Selective Fluoroalkylation of Cyclopentadienyl and Ethylene Ligands in Reactions of Perfluoroalkyl Iodides with Low-Valent Complexes of Molybdenum and Tungsten: Evidence for a Fluorocarbanion Mechanism

Russell P. Hughes* and Susan M. Maddock

*Department of Chemistry, 6128 Burke Laboratory
Dartmouth College, Hanover, New Hampshire 03755*

Arnold L. Rheingold and Louise M. Liable-Sands

*Department of Chemistry, University of Delaware
Newark, Delaware 19716*

Enhancement of the solubility of transition metal complexes in saturated fluorocarbons and supercritical CO_2 allows stoichiometric and catalytic chemistry to be conducted in these unusual media. Introduction of ligands bearing perfluoroalkyl groups has been shown to aid such solubility,[1] and consequently, methodology for direct fluoroalkylation of metal complexes is of considerable interest. The most common source of perfluoroalkyl groups are commercially available perfluoroalkyl iodides (R_FI), but almost all reactions of these compounds with transition metal complexes involve oxidative addition of the C–I bond at the metal center to give metal–fluoroalkyl complexes. However, we have recently shown that the site of reaction of R_FI with $[Rh(\eta^5\text{-}C_5H_5)L_2]$ (L = CO, PMe_3) can be changed by varying L; when L is CO, fluoroalkylation at the metal occurs to afford $[Rh(\eta^5\text{-}C_5H_5)R_FI(CO)]$, but when L is PMe_3 fluoroalkylation occurs chemo- and stereospecifically at the cyclopentadienyl ring to yield the diene complex **1**.[2] Two possible mechanisms were considered. Consistent with reactions of some hydrocarbon alkyl iodides with transition metal complexes, a radical mechanism, in which the first step is single electron transfer from the complex to R_FI, must be considered.[3] The radical anion thus generated, $[R_F\text{-}I]^{\bullet-}$, is known to give I^- and $R_F^{\bullet}$, at least when R_F is a primary fluoroalkyl.[4] $R_F^{\bullet}$ could then react at either the metal or the ring to give the observed products, with the selectivity controlled by the nature of L. However, a two-electron process involving nucleophilic attack by the metal on the iodine with formation of an intermediate fluorocarbanion R_F^- could not be discounted. Here, we report that reactions of $[MCp_2(C_2H_4)]$ (M = Mo, W) with secondary and tertiary fluoroalkyl iodides give products arising from selective fluoroalkylation at the cyclopentadienyl ring or the ethylene ligand, and evidence is presented that strongly supports a perfluoroalkyl carbanion rather than a perfluoroalkyl radical as the alkylating species.

Figure 1. Molecular Structure of **5**. Selected bond distances and angles: W–centroid (C1–C5), 1.95(1) Å; W–centroid (C6–C10), 1.96(1) Å; centroid–W–centroid, 142.9(4)°; W–H(1), 1.63(4) Å; W–I, 2.8199(14) Å; I–W–H, 76.2(2)°.

Figure 2. Molecular Structure of **7**. Selected bond distances and angles: W(1)–centroid (C1–C5), 1.977(9) Å; W(1)–centroid (C6–C10), 1.989(9) Å; centroid–W(1)–centroid, 138.4 (2)°; W(1)–I(1), 2.8565(8) Å; W(1)–C(11), 2.279(12) Å; I(1)–W(1)–C(11), 78.2(3)°; C(11)–C(12), 1.54(2) Å.

Reactions of 1 equiv of the secondary perfluoroalkyl iodide $ICF(CF_3)_2$ with $[MCp_2(C_2H_4)]$ (**2**, M = Mo; **3**, M = W)[5] afford the hydrido complexes **4** and **5** quantitatively as monitored by NMR; lower yields of the complexes could be isolated.[6] Free ethylene is observed when the reactions are conducted in NMR tubes. The structure of **5** has been confirmed by X-ray crystallography,[8] and an ORTEP is provided in Figure 1. In contrast, the tertiary perfluoroalkyl iodide $IC(CF_3)_3$ reacts with **2** or **3** cleanly at the ethylene ligand to give **6** and **7**.[6] X-ray crystallography confirms the structure of **7**,[8] and an ORTEP diagram of one of the two chemically identical, crystallographically independent molecules is presented in Figure 2.

