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# The Simplest Binary Fluorocarbon as a Ligand. Synthetic, Spectroscopic, Crystallographic, and Computational Studies of a Molybdenum Complex of Terminally Ligated Carbon Monofluoride (Fluoromethylidyne)

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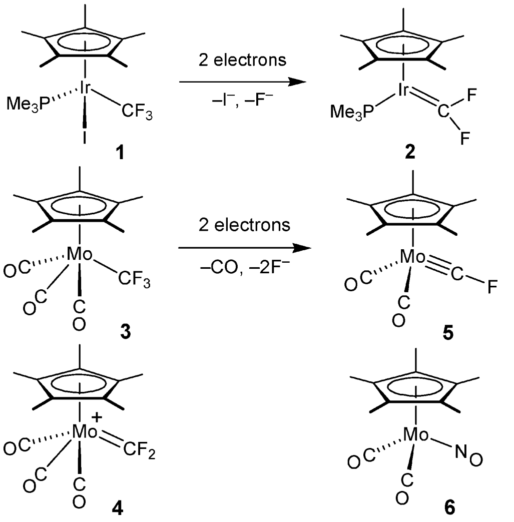
The simplest possible fluorocarbon is the CF molecule, which, unlike its isoelectronic analogue NO, is not an isolable, monomeric species.[1−3] While many terminal NO complexes of transition metals have been isolated and have a rich chemistry,[4,5] no terminally bound compounds of the CF ligand have been reported, although cluster compounds containing triply bridging CF have been crystallographically characterized.[6−15] Here we report the synthesis and characterization of a simple organometallic compound containing CF as a terminal ligand.

We have previously shown that two-electron reduction of iridium complex **1** provides a facile route to the corresponding complex **2**, which contains a difluorocarbene (difluoromethylidene) ligand.[16] Reasoning that stabilization of the $CF_2$ ligand requires a metal ligand fragment isolobal with $CH_2$, we sought a precursor, reduction of which should afford a metal ligand fragment isolobal with CH,[17] and which would therefore be capable of providing orbitals of suitable symmetry and occupancy to bind to the CF ligand.



Such a precursor is found in the known trifluoromethylmolybdenum complex **3**, which has previously been shown to afford cationic difluorocarbene derivative **4** by loss of fluoride.[18] Reduction of **3** using potassium graphite or magnesium graphite[19] affords two-electron reduction with loss of a CO ligand to give the terminal fluoromethylidyne complex **5** as a readily sublimable orange-yellow crystalline compound in 80−90% yield.

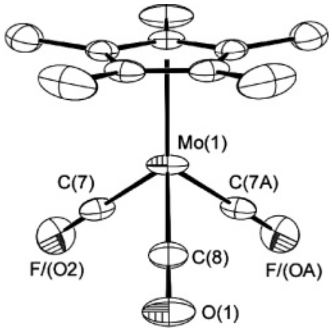


***Figure 1.*** ORTEP diagram and partial atom numbering scheme for **5**. The molecule resides on a crystallographic mirror plane which includes Mo(1)−C(8)−O(1). Selected distances (Å): Mo(1)−C(8), 1.970(3); C(8)−O(1), 1.154(3); Mo−C(7), 1.904(2); C(7)−O2/F, 1.222(2).

The overall structure of the compound is readily obtained spectroscopically. The IR spectrum (hexanes) of **5** shows two strong CO stretches (2002, 1930 $cm^{-1}$), just like **6** (2003, 1930 $cm^{-1}$).[20] The $^{19}F$ NMR spectrum of **5** shows a singlet resonance at $\delta$ +78.15, shifted significantly to low field compared to that of **3** ($\delta$ +0.7).[18] However, the $^{13}C$ NMR spectrum best provides a spectroscopic signature for this novel ligand. The CF resonance appears at low field ($\delta$ 219.12) with a very large doublet coupling to fluorine ($^{1}J_{CF} = 556$ Hz); similarly, the resonances of the CO ($\delta$ 229.56; $^{3}J_{CF} = 6.0$ Hz) and the ligated carbons of the Cp* ligands ($\delta$ 105.96; $^{3}J_{CF} = 1.5$ Hz) also show doublet couplings to the single fluorine of the CF ligand. The $^{1}J_{CF}$ value in **5** is significantly greater than those for the $CF_3$ (368 Hz) and $CF_2$ (465 Hz) ligands in compounds **3** and **4**,[18] and for the $\mu_3$-CF ligands (438−482 Hz) previously reported.[7,8,11,12] The corresponding value of $^{1}J_{CF}$ for the closest organic analogue, FC≡CF, is only 287 Hz.[21]

While compound **5** forms beautiful crystals, not surprisingly they exhibit crystallographic disorder of the CO and CF ligands; indeed, the NO analogue **6** suffers from the same issue.[20] An ORTEP diagram of **5** is shown in Figure 1. The molecule consists of the expected three-legged piano stool, which resides on a crystallographic mirror plane. While order would be preserved if the CF group resided on the mirror plane, refinement of this model resulted in an *R* factor of 2.79%. The thermal parameters suggested that a better model could be constructed by placing a CO group on the mirror plane and colocating CO and CF groups in the general position, each at half occupancy. This lowered the *R* factor to 2.29%.

