J. Am. Chem. Soc. **2001,** *123,* 3279−3288

Reactions of Halofluorocarbons with Group 6 Complexes $M(C_5H_5)_2L$ ($M = Mo, W; L = C_2H_4, CO$). Fluoroalkylation at Molybdenum and Tungsten, and at Cyclopentadienyl or Ethylene Ligands

Russell P. Hughes,*,[†] Susan M. Maddock,[†] Ilia A. Guzei,[‡] Louise M. Liable-Sands,[‡] and Arnold L. Rheingold[‡]

Contribution from the Departments of Chemistry Burke Chemistry Laboratory, Dartmouth College, Hanover, New Hampshire 03755-3564, and University of Delaware, Newark, Delaware 19716

Received September 11, 2000

Abstract: The molybdenum(II) and tungsten(II) complexes [MCp_2L] (Cp = η^5-cyclopentadienyl; L = C_2H_4, CO) react with perfluoroalkyl iodides to give a variety of products. The Mo(II) complex [$MoCp_2(C_2H_4)$] reacts with perfluoro-*n*-butyl iodide or perfluorobenzyl iodide with loss of ethylene to give the first examples of fluoroalkyl complexes of Mo(IV), $MoCp_2(CF_2CF_2CF_2CF_3)I$ (**8**) and $MoCp_2(CF_2C_6F_5)I$ (**9**), one of which (**8**) has been crystallographically characterized. In contrast, the CO analogue [$MoCp_2(CO)$] reacts with perfluorobenzyl iodide without loss of CO to give the crystallographically characterized salt, $[MoCp_2(CF_2C_6F_5)(CO)]^+I^-$ (**10**), and the W(II) ethylene precursor [$WCp_2(C_2H_4)$] reacts with perfluorobenzyl iodide without loss of ethylene to afford the salt $[WCp_2(CF_2C_6F_5)(C_2H_4)]^+I^-$ (**11**). These observations demonstrate that the metal−carbon bond is formed first. In further contrast the tungsten precursor [$WCp_2(C_2H_4)$] reacts with perfluoro-*n*-butyl iodide, perfluoro-*iso*-propyl iodide, and pentafluorophenyl iodide to give fluoroalkyl- and fluorophenyl-substituted cyclopentadienyl complexes $WCp(\eta^5\text{-}C_5H_4R_F)(H)I$ (**12**, $R_F = CF_2CF_2CF_2CF_3$; **15**, $R_F = CF(CF_3)_2$; **16**, $R_F = C_6F_5$); the Mo analogue $MoCp(\eta^5\text{-}C_5H_4R_F)(H)I$ (**14**, $R_F = CF(CF_3)_2$) is obtained in similar fashion. The tungsten(IV) hydrido compounds react with iodoform to afford the corresponding diiodides $WCp(\eta^5\text{-}C_5H_4R_F)I_2$ (**13**, $R_F = CF_2CF_2CF_2CF_3$; **18**, $R_F = CF(CF_3)_2$; **19**, $R_F = C_6F_5$), two of which (**13** and **19**) have been crystallographically characterized. The carbonyl precursors [$MCp_2(CO)$] each react with perfluoro-*iso*-propyl iodide without loss of CO, to afford the exo-fluoroalkylated cyclopentadiene M(II) complexes $MCp(\eta^4\text{-}C_5H_5R_F)(CO)I$ (**21**, M = Mo; **22**, M = W); the exo-stereochemistry for the fluoroalkyl group is confirmed by an X-ray structural study of **22**. The ethylene analogues [$MCp_2(C_2H_4)$] react with perfluoro-*tert*-butyl iodide to yield the products $MCp_2[(CH_2CH_2C(CF_3)_3]I$ (**25**, M = Mo; **26**, M = W) resulting from fluoroalkylation at the ethylene ligand. Attempts to provide positive evidence for fluoroalkyl radicals as intermediates in reactions of primary and benzylic substrates were unsuccessful, but trapping experiments with CH_3OD (to give R_FD, not R_FH) indicate that fluoroalkyl anions are the intermediates responsible for ring and ethylene fluoroalkylation in the reactions of secondary and tertiary fluoroalkyl substrates.

Introduction

There is considerable recent interest in the activation of aliphatic carbon−fluorine bonds by transition metal centers,[1,2] and in the use of fluorinated substituents to render catalytically active transition metal complexes more soluble in “fluorous” media.[3,4] As a consequence, we have focused renewed attention on the synthesis and chemistry of transition metal fluoroalkyl complexes, early examples of which have been known since the 1960s.[5]

One of the more widely used methods of synthesizing complexes with transition-metal perfluoroalkyl bonds ($M-R_F$) involves oxidative addition of the carbon−iodine bond of perfluoroalkyl iodides.[6,7] This route has been shown to be successful with low-valent late transition-metal centers to give perfluoroalkyl−metal complexes in which the $M-R_F$ bond is usually shorter than that in hydrocarbon analogues and is generally considered to be stronger. The mechanism of oxidative addition of perfluoroalkyl iodides has not been studied in any detail, and it is not known whether the reactions proceed by a concerted addition, a stepwise two-electron mechanism, or a radical pathway. It seems unlikely that a mechanism involving nucleophilic attack by the metal at carbon is operative, as the R_F-I bond is polarized to give a $\delta-$ charge on the carbon center.[8] We have concentrated our synthetic efforts in groups 9 and 10 and have recently described the syntheses and characterization of a series of perfluoroalkyl and perfluorobenzyl complexes of Co, Rh, and Ir (**1**) by oxidative addition of the appropriate R_F-I to $[M(\eta^5\text{-}C_5R_5)(CO)_2]$,[9−12] expanding considerably on the original examples reported by earlier

---

[†] Dartmouth College.

[‡] University of Delaware.

(1) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373−431.

(2) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recl.* **1997**, *130*, 145−154.

(3) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641−650.

(4) Studer, A.; Hadida, S.; Ferritto, R.; Kim, S.-Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823−826.

(5) Stone, F. G. A. *Endeavour* **1966**, *25*, 33−38.

(6) Morrison, J. A. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 293−316.

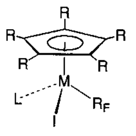
(7) Morrison, J. A. *Adv. Organomet. Chem.* **1993**, *35*, 211−239.

(8) Wakselman, C.; Lantz, A. In *Organofluorine Chemistry*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994; pp 177−194.

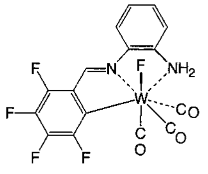
(9) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678−5686.

10.1021/ja003339u CCC: $20.00 © 2001 American Chemical Society
Published on Web 03/16/2001

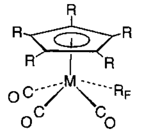
workers.[13−16] The chemistry of these compounds has proven interesting, and preliminary examples of facile hydrolysis[17] and hydrogenolysis[18] reactions of the α-fluorines have been documented.



1 M = Co, Rh, Ir
R = H, Me
L = CO, PR_3



2



3 R = H; M = Mo, W; $R_F = CF_3$
R = H; M = Mo, $R_F = C_2F_5$
R = Me; M = Mo; $R_F = CF_3$

The first complex (**2**) arising from the formal oxidative addition of a carbon−fluorine bond to a transition metal center was reported in 1987.[19] At the time, a considerable part of the driving force was considered to arise from formation of a strong tungsten−fluorine bond, but subsequent examples of aromatic C−F bond activation by group 9 and 10 metals illustrate that early metals are not essential for this process.[20−24] Nevertheless, we were intrigued by the paucity of examples of group 6 fluoroalkyl complexes in general, and with the idea that, if they could be prepared, they might afford examples of α− or β-fluorine elimination reactions, or agostic C−F−M interactions, analogous to those observed in hydrocarbon analogues. Previous examples of perfluoroalkyl complexes of group 6 metals in oxidation state (II) have been synthesized by decarbonylation of perfluoroacyl complexes, such as $[Mo(\eta^5\text{-}C_5R_5)(CO)_3COR_F]$ ($R_F = CF_3, CF_2CF_3$),[25,26] or by the metathesis reaction of $Cd(CF_3)_2$ with $[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ (M = Mo, W).[27,28] The tungsten(VI) complex $W(CF_3)_6$ has been reported as an unstable product of the reaction of $Cd(CF_3)_2$ with WBr_6.[6]

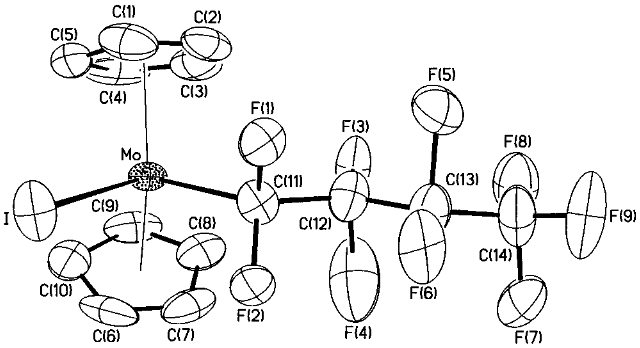


Figure 1. ORTEP diagram of the non-hydrogen atoms of **8**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

We reasoned that the well-known 18-electron M(II) complexes $[MCp_2L]$ (**4**−**7**) might provide useful entries to afford M(IV) fluoroalkyls by the oxidative addition route. Herein we report the reactions of primary, secondary, and tertiary perfluoroalkyl iodides with these complexes to give a variety of products resulting from fluoroalkylation at the metal or directly at the organic ligands. Part of this work has been the subject of a preliminary communication.[29]

Results and Discussion

Reaction of $[MoCp_2(C_2H_4)]$ (**4**) with perfluoro-*n*-butyl iodide in THF solution proceeds rapidly at room temperature with displacement of ethylene, to give the Mo(IV) fluoroalkyl complex **8**, resulting from formal oxidative addition of the C−I bond to the metal. In contrast to **4**, which is an air-sensitive solid, **8** is stable to air in solution for hours. The ^1H NMR spectrum of **8** shows a single peak for the cyclopentadienyl ligands and the ^{19}F NMR spectrum shows the expected four multiplets at δ −61.0, −80.8, −109.3, and −124.7 ppm for the perfluoro-*n*-butyl group. A single-crystal X-ray structural determination of **8** confirmed the overall molecular architecture. An ORTEP diagram is shown in Figure 1 and crystallographic information is presented in Table 1. The complex has the same general geometry as similar neutral complexes of the type $[M(\eta^5\text{-}C_5H_5)_2X_2]$ (M = Mo, W).[30−36] There is some disorder in the fluorine atom positions in the perfluorobutyl ligand. The Mo−C(11) bond length of 2.277(11) Å is not significantly different from the 2.284(10) Å observed in the ethyl complex $[MoCp_2(C_2H_5)Cl]$,[30]or those of 2.268(4) and 2.272(4) Å in the dibutyl complex $[MoCp_2(n\text{-}Bu)_2]$.[37] It is slightly longer than the 2.248(5) Å found in the Mo(II) complex $[Mo(\eta^5\text{-}C_5Me_5)(CO)_3(CF_3)]$.[26]

---

(10) Hughes, R. P.; Husebo, T. L.; Holliday, B. J.; Rheingold, A. L.; Liable-Sands, L. M. *J. Organomet. Chem.* **1997**, *548*, 109−112.

