60° rotation of the methyl groups to structure III either before or after IV (routes A and A′). In route B, ·$SiMe_3$ would invert through the highest energy structure, planar C_{3h} (V), via 30° rotations to II and without passing through III. The results thus predict an inversion through the planar C_{3v} geometry with separate rotations of the methyl groups.

Conclusions

Trimethylsilyl radical has been calculated to have a pyramidal geometry with a barrier to planarity of 13.3 kcal/mol. This value is about 8 kcal/mol larger than that estimated experimentally for ·SiMePhNp-α. The calculations also show, however, a substantial substituent dependence for the degree of pyramidalization of the preferred geometry and for the barrier to planarity in the silyl radicals. The calculated barriers range from 5 (·SiH_3) to 68 kcal/mol (·SiF_3). Qualitatively, the substituent effects on barrier heights, as well as the relative energies of different geometries for methyl-substituted silyl radicals, can be predicted from SOMO–LUMO energy differences. Specifically, upon substitution of F for H in ·SiH_3 there is a marked increase in the degree of pyramidalization and in the inversion barrier. Substitution of Me for H produces a similar, although attenuated, effect.

When a CH_3 group is substituted on a planar carbon radical center, several geometric effects are observed that can be explained in terms of a hyperconjugative model like that used to explain the calculated geometries of planar CH_3NH_2.[19] The effects include methyl group tilt, relative CCH bond angles, and relative CH bond lengths. The former two effects are clearly present in methyl-substituted silyl radicals, but the latter effect is not. The hyperconjugative effect may be smaller in the silyl radicals than in the carbon analogues, and the geometric parameter hardest to distort, i.e., bond length, is not affected. It is not straightforward to extend the orbital interaction reasoning used for the planar radicals to their pyramidal forms, either for carbon or silicon radicals.

Molecular mechanics calculations indicate that the preference for a C_{3h} planar geometry over a C_{3v} one for the *tert*-butyl radical may have a steric origin in small repulsive van der Waals forces in the C_{3h} form. The van der Waals forces are much smaller in the trimethylsilyl radical, which prefers the planar C_{3v} form. Surprisingly, molecular mechanics calculations do a fair job of duplicating the quantum mechanical calculations in predicting the relative energies of all five planar and pyramidal geometries considered here for ·$SiMe_3$.

Acknowledgment. The structures in Figure 1 and many of the initial sets of coordinates were produced by using PROPHET, a biomedical computer system sponsored by the National Institutes of Health, Division of Research Resources.

Registry No. H_3Si·, 13765-44-1; H_iCH_oSi·, 51220-22-5; H_2FSi·, 35427-70-4; trimethylsilyl radical, 16571-41-8; trifluorosilyl radical, 14835-14-4.

Electrophilic Halogen Exchange between Lewis Acids and Transition-Metal Perfluoroalkyl Complexes. Synthesis and Characterization of Transition-Metal α-Haloalkyl Complexes

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Facile halogen exchange takes place upon reaction of transition-metal perfluoroalkyl carbonyl complexes with BX_3 (X = Cl, Br, I). Treatment of $Mn(CO)_5CF_3$ with 1 equiv of BX_3 in a noncoordinating solvent affords $Mn(CO)_5CX_3$ (X = Cl, Br, I) in high yield under mild conditions. The stability of these new complexes decreases in the series Cl > Br > I. Mono- and dihalomethyl complexes, $Mn(CO)_5R$ (R = CHX_2, CH_2X; X = Cl, Br), were also prepared by this method from the appropriate fluoromethyl precursors. Application of the halogen-exchange reaction to other transition-metal systems enabled synthesis of $CpMo(CO)_3CX_3$ and $CpFe(CO)_2CX_3$ (X = Cl, Br). Regiospecific halogen exchange occurs at the carbon α to the metal center as shown by the synthesis of $Re(CO)_5CX_2CF_3$ (X = Cl, Br), $Mn(CO)_5CCl_2CF_3$, $CpMo(CO)_3CCl_2CF_3$, and $CpMo(CO)_3CCl_2C_2F_5$. The substituted ethyl complexes in CX_2CF_3 show hindered C–C bond rotation that is slow on the NMR time scale at room temperature. Further fluoride replacement is not observed when the above compounds are treated with additional BX_3 at room temperature. Similarly no exchange was observed when $Mn(CO)_5C(O)CF_3$ or $CpFe(CO)_2C_6F_5$ was treated with BCl_3. The ability of the transition-metal center to activate the α-C–F bond for halogen exchange results from the stabilization of the dihalocarbene complex which appears to be an intermediate in the exchange process.

Introduction

Perfluoroalkyl carbonyl complexes are readily prepared for nearly all of the late transition metals and have played an important role in the development of the chemistry of the metal–carbon bond.[1–3] These complexes are characterized by high thermal stability, and the perfluoroalkyl group is normally quite resistant to chemical attack. This parallels the known inertness of organic fluorocarbon compounds.[4,5] However, structural and spectroscopic

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(1) Treichel, P. L.; Stone, F. G. A. *Adv. Organomet. Chem.* **1964**, *1*, 143–220.

(2) Bruce, M. I.; Stone, F. G. A. *Prep. Inorg. React.* **1968**, *4*, 177–235.

(3) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417–427.

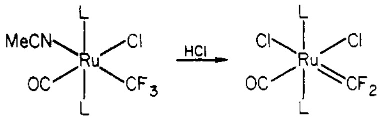
(4) Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry"; W. A. Benjamin: New York, 1969.

studies suggest that the α-C–F bond in transition-metal complexes is weaker than in aliphatic compounds. Carbon–fluorine bonds α to a transition metal show reduced C–F stretching frequencies[6-10] and increased bond lengths.[11-14] This phenomenon was first described in terms of the "no-bond" resonance form represented in eq 1.[7-9] More recent molecular orbital calculations suggest

$$F_3C\text{–}M \rightarrow F^-F_2C{=}M^+ \qquad (1)$$

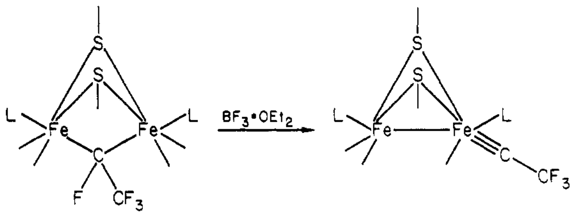
that the electron-withdrawing character of the CF_3 ligand is much more important than the metal–carbon π bonding depicted in eq 1 in the electronic structure of $Mn(CO)_5CF_3$.[15] However, this formulation is pendagogically useful and suggests that the fluorine atom may be susceptible to electrophilic attack. This has been experimentally observed in the generation of cationic metal carbene complexes in solution (eq 2).[16] More recently, stable difluorocabene complexes have been isolated by treating transition-metal trifluoromethyl complexes with anhydrous HCl (eq 3).[17] Other examples of molecular Lewis acid induced reactions in α-haloalkyl complexes include the formation[18] of $[Co_3(CO)_9CCO][AlCl_4]$ from $Co_3(CO)_9CCl$ and $AlCl_3$ and the transformation of a bridging perfluorocarbene ligand to a terminal carbyne ligand (eq 4).[19]

$$CpMo(CO)_3CF_3 + SbF_5 \rightarrow [CpMo(CO)_3(CF_2)][SbF_6] \qquad (2)$$



(3)

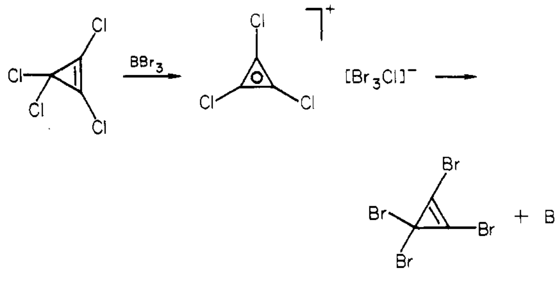
L = PPh_3



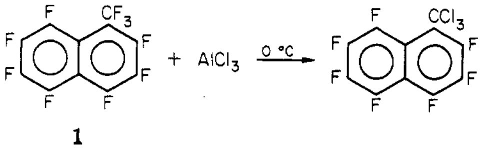
(4)

Our interest in the interactions of organometallic compounds with molecular Lewis acids prompted us to examine the reactions of perfluoroalkyl carbonyl complexes with Lewis acids.[20-23] We have exploited the susceptibility of the perfluoroalkyl ligand to electrophilic attack to synthesize a series of (α-halomethyl)metal carbonyl complexes by halogen-exchange reactions with boron trihalides (eq 5).[24] We note that similar halogen exchange reactions take place in activated organic halocarbons (eq 6 and 7). Thus

$$M\text{–}CF_3 + BX_3 \rightarrow M\text{–}CX_3 + BF_3 \qquad (5)$$



(6)[25]



(7)[26]

