.659 mmol) of $Mn(CO)_5CF_3$ was treated with 1.8 mmol of $BF_3$, and after the solution was stirred for 5 min at room temperature, the volume of the solvent was reduced to 3 mL. Addition of 20 mL of $Et_2O$ gave a fine white precipitate that was collected on a frit, washed with $Et_2O$, and dried under vacuum. The product (0.17 g, 0.55 mmol, 83% yield) was identified by its IR spectrum in $MeNO_2$ ($\nu_{CO}$ = 2101 cm$^{-1}$)[16] and its $^{55}Mn$ NMR resonance ($\delta$ -1453 upfield from external $KMnO_4$).[17] An alternative method involved precipitation of the product by addition of 50 $\mu$L of $H_2O$ through a septum into a $CH_2Cl_2$ (5 mL) solution prepared from 0.023 g (0.088 mmol) of $Mn(CO)_5CF_3$ and 0.18 mmol of $BF_3$. The $CH_2Cl_2$ and excess $BF_3$ were removed under vacuum, and the product was identified by its IR spectrum in MeCN ($\nu_{CO}$ = 2099 cm$^{-1}$).[16]

**Reactions with $HBF_4$(aq).** A solution of the trifluoromethyl complex ($CpFe(CO)_2CF_3$, $Mn(CO)_5CF_3$, or $CpMo(CO)_3CF_3$) was prepared in 5 mL of $MeNO_2$. Approximately 0.1 mL of 40% aqueous $HBF_4$ was added and the solution stirred for 5 min. An infrared spectrum taken at this time showed complete conversion to $[CpFe(CO)_3]^+$ ($\nu_{CO}$ = 2125 (s), 2076 (vs) cm$^{-1}$)[14] in the case of $CpFe(CO)_2CF_3$. For $Mn(CO)_5CF_3$ and $CpMo(CO)_3CF_3$, partial conversion to $[Mn(CO)_6]^+$ ($\nu_{CO}$ = 2099 cm$^{-1}$)[16] and $[CpMo(CO)_4]^+$ ($\nu_{CO}$ = 2123 (s), 2043 (vs, br) cm$^{-1}$)[18] respectively, was observed. Complete conversion to the carbonyl cations was observed after the mixture was stirred overnight.

Treatment of $CpMo(CO)_3C_2F_5$ with $HBF_4$(aq) in $MeNO_2$ for 12 h followed by removal of solvent under vacuum and extraction into hexane gave $CpMo(CO)_3C(O)CF_3$ as identified by its IR spectrum ($\nu_{C=O}$ = 1657 cm$^{-1}$).[19]

**Reactions with Olefins.** The trihalomethyl complexes were prepared in pentane solution immediately prior to use.[6] Residual Lewis acids and pentane solvent were removed under vacuum prior to dissolution of the complex in $C_6D_6$. Except as noted, reactions were carried out in normal room light for 16–20 h at room temperature employing a 1:3 mole ratio of olefin/metal

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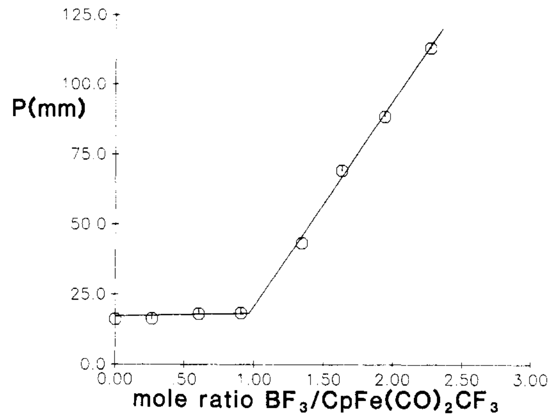

**Figure 1.** Tensimetric titration of $CpFe(CO)_2CF_3$ (0.578 mmol) with $BF_3$ at 0 °C in toluene solution. The break point occurs at 0.97 equiv of $BF_3/CpFe(CO)_2CF_3$.

