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Synthesis of η^6-Octafluorocyclooctatetraene and η^6-Cyclooctatetraene Complexes of Manganese(I). Molecular Structures of $[Mn(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_8X_8)]$ (R = H, Me, X = F; R = Me, X = H)

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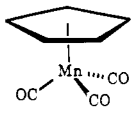
Irradiation of a mixture of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (1) and octafluorocyclooctatetraene (OFCOT) in toluene solution affords the air-stable, yellow, crystalline sandwich complex $[Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_8F_8)]$ (6). The air and thermal stability of 6 contrasts sharply with its hydrocarbon analogue $[Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_8H_8)]$ (5), which decomposes under a nitrogen atmosphere at 0 °C, as previously reported by others. The solid-state structure of 6 has been determined crystallographically: monoclinic, $P2_1/n$: a = 6.900 (2), b = 13.408 (4), c = 12.962 (4) Å; β = 91.93 (2)°; Z = 4. The yellow, air-stable pentamethylcyclopentadienyl analogue $[Mn(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_8F_8)]$ (9) has also been prepared in a similar fashion and crystallographically characterized: monoclinic, $P2_1/c$; a = 8.620 (2), b = 10.485 (2), c = 19.085 (3) Å; β = 94.96 (2)°; Z = 4. The red, crystalline, hydrocarbon analogue of 9, $[Mn(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_8H_8)]$ (11), has been synthesized. In contrast to 9, complex 11 is extremely air-sensitive, but it is considerably more stable thermally than its previously reported cyclopentadienyl analogue 5. For direct comparison of its solid-state structure with that of 9, complex 11 was also subjected to a crystallographic study: monoclinic, $P2_1/c$; a = 11.959 (3), b = 9.049 (2), c = 14.225 (5) Å; β = 98.90 (2)°; Z = 4. While the OFCOT ring in 6 and 9 does not show fluxional behavior on the ^{19}F NMR time scale, the cyclooctatetraene (COT) ring in the hydrocarbon analogue 11 does exhibit dynamic behavior attributed to either a [1,3] or a random shift mechanism for metal migration around the COT ring. Surprisingly, the solid-state structures of 6, 9, and 11 do not exhibit dramatically different features which might provide insight in to the differences in stability and dynamic behavior induced by fluorination of the eight-membered ring. Unsuccessful attempts to prepare OFCOT sandwich complexes with a variety of other metal complexes are briefly described. Irradiation of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ (2) with the tricyclic valence isomer of OFCOT, *anti*-perfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diene (16), afforded only the η^2-olefin complex 17 with no evidence for opening of the fluorocarbon ring to give a bicyclic or monocyclic isomer.

Introduction

The carbonyl substitution chemistry of $[Mn(\eta^5\text{-}C_5R_5)(CO)_3]$ (1, R = H; 2, R = Me) has been intensively investigated.[2] In view of the fact that 1 is quite inert to thermal substitution of CO, most syntheses of $[Mn(\eta^5\text{-}C_5H_5)(L)(CO)_2]$ (L = neutral two-electron ligand) have utilized photochemically activated dissociation of CO.[2] The substitution of more than one CO in 1 is unusual;[2a] however, complete photochemical replacement of the three carbonyl ligands by a series of six-electron ligands has afforded the manganese "sandwich" complexes (3–5).[2a,3–5] Changing the coordinated ring from the seven-membered cycloheptatriene ligand in 4 to the eight-membered cyclooctatetraene (COT) ligand in 5 had a dramatic effect on the thermal stability of these complexes; e.g., 4 is a thermally stable, air-sensitive complex, while 5 decomposed above −78 °C in the absence of excess COT.[3,4] A ^1H NMR spectrum of 5 was obtained at ca. 0 °C by filling the NMR tube at −196 °C and warming it up quickly just before measurement. The spectrum displayed, in addition to the signal assigned to the C_5H_5 ring protons, three resonances assigned to the C_8H_8 ring protons of relative intensities 2:4:2.[4]



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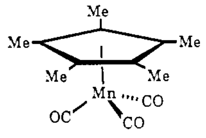

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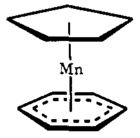

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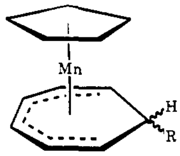

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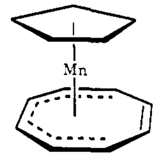

5

We have been interested in obtaining comparative structural information on transition-metal complexes of hydrocarbon ligands and their perfluorinated analogues to assess the effect of fluorine on bonding to the metal, since organometallic complexes that contain π-bound perfluorinated ligands are thought to be more thermally stable and possess stronger metal olefin bonds than their corresponding hydrocarbon analogues.[6] Stimulated by the above work, the syntheses of analogous manganese sandwich complexes derived from octafluorocyclooctatetraene (OFCOT) were attempted.

Results and Discussion

Reaction of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ with OFCOT. Irradiation of a toluene solution containing $[Mn(\eta^5\text{-}$

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(1) (a) Dartmouth College. (b) University of Delaware.

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Table I. Crystal, Data Collection, and Refinement Parameters for [Mn(η^5-C_5H_5)(η^6-C_8F_8)] (6), [Mn(η^5-C_5Me_5)(η^6-C_8F_8)] (9), and [Mn(η^5-C_5Me_5)(η^6-C_8H_8)] (11)

	6	9	11
formula	$C_{13}H_5F_8Mn$	$C_{18}H_{15}F_8Mn$	$C_{18}H_{23}Mn$
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	6.900 (2)	8.620 (2)	11.959 (3)
b, Å	13.408 (4)	10.485 (2)	9.049 (2)
c, Å	12.962 (4)	19.085 (3)	14.225 (5)
β, deg	91.93 (2)	94.96 (2)	98.90 (2)
V, Å^3	1198.5 (6)	1718.4 (6)	1520.8 (7)
Z	4	4	4
D(calcd), g cm^{-3}	2.040	1.694	1.285
size, mm	0.06 × 0.40 × 0.40	0.26 × 0.31 × 0.31	0.26 × 0.31 × 0.33
color	yellow	yellow	red-brown
μ(Mo Kα), cm^{-1}	11.71	9.02	9.0
scan limits, deg	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 52$	$4 \leq 2\theta \leq 45$
scan speed, deg min^{-1}	var 4–10	var 5–20	var 10–20
scan method	omega	omega	omega
std rflctns	3 std/197 rflctns	3 std/197 rflctns	3 std/197 rflctns
decay (I)	<1%	<1%	~6%
rflctns collctd	2077	3681	2247
indpdnt rflctns	1731	3374	1991
ovserved rflctns ($3\sigma(F_o)$)	1599	2263	1275
R(int), %	1.11	1.49	1.49
$R(F)$, %	3.29	5.48	5.73
$R(wF)$, %	3.92	6.48	6.14
GOF	1.175	1.723	1.172
Δ/σ	0.023	0.017	0.093
$\Delta(\rho)$, e Å^{-3}	0.23	0.57	0.31
N_o/N_v	7.30	9.27	7.41

C_5H_5)(CO)$_3$] in the presence of a 10% excess of OFCOT for 7 h under a purge of argon afforded, after column chromatography and crystallization, the air-stable, yellow, crystalline solid [Mn(η^5-C_5H_5)(η^6-C_8F_8)] (**6**). The solid-state structure of **6** was confirmed by a single-crystal X-ray diffraction study (see below).

The solution structure of **6** was determined by spectroscopic methods to be analogous to that observed in the solid state. The infrared and ^{19}F NMR spectra of the crude reaction mixture indicated only the formation of **6** and not any products arising from incomplete CO replacement. The solution infrared spectrum of **6** did not contain any bands in the metal carbonyl region but did display a band at 1770 cm^{-1} which was assigned to the uncoordinated olefin of the η^6-C_8F_8 ring based on a comparison with the FC=CF band at 1720 cm^{-1} in tetradecafluorocyclooctene.[7] The ^{1}H NMR spectrum of **6** exhibited a single resonance that was assigned to the cyclopentadienyl ring protons. The room-temperature ^{19}F NMR spectrum of **6** contained four resonances of equal intensity at δ 115.7, 152.0, 162.4, and 164.6 ppm upfield from internal $CFCl_3$. The three high-field signals were assigned to the fluorines bound to the carbons coordinated to the metal based on their upfield shift from the ^{19}F NMR chemical shift observed for free OFCOT (δ 123.2 ppm).[8] Consequently, the remaining ^{19}F NMR resonance at δ 115.7 ppm was assigned to the fluorines bound to the uncoordinated olefinic carbons.