1

the aromatic cyclopropylium cation intermediate in eq 6 provides a low-energy pathway for exchange. Similarly, the benzylic positions of 1 are subject to facile halogen exchange. In saturated fluorocarbon systems, halogen exchange is more difficult, mixtures of products are obtained, and yields are often low (eq 8).[26-28] In aliphatic compounds, the trifluoromethyl group is particularly resistant to electrophilic attack.[27,28]

$$CCl_2FCClF_2 \xrightarrow{AlCl_3} CCl_3CF_3 + CCl_3CClF_2 + CCl_3CCl_3 \qquad (8)^{27}$$

Although main-group trihalomethyl complexes are well-known and in some cases find application in organic synthesis,[29] transition-metal trihalomethyl (X = Cl, Br, I) complexes are rare.[30] Transition-metal trichloromethyl complexes have been postulated as intermediates in a number of metal-catalyzed reactions including olefin polymerization and addition of CCl_4 to olefins.[31] Similar intermediates have been implicated in the synthesis of $Co_3(CO)_9CX$ clusters.[32]

Herein we describe the synthesis and characterization of α-haloalkyl transition-metal carbonyl complexes prepared by halogen exchange with boron trihalides. The regiochemistry and generality of the halogen-exchange reactions are discussed. In the following paper the reactions of (trihalomethyl)metal carbonyl complexes with electrophiles, nucleophiles, and hydrogen sources are described.[33]

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(5) Chambers, R. B. "Fluorine in Organic Chemistry"; Wiley: New York, 1973.

(6) Pitcher, E.; Stone, F. G. A. *Spectrochim. Acta* **1962**, *18*, 585–594.

(7) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15–37.

(8) Cotton, F. A.; McCleverty, J. A. *J. Organomet. Chem.* **1965**, *4*, 490.

(9) Cotton, F. A.; Wing, R. M. *J. Organomet. Chem.* **1967**, *9*, 511–517.

(10) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315–321.

(11) Mason, R.; Russell, D. R. *Chem. Commun.* **1965**, 182–183.

(12) Churchill, M. R. *Inorg. Chem.* **1965**, *4*, 1734–1739.

(13) Churchill, M. R. *Inorg. Chem.* **1967**, *6*, 185–190.

(14) Churchill, M. R.; Fennessey, J. R. *Inorg. Chem.* **1967**, *6*, 1213–1220.

(15) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.

(16) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67–72.

(17) Clark, B. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9–C12.

(18) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758–765.

(19) Bonnet, J. J.; Mathieu, R.; Poilblanc, R.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7487–7496.

(20) Shriver, D. F. *J. Organomet. Chem.* **1975**, *94*, 259–271.

(21) Shriver, D. F. *Adv. Chem. Ser.* **1981**, *No. 152*, 1–18.

(22) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093–5100.

(23) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* **1982**, *12*, 1624–1628.

(24) Preliminary report: Richmond, T. G.; Shriver, D. F. *Organometallics* **1983**, *2*, 1061–1062.

(25) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 1459.

(26) Gething, B.; Patrick, C. R.; Smith, B. J. K.; Tatlow, J. C. *J. Chem. Soc.* **1962**, 190–193.

(27) Miller, W. T. Jr.; Fager, E. W.; Griswold, P. H. *J. Am. Chem. Soc.* **1950**, *72*, 705–707.

(28) Park, J. D.; Hopwood, S. L. *J. Org. Chem.* **1958**, *23*, 1169–1171.

(29) Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65–74.

(30) An iridium trichloromethyl complex has been prepared: Demming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1128–1134.

(31) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press, New York, 1978; Chapters 6 and 8.

(32) Booth, B. L.; Casey, G.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1980**, 403–406.

Table I. Infrared Spectral Data for α-Halomethyl Manganese Pentacarbonyl Complexes, $Mn(CO)_5R$, in Hexane Solution

R	ν_{CO}, cm^{-1}				ν_{C-X}, cm^{-1}
CF_3	2137 (vw)	2069 (vw)	2044 (s)	2020 (s)	1057 (m), 1028 (w)
CCl_3	2133 (w)	2071 (vw)	2046 (s)	2013 (m)	701 (m), 675 (w)
CBr_3	2131 (w)	2071 (vw)	2047 (s)	2013 (m)	
CI_3	2124 (w)	...	2042 (s)	2008 (m)	
CHF_2	2128 (vw)	2064 (w)	2031 (s)	2011 (m)	999 (w), 976 (w)
$CHCl_2$	2127 (w)	2071 (w)	2036 (s)	2009 (m)	689 (w), 678 (w)
$CHBr_2$	2127 (w)	2071 (w)	2037 (s)	2009 (m)	
CH_2F	2119 (vw)	2054 (w)	2020 (s)	2001 (m)	942 (w)
CH_2Cl	2120 (w)	2057 (w)	2024 (s)	2001 (m)	682 (w)
CH_2Br	2121 (w)	2060 (w)	2026 (s)	2002 (m)	
CH_2I[a]	2123 (w)	2063 (vw)	2029 (s)	2005 (m)	

[a] Reference 44.

Table II. Infrared and ^1H NMR Spectral Data for $CpFe(CO)_2CX_3$ and $CpMo(CO)_3CX_3$

complex	ν_{CO},[a] cm^{-1}	ν_{C-X}, cm^{-1}	$\delta(Cp)$
$CpFe(CO)_2CF_3$	2050 (s), 2002 (s)	1055 (m), 1037 (w), 1025 (w)[a]	
$CpFe(CO)_2CCl_3$	2049 (s), 2006 (s)	720 (m), 685 (s), 662 (m)[b]	4.93[c]
$CpFe(CO)_2CBr_3$	2049 (s), 2007 (s)		4.98[c]
$CpMo(CO)_3CF_3$	2054 (m), 1977 (vs), 1970 (s)	1055 (m), 1030 (m), 1021 (w)[a]	
$CpMo(CO)_3CCl_3$	2053 (m), 1979 (vs), 1967 (s)	722 (m, br)[b]	4.65[d]
$CpMo(CO)_3CBr_3$	2052 (m), 1980 (vs), 1965 (s)		4.65[d]

[a] Hexane solution. [b] Nujol mull. [c] $CDCl_3$ solution. [d] C_6D_6 solution.

Table III. Spectral Data for MCX_2CF_3 Complexes in Hexane Solution

complex	ν_{CO}, cm^{-1}	ν_{C-F},[a] cm^{-1}
$Mn(CO)_5CF_2CF_3$	2137 (w), 2077 (vw), 2047 (s), 2021 (m)	1304, 1185, 1040, 1018
$Mn(CO)_5CCl_2CF_3$	2134 (w), 2080 (vw), 2048 (s), 2016 (m)	1233, 1171, 1156
$Re(CO)_5CF_2CF_3$	2151 (w), 2078 (vw), 2042 (s), 2016 (m)	1191, 1180, 1049, 1004, 923
$Re(CO)_5CCl_2CF_3$	2150 (w), 2081 (vw), 2044 (s), 2009 (m)	1236, 1173, 1154
$Re(CO)_5CBr_2CF_3$	2149 (w), 2080 (vw), 2044 (s), 2008 (m)	1226, 1162, 1139
$CpMo(CO)_3CF_2CF_3$	2055 (s), 1979 (vs), 1970 (s)	1291, 1192, 1176, 1028, 989[b]
$CpMo(CO)_3CCl_2CF_3$[c]	2055 (s), 1983 (vs), 1965 (s)	1219, 1159[b]
$CpMo(CO)_3C_3F_7$	2054 (s), 1980 (vs), 1969 (s)	1225, 1192, 1172, 1160, 1082, 1021, 999
$CpMo(CO)_3CCl_2C_2F_5$[d]	2054 (s), 1980 (vs), 1967 (s)	1219, 1204, 1163, 1135, 1040

[a] Intensities of the C–F bands are weak relative to the CO vibrations. [b] CH_2Cl_2 solution. [c] ^1H NMR ($CDCl_3$) δ 5.56. [d] ^1H NMR ($(CD_3)_2CO$) δ 5.97.

Experimental Section

General Data. Aside from specific exceptions noted below, all manipulations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and syringe techniques, a Vacuum Atmospheres glovebox, or a high vacuum manifold equipped with grease-free Teflon in glass valves. Solvents were dried and freed of oxygen prior to use. Ethers and hydrocarbons were distilled from sodium benzophenone ketyl, and CH_2Cl_2, $MeNO_2$, and MeCN were dried with P_2O_5.

