MOLYBDENUM PERFLUOROCARBENE COMPLEXES *

D.L. REGER * and M.D. DUKES

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208 (U.S.A.)

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Summary

Treatment of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_3$, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)CF_3$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$ with SbF_5 in liquid SO_2 yielded the first known fluoro-carbene complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_2]SbF_6$, $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)CF_2]$-$SbF_6$, and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CFC_2F_5]SbF_6$. These have been shown to exist in solution using NMR spectroscopy, but could not be isolated as the pure solids. Also, BF_3 can apparently abstract fluoride ion from perfluoroalkyl compounds although in this case no carbene complexes could be observed directly by spectroscopic techniques. These results support earlier spectroscopic studies which indicated a weakening of the carbon—fluorine bonds at the α carbon in perfluoroalkylmetal complexes.

Introduction

The fact that perfluoroalkyl-transition metal complexes are generally more stable than the analogous alkyl complexes has been recognized for some time [1]. Both kinetic and thermodynamic factors are believed to account for this. The kinetic stability is believed to arise from a blocking of the main pathway of decomposition for alkyltransition metal complexes, β-hydride elimination to form metal hydride and olefin [2].

Infrared spectral studies by King and Bisnette [3] and by Cotton et al. [4,5] had indicated increased thermodynamic stability of the transition metal-to-carbon bond in perfluoroalkylmetal complexes. They reported that the carbon—fluorine stretching frequencies of the trifluoromethyl-transition metal compounds studied were roughly 100 cm^{-1} lower than expected by comparison to trifluoromethyl halides and trifluoroacetyl-transition metal compounds. Both groups attributed this lowering of carbon—fluorine stretching frequencies and the stability of the compounds to a π interaction between filled metal *d* orbitals
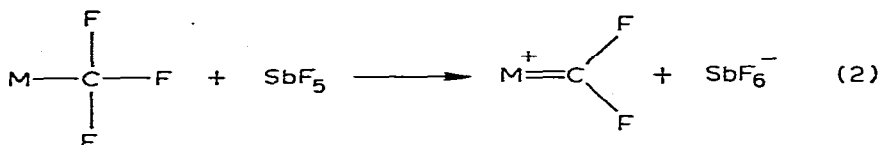
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and empty carbon orbitals. Cotton and McCleverty [4] proposed that filled metal d orbitals were donating electron density to empty carbon—fluorine σ antibonding orbitals. In valence bond terms, King and Bisnette [3] suggested fluorine hyperconjugation as pictured in eq. 1.

$$M—\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}—F \quad\longleftrightarrow\quad M\overset{+}{=}\underset{\underset{F}{|}}{C}—\overset{F^-}{}—F \qquad (1)$$
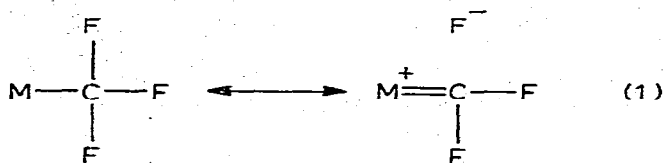
Fluorine-19 NMR spectral studies [3,6] also showed that there was something unusual about the α-fluorines of perfluoroalkyl-transition metal compounds. Fluorine atoms on carbons directly bonded to a transition metal resonate at considerably lower field than the corresponding fluorines in the respective perfluoroacyl-transition metal compounds.

X-ray crystallographic studies [7] verified what had been suspected from the infrared and NMR spectral data. The metal—carbon bond is short by comparison to similar bonds in other compounds and the α carbon—fluorine bonds are generally longer than the average sp^3 carbon—fluorine bond length of 1.38 Å. For example [7a], in the compound $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$ the $Mo—C_3F_7$ bond length is 2.288 Å, while for the analogous compound, $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3H_7$, the $Mo—C_3H_7$ bond length is 2.397 Å. Also, the average α carbon—fluorine bond length in $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$ is 1.40 Å, which is 0.02 Å longer than expected;

In view of the apparent weakness of the α carbon-fluorine bonds of perfluoroalkyl-transition metal complexes, it seemed likely that fluoride ion might be abstracted from the α carbon atoms with BF_3 or SbF_5 to yield novel fluorocarbene-transition metal complexes as pictured in eq. 2.

$$M—\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}—F \;+\; SbF_5 \quad\longrightarrow\quad M\overset{+}{=}C\underset{F}{\overset{F}{<}} \;+\; SbF_6^- \qquad (2)$$

Described in this paper are reactions of this type on selected perfluoroalkyl-transition metal compounds. These resulted in the preparation of the first fluorocarbene-transition metal complexes.