carbonyl complex. Reactions with a 1:1 mole ratio gave similar products, but significant amounts of the olefin were left unreacted after 16–20 h. The brown solids that precipitated during the course of the reaction were removed by centrifuge, and the soluble reaction products were identified by $^1H$ NMR and IR spectroscopic methods. Proton-containing products were quantified by integration of the $^1H$ NMR spectrum (Table II). Additional products were identified by GC–MS employing a 6-ft 3% SP2250 column, temperature programmed from 120 to 200 °C at 10 °C/min, and a HP5985A mass spectrometer with 70-eV ionization. Reactions with cumene and toluene were carried out by using the same procedures as for olefins.

**Reactions with $HSn(n\text{-}Bu)_3$.** Addition of 0.59 mmol of $HSn(n\text{-}Bu)_3$ to a solution of $Mn(CO)_5CBr_3$ (0.30 mmol) in 1 mL of $C_6D_6$ resulted in a rapid exothermic reaction to afford a 3:2 mole ratio of $Mn(CO)_5CH_2Br/Mn(CO)_5CHBr_2$. The identity of these products was confirmed by comparison of their NMR and IR spectra with those of authentic samples.[6] Some $Mn_2(CO)_{10}$ was also observed by IR spectroscopy. Fluoride displacement did not occur when $Mn(CO)_5CF_3$ (0.087 mmol), and $HSn(n\text{-}Bu)_3$ (0.19 mmol) were allowed to react for 1 h at room temperature. In a separate experiment, 0.37 mmol of $HSn(n\text{-}Bu)_3$ was added to a $C_6D_6$ solution (0.5 mL) of $Mn(CO)_5CH_2Br$ and the solution was heated to 60 °C for 1 h to afford $Mn(CO)_5Me$ as identified by its $^1H$ NMR spectrum ($\delta$ 0.10).[20]

## Results and Discussion

**Reactions with Electrophiles.** Treatment of $CpFe(CO)_2CF_3$ with $BF_3$ in benzene yields an ivory precipitate for which C, H, B, and F analyses are correct for $[CpFe(CO)_2(CF_2)][BF_4]$. The stoichiometry is confirmed by a tensimetric titration in which 0.97 equiv of $BF_3/CpFe(CO)_2CF_3$ were consumed (Figure 1). The solid-state infrared spectrum is shown in Figure 2. The CO bands at 2115 and 2071 cm$^{-1}$ are somewhat higher in energy than those observed for other cationic iron carbene complexes. The bands at 1223 and 1200 (sh) cm$^{-1}$ are assigned to the C–F stretching frequencies of the carbene ligand. As expected from the positive charge of the complex, the C–F bands are shifted to higher energy compared to those reported for $Ru(CO)(PPh_3)_2(CF_2)Cl_2$ at 1210 and 1155 cm$^{-1}$.[21] The broad absorption centered at 1050 cm$^{-1}$ is assigned to the tretrafluoroborate anion.[15] The complex is extremely moisture sensitive, and exposure of the mull to the atmosphere results in rapid hydrolysis to afford $[CpFe(CO)_3][BF_4]$ (Figure 2). Note the complete disappearance of the bands assigned to the difluorocarbene ligand. Dissolution of $[CpFe(CO)_2(CF_2)][BF_4]$ in polar solvents such as MeCN or $MeNO_2$ led to partial hydrolysis, and the complex is only slightly soluble in $CH_2Cl_2$.