The enhanced thermal stability observed for **6**, which melts in air without decomposition, compared to its hydrocarbon analogue (**5**),[4] provides a dramatic example of the effect of perfluorination of a ligand on the physical properties of a transition-metal complex. These two complexes are presumed to be structurally identical except for the substituents on the eight-membered ring (see below), yet **5** decomposed above −78 °C in the absence of excess COT,[4] while a toluene solution of pure **6** is unchanged even at temperatures as high as 100 °C, as evidenced by ^{19}F NMR spectroscopy.

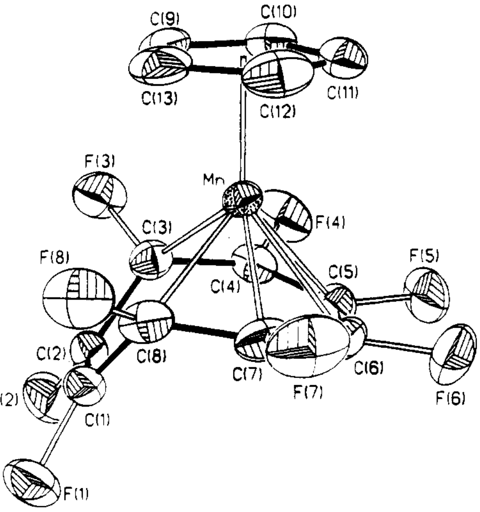

Figure 1. Molecular structure and atom labeling scheme for [Mn(η^5-C_5H_5)(η^6-C_8F_8)] (**6**).

Notably, irradiation of a toluene solution of **1** in the presence of a 10% excess of OFCOT at −15 °C for 7 h did not yield any fluorinated products arising from CO replacement. At this temperature either CO is not displaced from **1** or recombination of photodissociated CO to re-form **1** is favored. The observation that the photochemical reaction forms **6** at ambient temperature and not at −15 °C may indicate an activation barrier for the coordination of the eight-membered ring to the coordinatively unsaturated intermediate [Mn(C_5H_5)(CO)$_2$]; i.e., the mechanism for the formation of **6** may involve an initial photochemical displacement of one CO ligand followed by a thermally activated coordination of the ring with subsequent total CO replacement by the ligand to yield the observed product.

Solid-State Structure of [Mn(η^5-C_5H_5)(η^6-C_8F_8)] (6). An ORTEP of the molecular structure of **6** is shown in Figure

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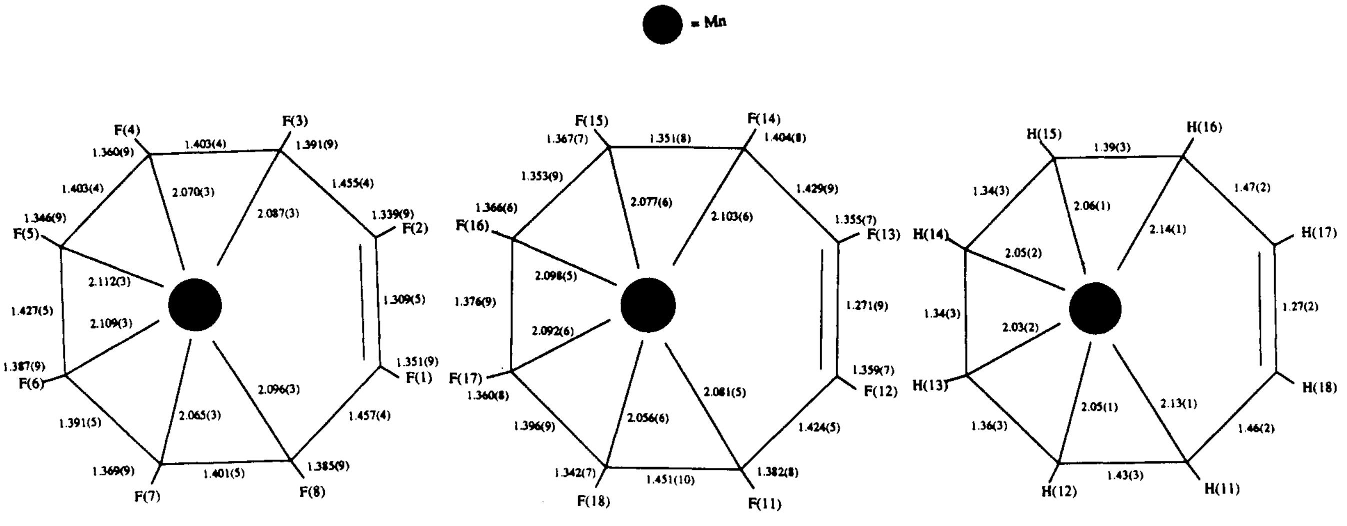
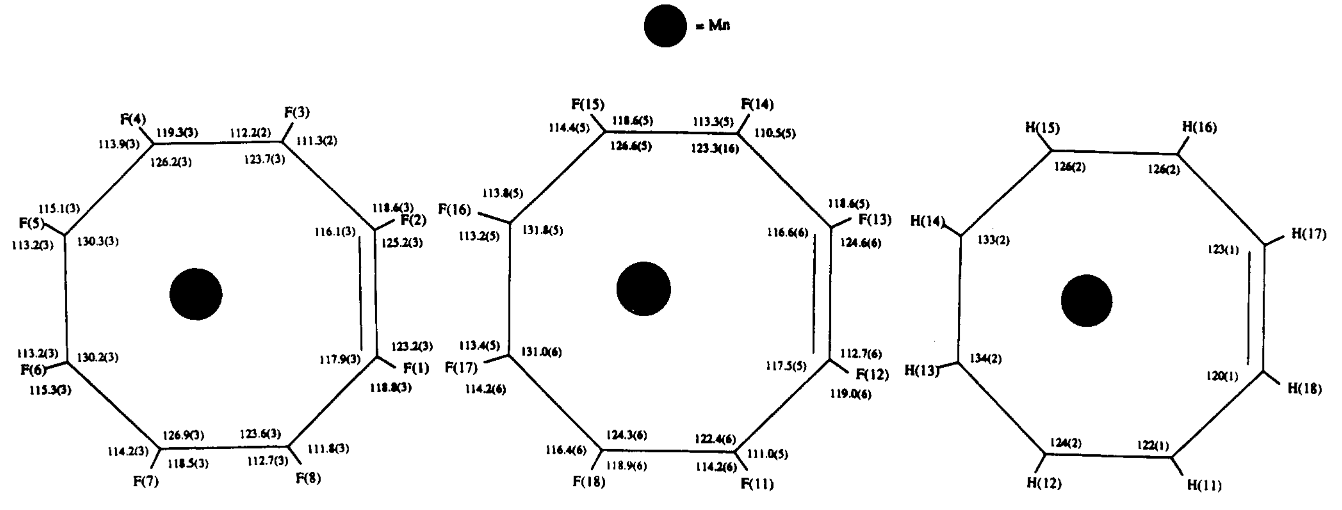


6 9 11

Figure 2. Selected bond distances (Å) for the OFCOT and COT rings in complexes **6**, **9**, and **11**.



6 9 11

Figure 3. Selected bond angles (deg) for the OFCOT and COT rings in complexes **6**, **9**, and **11**.

1. Details of the crystal structure determination are provided in Table I, and fractional atomic coordinates for **6** are given in Table II. Selected bond distances (Figure 2) and bond angles (Figure 3) in the C_8F_8 ligand of **6**, and additional distances and angles are listed in Table III for comparison with those of analogues to be discussed below. Various molecular planes and interplanar angles are described in Table IV.