(11) Hughes, R. P.; Husebo, T. L.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. *Organometallics* **1997**, *16*, 5−7.

(12) Hughes, R. P.; Smith, J. M.; Liable-Sands, L. M.; Concolino, T. E.; Lam, K.-C.; Incarvito, C.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **2000**, 873−879.

(13) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593−3597.

(14) Pitcher, E.; Buckingham, A. D.; Stone, F. G. A. *J. Chem. Phys.* **1962**, *36*, 124−129.

(15) McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1964**, 4200−4203.

(16) Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551−573.

(17) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1997**, *119*, 11544−11545.

(18) Hughes, R. P.; Smith, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 6084−6085.

(19) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091−8092.

(20) Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 264−266.

(21) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429−1440.

(22) Selmeczy, A. D.; Jones, W. D.; Partridge, M. D.; Perutz, R. N. *Organometallics* **1994**, *13*, 522−532.

(23) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Chem. Commun.* **1996**, 787−788.

(24) Cronin, L.; Higgitt, C. L.; Karch, R.; Perutz, R. N. *Organometallics* **1997**, *16*, 4920−4928.

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

(26) Koola, J. D.; Roddick, D. M. *Organometallics* **1991**, *10*, 591−597.

(27) Naumann, D.; Varbelow, H.-G. *J. Fluorine Chem.* **1988**, *41*, 415.

(28) Preut, H.; Varbelow, H. G.; Naumann, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 2460−2462.

(29) Hughes, R. P.; Maddock, S. M.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1997**, *119*, 5988−5989.

(30) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290.

(31) Schultz, A. J.; Stearley, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 3303.

(32) Hartwig, J. F.; Xiaoming, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 315.

(33) Hartwig, J. F.; Gala, S. R. D. *J. Am. Chem. Soc.* **1994**, *116*, 3661.

(34) Koloski, T. S.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 489.

(35) Forder, R. A.; Jefferson, I. W.; Prout, K. *Acta Crystallogr.* **1975**, *B31*, 618.

(36) Cameron, T. S.; Prout, C. K. *J. Chem. Soc., Dalton Trans.* **1972**, 1447.

(37) Calhorda, M. J.; Carrondo, M. A. A. F. d. C. T.; Dias, A. R.; Galvão, A. M.; Garcia, M. H.; Martins, A. M.; Piedade, M. E. M. d.; Pinheiro, C. I.; Ramão, C. C.; Simões, J. A. M.; Veiros, L. F. *Organometallics* **1991**, *10*, 483.

Table 1. Crystal Data and Summary of X-ray Data Collection

	8	**10**	**13**	**18**	**22**
formula	$C_{14}H_{10}F_9IMo$	$C_{18}H_{10}F_7IMoO$	$C_{14}H_9F_9I_2W$	C13H9F7I2W	$C_{14}H_{10}F_7IOW$
fw	572.06	598.10	785.86	735.85	637.97
space group	*P*2(1)/*c*	*Cc*	*C*2/*c*	*C*2/*c*	*P*2(1)/*c*
a, Å	16.9120(10)	11.790(2)	36.532(3)	31.887(3)	6.74920(10)
b, Å	7.4764(6)	10.270(2)	7.5414(6)	7.5394(10)	13.5373(4)
c, Å	12.991(2)	15.530(3)	13.9090(10)	13.9856(15)	37.3724(10)
α, deg	90	90	90	90	90
β, deg	92.796(6)	104.37(3)	104.090(7)	100.772(7)	90.5240(10)
γ, deg	90	90	90	90	90
V, $Å^3$	1640.6(3)	1821.6(6)	3716.7(5)	3303.1(6)	3414.42(15)
Z	4	4	8	8	8
D(calcd), g/cm^3	2.316	2.181	2.809	2.959	2.482
abs coeff, mm^{-1}	2.770	2.489	9.619	10.796	8.643
temp, K	298(2)	223(2)	298(2)	233(2)	223(2)
diffractometer			Siemens P4		
radiation			Mo Kα 0.71073 Å		
R(*F*),[a] %	4.56	4.45	3.79	3.88	6.16
R(*wF*²),[a] %	14.01	10.50	9.21	10.25	14.35

[a] Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

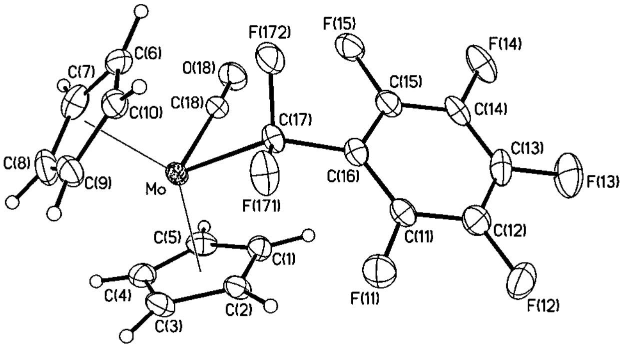


Figure 2. ORTEP diagram of the cation of **10**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

Similarly, reaction of **4** with perfluorobenzyl iodide in THF or benzene results in displacement of ethylene and oxidative addition at the metal center giving the dark green complex **9**. The ^{1}H NMR spectrum shows only one peak at δ 5.45 ppm consistent with two symmetrically equivalent unsubstituted cyclopentadienyl rings. In the ^{19}F NMR spectrum the benzylic fluorines appear as a triplet at δ −40.8 ppm (J_{FF} = 29.8 Hz) due to coupling to the *ortho* fluorines on the pentafluorophenyl ring. Three multiplets are observed for the fluorines on the pentafluorophenyl ring at −136.7, −158.7, and −163.6 ppm for the *ortho*, *para*, and *meta* positions, respectively.

In contrast to the ethylene precursor **4** the corresponding molybdenum carbonyl complex [MoCp$_2$(CO)] (**6**) reacts with perfluorobenzyl iodide in benzene to give a pale yellow precipitate of complex **10**, in which the CO ligand is retained as demonstrated by a strong υ_{CO} stretch at 2037 cm^{-1}. The insolubility of this complex in all but the most polar solvents (CH$_3$CN, DMSO) implied an ionic structure. The hydrogen nuclei on the cyclopentadienyl rings gave rise to a singlet in the ^{1}H NMR spectrum at δ 5.91 ppm, substantially downfield from that in **9**. As in **9** the ^{19}F NMR spectrum the benzylic fluorines gave rise to a triplet at δ −29.1 ppm, but shifted significantly downfield from the corresponding resonance in **9**, and the pentafluorophenyl fluorines appeared as three multiplets. The structure of **10** was confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 2. Crystallographic data are provided in Table 1. The overall geometry of the compound is very similar to that of **8** and other bent group 6 metallocenes.[30−36]

Reaction of the tungsten analogue [WCp$_2$(CO)] (**7**) with perfluorobenzyl iodide was not as clean, and gave a pale brown precipitate that contained several products as indicated by NMR spectroscopy. One of these appeared to be the tungsten analogue of **10**. This reaction was not pursued due to the difficulty of separating the components from the precipitate. However, when reaction of [WCp$_2$(C$_2$H$_4$)] (**5**) and perfluorobenzyl iodide was carried out in tetrahydrofuran there was immediate formation of an off-white precipitate, formulated as the ionic compound **11**. Like **10**, the insolubility of **11** in anything but very polar solvents such as acetonitrile and dimethyl sulfoxide was indicative of its ionic nature. The ^{1}H NMR spectrum in acetonitrile showed two multiplets at δ 2.81 and 2.57 ppm, each integrating for 2 hydrogens relative to the singlet at δ 5.79 for the 10 cyclopentadienyl hydrogens, indicating that the ethylene ligand was still bound to the metal, although not rotating fast on the NMR time scale. ^{19}F NMR spectroscopy confirmed coordination of the perfluorobenzyl group to the metal, with the triplet due to the benzylic fluorines exhibiting satellites due to coupling to the tungsten nuclear spin ($^2J_{FW}$ = 26 Hz). Refluxing an acetonitrile solution of **11** overnight did not result in loss of ethylene and formation of [W(η^5-C$_5$H$_5$)$_2$(CF$_2$C$_6$F$_5$)I], illustrating the kinetic stability of the tungsten ethylene bond.