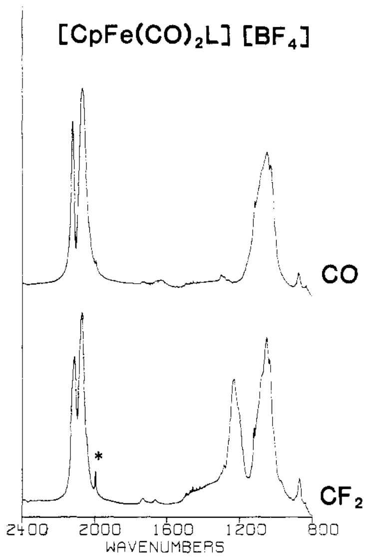

**Figure 2.** Lower trace: infrared spectrum of $[CpFe(CO)_2(CF_2)][BF_4]$ obtained as a Nujol mull. Upper trace: infrared spectrum of $[CpFe(CO)_3][BF_4]$ obtained by exposing the sample of $[CpFe(CO)_2(CF_2)][BF_4]$ to atmospheric moisture. The peak marked with an asterisk is a carbonyl band assigned to small amounts of unreacted $CpFe(CO)_2CF_3$ that are present in the sample. The bands of the mulling agent have been digitally subtracted from the spectra.

Reaction of $CpFe(CO)_2CF_3$ with 2 equiv of $BCl_3$ in toluene results in quantitative precipitation of a yellow powder (eq 1).

$$CpFe(CO)_2CF_3 + 2BCl_3 \rightarrow [CpFe(CO)_2(CCl_2)][BCl_4] + BF_3 \quad (1)$$

Large orange crystals (ca. 1 mm on edge) can be obtained from concentrated $CH_2Cl_2$ solution. The mull IR spectrum of the solid shows $\nu_{CO}$ = 2107 and 2078 cm$^{-1}$ as well as several strong bands consistent with the presence of a dichlorocarbene ligand at 872, 860, 834, and 810 cm$^{-1}$. The observation of four bands may be a consequence of solid-state splitting of the two expected bands. These are similar to the C–Cl bands reported for $Ru(CO)(PPh_3)_2(CCl_2)Cl_2$ at 860, 790, and 780 cm$^{-1}$.[22] The tetrachloroborate anion is detected by its absorption at 695 cm$^{-1}$.[15] This assignment is corroborated by the $^{13}C$ NMR spectrum that exhibits a singlet at low field ($\delta$ 319.5) which is characteristic of carbene carbons.[23,24] In contrast, the $^{13}C$ NMR resonance of the $CCl_3$ group in $CpFe(CO)_2CCl_3$ is observed at $\delta$ 107.6. Even large crystals of this complex darken on standing for several days at room temperature and some $CpFe(CO)_2CCl_3$ is formed. Hydrolysis of $[CpFe(CO)_2(CCl_2)]^+$ yields $[CpFe(CO)_3]^+$. Addition of [PPN][Cl] to a solution of $[CpFe(CO)_2(CCl_2)]^+$ cleanly affords $CpFe(CO)_2CCl_3$ (eq 2). In the course of preparing $CpFe(CO)_2CBr_3$, $[CpFe(CO)_2(CBr_2)]^+$ was detected and characterized by its infrared spectrum in $CH_2Cl_2$ solution (Table I).

$$[CpFe(CO)_2(CCl_2)][BCl_4] + [PPN][Cl] \rightarrow CpFe(CO)_2CCl_3 + [PPN][BCl_4] \quad (2)$$

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Table I. Infrared Spectral Data for $[CpFe(CO)_2(CX_2)]^+$ and $[CpFe(CO)_3]^+$

| complex | $\nu_{CO}$, cm$^{-1}$ | $\nu_{C-X}$, cm$^{-1}$ |
|---|---|---|
| $[CpFe(CO)_2(CF_2)][BF_4]$ | 2115 (s), 2071 (s)[a] | 1233 (s), 1200 (sh)[a] |
| $[CpFe(CO)_2(CCl_2)][BCl_4]$ | 2107 (s), 2078 (s)[b] | 872 (s), 860 (s), 834 (m), 810 (s)[a] |
| $[CpFe(CO)_2(CBr_2)]^+$ | 2105 (s), 2078 (s)[b] | |
| $[CpFe(CO)_3]^+$ | 2125 (s), 2076 (vs)[c] | |

[a] Nujol mull. [b] $CH_2Cl_2$ solution. [c] MeCN solution.