Experimental

General

All operations on complexes in solution were carried out under an atmosphere of purified nitrogen using solvents that were distilled and degassed. Infrared spectra were recorded on a Perkin—Elmer Model 337 spectrometer and are reported in cm^{-1}. Proton NMR spectra were recorded on a Perkin—Elmer R-32 spectrometer. Fluorine-19 spectra were recorded using a Varian XL-100 spectrometer. Carbon-13 NMR spectra were recorded with proton decoupling on a Varian CFT-20 spectrometer and were run at $-30°C$. Samples for NMR analysis were prepared using liquid SO_2 as the solvent. Chemical shifts of proton and carbon-13

NMR spectra are reported in δ (ppm) from TMS which was used as an external reference. Chemical shifts of fluorine-19 NMR spectra are reported in δ (ppm) from CF_3COOH which was used as the external reference. The reported shifts are positive to the low field side of CF_3COOH. The SbF_5 used in this study was obtained from Cationics Inc. All weighings of this compound were carried out in an inert atmosphere box. The BF_3 was obtained from Matheson Gas Products. Starting materials used in this study were prepared by the method of King et al. [3,8].

Reaction of $(\eta^5-C_5H_5)Mo(CO)_3CF_3$, $(\eta^5-C_5H_5)Mo(CO)_2(PPh_3)CF_3$, $(\eta^5-C_5H_5)Mo-(CO)_2(PPh_3)C_3F_7$, $(\eta^5-C_5H_5)Mo(CO)(Ph_2PCH_2CH_2PPh_2)CF_3$, and $(\eta^5-C_5H_5)Fe-(CO)_2CF_3$ with BF_3

A solution of $(\eta^5-C_5H_5)Mo(CO)_3CF_3$ (1.00 g, 2.18 mmol) in CH_2Cl_2 (30 ml) was cooled to $-78°C$. Gaseous BF_3 was bubbled into the solution for approximately 3 minutes. A yellow precipitate formed immediately upon addition of BF_3 gas. This solid was collected and recrystallized from hot-cold acetone to yield 0.656 g of yellow crystals that an IR spectrum and a C, H analyses showed to be $[(\eta^5-C_5H_5)Mo(CO)_4]BF_4$. The quantity of material isolated represented a yield of 77% based on the maximum amount of $[(\eta^5-C_5H_5)Mo(CO)_4]BF_4$ that could be formed in this reaction.

Using procedures analogous to that described above, $(\eta^5-C_5H_5)Mo(CO)_2-(PPh_3)CF_3$, $(\eta^5-C_5H_5)Mo(CO)(Ph_2PCH_2CH_2PPh_2)CF_3$, $(\eta^5-C_5H_5)Mo(CO)_2(PPh_3)-C_3F_7$ and $(\eta^5-C_5H_5)Fe(CO)_2CF_3$ were each allowed to react with BF_3. The results of these reactions were similar to that described above, with the respective disproportionation products, $[(\eta^5-C_5H_5)Mo(CO)_3(PPh_3)]BF_4$, $[(\eta^5-C_5H_5)-Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)]BF_4$, $[(\eta^5-C_5H_5)Mo(CO)_3(PPh_3)]BF_4$, and $[(\eta^5-C_5H_5)Fe(CO)_3]BF_4$, formed in each case.