The molecular structure clearly defines the η^6-coordination of the OFCOT ligand. The uncoordinated olefin of the C_8F_8 ligand is in the exo conformation which agrees with the overall conformation of the eight carbon ring in the related crystallographically characterized hydrocarbon complexes **7**[9] and **8**.[10] The six coordinated carbons of the C_8F_8 ring (plane II; Table IV) in **6** are planar with no atom displaced by more than 0.07 Å from the least-squares plane defined by those six atoms. The dihedral angle between the plane formed by the six coordinated carbon atoms [C(3)–C(8)] (plane II) and that formed by [C(8),C(1),C(2),C(3)] (plane III) is 117.5 (2)°, which is significantly

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for [Mn(η^5-C_5H_5)(η^6-C_8F_8)] (6)

	x	y	z	U^a
Mn	9162 (1)	6037 (1)	2348 (1)	34 (1)
F(1)	13189 (3)	6829 (2)	4777 (2)	77 (1)
F(2)	13162 (3)	4738 (2)	4531 (2)	73 (1)
F(3)	9617 (3)	4137 (1)	3612 (2)	68 (1)
F(4)	10682 (4)	3974 (1)	1714 (2)	75 (1)
F(5)	11923 (3)	5336 (2)	560 (2)	83 (1)
F(6)	11855 (3)	7178 (2)	787 (2)	88 (1)
F(7)	10569 (3)	8215 (1)	2244 (2)	85 (1)
F(8)	9577 (3)	7602 (2)	4048 (2)	78 (1)
C(1)	11938 (4)	6334 (2)	4136 (2)	50 (1)
C(2)	11948 (4)	5364 (2)	4028 (2)	48 (1)
C(3)	10611 (4)	4959 (2)	3243 (2)	44 (1)
C(4)	11060 (4)	4854 (2)	2202 (3)	45 (1)
C(5)	11643 (4)	5618 (3)	1541 (2)	49 (1)
C(6)	11608 (5)	6674 (3)	1671 (3)	54 (1)
C(7)	11002 (4)	7247 (2)	2495 (3)	52 (1)
C(8)	10583 (4)	6907 (2)	3485 (3)	49 (1)
C(9)	6457 (5)	5424 (3)	2784 (3)	58 (1)
C(10)	6727 (5)	5245 (2)	1741 (3)	52 (1)
C(11)	6876 (5)	6156 (3)	1226 (3)	55 (1)
C(12)	6702 (5)	6912 (3)	1963 (4)	65 (1)
C(13)	6444 (5)	6459 (3)	2937 (4)	70 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table III. Selected Bond Distances and Angles for $[Mn(\eta^5-C_5H_5)(\eta^6-C_8F_8)]$ (6), $[Mn(\eta^5-C_5Me_5)(\eta^6-C_8F_8)]$ (9), and $[Mn(\eta^5-C_5Me_2)(\eta^6-C_8H_8)]$ (11)[a]

6		9		11	
		(a) Bond Distances (Å)			
CENT(Cp)–Mn	1.753 (3)	CENT(Cp*)–Mn	1.780 (5)	CENT(Cp*)–Mn	1.760 (7)
C(3)–Mn	2.087 (3)	C(14)–Mn	2.103 (6)	C(11)–Mn	2.13 (1)
C(4)–Mn	2.070 (3)	C(15)–Mn	2.077 (6)	C(12)–Mn	2.05 (1)
C(5)–Mn	2.112 (3)	C(16)–Mn	2.098 (5)	C(13)–Mn	2.03 (2)
C(6)–Mn	2.109 (3)	C(17)–Mn	2.092 (6)	C(14)–Mn	2.05 (2)
C(7)–Mn	2.065 (3)	C(18)–Mn	2.056 (6)	C(15)–Mn	2.06 (1)
C(8)–Mn	2.096 (3)	C(11)–Mn	2.081 (5)	C(16)–Mn	2.14 (1)
C(3)–C(4)	1.403 (4)	C(14)–C(15)	1.351 (8)	C(16)–C(15)	1.39 (3)
C(4)–C(5)	1.403 (4)	C(15)–C(16)	1.353 (9)	C(15)–C(14)	1.34 (3)
C(5)–C(6)	1.427 (5)	C(16)–C(17)	1.376 (9)	C(14)–C(13)	1.34 (3)
C(6)–C(7)	1.391 (5)	C(17)–C(18)	1.396 (9)	C(13)–C(12)	1.36 (3)
C(7)–C(8)	1.401 (5)	C(18)–C(11)	1.451 (10)	C(12)–C(11)	1.43 (3)
C(8)–C(1)	1.457 (4)	C(11)–C(12)	1.489 (10)	C(11)–C(18)	1.46 (2)
C(1)–C(2)	1.309 (5)	C(12)–C(13)	1.271 (9)	C(18)–C(17)	1.27 (2)
C(2)–C(3)	1.455 (4)	C(13)–C(14)	1.429 (9)	C(17)–C(16)	1.47 (2)
C–F(av)	1.361 (9)	C–F(av)	1.37 (1)		
		(b) Bond Angles (deg)			
C(3)–C(4)–C(5)	126.2 (3)	C(14)–C(15)–C(16)	126.6 (5)	C(16)–C(15)–C(14)	126 (2)
C(4)–C(5)–C(6)	130.3 (3)	C(15)–C(16)–C(17)	131.8 (5)	C(15)–C(14)–C(13)	133 (2)
C(5)–C(6)–C(7)	130.2 (3)	C(16)–C(17)–C(18)	131.0 (6)	C(14)–C(13)–C(12)	134 (2)
C(6)–C(7)–C(8)	126.9 (3)	C(17)–C(18)–C(11)	124.3 (6)	C(13)–C(12)–C(11)	124 (2)
C(7)–C(8)–C(1)	123.6 (3)	C(18)–C(11)–C(12)	122.4 (6)	C(12)–C(11)–C(18)	122 (1)
C(8)–C(1)–C(2)	117.9 (3)	C(11)–C(12)–C(13)	117.5 (5)	C(11)–C(18)–C(17)	120 (1)
C(1)–C(2)–C(3)	116.1 (3)	C(12)–C(13)–C(14)	116.6 (6)	C(18)–C(17)–C(16)	123 (1)
C(2)–C(3)–C(4)	123.7 (3)	C(13)–C(14)–C(15)	123.3 (6)	C(17)–C(16)–C(15)	126 (2)

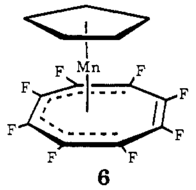
[a] Structurally equivalent bond parameters are shown on horizontal lines.

Table IV. Molecular Plane Calculations with Deviations (Å) and Interplanar Angles (deg) for $[Mn(\eta^5-C_5H_5)(\eta^6-C_8F_8)]$ (6), $[Mn(\eta^5-C_5Me_5)(\eta^6-C_8F_8)]$ (9), and $[Mn(\eta^5-C_5Me_5)(\eta^6-C_8H_8)]$ (11)

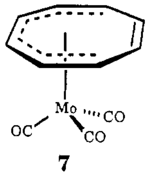
6		9		11	
atom	dev	atom	dev	atom	dev
		Plane I			
C(9)	−0.002 (6)	C(3)	0.007 (8)	C(1)	−0.010 (8)
C(10)	0.001 (6)	C(4)	−0.000 (8)	C(2)	0.003 (8)
C(11)	−0.000 (6)	C(5)	−0.007 (8)	C(3)	0.006 (8)
C(12)	−0.001 (6)	C(1)	0.011 (8)	C(4)	−0.012 (8)
C(13)	0.002 (6)	C(2)	−0.001 (8)	C(5)	0.013 (8)
		Plane II			
C(3)	0.025 (8)	C(14)	−0.034 (10)	C(16)	−0.034 (12)
C(4)	−0.067 (8)	C(15)	0.072 (10)	C(15)	0.084 (12)
C(5)	0.043 (8)	C(16)	−0.035 (10)	C(14)	−0.052 (12)
C(6)	0.035 (8)	C(17)	−0.044 (10)	C(13)	−0.045 (12)
C(7)	−0.072 (8)	C(18)	0.067 (10)	C(12)	0.081 (12)
C(8)	0.035 (8)	C(11)	−0.026 (10)	C(11)	−0.035 (12)
		Plane III			
C(8)	−0.003 (8)	C(11)	−0.005 (9)	C(11)	−0.000 (7)
C(1)	0.005 (8)	C(12)	0.011 (9)	C(18)	0.000 (7)
C(2)	−0.005 (8)	C(13)	−0.011 (9)	C(17)	−0.000 (7)
C(3)	0.003 (8)	C(14)	0.005 (9)	C(16)	0.000 (7)

angle	6	9	11
I–II	9.0 (2)	5.4 (3)	3.6 (5)
I–III	53.5 (2)	57.9 (3)	60.0 (5)
II–III	117.5 (2)	116.7 (3)	116.6 (5)