The carbonyl stretching frequencies of these complexes (Table I) are significantly higher than in other cationic iron carbene complexes such as $[CpFe(CO)_2(C(OMe)_2)]^+$ ($\nu_{CO}$ = 2063, 2015 cm$^{-1}$)[23] and $[CpFe(CO)_2(C(OMe)H)]^+$ ($\nu_{CO}$ = 2085, 2043 cm$^{-1}$),[25] indicating that the dihalocarbene ligand has a higher $\pi$-acceptor/$\sigma$-donor ratio than for the other carbene groups. Indeed, comprison of the IR bands with those of $[CpFe(CO)_3]^+$ ($\nu_{CO}$ = 2125, 2076 cm$^{-1}$)[14] suggests that the $CX_2$ ligand approaches CO as a $\pi$-acceptor. As observed for most other dihalocarbenes,[26] as well as for thiocarbenes,[27] the ligand is subject to facile hydrolysis to afford coordinated CO.[28] This property probably explains the failure of previous attempts[29] to prepare $[CpFe(CO)_2(CF_2)][BF_4]$.

Treatment of a $CH_2Cl_2$ solution of $Mn(CO)_5CF_3$ with excess $BF_3$ affords a cloudy white solution with carbonyl bands shifted to higher frequency and a decrease in the intensity of the $CF_3$ bands. This is consistent with the presence of $[Mn(CO)_5CF_2][BF_4]$ (eq 3). Removal of the

$$Mn(CO)_5CF + BF_3 \rightleftarrows [Mn(CO)_5(CF_2)][BF_4] \quad (3)$$

$BF_3$ under vacuum leads only to recovery of starting material. Hydrolysis of the reaction mixture affords $[Mn(CO)_6]^+$ as the only metal carbonyl product. This transformation is typically observed for difluorocarbene ligands and provides chemical evidence for eq 3. Similarly, $[Mn(CO)_6][BF_4]$ can be isolated in good yield by reaction of $Mn(CO)_5CF_3$ with $BF_3$ in $MeNO_2$ solution. The solvent (rather than adentitious moisture) is suspected to be the source of the oxygen atom in the CO ligand formed, but the other products of this reaction were not investigated. A tensimetric titration of $Mn(CO)_5CF_3$ with $BF_3$ shows a break point at 1.6 equiv of $BF_3/Mn(CO)_5CF_3$ (Figure 3). Perhaps stacking of the $BF_3$ to $[BF_4]^-$ to afford $[B_2F_7]^-$ contributes to the stability of the carbene complex in the solid state.[30] These observations are consistent with the reversible formation of a difluorocarbene ligand, but attempts to isolate a solid product were frustrated by facile $BF_3$ evolution from the solid. The manganese pentacarbonyl system does not stabilize the dihalocarbene ligand to the extent observed in the iron system. This is expected since the more basic metal center should be able to stabilize the electron-deficient carbene ligand.[31]

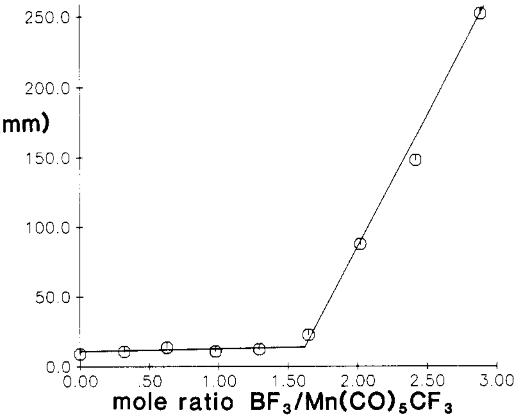
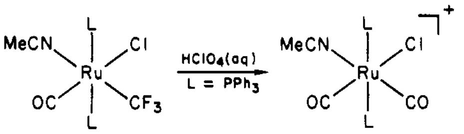


**Figure 3.** Tensimetric titration of $Mn(CO)_5CF_3$ (0.392 mmol) with $BF_3$ at 0 °C in toluene solution. The break point occurs at 1.6 equiv of $BF_3/Mn(CO)_5CF_3$.