The following perfluoroalkylmetal carbonyls were prepared by literature procedures: $Mn(CO)_5R$ (R = CF_3,[34] CHF_2,[35] CH_2F,[35] C_2F_5[36]), $Re(CO)_5C_2F_5$,[36] $Re(CO)_5CFCF_2$,[37] $CpFe(CO)_2CF_3$,[7] $CpFe(CO)_2C_6F_5$,[38] and $CpMo(CO)_3R'$ (R′ = CF_3, C_2F_5, n-C_3F_7).[7] Final purification was accomplished by vacuum sublimation, and the identity and purity of these complexes were verified by IR and ^1H and ^{19}F NMR spectroscopy. In the synthesis of $CpFe(CO)_2CF_3$, the chromatography step was omitted and the crude $CpFe(CO)_2C(O)CF_3$ was photolyzed to afford the desired complex in 50–70% overall yield from $[CpFe(CO)_2]_2$ compared to the reported yield of 6%.[7] The perfluoroalkyl complexes were stored under nitrogen but were weighed in air. R. J. Bosch kindly provided a sample of $HgPhCCl_3$ which was recrystallized from $CHCl_3$/hexane. Volatile Lewis acids ($SnCl_4$, $TiCl_4$, $SiCl_4$) were obtained commercially and purified by trap-to-trap distillation on the high vacuum line. Boron trifluoride was fractionated through a −112 °C trap, and BCl_3 was distilled and then degassed at −78 °C to remove HCl. Boron tribromide was stored over Hg metal to remove free Br_2 and then distilled. Diborane was freed of higher boranes by passage through a −112 °C trap. Vapor pressure measurements for these compounds were in agreement with literature values.[39] Boron triiodide was a gift from K. G. Moloy. Aluminum halides were sublimed from a mixture of Al powder and NaX (X = Cl, Br) and then resublimed prior to use.

Instrumentation. Solid-state IR spectra were obtained as Nujol mulls on KBr plates, and solution spectra were recorded by using 0.1-mm CaF_2 or 0.2-mm KBr cells on Nicolet 7199 FT-IR or Perkin Elmer 283 spectrometers. Variable-temperature ^1H (89.55 MHz), ^{11}B (28.69 MHz), ^{19}F (84.25 MHz), and ^{55}Mn (22.15 MHz) NMR spectra were recorded on a JEOL FX-90Q spectrometer with a variable-temperature accessory. Temperatures are believed to be accurate to ±1 °C. A JEOL FX-270 instrument was used for ^{13}C (67.80 MHz) NMR measurements. Carbon and proton chemical shifts are reported in parts per million relative to Me_4Si. Fluorine chemical shifts are reported relative to external CCl_3F. In all cases, a low-field shift is taken as positive. Spin simulations were performed by using JEOL software. Mass spectra were obtained by Dr. D. Hung of the Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using 15-eV ionization. Spectra are reported based on ^{35}Cl, ^{56}Fe, ^{79}Br, ^{92}Mo, and ^{185}Re. The relative intensities of the

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(33) Richmond, T. G.; Crespi, A. M.; Shriver, D. F., following paper in this issue.

(34) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1.

(35) Noack, K.; Schaerer, U.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *8*, 517–526.

(36) Kaesz, H. D.; King, R. B.; Stone, F. G. A. *Z. Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1960**, *15B*, 763–764.

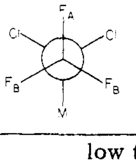
(37) Jolly, P. W.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5830–5837.

(38) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 38–43.

(39) Shriver, D. F. "Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

Table IV. Variable-Temperature ^{19}F NMR Data for MCX_2CF_3 Complexes in $(CD_3)_2CO$

compd	high temperature		
	T, °C	δ	$\nu_{1/2}$, Hz
$Re(CO)_5CF_2CF_3$	26	−83.78[a]	<1
$Re(CO)_5CCl_2CF_3$	64	−77.5	16
	28	−77.5	85
$Re(CO)_5CBr_2CF_3$	66	−70.4	7
	24	−70.4	44
$Mn(CO)_5CCl_2CF_3$	56	−72.9	26
	26	−72.9	92
$CpMo(CO)_3CCl_2CF_3$	20	−71.24	<1



compd	low temperature				
	T_c,[b] °C	T, °C	δ_A[c]	δ_B[c]	$^2J_{AB}$, Hz
$Re(CO)_5CF_2CF_3$	−90	d			
$Re(CO)_5CCl_2CF_3$	0	−85	−87.67	−72.62	103.2
$Re(CO)_5CBr_2CF_3$	4	−84	−74.60	−68.30	102.7
$Mn(CO)_5CCl_2CF_3$	7	−84	−81.10	−68.83	104.4
$CpMo(CO)_3CCl_2CF_3$	−69	−94[d]	−79[e]	−68[e]	

[a] Triplet, J = 1.8 Hz. [b] Coalescence temperature; estimated uncertainty ±2 °C. [c] Integrated intensity of δ_A multiplet to δ_B multiplet is 1:2. [d] Low-temperature limiting spectrum not attained. [e] Approximate chemical shifts.

peaks corresponding to each isotopomer were calculated on the basis of natural isotopic abundances of each of the above atoms. In all cases, the observed and calculated relative intensities of the isotopic envelopes were in good agreement. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of α-Haloalkyl Complexes. Halogen-exchange reactions were generally carried out by condensing (−196 °C) 1 equiv of BX_3 (quantified by PVT measurements) onto a frozen CH_2Cl_2 solution of the fluoroalkyl starting material. Reactions proceeded rapidly (<5 min) to completion upon warming the solution to room temperature. The boron trifluoride formed was removed on the vacuum line and identified by its gas-phase IR spectrum. Exchange reactions were quantitative and complete disappearance of the infrared bands assigned to the α-C–F stretches (ca. 950–1100 cm^{-1}) was observed in the solution infrared spectrum. Removal of the solvent under vacuum followed by sublimation or extraction with and recrystallization from pentane at −78 °C afforded analytically pure product. Details of selected preparations and characterization of the complexes are given below. Solution IR and NMR spectroscopic data are collected in Tables I through IV.

$Mn(CO)_5CCl_3$. A flask was charged with 0.50 g (1.89 mol) of $Mn(CO)_5CF_3$ and 10 mL of CH_2Cl_2. Boron trichloride (2.46 mmol) was condensed into the flask. A bright orange intermediate was observed at −78 °C that disappeared when the solution was warmed to room temperature. Boron trifluoride and CH_2Cl_2 were removed under vacuum, and sublimation under static vacuum (ca. 10^{-3} torr) at 50 °C onto a cold water probe afforded 0.54 g (1.72 mmol, 91% yield) of $Mn(CO)_5CCl_3$ as white crystals: mass spectrum, m/e (assignment, relative intensity) 312 (M^+, 1.4), 284 (M^+ − CO, 4.3), 277 (M^+ − Cl, 18.6), 256 (M^+ − 2CO, 2.4), 249 (M^+ − Cl − CO, 5.3), 228 (M^+ − 3CO, 9.3), 200 (M^+ − 4CO, 8.7), 195 (M^+ − CCl_3, 100). Anal. Calcd for $C_6Cl_3MnO_5$: C, 23.00; Cl, 33.95. Found: C, 23.12; Cl, 33.75.

$Mn(CO)_5CHCl_2$. Reaction of 0.115 g (0.518 mmol) of $Mn(CO)_5CHF_2$ with 0.49 mmol of BCl_3 and workup as for $Mn(CO)_5CCl_3$ gave 0.104 g (0.373 mmol) of colorless crystalline $Mn(CO)_5CHCl_2$ in 72% yield: ^{1}H NMR ($(CD_3)_2CO$) δ 6.62 (s). Anal. Calcd for $C_6H_2ClMnO_5$: C, 25.84; H, 0.36; Cl, 25.42. Found: C, 25.90; H, 0.33; Cl, 25.69.

$Mn(CO)_5CH_2Cl$. Reaction of 0.104 g (0.477 mmol) of $Mn(CO)_5CH_2F$ with 0.48 mmol of BCl_3 and workup as for $Mn(CO)_5CCl_3$ gave 0.090 g (0.369 mmol, 77% yield) of $Mn(CO)_5CH_2Cl$ as pale yellow crystals: ^{1}H NMR ($(CD_3)_2CO$) δ 3.66 (s); mass spectrum, m/e (assignment, relative intensity) 244 (M^+, 1.0), 216 (M^+ − CO, 100), 209 (M^+ − Cl, 3.9), 195 (M^+ − CH_2Cl, 33.4), 188 (M^+ − 2CO, 36.9), 160 (M^+ − 3CO, 64.0). Anal. Calcd for $C_6H_2ClMnO_5$: C, 29.48; H, 0.82; Cl, 14.50. Found: C, 29.45; H, 0.79; Cl, 14.34.

$Mn(CO)_5CBr_3$. Reaction of $Mn(CO)_5CF_3$ with 1 equiv of BBr_3 affords thermally unstable solutions of $Mn(CO)_5CBr_3$. Decomposition of a hexane solution is complete in ca. 1 day at room temperature. The white solid isolated by evaporation of a pentane solution of this complex is stable for several days at room temperature under nitrogen: mass spectrum, m/e (assignment, relative intensity) 444 (M^+, 0.3), 416 (M^+ − CO, 1.0), 388 (M^+ − 2CO, 4.1), 365 (M^+ − Br, 8.2), 360 (M^+ − 3CO, 17.7), 195 (M^+ − CBr_3, 100).