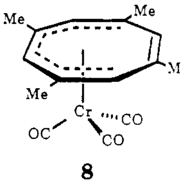
smaller than the corresponding angle in the hydrocarbon complex **7** [130 (2)°][9] but similar to that in **8** [119°].[10] The uncoordinated C═C bond distance in **6**, 1.309 (5) Å, is marginally shorter than the individual C═C bond distances in OFCOT.[11] The two longest C–C bond distances in the C_8F_8 ligand, 1.457 (4) Å for C(1)–C(8) and 1.455 (4) Å for C(2)–C(3), are not significantly different from any of the individual C–C bond lengths in OFCOT, which range from 1.442 (3) Å to 1.451 (3) Å.[11] The other five ring-carbon bond distances in **6**, which range from 1.391 (5) to 1.403 (4) Å, are longer than the C═C bond distances in OFCOT but shorter than the C—C bond lengths.[11] The C—F bond lengths of the fluorines bound to the carbon atoms of the uncoordinated olefin, 1.351 (9) Å for C(1)–F(1) and 1.339 (9) Å for C(2)–F(2) as well as to the C(5) and C(6) carbon atoms, 1.346 (9) Å for C(5)–F(5) and 1.347 (9) Å for C(6)–F(6), are not significantly different from any of the individual C–F bond distances in OFCOT, which range from 1.339 (3) to 1.350 (3) Å. The longest C–F bond distances in **6** are those on the terminal ends of the coordinated triene, i.e. 1.391 (9) Å for C(3)–F(3) and 1.385 (9) Å for C(8)–F(8), which are both significantly longer than any individual C–F bond length in OFCOT. The C–C–C bond angles in the C_8F_8 ligand are similar to those found in OFCOT, except for the smaller C(8)–C(1)–C(2) and C(1)–C(2)–C(3) bond angles of 117.9 (3)° and 116.1 (3)° respectively. As shown in Figure 2, the longest Mn–C bonds to the C_8F_8 ligand are to the middle carbon atoms of the coordinated triene, 2.112 (3) Å for Mn–C(5) and 2.109 (3) Å for Mn–C(6), while in the related hydrocarbon complex (**4**: R = *exo*-Ph) the longest Mn–C bonds to the seven-membered ring, 2.15 (3) Å, are to the terminal carbon atoms of the triene.[5] Finally, the Mn–C bond distances to the cyclopentadienyl ring in **6**, which ranged from 2.110 (3) to 2.125 (3) Å, are similar to the corresponding bond lengths in **4** (R = *exo*-Ph), which are between 2.10 (2) and 2.14 (2) Å.[5]



6



7



8

The six Mn–C bond distances to the fluorinated ring in **6** are not equivalent, although they can be separated into

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[11] Laird, B. B.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *B38*, 678–680.

nearly equal pairs, i.e. Mn–C(3) and Mn–C(8), 2.087 (3) and 2.096 (3) Å; Mn–C(4) and Mn–C(7), 2.070 (3) and 2.065 (3) Å; Mn–C(5) and Mn–C(6), 2.112 (3) and 2.109 (3) Å. The pattern of the C–C bond distances for the six-coordinated ring carbon atoms C(3)–C(8), 1.403 (4), 1.403 (4), 1.427 (5), 1.391 (5), and 1.401 (5) Å, suggests that significant delocalization is present. The significantly greater C(5)–C(6) bond length, 1.427 (5) Å, implies that the delocalization may be greater over C(3)–C(4)–C(5) and C(6)–C(7)–C(8) than over C(5)–C(6). Thus the metal–ligand bonding in **6** may be best represented by a bis(η^3-allyl) structure. There is a clear change in the hybridization of the terminal carbon atoms, C(3) and C(8), of the coordinated triene from sp^2 toward sp^3, as reflected in the longer C–F bond distances at these carbons.

Reaction of [Mn(η^5-C_5Me_5)(CO)$_3$] with OFCOT. We also attempted to generate the hydrocarbon analogue of **6** for crystallographic comparison. In agreement with literature reports,[4] the irradiation of a toluene solution of **1** with an excess of COT afforded the deep red, air-sensitive complex **5**, which decomposed at low temperature in the absence of excess COT. The instability of **5** precluded any direct comparison of its solid-state structure and fluxional behavior (see below) with that of **6**.

The availability of pentamethylcyclopentadiene in multigram quantities[12] has allowed the preparation of a large number of pentamethylcyclopentadienyl derivatives of transition-metal complexes.[13-18] Many of these comlexes have enhanced thermal stability relative to their cyclopentadienyl analogues.[19,20] Therefore, it was decided to attempt the syntheses of pentamethylcyclopentadienyl manganese sandwich complexes derived from OFCOT and COT to obtain a pair of complexes which would allow a direct comparison of their structural and fluxional properties.

We have reported elsewhere that the widely used manganese starting material thought to be pure [Mn(η^5-C_5Me_5)(CO)$_3$] (**2**), prepared according to the literature procedure,[21] was actually a mixture of **2** and the analogous tetramethylcyclopentadienyl complex.[22] Successive recrystallizations of the mixture did ultimately afford a sample of pure **2**.[22]

The irradiation of a toluene solution of pure **2** in the presence of a 10% excess of OFCOT for 7 h under a purge of argon gas afforded, after column chromatography and recrystallization, yellow crystals of the air-stable complex [Mn(η^5-C_5Me_5)(η^6-C_8F_8)] (**9**). There was no infrared or ^{19}F NMR evidence of any products formed from the incomplete replacement of the carbonyl ligands of **2**. The solution infrared spectrum of **9** did display a band at 1773 cm^{-1} which was assigned to the uncoordinated olefin of the C_8F_8 ring based on a comparison with **6**. The room-temperature ^{19}F NMR spectrum of **9** in benzene-d_6 solution displayed four distinct resonances at δ 118.2, 168.0, 174.6, and 179.5 ppm. On the basis of a comparison with the ^{19}F NMR spectrum of OFCOT and **6**, the three high-field ^{19}F NMR signals were assigned to the fluorines bound to the carbons coordinated to the metal, while the resonance at δ 118.2 was assigned to the fluorines bound to the uncoordinated olefinic carbon atoms.

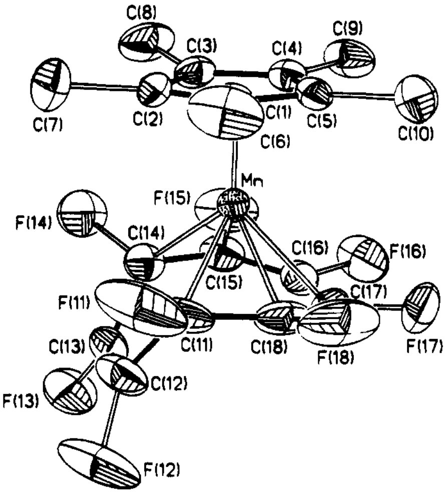

Figure 4. Molecular structure and atom labeling scheme for [Mn(η^5-C_5Me_5)(η^6-C_8F_8)] (**9**).

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [Mn(η^5-C_5Me_5)(η^6-C_8F_8)] (9)

atom	x	y	z	U[a]
Mn	2775 (1)	2440 (1)	6198 (1)	38 (1)
C(1)	4568 (6)	2875 (5)	7020 (3)	54 (2)
C(2)	3083 (7)	2983 (5)	7278 (3)	58 (2)
C(3)	2285 (6)	3977 (5)	6885 (3)	53 (2)
C(4)	3263 (6)	4421 (4)	6391 (3)	47 (2)
C(5)	4662 (5)	3743 (5)	6468 (3)	48 (2)
C(6)	5907 (8)	2064 (7)	7321 (4)	102 (3)
C(7)	2563 (11)	2307 (8)	7906 (3)	124 (4)
C(8)	782 (8)	4583 (7)	7064 (4)	103 (3)
C(9)	2904 (9)	5510 (5)	5876 (3)	87 (3)
C(10)	6075 (7)	3968 (7)	6067 (4)	92 (3)
C(11)	3090 (8)	474 (5)	6253 (4)	87 (3)
C(12)	1613 (8)	−253 (5)	6108 (4)	87 (3)
C(13)	354 (7)	382 (6)	6027 (3)	74 (2)
C(14)	484 (6)	1733 (6)	6111 (3)	62 (2)
C(15)	682 (7)	2540 (5)	5574 (3)	65 (2)
C(16)	1852 (7)	2514 (5)	5145 (3)	65 (2)
C(17)	3248 (7)	1868 (7)	5188 (3)	78 (3)
C(18)	3916 (7)	1031 (6)	5697 (4)	78 (2)
F(11)	4043 (6)	−100 (4)	6781 (3)	153 (3)
F(12)	1683 (7)	−1520 (4)	5962 (3)	162 (3)
F(13)	−1061 (5)	−123 (4)	5825 (2)	120 (2)
F(14)	−589 (5)	2179 (4)	6567 (3)	107 (2)
F(15)	−277 (5)	3576 (4)	5483 (2)	110 (2)
F(16)	1768 (6)	3463 (4)	4653 (2)	117 (2)
F(17)	4255 (5)	2310 (5)	4733 (2)	126 (2)
F(18)	5457 (4)	849 (5)	5704 (3)	143 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Solid-State Structure of [Mn(η^5-C_5Me_5)(η^6-C_8F_8)] (9). An ORTEP of the molecular structure of **9** is shown in Figure 4. Details of the crystallographic determination are given in Table I, and fractional atomic coordinates are listed in Table V. Selected bond distances and bond angles in the C_8F_8 ligand of **9** are shown in Figures 2 and 3, with additional data in Table III. Molecular planes and