In further contrast to the behavior of Mo complex **4**, reaction of tungsten analogue **5** with perfluoro-*n*-butyl iodide does not result in oxidative addition at the metal center. Instead the major product arises from fluoroalkyl substitution at one cyclopentadienyl ring with hydride migration to the metal occurring to form **12**. This reaction is analogous to that described in our preliminary communication,[29] and elaborated on below, for reaction of **5** with perfluoroisopropyl iodide. The ^{1}H NMR spectrum of **12** shows four different peaks, each of which integrates for one hydrogen, for the substituted cyclopentadienyl ring and a peak for the hydride at δ −10.92 ppm. Because the wedge ligands are inequivalent, there is no plane of symmetry in the molecule, and the α-fluorines on the perfluorobutyl group are diastereotopic, appearing as two strongly coupled doublets at δ −101.5 and −108.0 ppm (J_{FF} = 275 Hz) in the ^{19}F NMR spectrum. While **12** is not the only compound formed in this reaction, NMR analysis of the crude reaction mixture indicates that it is the major product (ca. 75%), and the ^{19}F NMR spectrum shows clearly that there is no formation of any metal fluoroalkyl product analogous to **8**. The chemical shift of the α-fluorines of the coordinated fluoroalkyl in **8** is δ −61.0 ppm whereas in **12** they appear at δ −101.5 and −108.0 ppm; in contrast to the W−fluorobenzyl complex **11**, no fluorine peaks with tungsten

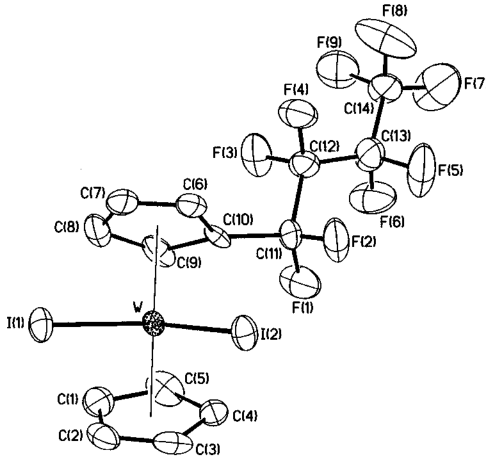
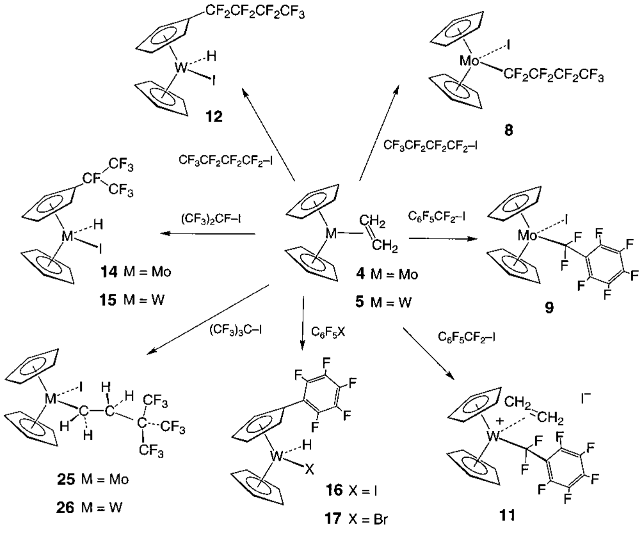


Figure 3. ORTEP diagram of the non-hydrogen atoms of **13**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

satellites can be observed in the crude reaction mixture. The reason for the difference in the site of reactivity in going from molybdenum to tungsten is not clear. Complex **12** is not stable and on recrystallization undergoes partial conversion to the diiodide **13**. A similar phenomenon has been described for the bromo hydrides [W(η^5-C_5H_5)(η^5-C_5H_4R)HBr] (R = Ph, *i*-Pr), which convert to the dibromides on workup.[38] The instability of **12** prevented a satisfactory elemental analysis from being obtained. The diiodide **13** can be synthesized more cleanly by adding an excess of CHI_3 to a dichloromethane solution of **12**. With two identical ligands in the wedge, **13** now has a mirror plane perpendicular to the plane that contains the metal and the two iodine atoms. Consequently, the α-fluorines are no longer diastereotopic and appear as a multiplet at δ −108.0 ppm in the ^{19}F NMR spectrum, and only two peaks rather than the four observed for **12** appear in the ^1H NMR spectrum for the substituted cyclopentadienyl ring. The X-ray crystal structure of **13** has been solved and confirms the molecular architecture. An ORTEP diagram of **13** is shown in Figure 3 and crystallographic information is presented in Table 1. The geometry is that expected for group 6 metallocene complexes (vide supra).[30−36,39]



Reactions of secondary perfluoroalkyl iodides differ from their primary analogues in that the reactions are much cleaner and selective for reaction at a cyclopentadienyl ring. Reaction of 1

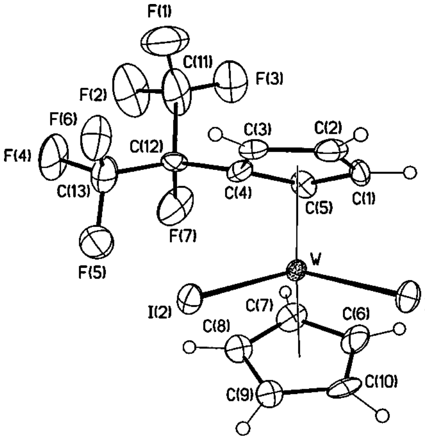


Figure 4. ORTEP diagram **18**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

molar equiv of perfluoroisopropyl iodide with molybdenum or tungsten precursors **4** or **5** at room temperature rapidly forms the hydrido complexes **14** and **15** in quantitative yield as monitored by NMR spectroscopy, although lower yields were isolated. The ethylene ligand is lost during the reaction and free ethylene is detected by ^1H NMR spectroscopy if the reaction is carried out in an NMR tube. The IR spectra of the products exhibited bands at 1958 (**14**) and 1935 cm^{-1} (**15**) attributable to υ_{M-H}, and their ^1H NMR spectra show hydride peaks at δ −7.82 (**14**) and −10.93 ppm (**15**), with the latter resonance exhibiting tungsten satellites (J_{HW} = 60.0 Hz). As with **12**, the hydrogens on the substituted cyclopentadienyl ring appear as four multiplets and the unsubstituted cyclopentadienyl ring gives rise to a singlet for all complexes. The ^{19}F NMR spectra of **14** and **15** are similar, with the diastereotopic trifluoromethyl groups appearing as two doublets of quartets in the ^{19}F NMR spectra. The quartet coupling and the doublet coupling are of similar magnitude (J_{FF} = 10 Hz) and the peaks appear as a quintet. The tertiary CF resonance couples to both CF_3 groups (J_{FF} = 10 Hz) and to one hydrogen on the cyclopentadienyl ring to which it is bound. The structure of **4** was determined by X-ray crystallography and has been published previously.[29] The NMR data are consistent with the solid-state structure and indicate that the compound in solution has the same geometry as that in the crystal structure.

This mode of reactivity is not confined to perfluoroalkyl iodides, since pentafluorophenyl iodide or bromide react in a similar manner with **5** to form **16** and **17**, respectively. The IR spectra shows a stretch due to υ_{M-H} at 1938 (**16**) and 1895 cm^{-1} (**17**) and the ^1H NMR spectra exhibit hydride resonances at δ −11.64 (J_{HW} = 56.4 Hz) and −11.18 (J_{HW} = 57.6 Hz) ppm, respectively. In the ^{19}F NMR spectra of **16** and **17** the pentafluorophenyl group gives rise to three multiplets of ratio 2:1:2 in the region δ −140 to −160 ppm for the *ortho*, *para*, and *meta* fluorines, respectively.

Exposure of solutions of **15**, **16**, and **17** to air results in a slow color change to green and precipitation of a dark blue/black solid that is insoluble in common solvents and was not characterized. From the green solution the diiodo complexes **18** and **19** and the dibromo complex **20** were isolated in low yield. These complexes can be formed in higher yield on reaction of the corresponding hydrido complexes with either CHI_3 or $CHBr_3$. In the ^1H NMR spectra of **18**−**20** there are

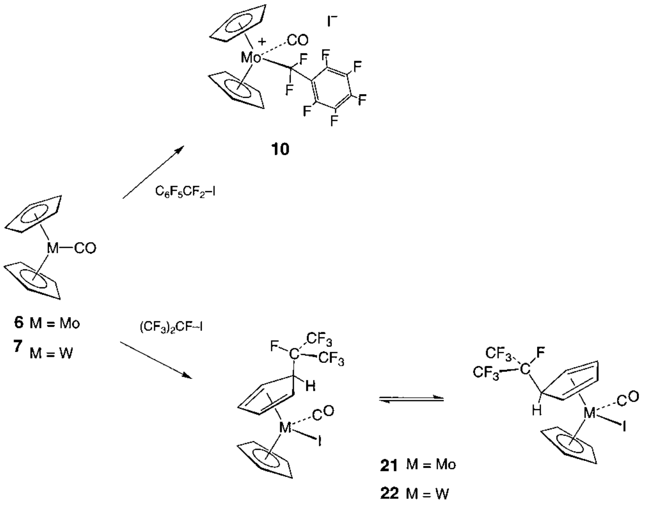
---

(38) McNally, J. P.; Glueck, D.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 4838.

(39) Jernakoff, P.; Fox, J. R.; Hayes, J. C.; Lee, S.; Foxman, B. M.; Cooper, N. J. *Organometallics* **1995**, *14*, 4493.

now only two peaks for the hydrogens on the substituted cyclopentadienyl ring which integrate for two hydrogens each. The trifluoromethyl groups in **18** are now equivalent and give rise to a doublet in the ^{19}F NMR spectrum at δ -74.4 ppm. The tertiary fluorine appears as a septet at δ -176.2 ppm. The solid-state structure of **18** was obtained by a single-crystal X-ray diffraction; an ORTEP diagram is presented in Figure 4 and crystallographic information is given in Table 1. The hydrogen on C(3) is 2.375 Å from F(6), which is less than the sum of the van der Waals' radii of 2.67 Å.[40]

Once again the carbonyl precursors **6** and **7** provide contrasting behavior, and afford new compounds whose structures shed some light on the pathway for formation of the previously observed hydrido compounds. When the reaction between ICF(CF_3)$_2$ and **6** or **7** is carried out in benzene, the orange diene complexes **21** (M = Mo) and **22** (M = W) are formed. These complexes are air stable and could be recrystallized in the open without decomposition. The ^{1}H NMR spectra of both complexes show an interesting temperature dependence. At room temperature the peaks in the ^{1}H spectrum of **21** are extensively broadened but those in the ^{19}F spectrum are not. The ^{1}H NMR spectrum at -60 °C shows two sets of peaks for all hydrogen nuclei indicating the presence of two isomers in an approximately 3:2 ratio. It seems reasonable that these isomers are simply due to different conformations of the diene ligand about the M$-$diene axis which interconvert only slowly on the NMR time scale by diene rotation. As the sample is warmed the isomer ratio remains constant, but the previously sharp peaks broaden somewhat and there is little change in the chemical shift of individual peaks, indicating that the broadening is probably not due to a fluxional process that interconverts the isomers, such as rotation about the M$-$diene bond. The ^{19}F NMR spectrum of **21** at -60 °C also shows the presence of two isomers in the same 3:2 ratio, but there is no broadening of the peaks on warming the sample to room temperature and the isomer ratio remains unchanged. The solution IR spectrum of **21** does not reflect the presence of two isomers as there is only one band for the carbonyl group at 1965 cm^{-1}. For **22** the difference between the ^{1}H NMR spectrum obtained at -60 °C and that obtained at room temperature is not so marked. Two isomers can also be observed for **22** by NMR spectroscopy but the minor one is in barely detectable quantities. In spectra of both **21** and **22** the solvent peaks remain sharp at all temperatures, as do the peaks in the ^{19}F spectra.