$Mn(CO)_5CHBr_2$. The reaction of $Mn(CO)_5CHF_2$ with BBr_3 in hexane, followed by removal of volatiles under vacuum, results in a fine white solid, which is formulated as $Mn(CO)_5CHBr_2$: ^{1}H NMR ($(CD_3)_2CO$) δ 6.32, (C_6D_6) 5.55.

$Mn(CO)_5CH_2Br$. Boron tribromide (0.30 mmol) was condensed onto a frozen CH_2Cl_2 solution containing 0.12 g (0.53 mmol) of $Mn(CO)_5CH_2F$. Sublimation at 40 °C afforded 0.12 g (0.42 mmol, 79% yield) of yellow crystalline product: ^{1}H NMR ($(CD_3)_2CO$) δ 3.29 (s); mass spectrum, m/e (assignment, relative intensity) 288 (M^+, 1.1), 260 (M^+ − CO, 78.2), 232 (M^+ − 2CO, 26.8), 209 (M^+ − Br, 21.3), 204 (M^+ − 3CO, 53.6), 195 (M^+ − CH_2Br, 5.1). Anal. Calcd for $C_6H_2BrMnO_5$: C, 24.94; H, 0.70; Br, 27.66. Found: C, 24.80; H, 0.77; Br, 27.87.

$Mn(CO)_5CI_3$. A solution of $Mn(CO)_5CI_3$ was prepared by reacting 0.059 g (0.16 mmol) of BI_3 with 0.025 g (0.095 mmol) of $Mn(CO)_5CF_3$ in 10 mL of hexane at −30 °C. Reaction occurred as the solution was warmed to room temperature, and the BF_3 released from the reaction mixture was identified by its gas-phase IR spectrum. An IR spectrum of the solution showed complete loss of the C–F bands (1057, 1028 cm^{-1}) of the starting material. The intensity of the carbonyl bands of the product (Table I) disappeared over the course of 1 h at room temperature. The violet color of the solution was similar to that of I_2 in hexane. Carbonyl infrared bands of similar intensity to those of $Mn(CO)_5CI_3$ were also observed at 2131 (w), 2040 (vs), and 2009 (m) cm^{-1} and assigned to $Mn(CO)_5I$.[40]

$Mn(CO)_5CCl_2CF_3$. A large excess of BCl_3 (2.9 mmol) was reacted with ca. 0.30 g (0.95 mmol) of $Mn(CO)_5C_2F_5$ (this compound is an oil at room temperature) in 20 mL of CH_2Cl_2. The product (0.2 g) was isolated as a waxy off-white solid by sublimation at 40 °C. Anal. Calcd for $C_7Cl_2F_3MnO_5$: C, 24.24; Cl, 20.44; F, 16.34. Found: C, 24.27; Cl, 20.18; F, 16.70.

$Re(CO)_5CCl_2CF_3$. Reaction of 0.128 g (0.29 mmol) of $Re(CO)_5C_2F_5$ with 0.31 mmol of BCl_3 in 5 mL of CH_2Cl_2 gave 0.11 g (0.23 mmol, 80% yield) of product after sublimation at 50 °C: mass spectrum, m/e (assignment, relative intensity) 476 (M^+, 1.8), 441 (M^+ − Cl, 5.2), 413 (M^+ − Cl − CO, 0.3), 385 (M^+ − Cl − 2CO, 2.3), 357 (M^+ − Cl − 3CO, 8.6), 325 (M^+ − CCl_2CF_3, 59.9). Anal. Calcd for $C_7F_3Cl_2O_5Re$: C, 17.58; F, 11.92; Cl, 14.83. Found: C, 17.48; F, 12.10; Cl, 15.04.

$Re(CO)_5CFCF_2$ + BCl_3. In 10 mL of CH_2Cl_2, 0.040 g (0.098 mmol) of $Re(CO)_5CFCF_2$ was treated with 0.09 mmol of BCl_3. Boron trifluoride was detected in the gas-phase IR spectrum as was unreacted BCl_3. The solution IR spectrum shows carbonyl bands at 2147 (w), 2036 (s), and 2008 (m, br) cm^{-1} assigned to $Re(CO)_5C_2ClF_2$ and 2154 (vw), 2045 (s), and 2004 (m, br) cm^{-1} assigned to $Re(CO)_5Cl$.[41] A new C–C stretch is observed at 1689 (w) cm^{-1}. Attempts to observe the ^{19}F NMR spectrum of this complex were frustrated by Re–C bond cleavage to afford $Re(CO)_5Cl$. The solid obtained by evaporation of the CH_2Cl_2 solution was analyzed by mass spectroscopy and found to contain $Re(CO)_5Cl$ and $Re(CO)_5C_2ClF_2$: mass spectrum (70 eV), m/e (assignment, relative intensity) 422 (M^+, 17.1), 394 (M^+ − CO, 8.3), 366 (M^+ − 2CO, 13.6), 338 (M^+ − 3CO, 36.6), 310 (M^+ − 4CO, 46.5), 282 (M^+ − 5CO, 49.2), 247 (M^+ − 5CO − Cl, 29.6), 232 (M^+ − 5CO − CF_2, 17.3), 197 (M^+ − 5CO − CF_2Cl, 27.3), 185 (M^+ − 5CO − C_2ClF_2, 31.4).

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(40) Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 161–163.
(41) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844–2851.

$CpFe(CO)_2CCl_3$. A CH_2Cl_2 solution (25 mL) containing 0.47 g (1.97 mmol) of $CpFe(CO)_2CF_3$ was treated with 1.98 mmol of BCl_3. While the solution was warmed to room temperature, BF_3 was removed from the system by occasionally opening the flask to the vacuum line. After 5 min at room temperature, CH_2Cl_2 was removed under vacuum and the product extracted (4 × 25 mL) with pentane. Yellow crystalline product (0.40 g, 1.4 mmol, 71% yield) was obtained when the pentane solution was cooled to −78 °C. Although the solid appeared to be reasonably stable for about 1 week at room temperature, impure samples and solutions darkened over the course of several days and HCl evolution was detected by gas-phase IR spectroscopy. An alternative synthesis involved reaction of $CpFe(CO)_2CF_3$ with 2 equiv of $SiCl_4$ for 12 h, and the product was isolated as described above. Silicon tetrafluoride was detected by its gas-phase IR spectrum:[42] ^{13}C NMR ($CDCl_3$, −40 °C) δ 212.7 (s, CO), 107.6 (s, CCl_3), 88.5 (d, J = 183 Hz, Cp); mass spectrum, m/e (assignment, relative intensity) 294 (M^+, 2.1), 266 ($M^+ - CO$, 24.5), 259 ($M^+ - Cl$, 22.9), 238 ($M^+ - 2CO$, 28.4), 177 ($M^+ - CCl_3$, 29.1), 112 (C_6H_5Cl, 100).

$CpFe(CO)_2CBr_3$. This complex was prepared from $CpFe(CO)_2CF_3$ and BBr_3 by using the procedure given for $CpFe(CO)_2CCl_3$: mass spectrum, m/e (assignment, relative intensity) 426 (M^+, 0.3), 398 ($M^+ - CO$, 4.6), 370 ($M^+ - 2CO$, 8.8), 347 ($M^+ - Br$, 9.9), 319 ($M^+ - CO - Br$, 3.1), 177 ($M^+ - CBr_3$, 9.2), 156 (C_6H_5Br, 45.5).

$CpMo(CO)_3CCl_3$. In 10 mL of CH_2Cl_2, 0.10 g (0.32 mmol) of $CpMo(CO)_3CF_3$ was treated with 0.369 mmol of BCl_3. The solvent was removed under vacuum, and yellow crystalline $CpMo(CO)_3CCl_3$ (0.085 g, 0.27 mmol, 84% yield) was isolated by cooling the pentane extracts from the reaction mixture to −78 °C. The mass spectrum showed a very weak parent ion, but the calculated and observed intensities for the ion $[CpMo(CO)_3CCl_3 - 2CO]^+$ were in good agreement.

$CpMo(CO)_3CCl_2R$ ($R = CF_3$ or C_2F_5). These complexes were synthesized in a similar manner to $CpMo(CO)_3CCl_3$ and isolated by crystallization from pentane at −78 °C. The observed and calculated mass spectra for $CpMo(CO)_3CCl_2R$ were in good agreement: ^{19}F NMR ($R = C_2F_5$, $(CD_3)_2CO$) δ −71.79 (s, 3, CF_3), −96.61 (s, 2, CF_2). Both singlets are slightly broadened because of unresolved coupling ($^3J_{FF} < 2$ Hz).