Reaction of $(\eta^5-C_5H_5)Mo(CO)_3C_3F_7$ with BF_3 gas

A solution of $(\eta^5-C_5H_5)Mo(CO)_3C_3F_7$ (0.25 g, 0.60 mmol) in CH_2Cl_2 (40 ml) was cooled to $-78°C$ and BF_3 gas bubbled through for 3 minutes causing a red solid to precipitate. While warming to room temperature, the red solid began to evolve a gas at approximately $-20°C$. Before reaching room temperature, all of the red precipitate had disappeared, leaving a yellow solution.

The above experiment was repeated as described except the solution over the red solid was decanted. The red solid was stable at $-78°C$, but upon warming to $-20°C$ it turned to a yellow solid. An IR spectrum of the yellow solid dissolved in CH_2Cl_2 showed it to be the starting material, $(\eta^5-C_5H_5)Mo(CO)_3C_3F_7$.

Tricarbonyl(η^5-cyclopentadienyl)(perfluoropropylidene)molybdenum(II) hexafluoroantimonate

The yellow solid $(\eta^5-C_5H_5)Mo(CO)_3C_3F_7$ (0.40 g, 0.98 mmol) was placed in a flask and cooled to $-78°C$. Liquid SO_2 (5 ml) was condensed into the flask. The resulting yellow solution was treated with one equivalent of SbF_5 dissolved in liquid SO_2, causing the solution to turn red. The red solution was diluted with CH_2Cl_2 (5 ml) and allowed to warm, causing slow evaporation of SO_2 and precipitating a red solid. The CH_2Cl_2 was decanted and the residue dried in vacuo yielding the red solid $[(\eta^5-C_5H_5)Mo(CO)_3CFC_2F_5]SbF_6$ (0.56 g, 92%).

This solid decomposes completely in two days at room temperature under an inert atmosphere. IR spectrum (nujol mull on KBr plates prepared in a dry box using freshly prepared material): ν(SbF) 640—680m, ν(CF) 1180—1210m, ν(CO) 2035s, 2120s, ν(C$_5$H$_5$) 3080m.

To prepare [(η^5-C$_5$H$_5$)Mo(CO)$_3$CFC$_2$F$_5$]Sb$_6$ for NMR analysis, (η^5-C$_5$H$_5$)Mo-(CO)$_3$C$_3$F$_7$ (0.24 g, 0.57 mmol) was placed in a 5 mm NMR tube fitted with a ground glass joint, and the tube and solid were cooled to —78°C. Using a syringe which had been cooled to —20°C, a 10% excess of SbF$_5$ in liquid SO$_2$, from a stock solution, was added to the cooled tube. The solvent in excess of what was needed for the NMR spectra (ca. 0.3 ml) was allowed to evaporate. The remaining solution was degassed by freezing and thawing, and then sealed in vacuo after refreezing the solution. Upon warming to room temperature all of the yellow solid starting material reacted and dissolved giving a deeply colored red solution. The NMR spectra were recorded immediately. ^{1}H NMR spectrum: 5.6 (s, C$_5$H$_5$). ^{19}F NMR spectrum: 185.03 (1, CF, triplet of quartets, J(CF—CF$_2$) 16.1 Hz, J(CF—CF$_3$) 8.0 Hz), —1.62 (3, CF$_3$, doublet of triplets, J(CF$_3$—CF) 8.0 Hz, J(CF$_3$—CF$_2$) 2.4 Hz), —28.35 (2, CF$_2$, doublet of quartets, J(CF$_2$—CF) 16.1 Hz, J(CF$_2$—CF$_3$) 2.4 Hz). Attempts to obtain a ^{13}C NMR spectrum were unsuccessfull, presumably because of fluorine coupling complicating the spectrum.