The observation of traces of $HCF(CF_3)_2$ or $HC(CF_3)_3$ (identified by ^{19}F NMR spectroscopy)[9] in all of these reactions suggested that a fluoroalkyl intermediate in the reaction was being intercepted by an H-atom- or proton-donor. When the

(1) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72. Gladysz, J. A. *Science* **1994**, *266*, 55. Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286. Curran, D. P.; Hadida, S. *J. Am. Chem. Soc.* **1996**, *118*, 2531. DiMagno, S. G.; Dussault, P. H.; Schultz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 5312. Curran, D. P. *Chemtracts: Org. Chem.* **1996**, *9*, 75. Zhu, D.-W. *Synthesis* **1993**, 953. DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945. Studer, A.; Hadida, S.; Ferrito, R.; Kim, S.-Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823.
(2) Hughes, R. P.; Husebo, T. L.; Rheingold, A. P.; Yap, G. P. A. *Organometallics* **1997**, *16*, 5.
(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 306 *et seq.* (provides an overview of this area).
(4) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pison, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509. Wakselman, C. *J. Fluorine Chem.* **1992**, *59*, 367.
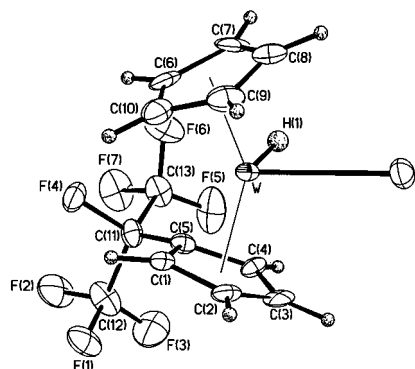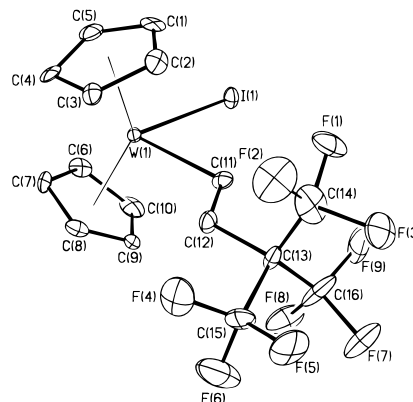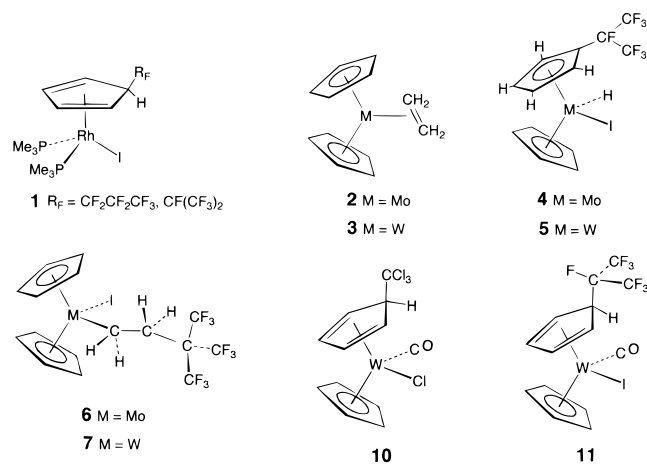
(5) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.
(6) Spectroscopic and analytical data for compounds **4**–**7** are provided as Supporting Information.
(7) The ^1H NMR spectrum of the substituted cyclopentadienyl system was simulated as an ABCDX system using the computer program gNMR (Cherwell Scientific).
(8) Crystal data for **5**: $C_{13}H_{10}F_7IW$, purple plate, monoclinic, $P2_1/c$, $a = 6.268(2)$, $b = 33.748(6)$, and $c = 7.616(2)$ Å, $\beta = 112.01(2)°$, $V = 1493.6(6)$ Å^3, $Z = 4$, $D_x = 2.713$ g cm^{-3}, $T = 298$ K, $R(F) = 5.89\%$, $R(wF^2) = 15.76\%$. H(1) was located and refined. Crystal data for **7**: $C_{16}H_{14}F_9IW$, green plate, monoclinic, $P2_1/n$, $a = 12.8936(1)$, $b = 7.5577$-(1), and $c = 38.9142(2)$ Å, $\beta = 95.0237(2)°$, $V = 3777.46(6)$ Å^3, $Z = 8$ (two chemically identical, crystallographically independent molecules), $D_x = 2.420$ g cm^{-3}, $T = 218$ K, $R(F) = 5.82\%$, $R(wF^2) = 21.90\%$.
(9) Andreades, S. *J. Am. Chem. Soc.* **1964**, *86*, 2003.