The ability of electrophiles to promote carbene formation in trifluoromethyl complexes is also evident in their reactions with proton acids. Treatment of $CpFe(CO)_2CF_3$, $CpMo(CO)_3CF_3$ or $Mn(CO)_5CF_3$ with aqueous $HBF_4$ in $MeNO_2$ results in quantitative spectroscopic conversion to the corresponding carbonyl cations (eq 4). Qualitatively, the rate of the overall reaction in eq 4 is greater for $CpFe(CO)_2CF_3$ than for $CpMo(CO)_3CF_3$ or $Mn(CO)_5CF_3$. This ordering parallels the stability of difluorocarbene ligands in these metal carbonyl systems. As observed for the halogen-exchange reactions,[6] this transformation is also $\alpha$-regiospecific. Proton acid promoted hydrolysis of $CpMo(CO)_3CF_2CF_3$ affords $CpMo(CO)_3C(O)CF_3$ as identified by its IR spectrum. Hydrolysis of a trifluoromethyl group by aqueous $HClO_4$ has recently been reported in a ruthenium complex (eq 5).[21] The mechanism for this

$$MCF_3 \xrightarrow{H^+} [M{=}CF_2]^+ \xrightarrow{H_2O} [M{-}C{\equiv}O]^+ \quad (4)$$



(5)

process (eq 4) probably involves initial formation of a cationic difluorocarbene group by electrophilic fluoride abstraction by $H^+$ followed by rapid hydrolysis at the $CF_2$ ligand. This mechanism is supported by the susceptibility of isolated dihalocarbene complexes to hydrolysis.[32,33]

**Reactions with Nucleophiles.** The reactions of $CpFe(CO)_2CCl_3$ with Lewis bases were explored. Hydrolysis in MeCN affords $[CpFe(CO)_3]^+$. Treatment of a $CH_2Cl_2$ solution with excess $NH_3$ affords a 78% isolated yield of $CpFe(CO)_2CN$ (eq 6). Control experiments show

$$CpFe(CO)_2CCl_3 + 4NH_3 \rightarrow CpFe(CO)_2CN + 3NH_4Cl \quad (6)$$

that $CpFe(CO)_2CF_3$ does not react with $H_2O$ or $NH_3$ under these conditions. Similarly, when $CpFe(CO)_2CCl_3$ is allowed to react with excess $i$-$PrNH_2$, $[CpFe(CO)_2(CN$-$i$-$Pr)]^+$ salt may be isolated in good yield. The phosphines $PH_3$ and $PH_2Ph$ react with $CpFe(CO)_2CBr_3$, but pure products could not be isolated. The crude product from the latter reaction contains two strong CO stretching bands at 2040 and 1995 cm$^{-1}$, indicating that the product is a neutral compounds; however it was not soluble in hexane or diethyl ether. The $Mn(CO)_5CX_3$ complexes are less

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Table II. Products Quantified by $^1H$ NMR in the Radical Reactions of $Mn(CO)_5CBr_3$[a]

| reagent | $Mn(CO)_5$-$CHBr_2$ | $CH_2Br_2$ | $CHBr_3$ | $C_2HBr_3$ |
|---|---|---|---|---|
| cyclohexene | 0.21 | 0.10 | 0.04 | 0.04 |
| 1-pentene | 0.08 | 0.06 | 0.04 | 0.02 |
| *trans*-2-butene | 0.15 | 0.04 | 0.04 | 0.02 |
| cumene | 0.04 | 0.16 | 0.07 | 0.07 |
| toluene | 0.08 | 0.07 | 0.05 | 0.05 |

[a] Moles of product per mole of $Mn(CO)_5CBr_3$. Mass spectral analysis indicates ca. 10% incorporation of deuterium from $C_6D_6$ solvent.

reactive with nucleophiles than the corresponding $CpFe(CO)_2CX_3$ compounds. Treatment of $Mn(CO)_5CCl_3$ with excess $NH_3$ affords an orange product ($\nu_{CO}$ = 2030 (m), 1925 (s, br) $cm^{-1}$) that is only partially soluble in $CH_3CN$ and may be polymeric in nature. As with $Mn(CO)_5CF_3$, no acetyl product is detected when $Mn(CO)_5CCl_3$ was exposed to 2 atm CO or treated with $PPh_3$. Similarly, no reaction is observed when $CpFe(CO)_2CCl_3$ or $[CpFe(CO)_2CCl_2]^+$ is treated with CO.