Tricarbonyl(η^5-cyclopentadienyl)(difluorocarbene)molybdenum(II) hexafluoroantimonate

A deep red solution containing [(η^5-C$_5$H$_5$)Mo(CO)$_3$CF$_2$]SbF$_6$ was prepared in an NMR tube by treating (η^5-C$_5$H$_5$)Mo(CO)$_3$CF$_3$ (0.095 g, 0.30 mmol) with a 10% excess of SbF$_5$ in liquid SO$_2$ as described above. The NMR spectra were recorded immediately. ^{1}H NMR spectrum: 5.6 (s, C$_5$H$_5$). ^{19}F NMR spectrum: 242.47 (s, CF$_2$). ^{13}C NMR spectrum: 99.8 (s, C$_5$H$_5$), 279.8 (t, J 471 Hz, CF$_2$), no resonance for the CO carbon was observed presumably because of its long relaxation time. Attempts to isolate solid [(η^5-C$_5$H$_5$)Mo(CO)$_3$CF$_2$]SbF$_6$ using procedures analogous to those described above for [(η^5-C$_5$H$_5$)Mo(CO)$_3$CFC$_2$F$_5$]-SbF$_6$ yielded only by the disproportionation product, [(η^5-C$_5$H$_5$)Mo(CO)$_4$]-SbF$_6$.

Dicarbonyl(η^5-cyclopentadienyl)(difluorocarbene)(triphenylphosphine)molybdenum(II) hexafluoroantimonate

A deep red solution containing [(η^5-C$_5$H$_5$)Mo(CO)$_2$(PPh$_3$)CF$_2$]SbF$_6$ was prepared in an NMR tube by treating *trans*-(η^5-C$_5$H$_5$)Mo(CO)$_2$(PPh$_3$)CF$_3$ with a 10% excess of SbF$_5$ in liquid SO$_2$ as described above. The NMR spectra were recorded immediately. ^{1}H NMR spectrum: 5.2 (s, C$_5$H$_5$), 6.9 (multiplet, PPh$_3$). ^{19}F NMR spectrum: 239.04 (s, CF$_2$). ^{13}C NMR spectrum: 98.3 (s, C$_5$H$_5$), 132.7 (multiplet, PPh$_3$), 264.1 (doublet of triplets, J(C—F) 392 Hz, J(C—P) 100 Hz, CF$_2$), no resonance for the CO carbon was observed. Attempts to isolate solid [(η^5-C$_5$H$_5$)Mo(CO)$_2$(PPh$_3$)CF$_2$]SbF$_6$ using procedures analogous to those described for [(η^5-C$_5$H$_5$)Mo(CO)$_3$CFC$_2$F$_5$]SbF$_6$ yielded only the disproportionation product, [(η^5-C$_5$H$_5$)Mo(CO)$_3$(PPh$_3$)]SbF$_6$.

Results and discussion

Reaction of (η^5-C$_5$H$_5$)Mo(CO)$_3$CF$_3$ and *trans*-(η^5-C$_5$H$_5$)Mo(CO)$_2$(PPh$_3$)CF$_3$ with SbF$_5$ in SO$_2$ solution gave the difluorocarbene complexes, [(η^5-C$_5$H$_5$)Mo-

$(CO)_3CF_2]SbF_6$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)CF_2]SbF_6$. Although these complexes could not be isolated they were shown to exist in liquid SO_2 solution using NMR spectroscopy. The ^{19}F NMR spectra of these complexes showed single resonances attributable to the CF_2 fluorines, at very low field. In addition, a ^1H decoupled ^{13}C NMR spectrum of a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_3$ and SbF_5 in sulfur dioxide recorded at $-30°C$ showed a triplet at 279.8 ppm which can readily be attributed to the carbene—carbon coupled to two fluorine atoms in the complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_2]SbF_6$. Other have shown that metal—carbene carbon atoms are highly deshielded [9]. A doublet of triplets was observed at 264.1 ppm in the ^{13}C NMR spectrum of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2$-$(PPh_3)CF_2]SbF_6$. In this case, the triplet pattern of the carbene—carbon resonance is caused by coupling to the two fluorine atoms and each of these resonances is split into a doublet by the triphenylphosphine phosphorous atom. Because no coupling is observed between the triphenylphosphine phosphorous atom and the protons of the cyclopentadienyl group, the $[(\eta^5\text{-}C_5H_5)Mo(CO)_2$-$(PPh_3)CF_2]SbF_6$ complex is assigned *cis* stereochemistry. *Trans* complexes of this type generally show ca. a 1 Hz coupling [10] whereas none is observed for *cis* isomers. The isomerization to *cis* geometry from the *trans* starting material must be rapid and is surprising in view of the fact that in the analogous complexes of 2-oxacyclopentylidene the *cis* isomer isomerizes to the *trans* isomer [10].

