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Facile Electrophilic Halogen Exchange between Boron Trihalides and Transition-Metal Perfluoroalkyl Complexes. A Novel Method for the Synthesis of Reactive Transition-Metal Haloalkyl Complexes

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Summary: Reaction of BX_3 (X = Cl, Br, I) with $Mn(CO)_5CH_nF_{3-n}$ (n = 0–2) affords the α-halomethyl complexes $Mn(CO)_5CH_nX_{3-n}$ (n = 0–2) in high yield under mild conditions. Treatment of $Re(CO)_5CF_2CF_3$ with excess BCl_3 yields exclusively $Re(CO)_5CCl_2CF_3$. This result shows that the metal activates the α-C–F bond for electrophilic attack. The highly reactive compound $CpFe(CO)_2CCl_3$ was prepared and converted to the known $CpFe(CO)_2CN$ complex by solvolysis with NH_3.

Our interest[1] in the interactions of organometallic compounds with Lewis acids prompted us to examine the reactions of perfluoroalkyl carbonyl complexes with molecular Lewis acids. Perfluoroalkyl 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.[2] In these compounds the carbon–fluorine bonds α to the metal are weaker than in aliphatic compounds as evidenced by their increased bond lengths[3] and reduced infrared stretching frequencies.[4] Thus, the C–F bond is susceptible to electrophilic attack.[5] This communication reports how we have exploited this property of metal fluorocarbon complexes to synthesize a series of α-halocarbon transition-metal carbonyl complexes.[6] This was achieved for the first time by halogen–exchange reactions with boron trihalides.

Treatment of (trifluoromethyl)manganese pentacarbonyl[7] with 1 equiv of BCl_3 in dichloromethane or pentane at −78 °C results in rapid halogen exchange to quantitatively produce (trichloromethyl)manganese pentacarbonyl (eq 1). The reaction is complete in minutes when the solution is warmed to 0 °C. Boron trifluoride was identified by its gas-phase IR spectrum, and $Mn(CO)_5CCl_3$ was isolated in 92% yield by evaporation of solvent followed by sublimation of the solid. The colorless crystalline complex was characterized by its IR spectrum, mass spectrum, and elemental analysis.[8] These physical measurements are all consistent with the formulation of the compound as $Mn(CO)_5CCl_3$. Similarly, the thermally unstable complexes $Mn(CO)_5CBr_3$ and $Mn(CO)_5CI_3$ were prepared from the reaction of $Mn(CO)_5CF_3$ with BBr_3 and BI_3, respectively, and characterized by IR spectroscopy and by the evolution of BF_3 gas from the reaction mixture. In the preparation of $Mn(CO)_5CI_3$, an approximately equimolar amount of $Mn(CO)_5I$[9] is also formed, apparently as a result of competitive cleavage of the Mn–C bond by BI_3. The frequencies of carbonyl stretching bands for these complexes are nearly identical, although the intensity of the high-frequency A_1 vibration increases in the series F < Cl < Br < I. Similar trends in frequencies and intensities have previously been observed[10] for the (trihalosilyl)-, (trihalogermyl)-, and (trihalostannyl)manganese pentacarbonyl complexes, $X_3MMn(CO)_5$. The carbon–chlorine stretching frequencies (701, 675 cm^{-1}) are lower in $Mn(CO)_5CCl_3$ compared to those observed[11] in aliphatic compounds. Thus, it is also possible to prepare $Mn(CO)_5CBr_3$ by reaction of $Mn(CO)_5CCl_3$ with BBr_3.

$$Mn(CO)_5CF_3 + BCl_3 \rightarrow Mn(CO)_5CCl_3 + BF_3 \quad (1)$$

Interestingly, the halogen-exchange reaction was found to be specific to the α position of the fluorocarbon ligand. For example, reaction of $Re(CO)_5CF_2CF_3$[12] and excess BCl_3 affords exclusively $Re(CO)_5CCl_2CF_3$[13] (eq 2). Comparison of the IR spectra of these complexes shows that the low-frequency bands assigned[4a] to the CF_2 group of 1 are absent in 2 although the peaks assigned to the CF_3 group are readily apparent. This complex exhibits a single broad ^{19}F NMR peak at room temperature which sharpens at higher temperatures. The spectrum coalesces near 0 °C and at −80 °C exhibits an ABX pattern indicating three inequivalent fluorine atoms. Similar NMR properties (presumably a consequence of slow carbon–carbon bond rotation) are observed for $Re(CO)_5CBr_2CF_3$ and for $Mn(CO)_5CCl_2CF_3$, and this behavior will be discussed more fully in a complete paper.

$$\underset{1}{Re(CO)_5CF_2CF_3} + BCl_3 \rightarrow \underset{2}{Re(CO)_5CCl_2CF_3} + BClF_2 \quad (2)$$

These results show that the metal is important in activating the carbon–fluorine bond for halogen exchange. Halogen exchange occurs readily only in noncoordinating solvents. Also, no reaction is observed when the relatively mild electrophiles BMe_3 or B_2H_6 are employed. This suggests that a strong Lewis acid is required for electrophilic attack at a fluorine substituent. The mechanism of exchange may involve an ionic intermediate 3 or be of a concerted nature 4. The formation of the strong B–F bond[14] is the thermodynamic driving force for the overall process. An analogous reaction in organic chemistry is the halogen exchange observed upon treatment of tetra-