The trihalomethyl complexes (X = Cl, Br, I) are much more reactive toward nucleophiles than their thermally robust trifluoromethyl precursors. This is particularly evident in the $CpFe(CO)_2CX_3$ systems that readily undergo nucleophilic attack. The similarity of these reactions with those reported[26] for dihalocarbene complexes suggests that a carbene intermediate is involved (eq 7 and 8). Alternatively, direct nucleophilic attack on the trichloromethyl ligand and expulsion of the halide may take place (eq 9).

$$CpFe(CO)_2CCl_3 \rightleftharpoons [CpFe(CO)_2CCl_2]^+Cl^- \qquad (7)$$

$$[CpFe(CO)_2(CCl_2)]^+ + Nu^- \rightarrow CpFe(CO)_2CCl_2\text{–}Nu \qquad (8)$$

$$CpFe(CO)_2CCl_3 + Nu^- \rightarrow CpFe(CO)_2CCl_2\text{–}Nu + Cl^- \qquad (9)$$

Kinetic studies would be required to differentiate between these two mechanisms. However, the scheme represented in eq 7 and 8 is supported by the greater reactivity of $CpFe(CO)_2CCl_3$ compared to $CpMo(CO)_3CCl_3$ or $Mn(CO)_5CCl_3$ since this order parallels the accessibility of cationic dihalocarbene complexes in these systems.

**Homolytic Reactions of $Mn(CO)_5CBr_3$.** Main-group trihalomethyl complexes such as $PhHgCBr_3$ are known to efficiently transfer dibromocarbene to olefins affording dibromocyclopropanes in high yield.[34] Therefore we have explored the reactions of the formally analogous transition-metal trichloromethyl complexes with olefins. We chose to examine the reactions of $Mn(CO)_5CBr_3$ with several electron-rich olefins that are known to readily form dibromocyclopropanes upon treatment with $PhHgCBr$.[34] The products detected by $^1H$ NMR spectroscopy following the room-temperature reaction of $Mn(CO)_5CBr_3$ with olefins in $C_6D_6$ for 16–20 h are collected in Table II. Reactions were usually carried out with a 1:3 mole ratio of olefin/$Mn(CO)_5CBr_3$ since this stoichiometry resulted in complete consumption of the olefin as evidenced by disappearance of the olefinic proton resonances from the $^1H$ NMR spectrum. Similar product distributions were observed in experiments employing a 1:1 mol ratio of reactants. Additional products detected by GC–MS for the olefin reactions include $C_2Br_4$, $C_6D_5CH_2Br$, $C_6D_5CHBr_2$, and $C_6D_5Br$. Free radical polymerization of the olefin may account for the paucity of olefin-derived products.