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(12) (a) Feilter, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466–469. (b) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5. (c) Manriquez, J.; Fagan, P. S.; Schertz, L. D.; Marks, T. J. *Inorg. Synth.* **1982**, *21*, 181–185. (d) Threlkel, R. S.; Bercaw, J. E.; Seidler, P. F. *Org. Synth.* **1987**, *65*, 42–46.

(13) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287–297.

(14) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1971**, *93*, 4950–4951.

(15) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773–3779.

(16) King, R. B.; Efraty, A.; Douglas, W. M. *J. Organomet. Chem.* **1973**, *60*, 125–137.

(17) King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53–63.

(18) Herrmann, W. A.; Kalcher, W. *Chem. Ber.* **1982**, *115*, 3886–3889.

(19) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238.

(20) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., III; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839–6846.

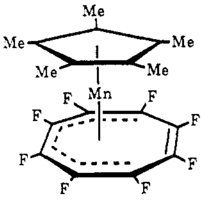
(21) Bernal, I. Korp, J. D.; Herrmann, W. A.; Serrano, R. *Chem. Ber.* **1984**, *117*, 434–444.

(22) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391–2392.

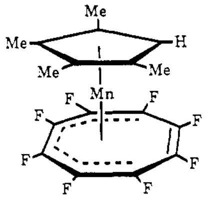
interplanar angles are described in Table IV. Complex 9 is clearly isostructural with 6. The dihedral angle between planes II and III, 116.7 (3)°, is identical within experimental error with the corresponding angle in 6 [117.5 (2)°].

The longest C–F bond distances are those on the terminal ends of the coordinated triene as found in 6, i.e. 1.382 (8) Å for C(11)–F(11) and 1.404 (8) Å for C(14)–F(14). The individual Mn–C bond distances to the C_8F_8 ligand are between 2.056 (6) Å to 2.103 (6) Å and are not significantly different from the corresponding bond lengths in 6, which range from 2.065 (3) and 2.112 (3) Å. The bis(η^3-allyl) representation proposed above for the structure of 6 is less evident in the C–C bond distances observed for 9. Also, the C–C–C bond angles between the coordinated carbon atoms in the C_8F_8 ligand are similar to those found in 6. As was observed for 6, the increase in the C–F bond distance for the fluorines bound to the terminal carbon atoms of the coordinated triene implies that their hybridization is closer to sp^3 than sp^2. However, this change is not reflected in their Mn–C bond distances, which are similar to the other metal-to-ring bond lengths. Curiously, the uncoordinated olefinic bond distance of 1.271 (9) Å for C(12)–C(13) is marginally shorter than the analogous distance in 6.

Reaction of [Mn(η^5-C_5Me_5)(CO)$_3$] with COT. After the successful synthesis of 9 the synthesis of its hydrocarbon analogue was attempted. The irradiation of a toluene solution of 2 in the presence of an excess of cyclooctatetraene for 7 h under a purge of argon afforded, after column chromatography and recrystallization, red crystals of the extremely air-sensitive complex [Mn(η^5-C_5Me_5)(η^6-C_8H_8)] (11).



9



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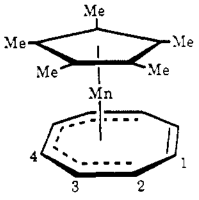


11

In contrast to the cyclopentadienyl derivative 5, this complex can be stored as a solid, at −20 °C under a nitrogen atmosphere, for at least 2 years without decomposition, and solutions of 11 can be heated to 80 °C without decomposition as evidenced by ^1H NMR spectroscopy. As discussed earlier, it was necessary to obtain the ^1H NMR spectrum of 5 at ca. 0 °C in order to avoid decomposition of the complex. However, partial decomposition to unidentified products occurs if a sample of 11 is stored in vacuo.

No infrared or ^1H NMR evidence was found for any products arising from incomplete CO replacement. The solution IR spectrum of 11 exhibited a band at 1665 cm^{-1} which was assigned to the uncoordinated olefin of the C_8H_8 ring based on a comparison of C=C values in related complexes (e.g. the band for the uncomplexed C_8H_8 double bond in 12[23] is at 1665 cm^{-1} and that of 13[24] is at 1670 cm^{-1}). The room-temperature $^{13}C\{^1H\}$ NMR spectrum of 11 exhibited resonances at δ 9.0 [Cp-CH_3] and 87.1 [$C_5(CH_3)_5$] as well as signals assigned to the four sets of C_8H_8 ring carbons at δ 74.7 [C_2], 95.0 [C_4], 96.8 [C_3], and 133.9 [C_1] based the corresponding $^{13}C\{^1H\}$ NMR chemical shift values for related complexes (e.g. δ 93.2 [C_2], 102.5 [C_4], 104.8 [C_3], and 130.6 [C_1] in 12 and δ 82.2 [C_2], 98.5 [C_4], 101.4 [C_3], and 133.3 [C_1] in 13.[25]

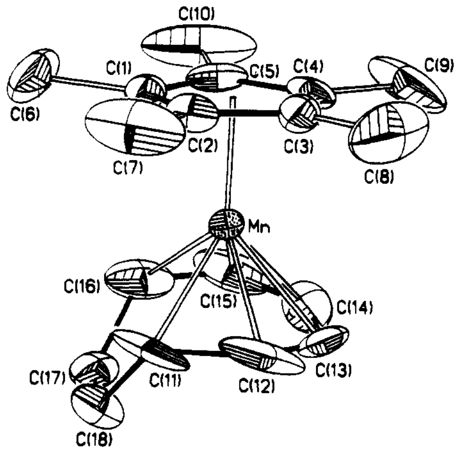


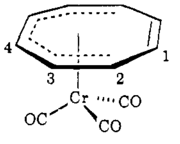
Figure 5. Molecular structure and atom labeling scheme for [Mn(η^5-C_5Me_5)(η^6-C_8H_8)] (11).

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [Mn(η^5-C_5Me_5)(η^6-C_8H_8)] (11)

	x	*y*	*z*	*U*[a]
Mn	2299 (1)	1374 (1)	2132 (1)	49 (1)
C(1)	3271 (7)	−79 (10)	1451 (6)	63 (3)
C(2)	3998 (7)	850 (9)	1992 (7)	60 (3)
C(3)	3885 (8)	681 (12)	2928 (6)	70 (4)
C(4)	3056 (9)	−383 (13)	2977 (7)	89 (5)
C(5)	2690 (7)	−889 (9)	2033 (8)	75 (4)
C(6)	3201 (13)	−322 (17)	382 (7)	178 (9)
C(7)	4868 (10)	1820 (14)	1644 (12)	164 (9)
C(8)	4583 (13)	1489 (17)	3744 (11)	206 (9)
C(9)	2689 (14)	−929 (22)	3888 (11)	268 (13)
C(10)	1900 (11)	−2167 (13)	1738 (17)	237 (13)
C(11)	2346 (11)	3495 (14)	1495 (14)	130 (7)
C(12)	2435 (16)	3556 (14)	2510 (14)	154 (10)
C(13)	1713 (22)	2851 (22)	3013 (12)	156 (12)
C(14)	935 (17)	1796 (27)	2802 (14)	147 (12)
C(15)	585 (11)	1013 (18)	2011 (15)	149 (9)
C(16)	791 (11)	1365 (17)	1104 (13)	121 (7)
C(17)	554 (11)	2827 (15)	676 (8)	98 (6)
C(18)	1294 (13)	3825 (15)	867 (9)	110 (7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The room-temperature ^1H NMR spectrum of 11 displayed a sharp singlet at δ 1.61 that was assigned to the pentamethylcyclopentadienyl ring protons as well as four broad resonances of equal intensity at δ 4.39 [H_2], 4.66 [H_4], 4.79 [H_3], and 5.03 [H_1] which were assigned to specific C_8H_8 ring protons by a two-dimensional HETCOR experiment. The ^1H NMR signals for the four sets of cyclooctatetraene ring protons in 12 are observed at δ 4.64 [H_2], 4.92 [H_1], 5.19 [H_3] and 6.28 [H_4], while those in 13 are at δ 4.23 [H_2], 5.26 [H_1], 5.40 [H_3], and 6.14 [H_4] ppm.[25] As discussed later, the C_8H_8 ligand in 11 is fluxional on the NMR time scale, in accordance with the observed dynamic behavior of 12 and 13.[25]