The ^{19}F NMR spectrum showed clearly that $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CFCF_2CF_3]$-$SbF_6$ formed in the reaction mixture of $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$ and SbF_5 in liquid SO_2. The spectrum (vs. external CF_3CO_2H) consists of a doublet of triplets centered at -1.62 ppm attributable to the CF_3 fluorines which are coupled to β-fluorines, giving the triplet structure, and the lone fluorine bonded to the carbene carbon giving doubled triplets. The resonance for the β-fluorines is centered at -28.35 ppm and is a doublet of quartets due to coupling with the α-fluorine and the CF_3 group, respectively. Both the β- and γ-fluorines couple more strongly to the α-fluorine than to each other and $J(CF\text{—}CF_3)$ is almost exactly half that of $J(CF\text{—}CF_2)$. As a result of the relative magnitude of the coupling constants, the α-fluorine resonance centered at 185.03 is an octet arising from the overlap of the expected triplet of quartets. The triplet and quartet patterns arise from the coupling of the α-fluorine to the CF_2 and the CF_3 groups, respectively. In addition to the distinctive coupling patterns, the integration of the three different resonances is correct for these assignments. It should be noted that a resonance for SbF_6^- is not observed for any of these compounds, presumably due to coupling with antimony and broadening by quadrupolar relaxation [11].

The red solid $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CFC_2F_5]SbF_6$ was precipitated from SO_2 solutions at $-20°C$ by the addition of CH_2Cl_2. This material was very unstable and decomposed completely within two days at room temperature under an inert atmosphere. The IR spectrum of this solid, run as a nujol mull, showed bands for the SbF_6^- group and carbonyl stretching bands at the locations expected for a cationic tricarbonyl complex of this type.

The reaction of gaseous BF_3 with $(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_3$ in CH_2Cl_2 at $-78°C$ was immediate, yielding yellow crystals which were shown to be $[(\eta^5\text{-}C_5H_5)Mo$-$(CO)_4]BF_4$ (77% isolated yield based on the carbon monoxide present). Similarly,

$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]BF_4$ crystallized immediately upon reaction of $(\eta^5\text{-}C_5H_5)Fe\text{-}(CO)_2CF_3$ with BF_3 at $-78°C$ in CH_2Cl_2. Analogous compounds were isolated from the room temperature work-up of the products from the reaction of BF_3 with $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)CF_3$, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C_3F_7$ and $(\eta^5\text{-}C_5H_5)\text{-}Mo(CO)(Ph_2PCH_2CH_2PPh_2)CF_3$. Although these are the types of product expected from known disproportionation reactions of cationic sixteen electron metal carbonyl complexes [12,13], other species probably are involved since one of the reasonable intermediates, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$, is known to be stable under the conditions of this reaction [13]. It is felt that these reactions are initiated by the removal of fluorine ion from the neutral metal complexes by BF_3. Although it could arise from other sources, high yields of BF_4^- are observed in these reactions. Attempts to trap free CF_2, which conceivably could be formed in these reactions, with 2-methyl-2-butene and benzoic acid failed.

Further indication that the BF_3 is removing a fluoride ion from the perfluoro-alkylmetal starting materials comes from the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$ with BF_3 at $-78°C$ in CH_2Cl_2. In this case, the yellow solution yielded a red precipitation when BF_3 was added. This red solid gave off gas when warmed to ca. $-20°C$ and returned to the yellow starting material, $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$. We believe that the red material which initially formed was $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{-}CFC_2F_5]BF_4$. This is the BF_4^- salt of the same carbenemetal complex mentioned earlier as an SbF_6^- salt. In this case the carbonium ion generated must be able to abstract fluoride ion from the BF_4^- above $-20°C$. The abstraction of fluoride ion from BF_4^- by carbonium ions is known [14]. We are at present attempting to prepare neutral difluorocarbene complexes which may be more stable.

Acknowledgement

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