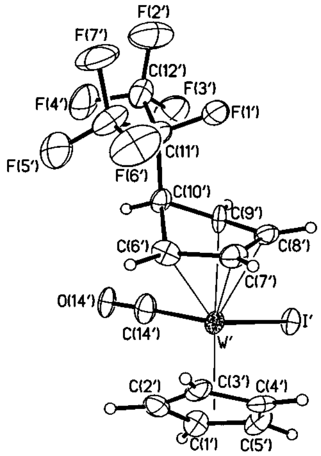
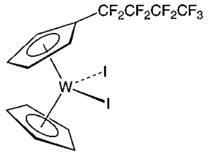
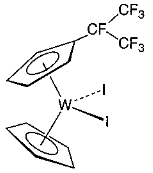


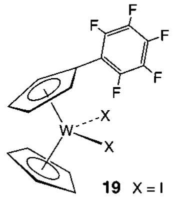
Figure 5. ORTEP diagram of one of two crystallographically independent molecules of **22**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.



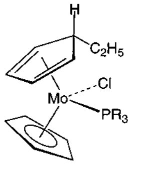
13



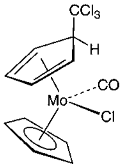
18



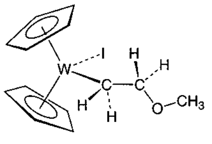
19 X = I
20 X = Br



23



24



27

We have no specific explanation for this behavior, but precedents exist. The ^{1}H NMR spectrum of **23** shows the presence of major and minor compounds which the authors suggest may be due to geometric isomers.[41] A similar NMR broadening phenomenon has been reported for the NMR spectra of the closely related complex **24**.[42] The authors suggested it may be due to an equilibrium between the complex and a coordinatively unsaturated derivative, which could be formed via dissociation of one of the double bonds of the diene ligand. Also considered as a cause for the broadening was electron exchange between the complex and a small amount of paramagnetic oxidation or reduction product.

A single-crystal X-ray structural determination of **22** confirmed formation of the substituted cyclopentadiene ligand and the *exo* orientation of the perfluoroisopropyl substituent. A ball-and-stick representation of the structure is shown in Figure 5, and crystallographic information is presented in Table 1. There are two crystallographically independent molecules in the unit cell, one of which shows disorder around the C(10)$-$C(11) bond.

---

(40) Smart, B. E. *Organofluorine Chemistry*; Plenum: New York, 1994.
(41) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1969**, 2215.
(42) Jernakoff, P.; Fox, J. R.; Cooper, N. J. *J. Organomet. Chem.* **1996**, *512*, 175.

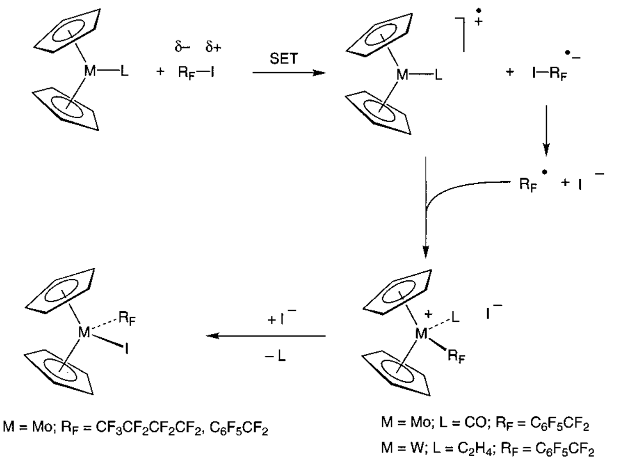
The overall architecture of the complex is very similar to that of **24**,[42] and as with other reported complexes resulting from substitution at a cyclopentadienyl ligand, the fluoroalkyl group is in the *exo* position.[11] As discussed below, complexes **21** and **22** can be viewed as model compounds for an intermediate in the formation of the hydride complexes **14**−**17**.

In further contrast to reactions of primary, secondary, and aryl halides, reaction of 1 molar equiv of the tertiary perfluoroalkyl iodide $IC(CF_3)_3$ with **4** or **5** does not result in fluoroalkylation at the metal or at a cyclopentadienyl ring, but instead reaction occurs at the ethylene ligand to give **25** or **26**. In the ^1H NMR spectra of **25** and **26** the substituted alkyl group gives rise to two multiplets at δ 1.90 and 1.56 ppm (**25**) and 2.09 and 1.28 ppm (**26**), which each integrate for two hydrogens. In the ^{13}C NMR spectrum the tungsten-bound carbon in **26** shows tungsten satellites ($J_{CW} = 60$ Hz) as do the cyclopentadienyl carbons ($J_{CW} = 6$ Hz). The resonance for the perfluoro-*tert*-butyl group in the ^{19}F NMR spectrum of **26** appears as a quintet. The coupling of 0.8 Hz was barely resolved and is presumably due to coupling to the hydrogen nuclei on the alkyl group. In the ^{19}F NMR spectrum of both **24** and **25** the perfluoro-*tert*-butyl group gave rise to a broad singlet at δ −66.0 ppm. The X-ray structure of **26** has been reported previously,[29] and is very similar to that of other Group 6 bent metallocene complexes. The W−alkyl σ-bond length (W−C(11)) of 2.279(12) Å is very similar to those in $[WCp_2(CH_2C_6H_3Me_2)_2]_2$ of 2.276 and 2.291 Å.[43]

At this stage of the discussion, some mechanistic considerations are appropriate. It has been reported that reaction of $[MCp_2(C_2H_4)]$ (M = Mo, W) with CH_3I gives the cationic complexes $[MCp_2(CH_3)(C_2H_4)]I$.[44,45] In this case the methyl carbon bears some positive charge and the first step is envisaged to be nucleophilic attack by the coordinatively saturated metal center on this carbon to form the metal−carbon bond. However, the carbon−iodine bond in perfluoroalkyl iodides is oppositely polarized $^{\delta-}C{-}I^{\delta+}$, so it is considered unlikely that the first step in their reactions with any nucleophiles involves nucleophilic attack at carbon.[8,46] Consequently, reactions of perfluoroalkyl iodides with electron-rich species involve either a single electron-transfer step to afford $(R_FI)^{\bullet-}$, which rapidly generates $R_F^{\bullet}$ and I^- (such electron transfer/dissociation may indeed be concerted),[47] or a nucleophilic attack at I to displace a fluoroalkyl carbanion.[8,46] The latter pathway may be favored when the fluorinated carbanion is secondary or tertiary, and therefore considerably stabilized by adjacent CF_3 groups.[48−51]

With these factors in mind, formation of bonds from primary and benzylic fluoroalkyls to Mo and W in compounds **8**−**11** cannot be rationalized in terms of the S_N2-type mechanism envisaged for CH_3I.[44,45] Two-electron attack by the metal on R_FI would be expected at I, not at C, and the metal−iodine bond would be formed first. While formation of **8** and **9** results in bonds from the metal to both carbon and iodine, observations of **10** and **11** as stable products indicate that the metal−carbon bond is formed first. We suggest the mechanism shown in Scheme 1. Initial electron transfer from metal to R_FI must be followed by very rapid decomposition of the radical anion to $R_F^{\bullet}$ and I^-;[47] recombination of the 17-electron radical cation with $R_F^{\bullet}$ then affords the metal fluoroalkyl cations, observed as stable products in the case of **10** and **11**. In the case of formation of **8** or **9**, loss of ethylene from molybdenum must be facile, allowing coordination of iodide and formation of the observed products. Notably CO loss from molybdenum must be considerably less facile than loss of ethylene, as **10** shows no tendency to lose CO and bind I^-. Similarly, the tungsten ethylene bond must be considerably stronger than the corresponding bond to molybdenum, as **11** is stable to ethylene loss, even on heating. The relative affinities for CO vs ethylene, and the greater lability of ethylene in cationic molybdenocene complexes compared to cationic tungstenocene complexes, is illustrated by displacement of ethylene from $[MoCp_2(C_2H_4)R]^+$ (R = H, CH_3) by CO in refluxing acetone.[44,45] These authors reported that the reaction of $[WCp_2(C_2H_4)H]^+$ with CO proceeds much more slowly, and attempts to repeat this reaction in our laboratory resulted in no observable formation of $[WCp_2(CO)H]^+$.

Scheme 1



If a fluoroalkyl radical were involved in the reaction pathway, it might be possible to observe other manifestations of its presence, provided it escaped the solvent cage before recombination at the metal. Fluoroalkyl radicals do not disproportionate to give fluoroalkanes and fluoroalkenes, as do hydrocarbon analogues, but instead undergo coupling reactions, initiate the polymerization of alkenes such as norbornene, and are much more voracious hydrogen atom abstractors than are hydrocarbon radicals.[52,53] Accordingly, the formation of compounds **8**−**11** was observed in the presence of a large molar excess of norbornene, with no change in the reaction outcome, and no observation of polymerization.[52] In addition, when reactions were carried out in toluene-d_8 no R_FD resulting from abstraction of benzylic $D^{\bullet}$ by $R_F^{\bullet}$ was observed. Similarly, carrying out the same reactions in the presence of 70 molar equiv of 9,10-dihydroanthracene as an H-atom donor resulted in no change in the organometallic products, and no observable R_FH. If fluoroalkyl radicals are indeed formed, they do not escape a fate other than recombination at the metal center. However, the less selective reaction of perfluoro-*n*-butyl iodide with the

---

(43) Prout, K.; Jefferson, I. W.; Forder, R. A. *Acta Crystallogr.* **1975**, *B31*, 618.

(44) Benfield, F. W. S.; Francis, B. R.; Green, M. L. H. *J. Organomet. Chem.* **1972**, *44*, C13.

(45) Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49.

(46) Wakselman, C. *J. Fluorine Chem.* **1992**, *59*, 367−378.

(47) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509−3520.

(48) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027−4031.