$CpFe(CO)_2CF_3 + B_2H_6$. Diborane (0.30 mmol) was condensed into a flask containing 0.062 g (0.25 mmol) of $CpFe(CO)_2CF_3$ and 5 mL of CH_2Cl_2. A deep red color rapidly developed when the flask was warmed to room temperature, and after 5 min the volatiles were removed under vacuum. The gas-phase IR spectrum shows characteristic B–F stretches at 1463, 1415, and 1362 cm^{-1}. The solid residue was redissolved in CH_2Cl_2, and the IR spectrum showed peaks assigned to $CpFe(CO)_2Me$ (2006 (s), 1946 (s) cm^{-1}),[34] $[CpFe(CO)_2]_2$ (1999 (s), 1955 (s), 177 4 (m) cm^{-1}),[34] and an unknown product (2126 (w), 2066 (s), 2043 (s) cm^{-1}). The identity of $CpFe(CO)_2Me$ was confirmed by ^1H NMR spectroscopy (($(CD_3)_2CO$) δ 4.90 (s, 5, Cp), 0.10 (s, 3, Me)), and the mole ratio of $[CpFe(CO)_2]_2/CpFe(CO)_2Me$ was 2.4/1 on the basis of integration of the NMR spectrum. A similar CH_2Cl_2 solution containing $CpFe(CO)_2CF_3$ and B_2H_6 was allowed to react for 1 h, and $[CpFe(CO)_2]$ was the only metal carbonyl product identified in the reaction mixture.

Results

Synthesis of α-Halomethyl Complexes. Treatment of the appropriate α-fluoromethyl complex with 1 equiv of BX_3 in a noncoordinating solvent results in rapid and quantitative halogen exchange to afford $Mn(CO)_5CH_nX_{3-n}$ (X = Cl, Br, I) (eq 9). Boron trifluoride is evolved from the reaction mixture and identified by its gas-phase IR spectrum. As detailed in the Experimental Section, evaporation of solvent from the reaction mixture and sublimation under static vacuum at 40–80 °C afford the desired complexes in high yield (Table I). A yellow-orange intermediate that is only partially soluble in CH_2Cl_2 forms when $Mn(CO)_5CF_3$ and BCl_3 are mixed at low temperature (ca. −78 °C). However, the color completely disappears when the solution is warmed to room temperature. Although hydrocarbon solvents are suitable for the exchange reaction, CH_2Cl_2 is preferred because of the relatively high solubility of the fluoromethyl starting materials and ease of solvent removal. Halogen exchange between $Mn(CO)_5CF_3$ and BCl_3 takes place slowly in Et_2O. Although a boron/manganese ratio of 1 was normally used in the preparation of the monohalomethyl complexes, complete reaction takes place even if this ratio is reduced to $^1/_3$.

$$Mn(CO)_5CH_nF_{3-n} + BX_3 \rightarrow Mn(CO)_5CH_nX_{3-n} + BF_{3-n}X_n \quad (9)$$

$$n = 0, 1, 2$$

The new complexes generally exhibit higher solubility in hydrocarbon solvents (e.g., pentane) than their fluorinated precursors. The thermal stability of the complexes decreases with increasing halogen content or with higher molecular weight halogens. Thus, $Mn(CO)_5CF_3$ is indefinitely stable in air, but $Mn(CO)_5CCl_3$ (although stable at room temperature under nitrogen) begins to yellow after several days in air and $Mn(CO)_5Cl$ is detected as a decomposition product. Similarly, $Mn(CO)_5Cl$ is also produced from $Mn(CO)_5CCl_3$ in refluxing benzene under N_2. Solutions of $Mn(CO)_5CBr_3$ decompose in 1–2 days at room temperature, but no decomposition is detected in solid samples over the same time period. Finally, $Mn(CO)_5CI_3$ is quite unstable and decomposes within 1 h after preparation to afford some $Mn(CO)_5I$ and the violet color of the solution suggests that I_2 is also present. It should be noted that in the synthesis of $Mn(CO)_5CI_3$ in solution, $Mn(CO)_5I$ is concurrently formed presumably by Mn–C bond cleavage by BI_3. Because of its instability, $Mn(CO)_5CI_3$ was characterized only by infrared spectroscopy and the detection of BF_3 gas evolution from the reaction mixture. The dihalomethyl and monohalomethyl complexes exhibit greater thermal stability than the trihalomethyl complexes. Thus the complete series of monohalomethyl complexes $Mn(CO)_5CH_2X$ (X = F, Cl,[43] Br, I[44]) have now been isolated as crystalline solids. The trihalomethyl compounds are subject to further electrophilic exchange, and this provides an alternative route to $Mn(CO)_5CBr_3$ (eq 10).

$$Mn(CO)_5CCl_3 + BBr_3 \rightarrow Mn(CO)_5CBr_3 + BCl_3 \quad (10)$$

Characterization of the new complexes was accomplished by IR and NMR spectroscopic methods as well as by mass spectroscopy and elemental analysis. The IR spectra in the carbonyl stretching region (Table I) show the typical four band pattern for octahedral C_{4v} $M(CO)_5R$ complexes.[45] The frequencies of the IR bands are nearly coincident with those of the fluoromethyl starting materials, but the relative intensity of the highest frequency (A_1) band increases with the increasing molecular weight of the halogen. These trends are also observed in the IR spectra of $Mn(CO)_5M'X_3$ (M′ = Si, Ge, Sn) complexes.[46] Exchange of the fluorine atoms is also evidenced by the complete disappearance of the C–F stretching bands of the fluoromethyl starting materials. These are replaced by new C–Cl stretches as illustrated in Figure 1. Similar spectroscopic changes are observed for the mono- and dihalomethyl complexes.

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(42) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 135.

(43) Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221–227.

(44) Brinkman, K. C.; Vaughn, G. P.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056–1060.

(45) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: London 1975.

(46) Onaka, S. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1721–1724.

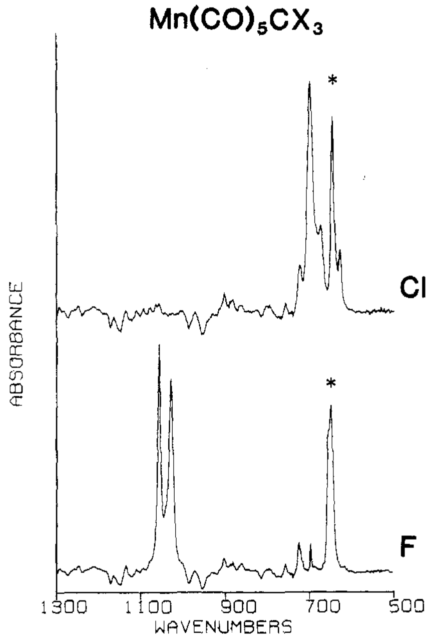

Figure 1. Infrared spectra of $Mn(CO)_5CF_3$ (lower trace) and $Mn(CO)_5CCl_3$ (upper trace) from 1300 to 500 cm^{-1} in hexane solution. The peak marked with an asterisk is assigned to Mn–CO vibrations.

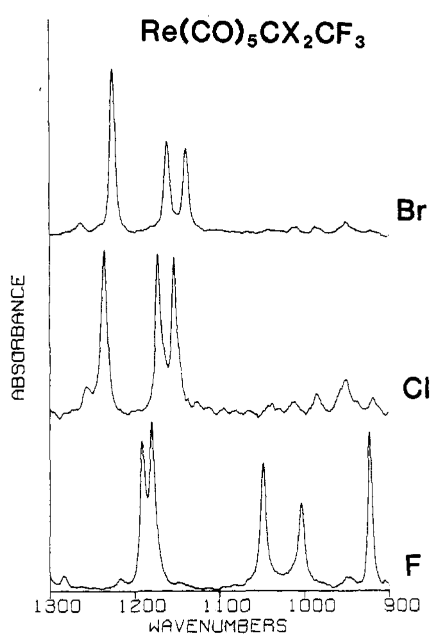

Figure 2. Infrared spectra of $Re(CO)_5CX_2CF_3$ (X = F, Cl, Br) in the carbon–fluorine stretching region in hexane solution.

Replacement of F by Cl or Br is also accompanied by loss of proton–fluorine coupling in the ^1H NMR spectra of the new complexes (see Experimental Section). Elemental analyses (C, H, X) were obtained for $Mn(CO)_5R$ (R = CCl_3, $CHCl_2$, CH_2Cl, and CH_2Br) and are in excellent agreement with the calculated values. Mass spectra of the other complexes gave parent ions with the appropriate isotopic cluster patterns. Peaks corresponding to loss of CO and halogen are observed.

Trihalomethyl complexes are also readily prepared from reaction of $CpMo(CO)_3CF_3$ or $CpFe(CO)_2CF_3$ with BX_3. Complete loss of the C–F stretching bands is observed by infrared spectroscopy, and BF_3 gas evolves from the reaction mixture. The new complexes can be isolated in good yield by crystallization from pentane at –78 °C and were characterized by their IR spectra in the carbonyl stretching region and by the singlets assigned to the Cp group in their ^1H NMR spectra (Table II). Mass spectra (see Experimental Section) confirmed the identity of the new complexes. As will be discussed in the following paper, further reaction of $CpFe(CO)_2CCl_3$ with BCl_3 occurs to afford $[CpFe(CO)_2(CCl_2)][BCl_4]$.[33] Indeed this latter reaction is so facile that small quantities of this salt (which are readily removed in the pentane crystallization process) are usually obtained in the preparation of $CpFe(CO)_2CCl_3$. Both the Mo and Fe complexes are thermally sensitive in solution and in the solid state so elemental analyses could not be obtained. Although the complexes can be sublimed at 80–100 °C under dynamic high vacuum, some decomposition occurs under these conditions. Hydrocarbon solutions decompose within 1 h at 60 °C evolving HCl gas.a No carbonyl stretching bands are observed in the IR spectrum of the black decomposition products.