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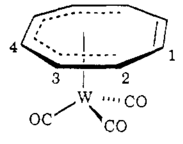

13

Solid-State Structure of [Mn(η^5-C_5Me_5)(η^6-C_8H_8)] (11). An ORTEP of the molecular structure of 11 is shown

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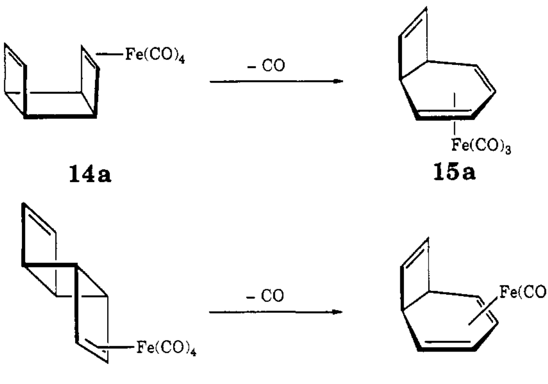
[23] King, R. B. *J. Organomet. Chem.* **1967**, *8*, 139–148.
[24] King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837–1846.
[25] Gibson, J. A.; Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1979**, 1021–1026.

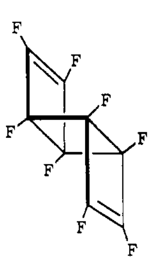
in Figure 5. Details of the crystallographic determination are given in Table I and fractional atomic coordinates in Table VI. Selected bond distances and bond angles in **11** are shown in Figures 2 and 3, with additional data in Table III. Molecular planes and interplanar angles are described in Table IV. The large thermal ellipsoids on the C_8H_8 ring carbons indicate some sign of disorder with the alternate site(s) less than 20% occupancy. The hydrocarbon complex **11** is isostructural with **9** and **6**. The dihedral angle between planes II and III [116.6 (5)°] is equal, within experimental error, to the corresponding angles in **9** and **6**. The C–C bond distances and C–C–C bond angles in **11** are not significantly different from those in the COT derivative **7**.[9] In **11**, the Mn–C bond distances to the coordinated carbon atoms of the C_8H_8 ring are similar to the Mn–C bond distances in the related complex **10**. Finally, the distance from the manganese atom to the centroid of the pentamethylcyclopentadienyl ring is marginally shorter in **11** [1.760 (7) Å] than in **9** [1.780 (5) Å].

In summary, the structural parameters of the hydrocarbon complex **11** appear to be closely related to those of the C_8H_8 complexes **10** and **7**. Surprisingly, the solid-state structure of **11** does not appear to be dramatically different from the solid-state structures of the fluorinated analogues **6** and **9**. Thus the observed differences in air and thermal stability are not manifested in significantly different Mn–C bond distances or a different mode of metal–ligand bonding in **11**.

Reaction of [Mn(η^5-C_5Me_5)(CO)$_3$] with *anti*-Perfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diene. It has been shown that the (*syn*-tricyclooctadiene)iron carbonyl complex **14a** readily undergoes stereospecific ring opening to afford the *exo*-bicyclooctatriene complex **15a**, and the (*anti*-tricyclooctadiene)iron carbonyl complex **14b** likewise opens to yield the endo isomer **15b**.[26]



These results indicated that there might be another route to **9** via reaction of **2** with the tricyclic valence isomer **16** of OFCOT. If a similar metal-induced ring opening occurred to give an analogous bicyclic product, it might be possible to open the bicyclic ring a second time by photochemical means to afford **9**. Unfortunately the reaction of [Mn(η^5-C_5Me_5)(CO)$_3$] with **16**, under identical photochemical conditions as those used for the production of **6** and **9**, afforded low yields of an air-stable, yellow solid characterized by microanalysis, IR, ^{1}H NMR, and ^{19}F NMR as the dicarbonyl product **17**. No ring opening was observed under these reaction conditions. A dicarbonyl complex containing an η^2-COT ligand, [Mn(C_5H_5)(CO)$_2$(η^2-C_8H_8)], has been isolated from the reaction of [Mn(C_5H_5)(CO)$_2$(THF)] with COT.[27]



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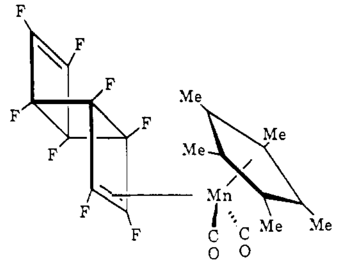

17

Attempted Synthesis of Other Sandwich Complexes Derived from OFCOT. The above results led to further synthetic efforts to generate other [ML$_n$(η^6-C_8F_8)] or [ML$_n$(η^8-C_8F_8)] complexes. As described briefly below, no fluorinated transition-metal complexes were observed by ^{19}F NMR spectroscopy in a wide range of reactions of OFCOT with different metal systems under either photochemical or thermal conditions.

Under conditions similar to those used with **1** and **2**, the photolysis of OFCOT in the presence of [Re(η^5-C_5Me_5)(CO)$_3$], [Mn(η^5-C_5Me_5)(CO)$_2$(CS)], [Nb(η^5-C_5H_5)(CO)$_4$], [V(η^5-C_5H_5)(CO)$_4$], [V(η^5-C_5Me_5)(CO)$_4$] ($\lambda > 170$ nm and $\lambda > 280$ nm), [V(CO)$_6$], [Mo(η^5-C_5H_5)(CO)$_3$]$_2$, and [Mo(η^5-C_5Me_5)(CO)$_3$]$_2$ did not afford complexes derived from OFCOT. Likewise, the thermal reaction of OFCOT with [Cr(CO)$_6$], [Cr(CO)$_3$(CH_3CN)$_3$], [Mo(CO)$_3$(CH_3CN)$_3$], [W(CO)$_3$(CH_3CH_2CN)$_3$], [Mo(η^5-C_5H_5)(CO)$_3$]$_2$, and [Mo(η^5-C_5Me_5)(CO)$_3$]$_2$ did not afford complexes containing OFCOT.

NMR Solution Studies of [M(η^5-C_5R_5)(η^6-C_8X_8)] Complexes. The observation of four resonances in the room-temperature ^{19}F NMR spectrum of [Mn(η^5-C_5H_5)(η^6-C_8F_8)] (**6**) indicated that there was no migration of the metal center around the perfluorinated ring on the NMR time scale. The temperature independence of the ^{19}F NMR spectrum of a toluene-d_8 solution of **6** up to 100 °C prevented the use of line-shape analysis to determine if the C_8F_8 ring was fluxional. Magnetization transfer experiments on **6** using a selective ^{19}F NMR decoupler pulse also demonstrated that the C_8F_8 ring in **6** was not fluxional; i.e. upon irradiation of each resonance, in turn, there was no observed decrease in the intensity in any of the three nondecoupled signals. The absence of coalescence in the ^{19}F NMR spectrum at 100 °C did allow a minimum value of $\Delta G^{\ddagger}_{398} > 18$ kcal/mol (72 kJ/mol) to be calculated.