1 R_F = $CF_2CF_2CF_3$, $CF(CF_3)_2$

2 M = Mo
3 M = W

4 M = Mo
5 M = W

6 M = Mo
7 M = W

10

11

Scheme 1

8

R_F = $C(CF_3)_3$

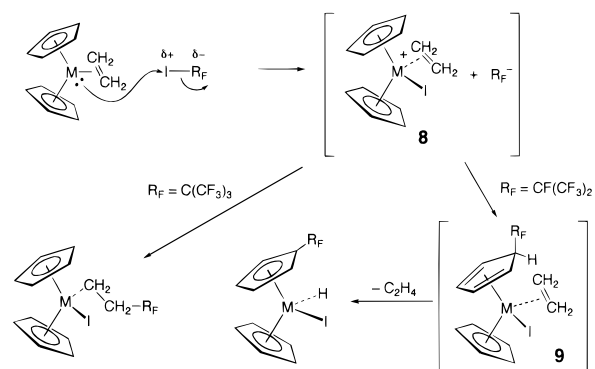R_F = $CF(CF_3)_2$

$- C_2H_4$

9

reaction of **3** with $ICF(CF_3)_2$ to give **5** was performed in perdeuterotoluene, the same traces of $HCF(CF_3)_2$ were detected, and no $DCF(CF_3)_2$[9] was observed. When the same reaction was carried out in C_6D_6 in the presence of up to 68 equiv of 9,10-dihydroanthracene, no more $HCF(CF_3)_2$ was detected than that detected in a control experiment with no 9,10-dihydroanthracene. Consequently, we attribute the traces of $HCF(CF_3)_2$ observed to trapping of a fluoroalkyl carbanion[10] by a proton source; adventitious moisture is the most likely candidate. Further support for a fluorocarbanion intermediate is provided by the observation of small amounts of $F_2C=CF(CF_3)$ and $F_2C=C(CF_3)_2$ among the reaction products from $ICF(CF_3)_2$ or $IC(CF_3)_3$ respectively, presumably arising from elimination of F^- from the corresponding fluorocarbanions.[11] In agreement with this hypothesis, addition of CH_3OD as a trap[12] resulted in the observation of $DCF(CF_3)_2$ or $DC(CF_3)_3$ with no increase in the amount of the corresponding protio compounds. A control experiment in which $ICF(CF_3)_2$ was photolyzed in CH_3OD afforded only $HCF(CF_3)_2$; photolysis is known to give to give $^\bullet CF(CF_3)_2$,[13] which, as expected, abstracts $H^\bullet$ from the weaker $C-H$ bond.[14] These results provide strong evidence that the fluoroalkyl species being trapped is R_F^- rather than $R_F^\bullet$. Finally the ratios of R_FD/**5** and R_FD/**7** vary linearly with [CH_3OD], indicating that the same species is responsible for production of R_FD and the fluoroalkylated organometallics.