Characterization of MCX_2R (R = CF_3, C_2F_5) Complexes. Regioselective replacement of the α-fluorines is observed when $Mn(CO)_5C_2F_5$, $Re(CO)_5C_2F_5$, $CpMo(CO)_3C_2F_5$, or $CpMo(CO)_3(n\text{-}C_3F_7)$ are treated with BX_3. Rapid, quantitative exchange occurs accompanied by BF_3 gas evolution. The infrared and ^1H NMR spectra of these complexes are collected in Table III, and the ^{19}F NMR parameters are given in Table IV. For $Mn(CO)_5CCl_2CF_3$ and $Re(CO)_5CCl_2CF_3$, elemental analyses (C, Cl, F) are consistent with the proposed stoichiometries. In addition, the mass spectra of all the complexes indicates replacement of only two fluorine atoms by chlorine or bromine. Further fluroine exchange does not take place when these complexes are treated with excess (2–5 equiv) BCl_3 at room temperature.

Analysis of the infrared spectra in the carbon–fluorine stretching region shows that the halogen exchange reaction is α-regioselective. The infrared spectra of $Re(CO)_5CX_2CF_3$ (X = F, Cl, Br) are reproduced in Figure 2. Complete disappearance of the low-energy bands that are assigned[6] to the α-CF_2 group are observed. The higher frequency bands assigned to the trifluoromethyl group undergo only a slight perturbation.

Interpretation of the ^{19}F NMR spectra of these complexes confirms that the reaction is α-regiospecific. In the case of $CpMo(CO)_3CCl_2CF_2CF_3$, only two ^{19}F NMR resonances are observed in the expected 3:2 intensity ratio. Importantly, the fluorine-fluorine coupling constant is less than 2 Hz which is typical for a perfluoroethyl group.[47] The alternative formulation $CpMo(CO)_3CF_2CCl_2CF_3$ would be expected to exhibit a F–F coupling constant on the order of 10 Hz which is normally observed for $^4J_{FF}$ in fluoropropanes.[47] Extraneous peaks indicative of random fluorine replacement are not detected in the ^{19}F NMR spectrum. The substituted ethyl complexes $M\text{–}CX_2CF_3$ exhibit temperature-dependent ^{19}F NMR spectra as shown in Figures 3 and 5. The chemical shift and coupling constant data derived from these spectra are given in Table IV. Analysis of the spectra obtained for $Re(CO)_5CX_2CF_3$ will be considered in detail. A single broad resonance is observed for $Re(CO)_5CBr_2CF_3$ (Figure 3) at room temperature which sharpens on warming the sample to 66 °C. Cooling the solution reverses this change and the signal coalesces at 4 °C. As the temperature of the sample is further reduced, new signals grow in and the low-temperature limiting spectrum at –84 °C is an AB_2 pattern. Integration of the low-temperature spectrum gives a 2:1 intensity ratio between the two groups of resonances. This

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[47] Brügel, W. "Handbook of NMR Spectral Parameters"; Hayden: London, 1979; pp 750–755.

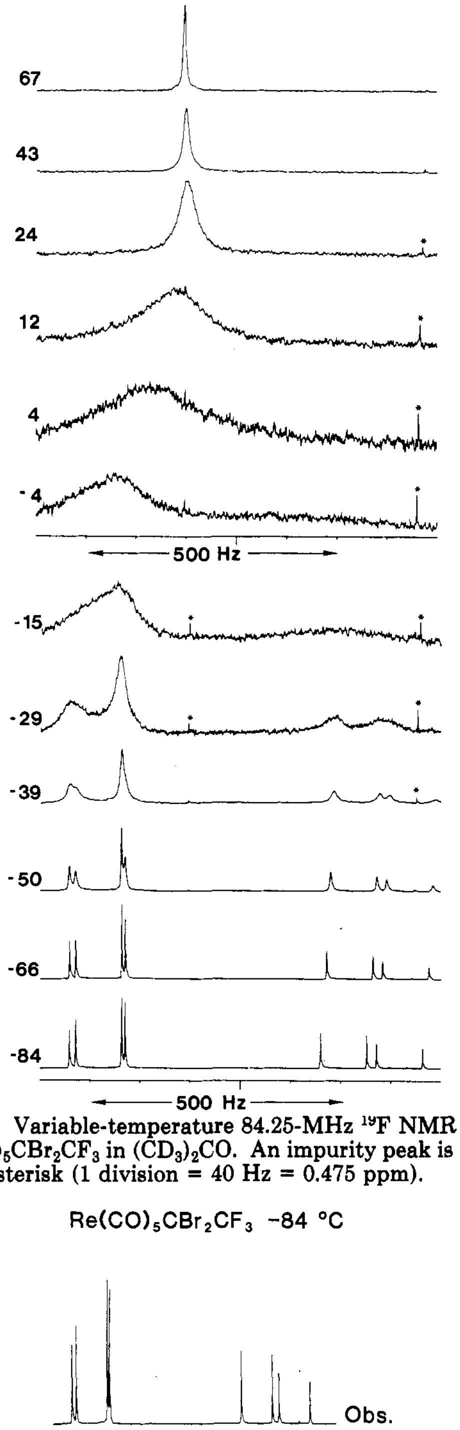


Figure 3. Variable-temperature 84.25-MHz ^{19}F NMR spectra of $Re(CO)_5CBr_2CF_3$ in $(CD_3)_2CO$. An impurity peak is marked with an asterisk (1 division = 40 Hz = 0.475 ppm).

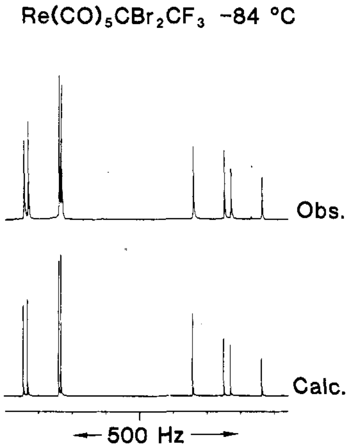


Figure 4. Calculated (lower trace) and observed (upper trace) ^{19}F NMRf spectra of $Re(CO)_5CBr_2CF_3$ in $(CD_3)_2CO$ at -84 °C.

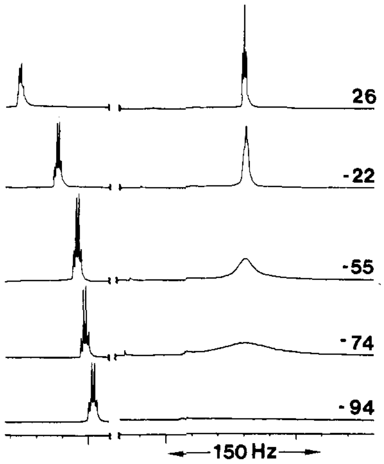


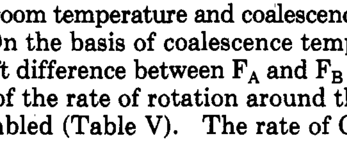
Figure 5. Variable-temperature 84.25-MHz ^{19}F NMR spectra of $Re(CO)_5CF_2CF_3$ in $(CD_3)_2CO$ (1 division = 25 Hz =0.297 ppm).

Table V. Coalescence Temperature and $\Delta G^\ddagger$ Data for C-C Bond Rotation in MCX_2CF_3 Compounds

M	X	T_c, °C	$\Delta G^\ddagger$,[a] kcal/mol
$Re(CO)_5$	Br	4	12.2
$Mn(CO)_5$	Cl	7	12.1
$Re(CO)_5$	Cl	0	11.6
$CpMo(CO)_3$	Cl	−69	8.7[c]
I	Cl	−72	8.5 (8.5)[b]
$Re(CO)_5$	F	−90	7.8[d]
CCl_3	Cl	−139	5.6 (5.6)[b]
I	F	−150	5.1 (5.5)[b]

[a] Approximate $\Delta G^\ddagger$ calculated[50] from $k_c = [\pi/(2)^{1/2}](\Delta\nu^2 + 6J^2)^{1/2}$ and $\Delta G^\ddagger = 2.303RT(10.32 + \log(T_c/k_c))$. [b] Value of $\Delta G^\ddagger$ in parentheses was obtained by complete line-shape analysis as reported in ref 49. [c] Coupling not resolved in low-temperature spectrum; J was assumed to be 100 Hz. [d] Low-temperature spectrum not obtained; $\Delta G^\ddagger$ calculated assuming $\Delta\nu$ = 10 ppm and J = 100 Hz.

assignment is confirmed by the excellent agreement between the experimental and simulated spectra (Figure 4). The geminal F–F coupling constants are similar to those observed in other chlorofluorocarbons.[48,49] The unique fluorine (anti to M) resonates at higher field than the two gauche fluorines.[49] The temperature dependence of the NMR spectra is a consequence of slow carbon–carbon bond rotation on the NMR time scale (eq 11).