(49) Smart, B. E.; Middleton, W. J.; Farnham, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 4905−4908.

(50) Farnham, W. B.; Dixon, D. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2607−2611.

(51) Farnham, W. B. *Chem. Rev.* **1996**, *96*, 1633−1640.

(52) Feiring, A. E. *J. Org. Chem.* **1985**, *50*, 3269−3274.

(53) Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557−1584.

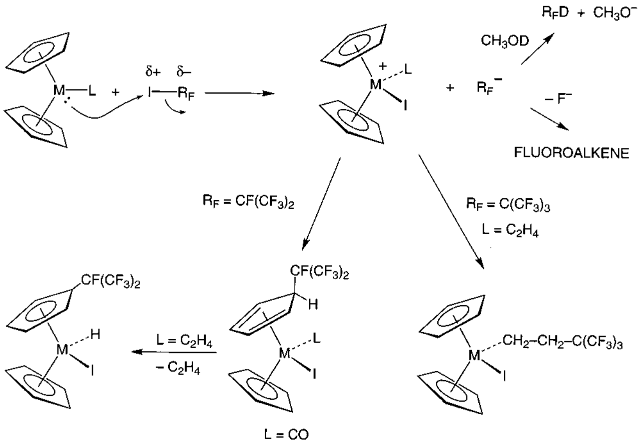
tungsten complex **5**, to give many unidentified products as well as the ring-substituted complex **12**, indicates that other reaction pathways are available to whatever reactive fluoroalkyl intermediate is formed. For example, we have previously observed metal-centered fluoroalkylation and *exo*-cyclopentadienyl ring fluoroalkylation in reactions of primary and secondary perfluoroalkyl iodides with cyclopentadienyl−rhodium[11] and −cobalt[10] complexes, and an identical sequence of steps has been proposed in tungsten systems.[38,41,54]

Since cyclopentadienyl ring fluoroalkyation is observed most selectively with perfluoroisopropyl iodide, we concentrated our efforts on this system, although this pathway is also observed for perfluoroaryl substrates. When carbonyl precursors **6** and **7** are used, the *exo*-fluoroalkylated products **21** and **22** are formed, but are inert to further reaction. It seems reasonable that formation of **14** and **15** occurs via intermediates which are ethylene analogues of **21** and **22**, but that the ethylene ligand is more labile. Notably the lability of ethylene in these formally M(II) intermediates must be greater than that in the isolable W(IV) cation **11**. Loss of ethylene generates a vacant coordination site, into which migrates the *endo*-hydrogen from the cyclopentadiene ring, reestablishing the coordinatively saturated metal center and rearomatizing the cyclopentadienyl ring. We have previously established this sequence of reactions for *exo*-fluoroalkyation of a cyclopentadienyl−rhodium complex to give an isolable cyclopentadiene compound; subsequent generation of a vacant site results in *endo*-H migration to give a cyclopentadienylrhodium hydrido product.[55] The stereochemistry of cyclopentadienyl ring fluoroalkylation is clearly *exo* in the cases reported here, but what is the nature of the fluoroalkylating agent? Closer monitoring of these reactions by NMR spectroscopy revealed the presence of small amounts (ca. 5%) of saturated $(CF_3)_2CFH$ and perfluoropropene, $CF_3CF{=}CF_2$. The former could arise by H-atom abstraction by the corresponding radical $(CF_3)_2CF^\bullet$, but this radical is not known to afford the fluoroalkene because of its very strong β-CF bonds.[53] Observation of fluoroalkenes is instead a characteristic signature of the corresponding perfluoroalkyl anion, in this case $(CF_3)_2CF^-$, which readily eliminates a β-fluoride.[51]

In an elegantly designed experiment, CH_3OD has been used to distinguish between an R_F^- and an $R_F^\bullet$ mechanism for the decomposition of $[Co(Py)(DH)_2(CF(CF_3)_2]$ by $NaBH_4$ to give $Na[Co(Py)(DH)_2]$ and $(CF_3)_2CFD$.[56] These results were interpreted in terms of formation of R_F^-, which reacts with the more acidic O−D bond in CH_3OD, rather than formation of $R_F^\bullet$, which would be expected to react with the weaker C−H bond[57] to give R_FH. The products $(CF_3)_2CFD$ and $(CF_3)_2CFH$ can easily be distinguished with ^{19}F NMR.[58]

In a control experiment $ICF(CF_3)_2$ was photolyzed in the presence of CH_3OD in a reaction known to afford the fluorinated radical; the only product detected was $(CF_3)_2CFH$ resulting from abstraction of $H^\bullet$ from the weaker C−H bond. However, when the reaction of **5** with $(CF_3)_2CFI$ was carried out in the presence of only 1 molar equiv of CH_3OD, the yield of organometallic product **15** was dramatically reduced and $(CF_3)_2CFD$ now made up approximately 45% of the fluorine-containing products, along with the same traces of $(CF_3)_2CFH$ observed in the absence of CH_3OD. This is only consistent with the formation of $(CF_3)_2CF^-$ and abstraction of D^+ from the trapping agent. Consequently, we interpret the traces of $(CF_3)_2CFH$ always observed as resulting from reaction of $(CF_3)_2CF^-$ with adventitious H_2O present in the reaction, and the previous observations of $CF_3CF{=}CF_2$ as resulting from fluoride elimination from the same perfluorocarbanion intermediate. To eliminate the possibility that the perfluoroalkyl species responsible for formation of the organometallic product **15** was not that responsible for formation of $(CF_3)_2CFD$, the reaction was carried out with varying concentrations of CH_3OD. The resultant ratio of $(CF_3)_2CFD$/**15** versus concentration of CH_3OD increases linearly, indicating that CH_3OD and the organometallic precursor to **15** are competing for the same perfluoroalkyl intermediate, which must be $(CF_3)_2CF^-$.

Scheme 2



Accordingly, we propose the mechanism outlined in Scheme 2. Initial nucleophilic attack on iodine by the tungsten center presumably results in formation of the ion pair $[MCp_2(C_2H_4)I]^+ R_F^-$. In an attempt to determine if the perfluorocarbanion escaped from the solvent cage to react with another molecule of the cation or it reacted with the tungsten cation with which it was formed, a series of reactions between **5** and $(CF_3)_2CFI$ were performed in which the concentrations were varied. If R_F^- were to escape the solvent cage, at low concentrations the amount of $CF_3CF{=}CF_2$ formed relative to **15** should increase as elimination of F^- would become more likely than reaction with a more difficult to find $[WCp_2(C_2H_4)I]^+$. While the results were clouded by the large amount of scatter observed for each data point, the amount of $F_2C{=}CF(CF_3)$ formed remained approximately constant. It seems probable that the $(CF_3)_2CF^-$ reacts within the ion pair of which it is initially a part. We note that this mechanism differs from that proposed for the reaction of **7** with CCl_4 to give **24**, in which a single electron transfer was proposed as the first step, followed by a radical coupling pathway.[42]

Similar observations were made for the reactions of perfluoro-*tert*-butyl iodide with **5** to give **26**. NMR monitoring of the reaction revealed small amounts of $(CF_3)_2C{=}CF_2$ in the product mixture, and trapping experiments using CH_3OD produced $(CF_3)_3CD$, not $(CF_3)_3CH$; both results are signatures for the perfluoro-*tert*-butyl carbanion.[51] We did not carry out analogous trapping experiments or explore further any reactions of perfluoroaryl substrates.

Given a mechanism in which a fluoroalkyl carbanion and $[WCp_2(C_2H_4)I]^+$ are formed initially, and the carbanion is trapped by CH_3OD, the amount of fluoroalkyated organometallic product produced decreases. What is the fate of the other intermediate $[WCp_2(C_2H_4)I]^+$ and the methoxide anion that must

---

(54) Forschner, T. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7420.

(55) Hughes, R. P.; Husebo, T. L.; Maddock, S. M.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1997**, *119*, 10231−10232.

(56) Toscano, P. J.; Brand, H.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 2101−2105.

(57) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(58) Andreades, S. *J. Am. Chem. Soc.* **1964**, *86*, 2003−2010.

also be formed? In each of the systems investigated, as the amount of added methanol was increased, a light orange precipitate, which could not be characterized, was formed, along with a green solution from which the 2-methoxyethyl complex **27** was isolated. This compound has similar spectroscopic properties to those of its crystallographically characterized analogue **26**[29] (see above). The 2-methoxyethyl group gives rise to multiplets in the ^{1}H NMR spectrum at δ 1.35 and 3.33 ppm for the methylene protons and a singlet at δ 3.26 ppm for the methoxy group. The resonance for the metal-bound carbon shows tungsten satellites (J_{CW} = 28 Hz) in the ^{13}C NMR spectrum. Complex **27** is not thermally stable and undergoes complete decomposition when stored overnight at room temperature under nitrogen. An X-ray structure of **27** was obtained which confirms the overall molecular connectivity, but was not of sufficient quality for accurate distances and angles to be obtained. Formation of **27** can be rationalized by nucleophilic attack by methoxide on the ethylene ligand of the putative intermediate $[WCp_2(C_2H_4)I]^+$.

However, such reaction selectivity raises the issue of why the $(CF_3)_2CF^-$ nucleophile reacts at cyclopentadienyl and *not* at ethylene. The Davies−Green−Mingos rules predict kinetically controlled attack by nucleophiles at the ethylene ligand of $[WCp_2(C_2H_4)I]^+$ rather than the cyclopentadienyl ligand, and this is apparently observed in the formation of **27**.[59] However, examples of multiple site attack by nucleophiles are not uncommon, and the kinetic site of attack is not always the one actually observed.[63−65] One possibility that we considered was that the reaction of $(CF_3)_2CF^-$ does indeed occur with kinetic selectivity for attack at ethylene, as observed for methoxide, but that the reaction of $(CF_3)_2CF^-$ is reversible, with the eventual outcome being the result of thermodynamically controlled attack at cyclopentadienyl. This is discounted by the observation that the more stable perfluoro-*tert*-butyl carbanion $(CF_3)_3C^-$ reacts at ethylene, but shows no signs of reversibility and subsequent attack at cyclopentadienyl. There could be some steric factor that disfavors the product of $(CF_3)_3C^-$ attack at cyclopentadienyl and results in a switching of thermodynamic product stabilities, but without further evidence that this is a straw worth grasping, the origins of differing selectivities in the case of $(CF_3)_2CF^-$ (and presumably $C_6F_5^-$) compared to $(CF_3)_3C^-$ remain a mystery.