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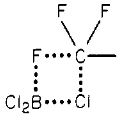
$[Cl_3BF]^-[F_2C{=}ML_n]^+$

3



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chlorocyclopropene with BBr_3 to afford tetrabromocyclopropene.[15,16]

Mono- and dihalomethyl complexes can also be prepared by this method from the appropriate fluoromethyl complexes[17] (eq 3). These complexes were characterized by

$$Mn(CO)_5CH_nF_{3-n} + BX_3 \xrightarrow[n = 1, 2]{} Mn(CO)_5CH_nX_{3-n} + BF_nX_{3-n} \quad (3)$$

their NMR, IR, and mass spectra and the thermally stable chloro derivatives by elemental analysis. The spectroscopic properties[18] of $Mn(CO)_5CH_2Cl$ agree with those recently reported[6b] for this complex. The previously unreported complex $Mn(CO)_5CH_2Br$ exhibits a singlet in its ^1H NMR spectrum at δ 3.29. The ^1H NMR spectra of the dihalo complexes $Mn(CO)_5CHX_2$ (X = Cl,[19] Br) show singlets at δ 6.62 and 6.32, respectively. Again the carbonyl infrared bands are nearly coincident with those of the fluoromethyl starting materials.

Extension of this reaction to other transition-metal systems has been briefly explored. Reaction of $CpFe(CO)_2CF_3$[4b] with 1 equiv of BCl_3 affords $CpFe(CO)_2CCl_3$. This compound was crystallized from pentane at −78 °C and characterized by its IR, ^1H NMR, and mass spectra[20] and by the evolution of BF_3 gas from the reaction mixture. Exposure of a CH_2Cl_2 solution of $CpFe(CO)_2CCl_3$ to excess NH_3 results in a rapid reaction according to eq 4 to yield

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

the known $CpFe(CO)_2CN$ complex,[21] which was characterized by its IR, NMR, and mass spectra. Ammonium chloride was identified by its mull IR spectrum.[22] Similarly, hydrolysis of $CpFe(CO)_2CCl_3$ in MeCN solution affords $[CpFe(CO)_3]^+$.[23] These types of solvolysis reactions have previously been observed[5,24] only for dihalocarbene transition-metal complexes. Electrophilic halogen exchange provides a mild, high yield synthetic route to a variety of α-haloalkyl complexes. These complexes are much more reactive than their thermally robust fluorocarbon homologues.

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Registry No. 1, 20774-63-4; 2, 86392-62-3; $Mn(CO)_5CF_3$, 13601-14-4; $Mn(CO)_5CHF_2$, 15022-34-1; $Mn(CO)_5CH_2F$, 15337-23-2; $CpFe(CO)_2CF_3$, 52409-72-0; $Mn(CO)_5CCl_3$, 86392-59-8; $Mn(CO)_5CBr_3$, 86392-60-1; $Mn(CO)_5CI_3$, 86392-61-2; $Mn(CO)_5CH_2Br$, 86392-63-4; $Mn(CO)_5CHCl_2$, 86392-64-5; $Mn(CO)_5CHBr_2$, 86392-65-6; $CpFe(CO)_2CCl_3$, 86392-66-7; $CpFe(CO)_2CN$, 12152-37-3; $CpFe(CO)_3^+$, 32660-74-5; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BI_3, 13517-10-7; NH_3, 7664-41-7.

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(19) Anal. Calcd for $C_6HCl_2MnO_5$: C, 25.84; H, 0.36; Cl, 25.42. Found: C, 25.90; H, 0.33; Cl, 25.69. IR (C_6H_{14}): 2127 (w), 2036 (s), 2009 (m) cm^{-1}.

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Alkylidyne–Alkyne Coupling on Triruthenium Clusters. A Potential Model for Fischer–Tropsch Chain Growth

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Summary: The clusters $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe, Me, Ph) react with alkynes C_2R_2 to form the corresponding alkene $C_2H_2R_2$ and $HRu_3(\mu_3\text{-}\eta^3\text{-}CXCRCR)(CO)_9$. Terminal alkynes yield mixtures of the two possible isomers in ratios dependent upon the steric bulk of the substituent. Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}C(OMe)CRCR)(CO)_9$ yields the corresponding $H_3Ru_3(\mu_3\text{-}CCHRCH_2R)(CO)_9$.

The implication of methylene coupling as a mechanism of chain growth in the metal suface-catalyzed Fischer–Tropsch (F–T) reaction has stimulated investigations of the chemistry of polynuclear alkylidene and alkylidyne complexes.[1,2] A number of examples of coupling between alkylidene ligands and unsaturated hydrocarbons on metal complexes have been reported.[3,4] A few examples of carbon–carbon bond formation between alkylidyne ligands and unsaturated hydrocarbons have also been reported,[5] and studies of hydrocarbons adsorbed on metal sufaces have identified alkylidyne fragments.[6] Mononuclear alkylidyne complexes react reversibly with alkynes to form metallacyclobutadienes,[7] while dibridged 1,3-dimetalloallyl moieties are produced from dimetallic alkylidynes.[5]

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