(11)

Coalescence is observed at 0 °C for $Re(CO)_5CCl_2CF_3$, and the larger chemical shift difference between F_A and F_B than for $Re(CO)_5CBr_2CF_3$ indicates faster C–C bond rotation in this complex. By way of comparison, $Re(CO)_5CF_2CF_3$ (Figure 5) exhibits a very sharp ^{19}F NMR spectrum at room temperature and coalescence is observed at −90 °C. On the basis of coalescence temperature and chemical shift difference between F_A and F_B (Table IV),[50] an ordering of the rate of rotation around the C–C bond can be assembled (Table V). The rate of C–C bond rotation in these complexes follows the series $Re(CO)_5CBr_2CF_3 \approx Mn(CO)_5CCl_2CF_3 \lesssim Re(CO)_5CCl_2CF_3 < CpMo(CO)_3CCl_2CF_3 < Re(CO)_5CF_2CF_3$.

Reactions of $CpFe(CO)_2CF_3$ with Other Lewis Acids. Excess $SiCl_4$ reacts with $CpFe(CO)_2CF_3$ to afford $CpFe(CO)_2CCl_3$ and SiF_4; no $[CpFe(CO)_2(CCl_2)]^+$ is detected in the reaction mixture. This reaction is slower than

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(48) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 3577–3578.

(49) Weigert, F. J.; Mahler, W. *J. Am. Chem. Soc.* **1972**, *94*, 5314–5318.

(50) Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: London, 1982.

the exchange reaction with BCl_3. Aluminum chloride reacts in a manner analogous to BCl_3 according to eq 12 and 13. Similar behavior is observed for $TiCl_4$. In contrast, when $CpFe(CO)_2CF_3$ is allowed to react with $SnCl_4$ in CH_2Cl_2, an off-white precipitate immediately forms and the mull IR shows the presence of some $[CpFe(CO)_2(CF_2)]^+$ in addition to at least one other metal carbonyl compound.[33] Hydrolysis of the solid affords predominantly $[CpFe(CO)_3]^+$. No exchange is observed when $CpFe(CO)_2CF_3$ is treated with a 10-fold excess of BMe_3. Treatment of $CpFe(CO)_2CF_3$ with B_2H_6 rapidly affords $CpFe(CO)_2Me$. However the methyl complex is unstable in the reaction mixture, and the solution turns deep red and $[CpFe(CO)_2]_2$ is the ultimate metal carbonyl product. No reaction occurs when $Mn(CO)_5CF_3$ is treated with B_2H_6 or BMe_3.

$$CpFe(CO)_2CF_3 + AlCl_3 \rightarrow CpFe(CO)_2CCl_3 + AlF_3 \quad (12)$$

$$CpFe(CO)_2CCl_3 + AlCl_3 \rightarrow [CpFe(CO)_2(CCl_2)][AlCl_4] \quad (13)$$

Other Reactions. Rapid halogen exchange with BF_3 evolution takes place when $Re(CO)_5CFCF_2$ is allowed to react with BCl_3 in CH_2Cl_2 to afford $Re(CO)_5C_2ClF_2$. The exchange is accompanied by formation of $Re(CO)_5Cl$. The infrared spectrum of the product is nearly identical with that of the starting material, but the C=C bond stretch decreases from 1709 to 1689 cm^{-1} upon replacement of F by Cl. On the basis of the reduction in C=C observed upon replacement of fluorine by chlorine in substituted ethylenes, a much larger decrease would be expected if all the fluorines were replaced.[51] The mass spectrum of the product (see Experimental Section), which shows the parent ion and peaks corresponding to sequential loss of five CO ligands with the expected isotopic intensity distribution, is consistent with the proposed formulation, and no $Re(CO)_5CCl{=}CCl_2$ was detected. Although we suspect that the α-fluorine is replaced in this transformation (eq 14), ^{19}F NMR studies that could confirm the regiochemistry of the halogen exchange were unsuccessful because of the instability of the product to Re–C bond cleavage.

$$Re(CO)_5CF{=}CF_2 + BCl_3 \rightarrow Re(CO)_5CCl{=}CF_2 + BCl_2F \quad (14)$$

The perfluorophenyl complex $CpFe(CO)_2C_6F_5$ is recovered unchanged following treatment with excess BCl_3 at 80 °C. This complex reacts with $AlBr_3$ in CH_2Cl_2 to afford $CpFe(CO)_2AlBr_4$ (ν_{CO} = 2076 (s), 2034 (s) cm^{-1})[52] as identified by its IR spectrum and presumably $AlBr_2C_6F_5$. Similarly, no exchange takes place between BCl_3 and $Mn(CO)_5C(O)CF_3$. In contrast to transition-metal trihalomethyl complexes, BCl_3 is not detected when $PhHgCCl_3$ is treated with BBr_3. Rather, alkyl group exchange reactions appear to take place.

Discussion

Facile halogen exchange takes place when transition-metal perfluoroalkyl complexes are treated with boron trihalides. This mild synthetic procedure, with volatile BF_3 as the only byproduct, enables isolation of thermally sensitive α-haloalkyl (X = Cl, Br, I) complexes in high yield. It should be noted that α-chloromethyl complexes are not accessible by thermal or photochemical decarbonylation of chloroacetyl precursors.[53] The electronic structures of the new complexes must be quite similar to that of their respective parent complexes since the carbonyl stretching frequencies are nearly identical within a given series of compounds. The halogen exchange reaction is thermodynamically favored because of the great strength of the B–F bond in the BF_3 produced.[54-57] Similar considerations show, in agreement with the experimental results, that halogen exchange with $AlCl_3$, $SiCl_4$, $TiCl_4$, and B_2H_6 is also thermodynamically allowed. Exchange of H by X with the concomitant formation of B_2H_6 is thermodynamically unfavorable and is not observed.[55-57] Of the metal halides studied, only $SnCl_4$ failed to undergo halide exchange with $CpFe(CO)_2CF_3$. Rather, the predominant product formed (2) arises simply from halide abstraction. This may be a consequence of the greater stability of higher coordination numbers with the large Sn atom compared to the other metalhalides investigated. The ability of the Lewis acid to shuttle between coordination numbers is apparently necessary for halogen exchange to occur. However, exchange would also be expected for BMe_3 which is contrary to the experimental result. Thus, the strength of the Lewis acid may be important in allowing the exchange reaction to take place. Furthermore, electrophilic fluoride replacement is expected to be thermodynamically favorable for nearly all C–F bonds. Thus the selectivity of the halogen exchange reaction cannot be explained on thermodynamic grounds alone.

$$[CpFe(CO)_2(CF_2)^+]_2[SnCl_4F_2]^{2-}$$

2

Regioselectivity of Halogen Exchange. Regioselective fluoride replacement occurs exclusively at the α-position of the perfluoroalkyl ligand in the compounds investigated (Table III; eq 15). Importantly, no exchange is observed when $CpFe(CO)_2C_6F_5$ or $Mn(CO)_5C(O)CF_3$ is allowed to react with BCl_3. This selectivity is remarkable in light of the strong thermodynamic preference for replacement of all of the fluorines. The apparent weakness of the α-C–F bond may be responsible in part for the selectivity observed. However, the energy difference between the α- and β-C–F bonds is probably small compared to the overall thermodynamic driving force for the exchange process. Thus it appears that kinetic factors are responsible for the regioselectivity of the halogen exchange reaction. In this regard the similarity to organic systems (eq 5, 6) should be noted. Fluorine replacement at benzylic or allylic positions occurs much more readily and selectively than in saturated systems.[25-28] Stabilization of the positive charge in the presumed carbocation intermediates is apparently necessary for facile halide abstraction and exchange. The isolation of several stable dihalocarbene complexes prepared by halide abstraction from metal trihalomethyl complexes suggests that this is a plausible pathway for halogen exchange.[33]

$$M{-}CF_2CF_3 + BCl_3 \rightarrow M{-}CCl_2CF_3 + BCl_2F \quad (15)$$

Mechanism of Halogen Exchange. The ability of the trifluoromethyl group to form a carbene ligand by electrophilic halide abstraction[16,33] suggests that this is a reasonable pathway for halogen exchange (eq 16–18).

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(51) Mann, D. E.; Fano, L.; Meal, J. H.; Shimanouchi, T. *J. Chem. Phys.* **1957**, *27*, 51–59.

(52) Pankowski, M.; Demerseman, B.; Borquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1972**, *35*, 51–59.

(53) Dilgassa, M.; Curtis, M. D. *J. Organomet. Chem.* **1979**, *172*, 177–184.