Conclusions

Oxidative addition reactions of perfluoroalkyl iodides with Mo(II) and W(II) precursors afford M(IV) products resulting from fluoroalkylation at the metal, at the cyclopentadienyl ring, or at ethylene ligands. In the case of primary or benzylic substrates, attempts to trap or provide other evidence for intermediate fluorinated radicals or carbanions have been unsuccessful, whereas with secondary and tertiary substrates positive evidence for fluorinated carbanion intermediates has been obtained. The reasons for differing selectivities for reactions of these intermediate fluoroalkylating agents remain a matter of conjecture. The products of fluoroalkylation at the metal center represent the first reported examples of fluoroalkyl complexes of Mo(IV) and W(IV).

Experimental Section

General Considerations. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of dinitrogen that had been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun Drybox. THF was distilled under nitrogen from potassium and benzophenone ketyl and benzene was distilled from sodium immediately before use. Dichloromethane and hexane were refluxed over calcium hydride under nitrogen and distilled immediately before use. IR spectra were recorded on a Perkin-Elmer FTIR 1600 Series spectrometer. NMR spectra were recorded on a Varian Unity Plus 300 FT spectrometer. ^{1}H NMR spectra were referenced to the protio impurity present in the solvent: C_6D_6 (δ 7.16 ppm), $CDCl_3$ (δ 7.27 ppm), CD_3CN (δ 1.94 ppm). ^{19}F NMR spectra were referenced to $CFCl_3$ (0.00 ppm). ^{13}C NMR spectra were referenced to CD_2Cl_2 (δ 53.8 ppm). Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. $I(CF_2)_3CF_3$ (Aldrich), $ICF_2C_6F_5$ (PCR), $ICF(CF_3)_2$ (PCR), and IC_6F_5 (Aldrich) were purified by washing with a solution of sodium thiosulfate to remove iodine, followed by washing with water and then drying over magnesium sulfate and deoxygenation by several freeze−evacuate−thaw cycles. BrC_6F_5 (Oakwood) was deoxygenated and used as received. $IC(CF_3)_3$ (PCR) was dissolved in deoxygenated benzene and used as received. CH_3OD (Aldrich) was used as received. $[MoCp_2(C_2H_4)]$ (**4**),[60] $[WCp_2(C_2H_4)]$ (**5**),[60] $[MoCp_2(CO)]$ (**6**),[61] and $[WCp_2(CO)]$ (**7**)[62] were prepared according to literature procedures.

$Mo(\eta^5\text{-}C_5H_5)_2[(CF_2)_3CF_3]I$ (8). $MoCp_2(C_2H_4)$ (0.030 g, 0.118 mmol) was dissolved in tetrahydrofuran (4 mL). $I(CF_2)_3CF_3$ (0.021 mL, 0.122 mmol) was added to give a brown solution. The reaction mixture was stirred for 10 min, then filtered under nitrogen, and the solvent removed in vacuo. The light brown solid was recrystallized from dichloromethane/ethanol then dichloromethane/hexane (0.032 g, 47%). Crystals suitable for an X-ray study were grown from dichloromethane/hexane. Mp: 170−172 °C. ^{1}H NMR (C_6D_6) δ 4.56 (s, 10H, C_5H_5). ^{19}F NMR (C_6D_6) δ −61.0 (m, 2F, α-CF_2), −80.8 (tt, J_{FF} = 10 Hz, J_{FF} = 4 Hz, 3F, CF_3), −109.3 (m, 2F, β-CF_2), −124.7 (m, 2F, γ-CF_2). Anal. Calcd for $C_{14}H_{10}F_9IMo$ (572.02): C, 29.39; H, 1.76. Found: C, 29.39; H, 1.55.

$Mo(\eta^5\text{-}C_5H_5)_2(CF_2C_6F_5)I$ (9). $MoCp_2(C_2H_4)$ (0.100 g, 0.393 mmol) was dissolved in tetrahydrofuran (12 mL). $ICF_2C_6F_5$ (0.07 mL, 0.41 mmol) was added dropwise to give a brownish solution that was stirred at room temperature for half an hour. The solution was filtered under nitrogen, the solvent volume was reduced to approximately 1 mL, and hexane (5 mL) was added to complete precipitation of the product. The green solid was washed with hexane (2 × 5 mL) and dried in vacuo (0.115 g, 51%). Mp: decomposition at ca. 120 °C. ^{1}H NMR (CD_3CN) δ 5.45 (s, 10H, C_5H_5). ^{19}F NMR (CD_3CN) δ −40.8 (t, $^4J_{FF}$ = 29 Hz, 2F, CF_2), −136.7 (m, 2F, C_6F_5 *ortho*), −158.7 (tm, $^3J_{FF}$ = 19 Hz, 1F, C_6F_5 *para*), −163.6 (m, 2F, C_6F_5 *meta*). Anal. Calcd for $C_{17}H_{10}F_7IMo$ (570.10): C, 35.82; H, 1.77. Found: C, 35.85; H, 1.88.

$[Mo(\eta^5\text{-}C_5H_5)_2(CF_2C_6F_5)(CO)]I$ (10). $MoCp_2(CO)$ (0.040 g, 0.157 mmol) was dissolved in benzene (4 mL) and $ICF_2C_6F_5$ (0.03 mL, 0.17 mmol) was added. A pale yellow precipitate formed immediately. This was collected by filtration and washed with benzene (5 mL) and hexane (2 × 5 mL) to give analytically pure product (0.075 g, 82%). Mp: decomposition at ca. 190 °C. IR (Nujol) υ_{CO} 2037 cm^{-1}. ^{1}H NMR (CD_3CN): δ 5.91 (s, 10H, C_5H_5). ^{19}F NMR (CD_3CN): δ −29.1 (t, $^4J_{FF}$ = 28 Hz, 2F, CF_2), −138.4 (m, 2F, C_6F_5 *ortho*), −154.4 (t, $^3J_{FF}$ = 20 Hz, 1F, C_6F_5 *para*), −160.8 (m, 2F, C_6F_5 *meta*). Anal. Calcd for $C_{18}H_{10}F_7IMoO$ (582.11): C, 36.15; H, 1.69. Found: C, 36.33; H, 1.73.

$[W(\eta^5\text{-}C_5H_5)_2(CF_2C_6F_5)(C_2H_4)]I$ (11). $WCp_2(C_2H_4)$ (0.140 g, 0.041 mmol) was dissolved in THF (10 mL). $ICF_2C_6F_5$ (0.075 mL, 0.436 mmol) was added dropwise and an off-white precipitate formed. The reaction mixture was stirred for 15 min. The solvent was removed by filtration and the product was washed with hexane (2 × 5 mL) and filtered to give analytically pure product (0.200 g, 77%). Mp: 114−116 °C. ^{1}H NMR (CD_3CN): δ 5.79 (s, 10H, C_5H_5), 2.81 (m, 2H, $CH_2{=}CH_2$), 2.56 (m, 2H, $CH_2{=}CH_2$). ^{19}F NMR (CD_3CN): δ −30.8 (t, W

---

[59] Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

[60] Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

[61] Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.

[62] Francis, B. R.; Green, M. L. H.; Luong-thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1339.

[63] Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *333*, 36.

[64] Jaouen, G. *Pure. Appl. Chem.* **1986**, *58*, 597.

[65] Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K.; Taylor, T. H. *Organometallics* **1986**, *5*, 158.

satellites, $^4J_{FF} = 33$ Hz, $J_{FW} = 26$ Hz, 2F, CF_2), −135.9 (m, 2F, C_6F_5, *ortho*), −154.5 (t, $^3J_{FF} = 21$ Hz, 1F, C_6F_5, *para*), −160.9 (m, 2F, C_6F_5, *meta*). Anal. Calcd for $C_{19}H_{14}F_7IW$ (686.07): C, 33.26; H, 2.06. Found: C, 33.44; H, 1.94.

W(η^5-C_5H_5)[C_5H_4((CF_2)$_3$$CF_3$)]HI (12). $WCp_2(C_2H_4)$ (0.050 g, 0.146 mmol) was dissolved in benzene (6 mL) and $I(CF_2)_3CF_3$ (0.028 mL, 0.163 mmol) was added. The resulting brown solution was stirred for 15 min and then filtered. The solvent was removed from the filtrate giving a brown residue. This residue contained impure **12**. Attempts to recrystallize the product resulted in partial conversion to **13**. ^{1}H NMR (C_6D_6): δ 4.79 (m, 1H, C_5H_4), 4.57 (m, 1H, C_5H_4), 4.46 (s, 5H, C_5H_5), 4.05 (br s, 1H, C_5H_4), 3.75 (br s, 1H, C_5H_4), −10.92 (s, W satellites, $J_{HW} = 63.0$ Hz, 1H, W−H). ^{19}F NMR (C_6D_6): δ −81.4 (tt, $^3J_{FF} = 3.0$ Hz, $^4J_{FF} = 10$ Hz, 3F, CF_3), −101.5 (dm, $^2J_{FF} = 275$ Hz, 1H, α-CF_2), −108.0 (dm, $^2J_{FF} = 275$ Hz, 1H, α-CF_2), −122.7 (m, 2F, β-CF_2), −125.5 (m, 2F, γ-CF_2).

W(η^5-C_5H_5)[C_5H_4((CF_2)$_3$$CF_3$)]$I_2$ (13). $WCp_2(C_2H_4)$ (0.150 g, 0.438 mmol) was dissolved in benzene (6 mL) and $I(CF_2)_3CF_3$ (0.075 mL 0.442 mmol) was added giving a brown solution. This was filtered and the benzene removed in vacuo. Dichloromethane (10 mL) and iodoform (0.861 g, 2.19 mmol) were added to the residue. The solution was stirred for 4 h during which time it turned dark green. Filtration followed by removal of all the solvent gave a dark green/brown product. This was dissolved in a minimum of dichloromethane and filtered to remove iodoform. The filtrate was placed on a silica gel column (6 × 1.5 cm) and eluted with dichloromethane. The first dark yellow/brown fraction contained excess CHI_3 and was discarded. The second dark green fraction was collected, the solvent volume was reduced under reduced pressure, and hexane was added giving a dark green precipitate that was recrystallized from dichloromethane/hexane (0.050 g, 15%). Mp: 220−223 °C. ^{1}H NMR ($CDCl_3$): δ 5.91 (m, $^3J_{HH} = 2.7$ Hz, $^4J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.6$ Hz, $^4J_{HF} = 1.0$ Hz, 2H, C_5H_4), 5.70 (s, 5H, C_5H_5), 5.27 (t, $^3J_{HH} = 2.7$ Hz, 2H, C_5H_4). ^{19}F NMR ($CDCl_3$): δ −81.4 (m, 3F, CF_3), −108.0 (m, 2F, α-CF_2), −122.8 (m, 2F, β-CF_2), −125.8 (m, 2F, γ-CF_2). Anal. Calcd for $C_{14}H_9F_9I_2W$ (785.87): C, 21.40; H, 1.15. Found: C, 21.31; H, 1.19.