It is clear from the nature and large number of products that simple cyclopropane formation occurs only to a small extent, if at all. In the case of *trans*-2-butene, three isomers of $C_5H_8Br_2$, which may be dibromocyclopropanes, are detected by GC–mass spectroscopy, but the low yield of these products precluded further characterization. The diversity and character of the products led us to suspect that radical processes are important in this reaction. Thus, we also explored the reactivity of $Mn(CO)_5CBr_3$ with cumene and toluene, which are representative hydrocarbons that are known to be susceptible to radical reactions.[35] The products observed by $^1H$ NMR spectroscopy are listed in Table II. Products expected from cumyl radical coupling and disproportionation including $PhCMe_2C_6D_5$, $(PhC_2H_3)_{2,37}$ and $(PhCMe_2)_2$ are detected by GC–MS. The reaction with cumene proceeds more rapidly than with olefins and will take place in the absence of room light. $PhCH_2C_6D_5$ is observed as a product in the reaction with toluene in $C_6D_6$ solvent. In addition, it should be noted that $Mn(CO)_5CBr_3$ reacts slowly with benzene. The phenyl group is detected in several reaction products, and deuterium incorporation is observed from $C_6D_6$ solvent. The major metal carbonyl products detected are $Mn(CO)_5CHBr_2$ and $Mn(CO)_5Br$.[36] Further reaction os isolated $Mn(CO)_5CHBr_2$ with 1-pentene is not observed after 20 h at room temperature. Control experiments indicate that $Mn(CO)_5CF_3$ is completely unreactive with these reagents under the conditions employed. In addition, the trichloromethyl complex $Mn(CO)_5CCl_3$ is less reactive than $Mn(CO)_5CBr_3$.

Although radical processes are undoubtedly important in the reactions discussed above, the complexity of the reaction mitigrates against detailed mechanistic analysis. However, several generalizations are suggested by the experimental observations. Foremost among these is the greatly enhanced ability of $Mn(CO)_5CBr_3$ to participate in radical processes compared to $Mn(CO)_5CF_3$. The radical type of reactivity also is in contrast to that observed for $PhHgCBr_3$ and related compounds.[34]

Control experiments indicate that $Mn(CO)_5CBr_3$ is significantly more reactive toward cumene or 1-pentene than $CBr_4$. The latter reagent required initiation by UV light as no reaction was observed under our experimental conditions after 17 h at room temperature. Two initiation steps are plausible for this radical process. The observation of $Mn(CO)_5CHBr_2$ as a major product suggests that C–Br bond homolysis is the dominant step (eq 10). The alternative initiation step may involve Mn–C bond cleavage (eq 11). Hydrogen abstract by $CBr_3\cdot$ could yield $CHBr_3$.

$$Mn(CO)_5CBr_3 \rightarrow Mn(CO)_5CBr_2\cdot + Br\cdot \qquad (10)$$

$$Mn(CO)_5CBr_3 \rightarrow Mn(CO)_5\cdot + CBr_3\cdot \qquad (11)$$

Any $Mn(CO)_5\cdot$ formed must be efficiently scavenged by $Br\cdot$ to afford $Mn(CO)_5Br$ since $Mn_2(CO)_{10}$ is not detected as a reaction product. The formation of several $C_2$ fragments including $C_2HBr_3$ and $C_2Br_4$ may indicate that the lifetime of the $Mn(CO)_5CBr_2\cdot$ species is sufficient to allow coupling reactions to take place. The apparent role of the metal carbonyl center in stabilizing the radical merits further investigation. The known substitution lability of many 17-electron species may provide an avenue for further reaction chemistry.[37,38]

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The tribromomethyl group in $Mn(CO)_5CBr_3$ is subject to facile homolytic replacement of Br by H upon treatment with $HSn(n\text{-}Bu)_3$. Rapid exothermic reaction occurs when $Mn(CO)_5CBr_3$ is treated with 2 equiv of $HSn(n\text{-}Bu)_3$ to afford a mixture of $Mn(CO)_5CHBr_2$ and $Mn(CO)_5CH_2Br$. Complete replacement of all the bromine atoms by hydrogen to yield $Mn(CO)_5Me$ requires heating to 60 °C (eq 12). Some $Mn_2(CO)_{10}$ is detected in the reaction mixture

$$Mn(CO)_5CH_2Br + HSn(n\text{-}Bu)_3 \rightarrow Mn(CO)_5Me + BrSn(n\text{-}Bu)_3 \quad (12)$$

implying that Mn–C bond cleavage also takes place. No reaction is observed between $Mn(CO)_5CF_3$ and excess $HSn(n\text{-}Bu)_3$ under similar conditions. Homolytic halide replacement by $HSn(n\text{-}Bu)_3$ also has been observed in halomethylidyne cluster complexes.[39]

## Conclusion

The reaction chemistry of transition-metal trihalomethyl complexes (X = Cl, Br) is much more diverse than that of their thermally stable trifluoromethyl precursors. The enhanced reactivity is particularly evident in reactions with nucleophiles or in homolytic processes. Cation dihalocarbene complexes are implicated as intermediates in heterolytic reactions, whereas transition-metal dihalocarbene radicals may be involved in the free radical reactions.