Similarly, the ^{19}F NMR spectrum of [Mn(η^5-C_5Me_5)(η^6-C_8F_8)] (**9**) also exhibited four resonances at 100 °C. Magnetization transfer studies on **9** also demonstrated that the C_8F_8 ring was static in solution. The absence of coalescence in the ^{19}F NMR spectrum at 100 °C did allow a minimum value of $\Delta G^{\ddagger}_{398} > 17.3$ kcal/mol to be calculated.

In contrast, the room-temperature ^{1}H NMR spectrum of the hydrocarbon analogue [Mn(η^5-C_5Me_5)(η^6-C_8H_8)] (**11**) exhibited four broad resonances assigned to the C_8H_8 ring protons as well as a sharp singlet due to the pentamethylcyclopentadienyl ring protons. Upon warming a toluene-d_8 solution of **11**, all four COT signals broadened at the same rate and appeared as a singlet at 79 °C. The low-temperature-limiting spectrum for the cyclooctatetraene ring protons was obtained at −30 °C, while the ^{1}H NMR spectrum at −90 °C still exhibits a singlet for

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the methyl protons of the pentamethylcyclopentadienyl ligand.

The equal broadening rate of the ^{1}H NMR resonances is consistent with either a [1,3] or a random shift mechanism for metal migration around the COT ring. A $^{13}C\{^1H\}$ NMR magnetization transfer experiment would further elucidate the mechanism of the fluxional behavior of **11** and allow the determination of accurate activation parameters.[28,29] Unfortunately, our NMR facilities are incapable of this type of experiment.

Concluding Remarks

Perfluorination of the cyclooctatetraene ligand clearly results in enormous enhancement of thermal and air stability of the η^6-complexes described in this paper and also slows the rate of metallatropic shifts around the ring. While the effect of perfluorination on the spectroscopic and physical properties of the compounds is dramatic, it is somewhat surprising that the solid-state structures of fluorocarbon and hydrocarbon relatives do not reveal significant changes in structural parameters.

Experimental Procedures

General Data. Infrared spectra were recorded on a Perkin-Elmer 257 or 599 dispersive infrared spectrophotometer, calibrated against the 1601 cm^{-1} peak of polystyrene or on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer. ^{1}H NMR spectra (300 MHz) and $^{13}C\{^1H\}$ spectra (75 MHz) were recorded on a Varian Associates XL-300 spectrometer at 25 °C unless otherwise noted. ^{19}F NMR spectra were recorded on a JEOL FX60Q spectrometer (56.2 MHz) or on a Varian Associates XL-300 spectrometer (282 MHz) at 25 °C unless otherwise noted. All ^{19}F NMR shifts were recorded as parts per million upfield from the internal standard of $CFCl_3$. All ^{1}H and $^{13}C\{^1H\}$ shifts were recorded as parts per million downfield from tetramethylsilane. All variable-temperature NMR spectra were taken on a Varian Associates XL-300 spectrometer. The probe was calibrated at various temperatures by using samples of methanol (low temperaure),[30] and ethylene glycol (high temperature).[31] Melting points were determined by using an Electrothermal capillary melting point apparatus and are uncorrected. Positive ion fast atom bombardment (FAB) mass spectra were recorded at the Johns Hopkins School of Medicine Middle Atlantic Mass Spectrometry Laboratory. Microanalyses were done at Atlantic Microlab, Inc., Atlanta, GA, or Spang Microanalytical Laboratory, Eagle Harbor, MI. Gradient sublimation was performed on a Scientific Instrument Accessories (Austin, TX) Model 240 thermal gradient sublimer.

Reaction solvents, crystallization solvents, and chromatography solvents were dinitrogen saturated and distilled over a variety of drying agents. Benzene and tetrahydrofuran were dried over potassium, toluene was dried over sodium, hexane, petroleum ether, and diethyl ether were dried over sodium–potassium alloy, and methylene chloride was dried over P_4O_{10}. All organometallic reactions were run in oven-dried glassware by using conventional Schlenk techniques, under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried with Aquasorb or in a Vacuum Atmospheres drybox equipped with a HE-492 gas purification system. Column chromatography was done under dinitrogen in jacketed columns with dry, N_2-saturated chromatography supports and solvents. All deuterated solvents were dried over P_4O_{10} and degassed prior to use. Photolyses were performed by using the borosilicate glass filtered output of a Hanovia 450W Hg arc lamp unless otherwise noted.

Silica gel (Davisil 62, activity III) was obtained from Davison Chemical, Inc. Alumina (activity III) was obtained form ICN Pharmaceuticals, Inc. Florisil was obtained from Fisher Scientific Co. Hexacarbonylchromium was obtained from Pressure Chemical Co. 1,3,5,7-Cyclooctatetraene (COT) was obtained from Aldrich Chemical Co. and purified by chromatography on alumina before use. (Cyclopentadienyl)tricarbonylmanganese was obtained from Strem Chemical Co. 1,3,5,7-Octafluorocyclooctatetraene (OFCOT) and *anti*-perfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diene were prepared according to the method of Lemal.[32] Pentamethylcyclopentadiene,[12] $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$,[33] $[V(CO)_6]$,[34] $[V(\eta^5\text{-}C_5Me_5)(CO)_4]$,[34] $[Mo(\eta^5\text{-}C_5Me_5)(CO)_3]_2$,[35] $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$,[36] $[Cr(CO)_3(CH_3CN)_3]$,[37] $[Mo(CO)_3(CH_3CN)_3]$,[37] and $[W(CO)_3(CH_3CH_2CN)_3]$[37] were prepared by literature procedures. A sample of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(CS)]$ was generously donated by Professor John Hubbard at the University of Vermont. Samples of $[V(\eta^5\text{-}C_5H_5)(CO)_4]$ and $[Nb(\eta^5\text{-}C_5H_5)(CO)_4]$ were generously donated by Professor Wolfgang A. Herrmann at the University of Munich. Samples of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ were prepared by the literature procedure,[21] followed by successive recrystallizations to remove the tetramethylcyclopentadienyl coproduct.[22]

Reaction of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ with OFCOT. To a stirred solution of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (**1**) (0.54 g, 2.6 mmol) in toluene (70 mL), in a Pyrex photolysis well, was added OFCOT (0.70 g, 2.8 mmol) under an argon atmosphere. The reaction mixture was irradiated at room temperature under a purge of argon gas for 7 h. The reaction solvent was removed under reduced pressure, and the products were redissolved in CH_2Cl_2 (25 mL) and filtered through Celite. The solvent was then removed under reduced pressure and the residue subjected to column chromatogaphy on silica gel at −10 °C. Elution with hexane (total amount of solvent = 100 mL) gave a bright yellow band from which unreacted $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (0.13 g, 24%) was obtained. Elution with toluene–hexane (5:95) (total amount of solvent = 200 mL) gave a bright yellow band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded yellow crystals of **6** (0.11 g, 15%): mp 156–158 °C; ^{19}F NMR ($CDCl_3$) δ 115.7 (m, 2 F), 152.0 (m, 2 F), 162.4 (m, 2 F), 164.6 (m, 2 F); ^{1}H NMR ($CDCl_3$) δ 4.88 (C_5H_5); IR (CH_2Cl_2) $\nu_{FC=CF}$ = 1770 cm^{-1}; MS *m/e* 368 (M$^+$). Anal. Calcd for $C_{13}H_5F_8Mn$: C, 42.42; H, 1.37. Found: C, 42.61; H, 1.54.

Reaction of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ with OFCOT. To a stirred solution of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ (**2**) (0.95 g, 3.5 mmol) in toluene (70 mL) was added OFCOT (0.90 g, 3.6 mmol) under an argon atmosphere. The reaction mixture was irradiated in a Pyrex photolysis well at room temperature under a purge of argon gas for 7 h. The reaction solvent was removed under reduced pressure, and the products were redissolved in CH_2Cl_2 (20 mL). The solution was then filtered through Celite, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel at −25 °C. Elution with hexane (total amount of solvent = 200 mL) gave a bright yellow band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded bright yellow crystals of **9** (0.70 g, 55%): mp 171–172 °C; ^{19}F NMR ($CDCl_3$) δ 119.3 (m, 2 F), 168.2 (m, 2 F), 176.2 (m, 2 F), 180.2 (m, 2 F); ^{1}H NMR ($CDCl_3$) δ 1.79 (C_5Me_5); IR (CH_2Cl_2) $\nu_{FC=CF}$ = 1773 cm^{-1}. MS *m/e* 438 (M$^+$). Anal. Calcd for $C_{18}H_{15}F_8Mn$: C, 49.33; H, 3.45. Found: C, 49.35; H, 3.37.