Mo(η^5-C_5H_5)[C_5H_4(CF(CF_3)$_2$)]HI (14). $MoCp_2(C_2H_4)$ (0.040 g, 0.157 mmol) was dissolved in benzene (3 mL) and $ICF(CF_3)_2$ (0.022 mL, 0.157 mmol) was added. The solution was stirred for 30 min and filtered and the solvent was removed in vacuo. The brown residue was dissolved in benzene, the volume was reduced to ca. 1 mL, and a similar volume of hexane was added to precipitate the product. It was recrystallized from benzene/hexane (0.037 g, 45%). Mp: decomposition at ca. 55 °C. IR (C_6H_6): υ_{MoH} 1958 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 4.78 (m, $^3J_{HH} = 3.1$ Hz, $^4J_{HH} = 2.5$ Hz, $^4J_{HH} = 2.9$ Hz, 1H, C_5H_4), 4.52 (s, 5H, C_5H_5), 4.43 (br s, 1H, C_5H_4), 4.29 (m, $^4J_{HH} = 2.5$ Hz, $^4J_{HH} = 0.5$ Hz, $^3J_{HH} = 2.7$ Hz, $^4J_{HF} = 2.4$ Hz, 1H, C_5H_4), 4.03 (br s, 1H, C_5H_4), −7.82 (s, 1H, Mo−H). ^{19}F NMR (282 MHz, C_6D_6): δ −74.1 (dq, $^3J_{FF} = 10$ Hz, $^4J_{FF} = 10$ Hz, 3F, CF_3), −75.4 (dq, $^3J_{FF} = 10$ Hz, $^4J_{FF} = 10$ Hz, 3F, CF_3), −171.2 (sept d, $^3J_{FF} = 10$ Hz, $^3J_{FF} = 10$ Hz, $^4J_{FH} = 2$ Hz, 1F, CF). Anal. Calcd for $C_{13}H_{10}F_7IMo$ (522.06): C, 29.90; H, 1.93. Found: C, 29.66; H, 1.85.

W(η^5-C_5H_5)[C_5H_4(CF(CF_3)$_2$)]HI (15). $WCp_2(C_2H_4)$ (0.275 g, 0.804 mmol) was dissolved in THF (10 mL) and $ICF(CF_3)_2$ (0.121 mL, 0.859 mmol) was added dropwise. The solution was stirred at room temperature for 30 min during which time the color changed to purple/brown. The solution was filtered under nitrogen and the solvent was removed in vacuo. The purple residue was washed twice with hexane (2 × 5 mL) (0.434 g, 86%). Crystals suitable for X-ray diffraction were grown from benzene. Mp: 95−98 °C. IR (Nujol mull): υ_{WH} 1935 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) δ 4.77 (m, $^3J_{HH} = 3.4$ Hz, $^4J_{HH} = 2.0$ Hz, $^4J_{HH} = 3.3$ Hz, 1H, C_5H_4), 4.46 (s, 6H, C_5H_5, C_5H_4), 3.89 (br s, 1H, C_5H_4) 3.82 (br s, 1H, C_5H_4), −10.93 (s, W satellites, $J_{HW} = 60.0$ Hz, 1H, W−H). ^{19}F NMR (282 MHz, C_6D_6): δ −73.5 (dq, $^3J_{FF} = 10$ Hz, $^4J_{FF} = 10$ Hz, 3F, CF_3), −75.7 (dq, $^3J_{FF} = 10$ Hz, $^4J_{FF} = 10$ Hz, 3F, CF_3), −171.7 (sept d, $^3J_{FF} = 10$ Hz, $^3J_{FF} = 10$ Hz, $^4J_{HF} = 1.0$ Hz, 1F, CF). Anal. Calcd for $C_{13}H_{10}F_7IW$ (609.97): C, 25.60; H, 1.65. Found: C, 25.35; H, 1.79.

W(η^5-C_5H_5)[C_5H_4(C_6F_5)]HI (16). $WCp_2(C_2H_4)$ (0.058 g, 0.170 mmol) was dissolved in THF (7 mL) and IC_6F_5 (0.023 mL, 0.170 mmol) was added resulting in a yellow/brown solution. This mixture was stirred at room temperature for 30 min then filtered under nitrogen. The solvent was removed in vacuo and the residue was washed with hexane (2 × 5 mL) and recrystallized from benzene/hexane (0.051 g, 49%). Mp: decomposition at ca. 114 °C. IR (Nujol mull): υ_{WH} 1938 cm^{-1}. ^{1}H NMR (300 MHz, C_6H_6): δ 5.24 (m, 1H, C_5H_4), 5.01 (m, 1H, C_5H_4), 4.38 (s, 5H, C_5H_5), 4.21 (m, 1H, C_5H_4), 3.70 (m, 1H, C_5H_4), −11.64 (s, W satellites, $J_{HW} = 56.4$ Hz, 1H, W−H). ^{19}F NMR (282 MHz, C_6H_6): δ −141.3 (dd, $J_{FF} = 22$ Hz, $J_{FF} = 7$ Hz, 2F, C_6F_5 *ortho*), −158.6 (t, $J_{FF} = 22$ Hz, 1F, C_6F_5 *para*), −163.4 (m, 2F, C_6F_5 *meta*). Anal. Calcd for $C_{16}H_{10}F_5IW$ (608.00): C, 31.61; H, 1.66. Found: C, 31.53; H, 1.89.

W(η^5-C_5H_5)[C_5H_4(C_6F_5)]HBr (17). $WCp_2(C_2H_4)$ (0.150 g, 0.438 mmol) was dissolved in THF (6 mL). On addition of BrC_6F_5 (0.056 mL, 0.441 mmol) the orange solution turned brown/yellow. It was stirred for 1 h at room temperature then filtered under nitrogen. Reduction of the solvent volume gave a brown solid that was washed with hexane then recrystallized from dichloromethane/hexane (0.159 g, 65%). Mp: decomposition at ca. 100 °C. IR (Nujol mull): υ_{WH} 1895 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 5.20 (m, 1H, C_5H_4), 5.03 (m, 1H, C_5H_4), 4.39 (s, 6H, C_5H_5, C_5H_4), 4.30 (m, 1H, C_5H_4), −11.18 (s, W satellites, $J_{HW} = 57.6$ Hz, 1H, W−H). ^{19}F NMR (282 MHz, C_6D_6): δ −141.4 (dd, $J_{FF} = 23$ Hz, $J_{FF} = 6$ Hz, 2F, C_6F_5 *ortho*), −158.9 (t, $J_{FF} = 23$ Hz, 1F, C_6F_5 *para*), −163.5 (m, 2F, C_6F_5). Anal. Calcd for $C_{16}H_{10}BrF_5W$ (561.00): C, 34.26; H, 1.80. Found: C, 34.40; H, 1.70.

W(η^5-C_5H_5)[C_5H_4(CF(CF_3)$_2$)]I_2 (18). W(η^5-C_5H_5)[C_5H_4(CF(CF_3)$_2$)]HI (**15**) (0.027 g, 0.044 mmol) was dissolved in dichloromethane (3 mL) and iodoform (0.017 g, 0.046 mmol) was added. The solution was stirred at room temperature for 3 h during which time it turned green. Filtration in the open followed by reduction of the solvent volume and addition of hexane afforded green microcrystals. The product was recrystallized from dichloromethane/hexane (0.018 g, 55%). Crystals suitable for diffraction were grown from dichloromethane/hexane. Mp: 211−212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.95 (m, 2H, C_5H_4), 5.67 (s, 5H, C_5H_5), 5.20 (t, $J_{HH} = 2.5$ Hz, 2H, C_5H_4). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.4 (d, $^3J_{FF} = 9$ Hz, 6F, CF_3), −176.2 (sept, $^3J_{FF} = 10$ Hz, 1F, CF). Anal. Calcd for $C_{13}H_9F_7I_2W$ (735.86): C, 21.22; H, 1.23. Found: C, 21.17; H, 0.96.

W(η^5-C_5H_5)[C_5H_4(C_6F_5)]I_2 (19). W(C_5H_5)[C_5H_4(C_6F_5)]HI (**16**) (0.075 g, 0.123 mmol) was dissolved in dichloromethane (5 mL) in the open. Iodoform (0.486 g, 1.23 mmol) was added and the solution was stirred for 1 h during which time it turned green. Filtration followed by reduction of the solvent volume under reduced pressure and addition of hexane gave a green crystalline product that was recrystallized from dichloromethane/hexane and washed well with ethanol then hexane (0.069 g, 76%). Mp: decomposition at ca. 210 °C with apparent loss of I_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91 (t, $J_{HH} = 2.7$ Hz, 2H, C_5H_4), 5.58 (m, 2H, C_5H_4), 5.55 (s, 5H, C_5H_5). ^{19}F NMR (282 MHz, $CDCl_3$): δ −139.0 (d, $J_{FF} = 16$ Hz, 2F, C_6F_5 *ortho*), −154.2 (t, $J_{FF} = 21$ Hz, 1F, C_6F_5 *para*), −161.9 (m, 2F, C_6F_5 *meta*). Anal. Calcd for $C_{16}H_9F_5I_2W$ (733.90): C, 26.19; H, 1.24. Found: C, 25.81; H, 1.25.