(54) Muetterties, E. L. "The Chemistry of Boron and Its Compounds"; Wiley: New York, 1967; pp 13–14.

(55) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Inorganic Compounds"; Academic Press: New York, 1970.

(56) Barin, I.; Knacke, O. "Thermochemical Properties of Inorganic Substances"; Springer-Verlag: Berlin, 1973.

(57) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1971, *37*.

$$\mathrm{M{-}CF_3 + BX_3 \rightarrow [M{=}CF_2]^+[F{-}BX_3]^-} \quad (16)$$

$$\mathrm{[M{=}CF_2]^+[F{-}BX_3]^- \rightarrow [M{=}CF_2]^+[X{-}BFX_2]^-} \quad (17)$$

$$\mathrm{[M{=}CF_2]^+[X{-}BFX_2]^- \rightarrow M{-}CF_2X + BFX_2} \quad (18)$$

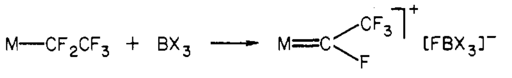
Further repetitions of this sequence results in complete replacement of F by X. On the basis of the thermodynamics of the reaction, the final step (eq 18) should be irreversible. A similar mechanism has been proposed to explain the fluorination of the trichlorosilyl ligand by $AgBF_4$ (eq 19).[58] A silylene intermediate was postulated

$$\mathrm{CpFe(CO)_2SiCl_3 + 3AgBF_4 \rightarrow CpFe(CO)_2SiF_3 + 3BF_3 + 3AgCl} \quad (19)$$

in this transformation (eq 20). This mechanism provides

$$\mathrm{CpFe(CO)_2SiCl_3 + AgBF_4 \rightarrow [CpFe(CO)_2(SiCl_2)][BF_4] + AgCl} \quad (20)$$

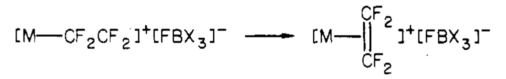
a basis for the α-regiochemistry of the reaction (eq 21).



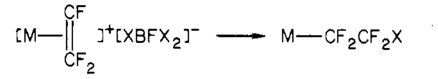
$$\mathrm{M{-}CF_2CF_3 + BX_3 \longrightarrow \left[M{=}C{\begin{smallmatrix}CF_3\\F\end{smallmatrix}}\right]^+[FBX_3]^-} \quad (21)$$

The cationic carbene intermediate is stabilized by π-bonding to the transition metal center. Electrophilic attack at the β-position would yield an unstabilized carbonium ion (eq 22), and this complex might be expected to rearrange to an olefin complex (eq 23). The metal carbonyl systems under investigation are known to form stable olefin complexes as depicted in eq 23 for nonfluorinated olefins.[59] Even if the olefin formation is reversible (eq 24), the halogen exchange would occur in the β-position. Additionally, the symmetrical olefin intermediate in eq 23 would lead to loss of selectivity in further exchange cycles. The greater reactivity of $CpFe(CO)_2CF_3$ compound compared with $Mn(CO)_5CF_3$ on treatment with B_2H_6 parallels the greater propensity of the iron complex to stabilize a dihalocarbene ligand. It is difficult to rule out a concerted mechanism as illustrated in **3**. The role of the metal in stabilizing such a transition state is not obvious, but the longer α-C–F bonds in transition-metal carbonyl complexes may facilitate such an arrangement.

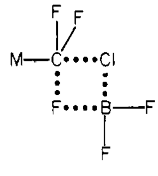
$$\mathrm{M{-}CF_2CF_3 + BX_3 \rightarrow [M{-}CF_2CF_2]^+[FBX_3]^-} \quad (22)$$



$$\mathrm{[M{-}CF_2CF_2]^+[FBX_3]^- \longrightarrow \left[M{-}\begin{smallmatrix}CF_2\\\Vert\\CF_2\end{smallmatrix}\right]^+[FBX_3]^-} \quad (23)$$

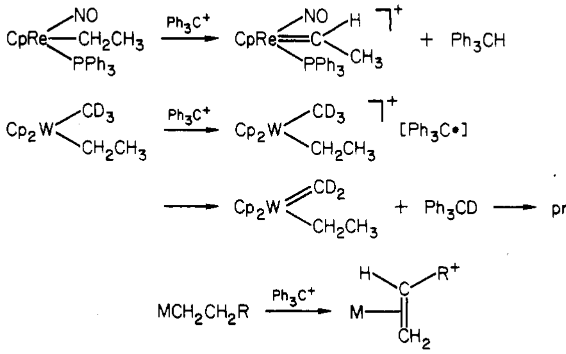


$$\mathrm{\left[M{-}\begin{smallmatrix}CF\\\Vert\\CF_2\end{smallmatrix}\right]^+[XBFX_2]^- \longrightarrow M{-}CF_2CF_2X} \quad (24)$$



3

α-Regiochemistry has recently been demonstrated in a number of reactions involving hydride abstraction by the trityl cation (eq 25, 26). This contrasts with the β-hydride abstraction usually observed with this reagent to yield metal olefin complexes (eq 27). In the $Cp_2W(CD_3)(C_2H_5)$ system detailed investigations indicate that electron transfer takes place prior to hydride abstraction and it has been suggested that prior electron transfer is uniquely associated with α-hydride loss.[60,61] However, in the present systems involving BX_3 and perfluoroalkyl ligands, electron transfer does not seem likely. Rather, stabilization of the cationic carbene intermediate by π-bonding to the transition-metal center appears to be crucial in directing the regiochemistry of this transformation. In the case of $Re(CO)_5CFCF_2$, exchange may take place through a cationic vinylidene[62] intermediate $[Re(CO)_5C{=}CF_2]^+$. Interestingly, no halogen exchange is observed when $HgPhCCl_3$ is treated with BBr_3. Other workers have noted that reactions of $HgPhCCl_3$ with silicon halides results in redistribution reactions of the Hg–C bonds with SiX_4.[63]



(25)[60]

(26)[61]

(27)[60]

Hindered C–C Bond Rotation in MCX_2CF_3. Rotation about the C–C single bond of the substituted ethyl group in several of the new complexes is extremely slow. Coalescence temperatures and approximate free energies of activation for this process in the complexes studied and in several organic analogues are collected in Table V. Complete line-shape analysis of the experimental data was not undertaken because we felt that it would add little to the qualitative conclusions obtained from an approximate treatment of the data. The computed $\Delta G^{\ddagger}$ based on the formula[50,64] given in Table V are in reasonable agreement with those derived from a complete line-shape analysis for ICF_2CF_3, $ICCl_2CF_3$, and $CCl_3CCl_2CF_3$.[49] As expected by comparison with organic systems, the ease of C–C bond rotation in the transition-metal systems decreases with increasing molecular weight of the halogen substituent X.[50,64] Thus replacement of F by Cl or Br results in a 4 kcal/mol increase in the rotation barrier. The dramatic effect of the metal carbonyl group $M'(CO)_5$ (M′ = Mn, Re) in raising the barrier to C–C bond rotation is evident from the data in Table V. For example, the barrier to rotation increases by 4 kcal/mol when M is changed from I to $Re(CO)_5$ in the MCX_2CF_3 compounds. The superposition of these two effects results in C–C single bond rotation which is slow on the NMR time scale at room temperature. We attribute this behavior to steric interactions between the CF_3 group and the four equatorial CO ligands in $M'(CO)_5$. Rotation about the C–C bond requires two eclipsed F–Cl interactions, and the unique fluorine is forced into the plane of the cis carbonyl ligands. We have no evidence which suggests that restricted M–C bond rotation takes place in these complexes. NMR relaxation studies indicate that the activation energy for Re–C bond rotation in $Re(CO)_5Me$ is very low.[65] The barrier to Fe–C bond rotation in $CpFe(CO)_2C(SMe)_3$ has been estimated to be ~8.7

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[58] Seyam, A.; Marks, T. J. *Inorg. Chem.* **1974**, *13*, 1624–1627.

[59] Green, M. L. H.; Nagy, P. L. I. *Adv. Organomet. Chem.* **1964**, *2*, 323–363.

[60] Kiel, W.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958–4972.

[61] Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570–5572.

[62] Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635–639.

[63] Weidenbach, M.; Pierrand, C. *Chem. Ber.* **1977**, *110*, 1545–1554.

[64] Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219–235.

[65] Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4853–4858.

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, ΔG^* 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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(66) McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* **1981**, *20*, 4108–4111.

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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(1) Treichel, P. L.; Stone F. G. A. *Adv. Organomet. Chem.* **1964**, *1*, 143–220.

(2) Bruce, M. I.; Stone, F. G. A. *Prep. Inorg. React.* **1968**, *4*, 177–235.

(3) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417–427.

(4) Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry"; W. A. Benjamin: New York, 1969.

(5) Chambers, R. B. "Fluorine in Organic Chemistry"; Wiley: New York, 1973.

(6) Richmond, T. G.; Shriver, D. F., Preceding paper in this issue.

0276-7333/84/2303-0314$01.50/0