Assuming that the Mo−C(8)−O(1) distances are typical of the Mo−C−O ligand in any environment, and that the Mo−C(7)−X distances are the arithmetic mean value of the 50/50 disordered Mo−C(7)−O(2) and Mo−C(7)−F units, this gives values for the bond lengths in the Mo−C(7)−F ligand of Mo−C = 1.838 Å and C−F = 1.290 Å.

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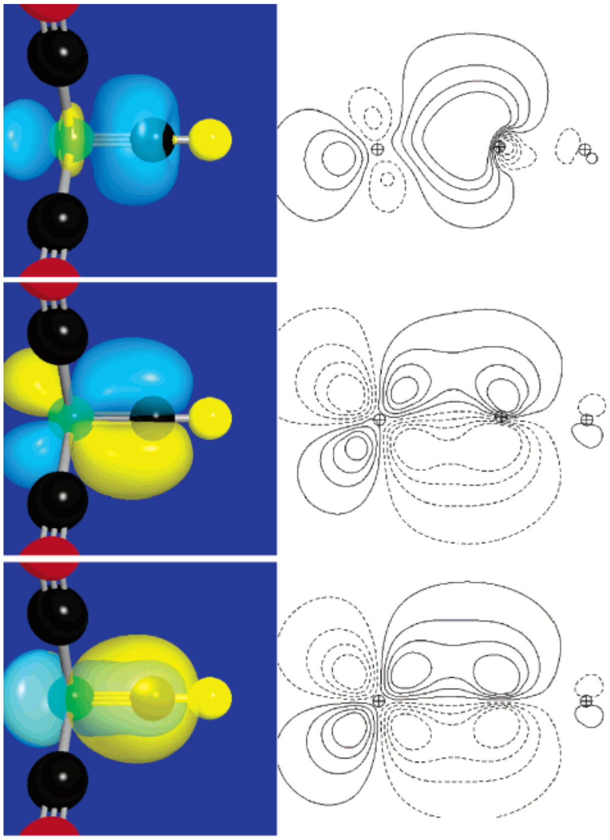


***Figure 2.*** Surfaces and cross-sectional plots of the $\sigma$- and $\pi$-components for the Mo−C−F interaction in compound **5**.

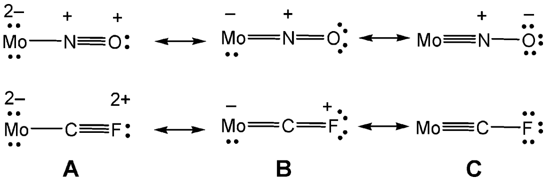


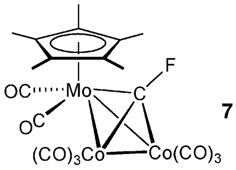
***Figure 3.*** Resonance structures for the Mo−N−O and Mo−C−F interactions in compounds **5** and **6**.

Computational DFT (B3LYP/LACV3P**++) studies of **5** provided an optimized structure that agrees well this crystallographic model, generating Mo−CO distances of 2.01 Å and C−O distances of 1.15 Å, with a Mo−CF distance of 1.82 Å and a C−F distance of 1.28 Å.

Figure 2 illustrates some of the computational results concerning the Mo−C−F interactions, in which the Mo−C bond clearly has a $\sigma$-component and two $\pi$-components. DFT computations agree with empirical results: the computed CO stretching frequencies of **5** (2017, 2077 cm$^{-1}$) and **6** (2017, 2081 cm$^{-1}$) are nearly identical. Although the Mo−CO bonding metrics are little perturbed by substitution of CF for NO, the Mo−CF and Mo−NO interactions are substantially different. Natural bond order (NBO) and natural resonance theory analyses of **5** and the cations resulting from removal of the Cp$^{-}$ clearly reveal triple bond character. In contrast, the Mo−NO bond order of the nitrosyl analogues lies closer to two. In terms of single Lewis-like structures, the CF ligand bonding is best described as Mo≡C−F, whereas the metal−NO is Mo=N=O.

These computational findings are perhaps not unexpected, considering the resonance structures shown for Mo−NO (linear) and Mo−CF bonding in Figure 3. The best resonance structure for the CF complex is clearly C, while those for the NO analogue are B and C.

In agreement with these ideas, complex **5** reacts as a metallaalkyne with Co$_2$(CO)$_8$ to afford cluster complex **7**, which has been crystallographically characterized (see Supporting Information).



**7**

This combination of spectroscopic, crystallographic, and computational methodology clearly defines **5** as a new member of the family of metal-alkylidyne complexes[22−24] and the first terminal compound of fluoromethylidyne; a terminal chloromethylidyne complex was reported some years ago.[25,26] We anticipate a rich chemistry for this new ligand and are exploring analogous reduction of CF$_3$ ligands bound to other isolobally competent metal−ligand templates; known compounds containing terminal nitrosyl ligands should provide a guide for exploration.

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**Supporting Information Available:** Full experimental details on the synthesis of **5** and **7**, their CIF files, and details of the computational work on **5**. This information is available free of charge via the Internet at http://pubs.acs.org.

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