Reaction of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ with COT. To a stirred solution of $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ (**2**) (1.1 g, 4.0 mmol) in toluene (80 mL) was added COT (2.0 mL, 17.8 mmol) under an argon atmosphere. The reaction solution was then irradiated in a Pyrex photolysis well at room temperature under a purge of argon gas for 7 h. The extremely air-sensitive, deep cherry red solution was then transferred to a Schlenk flask and the reaction solvent

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removed under reduced pressure. The residue was then subjected to column chromatography on silica gel at -50 °C. Elution with CH_2Cl_2/hexane (15:85) (total amount of solvent = 200 mL) gave a deep red-yellow band. Removal of the solvent under reduced pressure followed by crystallization in the glovebox from CH_2Cl_2/hexane afforded deep red, air-sensitive crystals of **11** (0.70 g, 60%): mp 178–180 °C dec; ^1H NMR ($CDCl_3$, 20 °C) δ 1.61 ($C_5\mathit{Me}_5$), 4.39 (br, s, H_2), 4.66 (br, s, H_4), 4.79 (br, s, H_3), 5.03 (br, s, H_1); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 9.0 (C_5CH_3), 74.7 (*C*H, C_2), 87.1 (C_5Me_5), 95.0 (*C*H, C_4), 96.8 (*C*H, C_3), 133.9 (*C*H, C_1); IR (CH_2Cl_2) $\nu_{HC=CH}$ = 1665 cm^{-1}. Anal. Calcd for $C_{18}H_{23}Mn$: C, 73.46; H, 7.88. Found: C, 73.37; H, 7.77.

Reaction of [Mn(η^5-C_5Me_5)(CO)$_3$] with *anti*-Octafluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diene (16). To a stirred solution of [Mn(η^5-C_5Me_5)(CO)$_3$] (**2**) (0.64 g, 2.3 mmol) in toluene (80 mL) was added (**16**) (0.69 g, 2.8 mmol) under an atmosphere of argon. The reaction solution was irradiated in a Pyrex photolysis well at room temperature under a purge of argon gas for 7.5 h. The reaction solvent was removed under reduced pressure, and the products were redissolved in THF/hexanes (50:50) and filtered through Celite (total amount of solvent = 100 mL). The solvent was removed under reduced pressure and the residue subjected to column chromatography on Florisil at -5 °C. Elution with Et_2O/hexane (15:85) (total amount of solvent = 200 mL) produced a yellow band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded yellow crystals of **17** (0.08 g, 0.2 mmol, 9%): mp 139–140 °C; ^{19}F NMR ($CDCl_3$) δ 120.9 (m, 2 F, F_1), 156.1 (m, 2 F, F_2), 174.8 (m, 2 F, F_3), 185.6 (m, 2 F, F_4); ^1H NMR ($CDCl_3$) δ 1.86 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) ν_{CO} = 2000, 1952 cm^{-1}, $\nu_{FC=CF}$ = 1758 cm^{-1}. Anal. Calcd for $C_{20}H_{15}F_8MnO_2$: C, 48.60; H, 3.06. Found: C, 48.51; H, 3.14.

Attempted Reactions of Other Metal Carbonyl Complexes with OFCOT. I. Photochemical Reactions. Attempted Reaction of [Re(η^5-C_5Me_5)(CO)$_3$] with OFCOT. To a stirred solution of [Re(η^5-C_5Me_5)(CO)$_3$] (0.73 g, 1.8 mmol) in toluene (80 mL) was added OFCOT (0.57 g, 2.3 mmol). The reaction mixture was then irradiated at room temperature through quartz under a purge of argon gas for 20 h. The reaction was monitored by ^{19}F NMR spectroscopy and displayed only the resonance of unreacted OFCOT. Similar results were obtained by using Mn(η^5-C_5Me_5)(CO)$_2$(CS)], [Nb(η^5-C_5H_5)(CO)$_4$], [V(η^5-C_5H_5)(CO)$_4$], [V(η^5-C_5Me_5)(CO)$_4$], [V(CO)$_6$], [Mo(η^5-C_5H_5)(CO)$_3$]$_2$, and [Mo(η^5-C_5Me_5)(CO)$_3$]$_2$.

II. Thermal Reactions. Attempted Reaction of [Cr(CO)$_6$] with OFCOT. To a stirred solution of [Cr(CO)$_6$] (0.15 g, 0.7 mmol) in diglyme (8 mL) was added OFCOT (0.32 g, 1.3 mmol). The reaction mixture was refluxed (162 °C) for 4.5 h and then allowed to stir at room temperature for 20 h. The reaction was monitored by ^{19}F NMR spectroscopy and displayed only the signal of unreacted OFCOT.

Similar results were obtained by using [Cr(CO)$_3$(CH_3CN)$_3$] in refluxing hexanes, [Mo(CO)$_3$(CH_3CN)$_3$] in refluxing CH_3CN, [W(CO)$_3$(CH_3CH_2CN)$_3$] in refluxing THF, [Mo(η^5-C_5H_5)(CO)$_3$]$_2$ in refluxing octane, and [Mo(η^5-C_5Me_5)(CO)$_3$]$_2$ in refluxing benzene.

X-ray Structural Determinations. Table I provides crystal, data collection, and refinement parameters for **6**, **9**, and **11**. All samples were mounted on glass fibers and coated with three thin layers of epoxy cement. The structures were determined at 293 ± 2 K with a Nicolet R3m/μ system using graphite-monochromated Mo Kα radiation. Unit cell parameters were determined from the least-squares fit of the angular settings of 25 reflections ($22 \leq 2\theta \leq 28°$) which included Friedel-related sets to inspect optical and diffractometer alignment. The monoclinic space group $P2_1/c$ or $P2_1/n$ was uniquely determined from systematic absences in the diffraction data. Crystals of the COT complex **11** scattered weakly; the large, but appropriately shaped, thermal ellipsoids for this complex are consistent with a very thermally active structure. A ~6% linear intensity decay was observed for **11** and was corrected for absorption; the other two showed <1% decay. Corrections for absorption were omitted for the pentamethylcyclopentadienyl complexes **9** and **11** but were applied to the cyclopentadienyl complex **6**, which crystallized as thin plates. Reflections making a glancing angle of ≤3.5° to the major face (001) were neglected in performing the empirical correction; this resulted in discarding 12 of 216 ψ-scan data and 154 of 2077 collected reflections. In all cases data were collected to the limits of availability.

The structures were solved by heavy-atom methods and subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters, and for the two complexes **9** and **11**, hydrogen atom contributions were idealized [d(C–H) = 0.96 Å]; methyl group orientations were determined from found hydrogen atom locations. For **6** all hydrogen atoms were found and isotropically refined.

All computations used the SHELXTL (5.1) program library (Nicolet Instrument Co. Madison, WI).

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Registry No. **1**, 12079-65-1; **2**, 34807-89-1; **6**, 119743-21-4; **9**, 119743-23-6; **11**, 119743-24-7; **16**, 72777-10-7; **17**, 119743-22-5; COT, 629-20-9; OFCOT, 57070-35-6; [Re(η^5-C_5Me_5)(CO)$_3$], 12130-88-0; [V(CO)$_6$], 14024-00-1; [V(η^5-C_5Me_5)(CO)$_4$], 84270-55-3; [Mo(η^5-C_5Me_5)(CO)$_3$], 56200-14-7; [Mo(η^5-C_5H_5)(CO)$_3$]$_2$, 12091-64-4; [Cr(CO)$_3$(CH_3CN)$_3$], 16800-46-7; [Mo(CO)$_3$(CH_3CN)$_3$], 15038-48-9; [W(CO)$_3$(CH_3CH_2CN)$_3$], 84580-21-2; [Mn(η^5-C_5Me_5)(CO)$_2$(CS)], 105693-60-5; (V(η^5-C_5H_5)(CO)$_4$], 12108-04-2; [Nb(η^5-C_5H_5)(CO)$_4$], 12108-03-1; [Cr(CO)$_6$], 13007-92-6.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters for **11** (Tables 2A–5A), **6** (Tables 2B–5B), and **9** (Tables 2C–5C) (14 pages); listings of observed vs calculated structure factors for **11** (Table 1A), **6** (Table 1B), and **9** (Table 1C) (30 pages). Ordering information is given on any current masthead page.