W(η^5-C_5H_5)[C_5H_4(C_6F_5)]Br_2 (20). WCp[C_5H_4(C_6F_5)]HBr (**17**) (0.100 g, 0.178 mmol) was dissolved in dichloromethane (3 mL) and bromoform (0.301 g, 1.19 mmol) was added. The solution was stirred for 3 h during which time it turned green and a small amount of dark precipitate appeared. It was filtered in the open, the volume of the solvent was reduced, and hexane was added to precipitate the product, which was recrystallized from dichloromethane/hexane (0.072 g, 63%). Mp: decomposition at ca. 214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94 (br s, 2H, C_5H_4), 5.62 (br s, 7H, C_5H_5, C_5H_4). ^{19}F NMR (282 MHz, $CDCl_3$): δ −138.8 (d, $J_{FF} = 18$ Hz, 2F, C_6F_5 *ortho*), −154.2 (t, $J_{FF} = 22$ Hz, 1F, C_6F_5 *para*), −161.9 (m, 2F, C_6F_5 *meta*). Anal. Calcd for $C_{16}H_9Br_2F_5W$ (639.90): C, 30.30; H, 1.42. Found: C, 30.16; H, 1.48.

Mo(η^5-C_5H_5)[C_5H_5(CF(CF_3)$_2$)]I(CO) (21). $MoCp_2(CO)$ (0.051 g, 0.201 mmol) was dissolved in tetrahydrofuran (4 mL) and $ICF(CF_3)_2$ (0.030 mL, 0.219 mmol) was added giving a red/brown solution. This mixture was stirred for 10 min then the solvent was removed in vacuo. The orange residue was extracted with dichloromethane and filtered in the open. Reduction of the solvent volume and addition of hexane afforded an orange powder that was recrystallized from dichloromethane/hexane (0.079 g, 71.6%). Mp: 112−113 °C. IR (Nujol mull): υ_{CO} 1952 cm^{-1}. ^{1}H NMR (300 MHz, $C_6D_5CD_3$; −60 °C): δ 5.30 (m, 1H, C_5H_5), 4.21 (br s, 1H, C_5H_5), 4.09 (s, 5H, C_5H_5), 4.01 (d, $^{3}J_{HF}$ = 24.9 Hz, 1H, H-endo), 3.89 (m, 1H, C_5H_5), 1.90 (m, 1H, C_5H_5) (major isomer); 5.02 (br s, 1H, C_5H_5), 4.95 (m, 1H, C_5H_5), 4.36 (s, 5H, C_5H_5), 3.73 (br s, 1H, C_5H_5), 3.08 (d, $^{3}J_{HF}$ = 23.4 Hz, 1H, H-endo), 1.60 (br s, 1H, C_5H_5) (minor isomer). ^{19}F NMR (282 MHz, $C_6D_5CD_3$; −60 °C): δ −73.7 (br s, 6F, CF_3), −191.2 (m, $^{3}J_{FF}$ = 8 Hz, $^{3}J_{FH}$ = 24 Hz, 1F, CF) (major isomer); −73.2 (dq, $^{3}J_{FF}$ = 8 Hz, $^{4}J_{FF}$ = 8 Hz, 3F, CF_3), −73.9 (dq, $^{3}J_{FF}$ = 8 Hz, $^{4}J_{FF}$ = 8 Hz, 3F, CF_3), −189.0 (m, $^{3}J_{FF}$ = 8 Hz, $^{3}J_{FH}$ = 24 Hz, 1F, CF) (minor isomer). Anal. Calcd for $C_{14}H_{10}F_7IMoO$ (550.07): C, 30.57; H, 1.83. Found: C, 30.77; H, 1.97.

W(η^5-C$_5$H$_5$)[C$_5$H$_5$(CF(CF$_3$)$_2$)]I(CO) (22). $WCp_2(CO)$ (0.060 g, 0.175 mmol) was dissolved in tetrahydrofuran (4 mL) and $ICF(CF_3)_2$ (0.025 g, 0.177 mmol) was added giving a yellow/brown solution. This mixture was stirred for 10 min then filtered in the open. The solvent was removed and the residue was extracted with benzene. On slow reduction of the solvent volume a small amount of dark precipitate appeared. This was removed by filtration and the volume of the resulting orange solution was reduced further and hexane was added to precipitate the product. Recrystallization from dichloromethane/hexane gave orange crystals (0.070 g, 63%). Crystals suitable for X-ray diffraction were grown from toluene/hexane. Mp: 135−137 °C. IR (Nujol mull): υ_{CO} 1943 cm^{-1}. ^{1}H NMR (300 MHz, $C_6D_5CD_3$; −60 °C): δ 5.15 (s, 1H, C_5H_5), 4.28 (d, $^{3}J_{HF}$ = 25.1 Hz, 1H, H-endo), 4.03 (s, 5H, C_5H_5), 3.74 (s, 1H, C_5H_5), 3.66 (m, 1H, C_5H_5), 1.74 (s, 1H, C_5H_5). ^{19}F NMR (282 MHz, $C_6D_5CD_3$; −60 °C): δ −73.4 (d, $^{3}J_{FF}$ = 7.0 Hz, 6F, CF_3), −189.2 (m, $^{3}J_{FF}$ = 7 Hz, $^{3}J_{FH}$ = 25 Hz, 1F, CF). Anal. Calcd for $C_{14}H_{10}F_7IOW$ (637.98): C, 26.36; H, 1.58. Found: C, 26.46; H, 1.55.

Mo(η^5-C$_5$H$_5$)$_2$[CH$_2$CH$_2$C(CF$_3$)$_3$]I (25). $MoCp_2(C_2H_4)$ (0.039 g, 0.153 mmol) was dissolved in tetrahydrofuran (4 mL) and a solution of $IC(CF_3)_3$ (0.190 mL, 0.157 mmol) in benzene was added. The orange/brown solution turned brown and was stirred for half an hour. Removal of the solvent volume gave the crude product as a light brown solid. Recrystallization from dichloromethane/hexane gave the pure product (0.050 g, 54%). Mp: decomposition at ca. 160 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 4.28 (s, 10H, C_5H_5), 1.90 (m, 2H, CH_2), 1.56 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (75 MHz, CD_2Cl_2): δ 122.5 (q, J_{CF} = 288 Hz, CF_3), 92.7 (s, C_5H_5), 60.9 (dec, $^{2}J_{CF}$ = 25 Hz, *C*CF$_3$), 36.7 (s, CH_2), −5.7 (s, Mo−CH$_2$). ^{19}F NMR (282 MHz, C_6D_6): δ −66.0 (br s, 9F, CF_3). Anal. Calcd for $C_{16}H_{14}F_9IMo$ (600.12): C, 32.02; H, 2.35. Found: C, 32.00; H, 2.39.

W(η^5-C$_5$H$_5$)$_2$[CH$_2$CH$_2$C(CF$_3$)$_3$]I (26). $WCp_2(C_2H_4)$ (0.030 g, 0.088 mmol) was dissolved in tetrahydrofuran (4 mL) and a solution of $IC(CF_3)_3$ in benzene (0.11 mL, 0.09 mmol) was added dropwise giving a green solution. The reaction mixture was stirred for 15 min then the solvent was removed in vacuo giving the crude product. The green residue was dissolved in dichloromethane and filtered. Reduction of the solvent volume and addition of hexane gave a green crystalline product (0.041 g, 60%). Crystals suitable for X-ray diffraction were grown from dichloromethane/hexane. Mp: decomposition at ca. 200 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.03 (s, 10H, C_5H_5), 2.09 (m, 2H, CH_2), 1.28 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (75 MHz, CD_2Cl_2): δ 122.5 (qm, J_{CF} = 288 Hz, CF_3), 88.9 (s, W satellites, J_{CW} = 6 Hz, C_5H_5), 61.5 (dec, $^{2}J_{CF}$ = 25 Hz, *C*CF$_3$), 39.7 (s, CH_2), −20.8 (s, W satellites, J_{CW} = 60 Hz, W−CH$_2$). ^{19}F NMR (282 MHz, C_6D_6): δ −66.0 (quintet, 9F, CF_3). Anal. Calcd for $C_{16}H_{14}F_9IW$ (688.93): C, 27.93; H, 2.05. Found: C, 28.10; H, 2.01.

W(η^5-C$_5$H$_5$)$_2$[CH$_2$CH$_2$OCH$_3$]I (27). $WCp_2(C_2H_4)$ (0.050 g, 0.146 mmol) was dissolved in benzene (5 mL) and methanol (0.057 mL, 1.41 mmol) was added followed by $ICF(CF_3)_2$ (0.021 mL, 0.149 mmol). A light orange precipitate and a green/brown solution resulted. The solution was stirred for 15 min and then filtered to remove the precipitate. The solvent was removed in vacuo and the residue was washed with hexane. Recrystallization from dichloromethane/hexane gave a dull green powder (0.022 g, 30%). ^{1}H NMR (300 MHz, CD_2Cl_2):; δ 5.02 (s, 10H, C_5H_5), 3.33 (m, 2H, CH_2), 3.26 (s, 3H, OCH_3), 1.35 (m, 2H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 88.5 (s, W satellites, J_{CW} = 6 Hz, Cp), 84.5 (s, CH_2), 57.2 (s, CH_3), −11.3 (s, W satellites, J_{CW} = 58 Hz, W−CH$_2$). Anal. Calcd for $C_{13}H_{17}IOW$ (500.03): C, 31.23: H, 3.43.

Crystallographic Structural Determinations. Crystal, data collection, and refinement parameters are collected in Table 1. The systematic absences in the diffraction data were consistent for the reported space groups. For **10**, **13**, and **18** either of the monoclinic space groups *Cc* and *C*2/*c* was indicated; the noncentrosymmetric group *Cc* was chosen for **10** and the centrosymmetric space group *C*2/*c* was chosen for **13** and **18** to yield the chemically reasonable and computationally stable results of refinement. The structures were solved by using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Absorption corrections were not required for structures **10** and **13** because the variation in the ψ-scan intensities was less than 10%. Empirical corrections for absorption (DIFABS) were applied to the data for **18** and **22**. In **8**, atoms F(3), F(5), F(6), and F(7) are disordered over two positions with an occupancy distribution 70/30 for atom F(3) and 60/40 for the other fluorine atoms. In **22** the asymmetric unit contains two crystallographically independent, but chemically similar, molecules. In one of the two molecules, disorder is found in the $CF(CF_3)_2$ group and two sites of approximately equal occupancy were refined. All non-hydrogen atoms were refined with anisotropic displacement coefficients, except for atoms of the disordered group in **22.** Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.

Acknowledgment. R.P.H. is grateful to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

Supporting Information Available: Atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for **8, 10, 13, 18, 22,** and **27** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003339U