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**Registry No.** $[CpFe(CO)_2(CF_2)][BF_4]$, 88211-34-1; $[CpFe(CO)_3][BF_4]$, 12244-69-8; $[CpFe(CO)_2(CCl_2)][BCl_4]$, 88211-36-3; $[CpFe(CO)_2(CN\text{-}i\text{-}Pr)][PF_6]$, 69532-19-0; $CpFe(CO)_2CF_3$, 52409-72-0; $CpFe(CO)_2CCl_3$, 86392-66-7; $CpFe(CO)_2CN$, 12152-37-3; $CpFe(CO)(CN\text{-}i\text{-}Pr)(C(O)NH(i\text{-}Pr))$, 88211-37-4; $[CpFe(CO)_3]^+$, 32660-74-5; $Mn(CO)_5CF_3$, 13601-14-4; $[Mn(CO)_6][BF_4]$, 15557-71-8; $Mn(CO)_5CBR_3$, 86392-60-1; $Mn(CO)_5CH_2BR$, 86392-63-4; $Mn(CO)_5CHBr_2$, 86392-65-6; $Mn(CO)_5Me$, 13601-24-6; $CpMo(CO)_3CF_3$, 12152-60-2; $[CpMo(CO)_4]^+$, 48138-37-0; $CpMo(CO)_3C_2F_5$, 88180-66-9; $BF_3$, 7637-07-2; $BCl_3$, 10294-34-5; $NH_3$, 7664-41-7; $i\text{-}PrNH_2$, 75-31-0; $HSn(n\text{-}Bu)_3$, 688-73-3; $HBF_4$, 16872-11-0; cyclohexene, 110-83-8; 1-pentene, 109-67-1; *trans*-2-butene, 624-64-6; cumene, 98-82-8; toluene, 108-88-3.

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# Olefin Oligomerization on Nickel. A Theoretical Study of the Barrier to Olefin Rotation and Insertion

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The mechanism of Ziegler–Natta catalysis has been investigated by using the atom superposition and electron delocalization moleculer orbital theory. Model nickel compounds of the form $Ni(C_2H_4)(CH_3)LX$ ($L = PH_3$, X = Cl) were studied. Polymerization was examined by assuming a Cossee mechanism. From MO symmetry considerations, a rearrangement involving rotation of the olefin around its bond to the metal is required before the reaction will occur. The barrier to this rotation is found to be a function of the ligand trans effect and steric interactions with the cis ligands. Calculated barriers for Pt(II) and Rh(I) compounds compare favorably with results obtained from NMR experiments.

## Introduction

Typical Ziegler–Natta catalysts are formed from transition-metal salts and main-group (usually aluminum) metal alkyl, metal aryl, and alkyl metal halides.[1,2] These catalysts are used for polymerization of $\alpha$-olefins such as ethylene, propylene, etc.[3-5] Only moderate pressures (8–30 atm) and slightly elevated temperatures (20–120 °C) are required for the reaction to proceed. The products of polymerization, in contrast to the polymers produced by free radical reactions, have a narrow molecular weight distribution and high stereospecificity.[3,6-8] The reaction offers the possibility of forming a well-controlled product through the choice of an appropriate metal center, with appropriate conditions of temperature and pressure. A polymer of a lower molecular weight usually is produced at elevated temperatures.[9]

A most interesting question about the polymerization mechanism is the origin of high stereoselectivity. This stereoselectivity can lead to a polymer with special characteristics such as crystallinity or (with dienes) high tacticity. A number of theories exist that attempt to explain the stereoregularity.[2,6,10,11] Most involve formation of a

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