A suggested mechanism is outlined in Scheme 1 in which initial nucleophilic attack by the metal center at the $\delta+$ iodine of R_FI[15] produces the fluoroalkyl anion R_F^- and organometallic cation **8**. For the secondary $^-CF(CF_3)_2$ anion, attack at the Cp ring is observed for both Mo and W, with subsequent loss of ethylene from intermediate **9** and migration of the *endo*-H to the metal. This series of steps is analogous to those observed for the corresponding rhodium systems[2] and may cast doubt upon a radical pathway in that system. The reason why the tertiary $^-C(CF_3)_3$ attacks **8** at ethylene rather than at a Cp ring is less clear; it may be that this very stable carbanion[10,11] reacts reversibly at the Cp ligand and then irreversibly at ethylene, so the observed products are those of thermodynamic rather than kinetic control.

Precedent for attack at the Cp ring by anionic carbon nucleophiles exists in various reactions of [$WCp_2(SMe_2)Br$]$^+$ [16]

and [WCp_2Cl_2][17] which result in substitution at one cyclopentadienyl ring. Unfortunately we, and others,[18] have been unable to prepare the cation **8**, and it is unsettling that the Davies−Green−Mingos rules[19] predict kinetically controlled attack by nucleophiles at the ethylene ligand of **8** in preference to attack at Cp. A related reaction of [$WCp_2(CO)$] with CCl_4 to give **10** has been reported, although a radical mechanism involving SET as the initial step was proposed.[20] We find that reaction of [$WCp_2(CO)$] with $ICF(CF_3)_2$ results in formation of **11**[21] with traces of $F_2C=CF(CF_3)$; when CH_3OD is used as a trap, $DCF(CF_3)_2$ is observed. An X-ray crystallographic determination has confirmed the structure of **11** and, in particular, the *exo*-stereochemistry of the fluoroalkyl group.[22] These results also support a carbanionic mechanism for this reaction; loss of CO from **11** is clearly less favorable than loss of ethylene from **9**, and *endo*-H-migration to the metal is blocked.

In summary, we have shown that the products obtained from reaction of [$MCp_2(C_2H_4)$] with perfluoroalkyl iodides depend on the nature of the perfluoroalkyl iodide. A secondary perfluoroalkyl iodide ($ICF(CF_3)_2$) reacts at a cyclopentadienyl ring and a tertiary one ($IC(CF_3)_3$) at the ethylene ligand. While the reasons for the different selectivity are unclear, no evidence has been obtained for fluoroalkyl radicals as intermediates, and two positive signatures for fluorocarbanion intermediates have been obtained. This represents a new type of reaction mechanism for the transition metal promoted reactions of fluoroalkyl halides that differs from any previously encountered for hydrocarbon analogues.

(10) Farnham, W. B. *Chem. Rev.* **1996**, *96*, 1633.
(11) Smart, B. E.; Middleton, W. J.; Farnham, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 4905.
(12) Toscano, P. J.; Brand, H.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 2101.
(13) Dolbier, W. R. *Chem. Rev.* **1996**, *96*, 1557.
(14) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
(15) Wakselman, C.; Lantz, A. In *Organofluorine Chemistry; Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994; Chapter 8 and references cited therein.

(16) Forschner, T. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7420.
(17) McNally, J. P.; Glueck, D.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 4838.
(18) Miller, G. A.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709.
(19) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.
(20) Jernakoff, P.; Fox, J. R.; Cooper, N. J. *J. Organomet. Chem.* **1996**, *512*, 175.
(21) Spectroscopic and analytical data for compound **11** are provided as Supporting Information.
(22) Hughes, R. P.; Maddock, S. M.; Liable-Sands, L. M.; Rheingold, A. L. Unpublished results.